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Biodiesel manufacturing processes

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Biodiesel Manufacturing Processes

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Government of India

Submitted by

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Principal Investigator
Somnath Bhattacharjee

Project Team
Shankar Haldar
Arvind Reddy
Nilanjan Ghose
Sharda Gautam
Aniruddha Bhattacharjee

Principal Advisor
Sudhir Singhal
Volume II

ANNEXURE

Annexure 1: S.P. Singh, et al., Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review, Renewable and Sustainable Energy Reviews, 2010

Annexure 2: Balat et al., Progress in biodiesel processing, Applied Energy, 2010

Annexure 3: Kraai et al., Novel highly integrated biodiesel production technology in a centrifugal contactor separator device, 2009

Annexure 4: T. Eevera, et al., Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions, Renewable Energy, 2009


Annexure 8: Ru Yang, et al., One-pot process combining trans-esterification and selective hydrogenation for biodiesel production from starting material of high degree of unsaturation, Bioresource Technology, 2010

Annexure 9: J.M. Marchetti, et al., Biodiesel production from acid oils and ethanol using a solid basic resin as catalyst, Science direct, 2010


Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review

S.P. Singh, Dipti Singh *

School of Energy and Environmental Studies, Devi Ahilya University, Khandwa Road, Takshila Campus, Indore 452011, Madhya Pradesh, India

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ABSTRACT

The world is confronted with the twin crises of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves. Petroleum based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain region of the world. Therefore, those countries not having these resources are facing a foreign exchange crisis, mainly due to the import of crude petroleum oil. Hence it is necessary to look for alternative fuels, which can be produced from materials available within the country. Although vegetative oils can be fuel for diesel engines, but their high viscosities, low volatilities and poor cold flow properties have led to the investigation of its various derivatives. Among the different possible sources, fatty acid methyl esters, known as Biodiesel fuel derived from triglycerides (vegetable oil and animal fates) by transesterification with methanol, present the promising alternative substitute to diesel fuels and have received the most attention now a day. The main advantages of using Biodiesel are its renewability, better quality exhaust gas emission, its biodegradability and the organic carbon present in it is photosynthetic in origin. It does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the green house effect. This paper reviews the source of production and characterization of vegetable oils and their methyl ester as the substitute of the petroleum fuel and future possibilities of Biodiesel production.

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Contents

1. Introduction .......................................................................................................................... 201
2. Source of Biodiesel ............................................................................................................. 201
3. Chemical composition of alternative fuels (oil and Biodiesel) and diesel ......................... 201
4. Processes or method to produce Biodiesel ................................................................. 203
   4.1. Pyrolysis ....................................................................................................................... 203
   4.2. Dilution ....................................................................................................................... 203
   4.3. Microemulsion ........................................................................................................... 206
   4.4. Transesterification ...................................................................................................... 206
5. Properties of alternative fuel or diesel ............................................................................. 208
   5.1. Properties of oil .......................................................................................................... 208
   5.2. Properties of Biodiesel .............................................................................................. 209
   5.3. Determination and measurement methods for oil/Biodiesel properties ..................... 209
6. Performance of alternative fuel (oil and Biodiesel) as a fuel ............................................. 210
   6.1. Use of oils as fuel and their performance ................................................................. 210
   6.2. Need of blending and its effect on performance ....................................................... 210
   6.3. Use of esters as fuel and their performance .............................................................. 211

* Corresponding author. Tel.: +91 0731 2460309; fax: +91 0731 2467378/2462366.
E-mail address: dipti5683@rediffmail.com (D. Singh).

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1. Introduction

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative source of energy, which can supplement or replace fossil fuels.

One hundred years ago, Rudolf Diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893 [1]. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, usually only in emergency. The first International conference on plant and vegetable oils as fuels was held in Fargo, North Dakota in August 1982. The primary concern discussed were the cost of fuel, the effect of vegetable oil fuels on engine performance and durability and fuel preparation specification and additives. Oil production, oil seed processing and extraction also were considered in this meeting [2]. Vegetable oils hold promise as alternative fuels for diesel engines [3,4]. But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as Biodiesel, derived from triglycerides by transesterification with methanol have received the most attention [5,6].

The name Biodiesel was introduced in the United States during 1992 by the National Soy diesel Development Board (presently national bio diesel board) which has pioneered the commercialization of Biodiesel in the United States. Biodiesel can be used in any mixture with petroleum diesel as it has very similar characteristics but it has lower exhaust emissions. Biodiesel has better properties than that of petroleum diesel such as renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens [7]. Ma et al. [8] stated that Biodiesel has become more attractive recently because of its environmental benefits and fact that it is made from renewable resources. The raw materials being exploited commercially by the Biodiesel are the edible fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, linseed, etc. [9]. In recent years, research has been directed to explore plant based fuels, have high bright future [10]. This chapter focused on the source of oils, problems associated with the use of oils, production of Biodiesel from non-edible oil, Physical and chemical properties of oils and esters; advantages, disadvantages and challenges.

2. Source of Biodiesel

Alternative diesel fuels made from natural, renewable sources such as vegetable oil and fats [11,12]. The most commonly used oils for the production of Biodiesel are soybean [13,14], sunflower [15,16], palm [17], rapeseed [18], canola [19], cotton seed [20] and Jatropha [21]. Since the prices of edible vegetable oils are higher than that of diesel fuel, therefore waste vegetable oils and non-edible crude vegetable oils are preferred as potential low priced Biodiesel sources. Use of such edible oil to produce Biodiesel in India is also not feasible in view of big gap in demand and supply of such oils. Under Indian condition only such plants can be considered for Biodiesel, which produce non-edible oil in appreciable quantity and can be grown on large scale on non-cropped marginal lands and waste lands. Animal fats, although mentioned frequently, have not been studied to the same extent, as vegetable oils because of natural property differences. Animal fats contain higher level of saturated fatty acids therefore they are solid at room temperature [22]. The source of Biodiesel in the form of vegetable oils, non-edible oils, animal fats and some other biomass are listed in Table 1.

The source of Biodiesel usually depends on the crops amenable to the regional climate. In the United States, soybean oil is the most commonly Biodiesel feedstock, whereas the rapeseed (canola) oil and palm oil are the most common source for Biodiesel, in Europe, and in tropical countries respectively [68]. A suitable source to produce Biodiesel should not competent with other applications that rise prices, for example pharmaceutical raw materials. But the demand for pharmaceutical raw material is lower than for fuel sources. As much as possible the Biodiesel source should fulfill two requirements: low production costs and large production scale. Refined oils have high production costs, but low production scale: on the other side, non-edible seeds, algae and sewerage have low production costs and are more available than refined or recycled oils.

The oil percentage and the yield per hectare are important parameters to consider as Biodiesel source. Productions of non edible oil seeds percentage of oil content are given in Table 2.
methyl ester. Chemically, most Biodiesel consists of alkyl (usually methyl) esters instead of the alkanes and aromatic hydrocarbons of petroleum derived diesel.

Oil, ester and diesel have different number of carbon and hydrogen compound. Diesel has no oxygen compound. It is a good quality of fuel. On the other hand, in the case of vegetable oils Oxidation resistance is markedly affected by the fatty acid composition. The large size of vegetable oil molecules (typically three or more times larger than hydrocarbon fuel molecules) and the presence of oxygen in the molecules suggests that some fuel properties of vegetable oil would differ markedly from those of hydrocarbon fuels [3]. Chemical structure of oil, Biodiesel and petroleum diesel are given Table 3.

Table 1
Source of oil.

<table>
<thead>
<tr>
<th>Vegetable oils</th>
<th>Non-edible oils</th>
<th>Animal Fats</th>
<th>Other Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut [23,26,27]</td>
<td>B. nobilis [36]</td>
<td></td>
<td>Latexes [66]</td>
</tr>
<tr>
<td>Copra [28]</td>
<td>Camelina [37]</td>
<td></td>
<td>Cooking Oil (Yellow Grease) [64]</td>
</tr>
<tr>
<td>Groundnut [23,28–30]</td>
<td>Cynara cardunculus [38]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oat [25]</td>
<td>Jatropha curcas [21,39,40]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice [25,28,31]</td>
<td>Jatropha nana [41]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wheat [25]</td>
<td>Pongamia glabra [43,44]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Winter rapeseed oil [32]</td>
<td>Laurel [23]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Production of non-edible oil seeds and bio-residues in India [69].

<table>
<thead>
<tr>
<th>Species</th>
<th>Oil faction (%)</th>
<th>Seed estimate (10^6 tones/y)</th>
<th>Oil (tons/ha/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor</td>
<td>45–50</td>
<td>0.25</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Jatropha</td>
<td>50–60</td>
<td>0.20</td>
<td>2.0–3.0</td>
</tr>
<tr>
<td>Mahua</td>
<td>35–40</td>
<td>0.20</td>
<td>1.0–4.0</td>
</tr>
<tr>
<td>Sal</td>
<td>10–12</td>
<td>0.20</td>
<td>1.0–2.0</td>
</tr>
<tr>
<td>Linseed</td>
<td>35–45</td>
<td>0.15</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Neem</td>
<td>20–30</td>
<td>0.10</td>
<td>2.0–3.0</td>
</tr>
<tr>
<td>Pongamia (Karanja)</td>
<td>30–40</td>
<td>0.08</td>
<td>2.0–4.0</td>
</tr>
<tr>
<td>Others</td>
<td>10–50</td>
<td>0.50</td>
<td>0.5–2.0</td>
</tr>
<tr>
<td>Others</td>
<td>10–50</td>
<td>0.50</td>
<td>0.5–2.0</td>
</tr>
</tbody>
</table>

Fig. 1. Chemical structure of vegetable oil [71].

Table 3
Chemical structure of oil, ester and diesel.

<table>
<thead>
<tr>
<th>Chemical structure of Monoglyceride</th>
<th>Chemical structure of Diglyceride</th>
<th>Chemical structure of Fat &amp;Oil</th>
<th>Chemical Structure of Ester</th>
<th>Chemical structure of Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂C–O–COR₁</td>
<td>H₂C–O–COR₂</td>
<td>R₁ H₃C–O–COR₃</td>
<td>C₁₂H₂₃</td>
<td></td>
</tr>
<tr>
<td>H₃C–OH</td>
<td>H₃C–OH</td>
<td>R₂ H₃C–O–COR₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R₃ H₃C–O–COR₅</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chemical structure of Monoglyceride.
Table 4

<table>
<thead>
<tr>
<th>Name of fatty acid</th>
<th>Chemical name of fatty acids</th>
<th>Structure (xx:y)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>Dodecanoic</td>
<td>12:0</td>
<td>C_{12}H_{24}O_{2}</td>
</tr>
<tr>
<td>Myristic</td>
<td>Tetradecanoic</td>
<td>14:0</td>
<td>C_{14}H_{26}O_{2}</td>
</tr>
<tr>
<td>Palmitic</td>
<td>Hexadecanoic</td>
<td>16:0</td>
<td>C_{16}H_{32}O_{2}</td>
</tr>
<tr>
<td>Stearic</td>
<td>Octadecanoic</td>
<td>18:0</td>
<td>C_{18}H_{36}O_{2}</td>
</tr>
<tr>
<td>Oleic cis-9-cis-12-</td>
<td>Octadecenoic</td>
<td>18:2</td>
<td>C_{18}H_{36}O_{2}</td>
</tr>
<tr>
<td>Linolenic</td>
<td>cis-9,cis-12,cis-15-Octadecatrienoic</td>
<td>18:3</td>
<td>C_{18}H_{36}O_{2}</td>
</tr>
<tr>
<td>Arachidic</td>
<td>Eicosanoic</td>
<td>20:0</td>
<td>C_{20}H_{43}O_{2}</td>
</tr>
<tr>
<td>Behenic</td>
<td>Docosanoic</td>
<td>22:0</td>
<td>C_{22}H_{45}O_{2}</td>
</tr>
<tr>
<td>Erucic</td>
<td>cis-13-Docosenoic</td>
<td>22:1</td>
<td>C_{22}H_{45}O_{2}</td>
</tr>
<tr>
<td>Lignoceric</td>
<td>Tetracosanoic</td>
<td>24:0</td>
<td>C_{24}H_{49}O_{2}</td>
</tr>
</tbody>
</table>

Petroleum based diesel fuels have different chemical structures from vegetable oils and esters. The former contain only carbon and hydrogen atoms, which are arranged in normal (straight chain) or branched chain structures, as well as as aromatics configuration. The normal structures preferred for better ignition quality [73]. Diesel fuel can contain both saturated and unsaturated hydrocarbons, but the latter are not present in large enough amounts to make fuel oxidation problem. Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including oxidation problem. Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes) [74]. The average chemical formula for common diesel fuel is C_{12}H_{23}, ranging from approximately C_{10}H_{20} to C_{15}H_{28}.

Vegetable oils contain fatty acid, free fatty acids (generally 1–5%), phospholipids, phosphatides, carotenes, tocopherols, sulfur compound and traces of water [75]. The fatty acids, which are commonly found in vegetable oils, are stearic, palmitic, oleic, linoleic and linolenic. Table 4 summarizes the fatty acid composition of some vegetable oils [4,33,35,64].

Triglyceride molecules have molecular weights between 800 and 900 and are thus nearly four times larger than typical diesel fuel molecules [76]. The various vegetable oils and esters are distinguished by their fatty acid compositions. In Tables 5 and 6 different fatty acids are shown by their respective number of carbon present in the structure of oils and esters.

Table 5 summarized the fatty acid composition of fifty-one samples of vegetable oils and fat. Twenty one fatty acids are screened in all the samples. The fatty acids which are commonly found in vegetable oil and fat are stearic, palmitic, oleic, linoleic. The other fatty acids which are also present in many of the oils and fats are myristic (tetradecanoic), palmitoleic, acachidic, linolenic and octadecatetraenolic. There are many other fatty acids which are also found in oils with the above-mentioned common fatty acids. Lauric fatty acid is present only in bay laurel leaf, coconut, Babassu and Luphea. Myristoleic and ecosenoic fatty acids are found in beef tallow, choice white and poultry fat. Eicosanoic fatty acid is present in beef tallow, choice white, poultry fat, yellow grease and camalina. Behenic, lignoceric fatty acids are detected in peanut kernel and crambe. Erucic fatty acid is found only in three oils, i.e. crambe camellia oil and Brassica carinata.

In the oil of Cotton, Tobbaco, rapeseed, safflower, sunflower, Sesame, linside, palm, corn, soyabea, peanut and rice bran, the content of the fatty acid is different in the same plant species that may be either due to the varital or instrumental difference or in the different parts of plants.

Fatty acid profiles of seed oil methyl esters of 75 plant species having 30% or more fixed oil in their seed/kernel were examined (Table 6). Fatty acid compositions were used to predict the quality of fatty acid methyl esters of oil for use as Biodiesel. Fatty acid methyl ester of oils of 26 species including Azadirachta indica, Calophyllum inophyllum, Jatropha curcas and Pongamia pinnata were found most suitable for use as Biodiesel and they meet the major specification of Biodiesel standards of USA, Germany and European Standard Organization [97].

The fatty acid methyl esters of another 11 species meet the specification of Biodiesel standard of USA only. These selected plants have great potential for Biodiesel [81].

4. Processes or method to produce Biodiesel

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of hydrocarbons-based diesel fuels. The problem with substituting triglycerides for diesel fuel is mostly associated with high viscosity, low volatility and polyunsaturated characters. These can be changed in at least four ways: pyrolysis, microemulsion, dilution and transesterification.

4.1. Pyrolysis

Pyrolysis is a method of conversion of one substance into another by mean of heat or by heat with the aid of the catalyst in the absence of air or oxygen [98]. The process is simple, wasteless, pollution free and effective compared with other cracking processes. The reaction of thermal decomposition is shown in Fig. 2.

4.2. Dilution

The vegetable oil is diluted with petroleum diesel to run the engine. Caterpillar Brazil, in 1980, used pre-combustion chamber engines with the mixture of 10% vegetable oil to maintain total power without any alteration or adjustment to the engine. At that point it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Vegetable oil</th>
<th>Fatty acid composition (wt.%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cottonseed</td>
<td>28.7 - 1.0 - 0.9 - 0.2 - 0.8 - 13.0</td>
<td>[33]</td>
</tr>
<tr>
<td>2.</td>
<td>Cottonseed</td>
<td>28.7 - 1.0 - 0.9 - 0.2 - 0.8 - 13.0</td>
<td>[33]</td>
</tr>
<tr>
<td>3.</td>
<td>Tobacco</td>
<td>10.96 - 0.2 - 3.34</td>
<td>14.54</td>
</tr>
<tr>
<td>4.</td>
<td>Tobacco</td>
<td>10.96 - 0.2 - 3.34</td>
<td>14.54</td>
</tr>
<tr>
<td>5.</td>
<td>Rapseed</td>
<td>3.5 - 0.9 - 0.4 - 0.8 - 0.8 - 0.8 - 24.1</td>
<td>[33]</td>
</tr>
<tr>
<td>6.</td>
<td>Rapseed</td>
<td>3.5 - 0.9 - 0.4 - 0.8 - 0.8 - 0.8 - 24.1</td>
<td>[33]</td>
</tr>
<tr>
<td>7.</td>
<td>Ruffle</td>
<td>7.3 - 1.9 - 1.3 - 1.3 - 1.3 - 1.3</td>
<td>13.6</td>
</tr>
<tr>
<td>8.</td>
<td>Ruffle</td>
<td>7.3 - 1.9 - 1.3 - 1.3 - 1.3 - 1.3</td>
<td>13.6</td>
</tr>
<tr>
<td>9.</td>
<td>H.O. Ruffle</td>
<td>5 - 2 Tr - 0.0</td>
<td>79</td>
</tr>
<tr>
<td>10.</td>
<td>Sunflower</td>
<td>6.4 - 0.1 - 2.9 - 17.7</td>
<td>6.4</td>
</tr>
<tr>
<td>11.</td>
<td>Sunflower</td>
<td>6.4 - 0.1 - 2.9 - 17.7</td>
<td>6.4</td>
</tr>
<tr>
<td>12.</td>
<td>Sesame</td>
<td>13.1 - 3.9 - 52.8</td>
<td>30.2</td>
</tr>
<tr>
<td>13.</td>
<td>Sesame</td>
<td>13.1 - 3.9 - 52.8</td>
<td>30.2</td>
</tr>
<tr>
<td>14.</td>
<td>Linseed</td>
<td>5.1 - 0.3 - 2.5</td>
<td>18.9</td>
</tr>
<tr>
<td>15.</td>
<td>Linseed</td>
<td>5.1 - 0.3 - 2.5</td>
<td>18.9</td>
</tr>
<tr>
<td>16.</td>
<td>Palm</td>
<td>42.6 - 0.3 - 4.4</td>
<td>40.5</td>
</tr>
<tr>
<td>17.</td>
<td>Palm tree</td>
<td>35 - 7</td>
<td>44</td>
</tr>
<tr>
<td>18.</td>
<td>Corn marrow</td>
<td>11.8 - 2.0</td>
<td>24.8</td>
</tr>
<tr>
<td>19.</td>
<td>Corn</td>
<td>12 - 2 Tr</td>
<td>0</td>
</tr>
<tr>
<td>20.</td>
<td>Tallow</td>
<td>23.3 - 0.1</td>
<td>19.3</td>
</tr>
<tr>
<td>21.</td>
<td>Beef tallow</td>
<td>22.98 - 0.50</td>
<td>22.98</td>
</tr>
<tr>
<td>22.</td>
<td>Soybean</td>
<td>13.9 - 0.3</td>
<td>2.1</td>
</tr>
<tr>
<td>23.</td>
<td>Soya bean</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>24.</td>
<td>Soya bean</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>25.</td>
<td>Peanut kernel</td>
<td>11.4</td>
<td>4</td>
</tr>
<tr>
<td>26.</td>
<td>Peanut</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>27.</td>
<td>Hazelnut kernel</td>
<td>4.9</td>
<td>0.2</td>
</tr>
<tr>
<td>28.</td>
<td>Walnut kernel</td>
<td>7.2</td>
<td>0.2</td>
</tr>
<tr>
<td>29.</td>
<td>Almond kernel</td>
<td>6.5</td>
<td>0.5</td>
</tr>
<tr>
<td>30.</td>
<td>Olive kernel</td>
<td>5.0</td>
<td>0.3</td>
</tr>
<tr>
<td>31.</td>
<td>Coconut</td>
<td>19.9</td>
<td>7.8</td>
</tr>
<tr>
<td>32.</td>
<td>Choice white</td>
<td>22.04</td>
<td>5.03</td>
</tr>
<tr>
<td>33.</td>
<td>Poultry fat</td>
<td>22.76</td>
<td>8.37</td>
</tr>
<tr>
<td>34.</td>
<td>Yellow grease</td>
<td>14.26</td>
<td>8.23</td>
</tr>
<tr>
<td>35.</td>
<td>Babassu</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>36.</td>
<td>Cumaru</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>37.</td>
<td>Piqui</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>38.</td>
<td>Castor</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>39.</td>
<td>Poppy seed</td>
<td>12.6</td>
<td>1.0</td>
</tr>
<tr>
<td>40.</td>
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Table 6 (Continued)

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Osa: Other saturated acid; u.k.: unknown; e.a.: elaeostearic acid; K.a.: kamlolenic acid; H.a.: hydnocarpic acid; G.a.: gadoleic acid; X.a.: ximenic acid.

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Excess alcohol is used to shift the equilibrium toward the product because of reversible nature of reaction. For this purpose primary and secondary monohybrid aliphatic alcohols having 1-8 carbon atoms are used [105].

(a) Chemistry of transesterification process: Transesterification consist of a number of consecutive, reversible reactions [14,99]. The triglycerides are converted step wise to triglycerides, monoglyceride and finally glycerol. A mole of ester liberated at each step (Fig. 3).

(i) Alkali catalyzed transesterification: In transesterification method we can use different catalyst. The reaction mechanism for alkali catalyzed transesterification was formulated in three steps [106] as explained in Fig. 4. The first step is an attack on the carbonyl carbon atom of the triglycerides molecule by the anion of the alcohol (Methoxide ion) to form a tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of alcohol (methoxide ion). In the last step, rearrangement of tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. When NaOH, KOH, K$_2$CO$_3$ or other similar catalysts were mixed with alcohol, the actual catalysts, alkoxide group is formed [107]. Kim et al [108] have developed a process for the production of Biodiesel from vegetable oils using heterogeneous catalyst Na$_2$CO$_3$/Al$_2$O$_3$. These catalysts showed almost the same activity under the optimized reaction conditions compared to conventional homogeneous NaOH catalyst. For an alkali catalyzed transesterification, the glycericed and alcohol must be substantially anhydrous [109] because water makes the reaction partially change to saponification, which produces soap. A number of researchers have worked with feed stokes that have elevated FFA (free fatty acid) levels [61,110–113]. However, in most cases, alkaline catalysts have been used and the FFAs (free fatty acids) were removed from the process stream as soap and considered waste. Waste greases typically contain from 10 to 25% FFAs. This is far beyond the level that can be converted to Biodiesel using an alkali catalyst.

![Fig. 3. Transesterification reaction.](image-url)
Acid catalyst transesterification: An alternative process is to use acid catalyst that some researchers have claimed are more tolerant of free fatty acids [114–116]. The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Fig. 5: However, it can be extended to di- and triglycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst. We can use acid alkali and biocatalyst in transesterification method. If more water and free fatty acids are in triglycerides, acid catalyst can be used [117]. Transemethylation occur approximately 4000 times faster in the presence of an alkali catalyst than those catalyzed by the same amount of acidic catalyst [118].

Lipase catalyst transesterification: This transesterification process is like alkali transesterification, only ratio of catalyst and solvent a stirring time different, and in this transesterification we have used lipase catalyst. The process is explained in the following Fig. 6.

Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones [119]. Thus, in general, the efficiency of the transesterification of triglycerides with methanol (methanlysis) is likely to be very low compared to that with ethanol in systems with or without a solvent.

Various studies have been conducted for transesterification reaction for different catalyst, alcohol and molar ratios at different temperature. The results and experimental conditions of some studies are summarized in Tables 7 and 8.

Various types of alcohols – primary, secondary, and straight- and branched-chain – can be employed in transesterification using lipases as catalysts (Table 8). Linko et al. [128] have demonstrated the production of a variety of biodegradable esters and polyesters with lipase as the biocatalyst. In the transesterification of rapeseed oil with 2-ethyl-l-hexanol, 97% conversions of esters was obtained using Candida rugosa lipase powder. De et al. [129] investigated the conversion of fatty alcohol esters (C4–C18:1) using immobilized Rhizomucor miehei lipase (Lipozyme IM-20) in a solvent-free system. The percentage of molar conversions of all corresponding alcohol esters ranged from 86.8 to 99.2%, while the slip melting points of the esters were found to increase steadily with increasing alcohol chain length (from C4 to C18), and to decline with the incorporation of unsaturation for the same chain length (as from C18 to C18:1). Transesterification of the triglycerides sunflower oil, fish oil, and grease with ethanol, i.e. ethanolysis, has also been studied. In each case, high yields beyond 80% could be achieved using the lipases from M. miehei [130], Candida antarctica [131], Pseudomonas cepacia [132], respectively. Nelson et al. [133]
investigated the abilities of lipases in transesterification with short-chain alcohols to give alkyl esters. The lipase from *M. miehei* was the most efficient for converting triglycerides to their alkyl esters with primary alcohols, whereas that from *C. antarctica* was the most efficient for transesterifying triglycerides with secondary alcohols to give branched alkyl esters. Maximum conversions of 94.8–98.5% for the primary alcohols methanol, ethanol, propanol, butanol, and isobutanol, and of 61.2–83.8% for the secondary alcohols isopropanol and 2-butanol were obtained in the presence of hexane as a solvent. In solvent-free reactions, however, yields with methanol and ethanol were lower than those obtained with hexane; in particular, the yield with methanol decreased to 19.4%. Mittelbach [134] reported transesterification using the primary alcohols methanol, ethanol, and 1-butanol, with and without petroleum ether as a solvent. Although the ester yields with ethanol and 1-butanol were relatively high, even in reactions without a solvent, with methanol only traces of methyl esters were obtained. Abigor et al. [135] also found that in the conversion of palm kernel oil to alkyl esters using *p. cepacia* lipase, ethanol gave the highest conversion of 72%, while only 15% methyl esters was obtained with methanol. Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones [119]. Thus, in general, the efficiency of the transesterification of triglycerides with methanol (methanolysis) is likely to be very low compared to that with ethanol in systems with or without a solvent.

5. Properties of alternative fuel or diesel

5.1. Properties of oil

The vegetative oils are mainly characterized by some fuel related properties. Some of them are listed in Table 9 [3,139]. The kinematics viscosity of vegetable oils varies in the range of 30–40 cSt at 38 °C. High viscosity of these oils is due to large molecular mass and chemical structure. The fatty acid methyl esters of seed oils and fats have already been found suitable for use as fuel in diesel engine [140] because transesterification provides a fuel viscosity that is close to that diesel.

Vegetable oils have high molecular weights in the range of 600–900, which are three or more times higher than diesel fuels. The volumetric heating values of these oils are in the range of 39–
Table 9
Vegetable oil | Kinematic viscosity at 38 °C (mm²/s) | Cetane No. | Heating Value (MJ/kg) | Cloud Point (°C) | Pour Point (°C) | Flash Point (°C) | Density (kg/l) | Carbon residue (wt.%) |
---|---|---|---|---|---|---|---|---|
Corn | 34.9 | 37.6 | 39.5 | – | – | 277 | 0.9095 | 0.24 |
Cottonseed | 33.5 | 41.8 | 39.5 | 1.7 | – | 273 | 0.9148 | 0.24 |
Crambe | 53.6 | 44.6 | 40.5 | 12.8 | – | 271 | 0.9026 | 0.24 |
Linseed | 27.2 | 34.6 | 39.3 | – | – | 241 | 0.9236 | 0.22 |
Peanut | 39.6 | 41.8 | 39.8 | – | – | 264 | 0.9115 | 0.30 |
Rapeseed | 37.0 | 37.6 | 39.7 | – | – | 265 | 0.9144 | 0.25 |
Safflower | 31.3 | 41.3 | 39.5 | 18.3 | – | 260 | 0.9113 | 0.24 |
Sesame | 35.5 | 40.2 | 39.3 | – | – | 260 | 0.9138 | 0.25 |
Soya bean | 32.6 | 37.9 | 39.6 | – | – | 260 | 0.9180 | 0.23 |
Sunflower | 33.9 | 37.1 | 39.6 | 7.2 | – | 274 | 0.9161 | 0.27 |
Palm | 39.6 | 42.0 | – | – | 267 | 0.9180 | 0.23 |
Babassu | 30.3 | 38.0 | – | 20.0 | – | 150 | 0.9460 | – |
Diesel | 3.06 | 50 | 43.8 | – | – | 76 | 0.855 | – |

40 MJ/kg, which are low, compared to diesel fuels (about 45 MJ/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The cetane numbers are in the range of 34–42. The cloud and pour points of vegetable oils are higher than that of diesel fuels.

5.2. Properties of Biodiesel

The characteristics of Biodiesel are close to diesel fuels, and therefore Biodiesel becomes a strong source to replace the diesel fuels. The conversion of triglycerides into methyl or ethyl esters through the transesterification process, reduces the molecular weight to one-third that of the triglyceride and also reduces the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to diesel fuels. These esters contain 10–11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine. The cetane number of Biodiesel is around 50. The use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties. Since the volatility increases marginally, the starting problem persists in cold climates. Four cold flow improver additives were tested at 0.1–2% with pour point depressants, toward the objective of identifying approaches to transport and mix Biodiesel with diesel in cold climates. Four cold flow improver additive were tested at 0.1–2% in B80, B90, and B100 blends. Two additives significantly—a mixture of 0.2% additives, 79.8% Biodiesel, and 20% kerosene reduced the pour point of B100 by 27 °C. The unrefined Biodiesels showed higher lubricity properties than refined Biodiesel. The chemical factors influencing the lubricity properties of Biodiesels were investigated by Hu et al. [146]. Methyl ester and monoglycerides are the main composition that determines the lubricity of Biodiesel that meets international standards. Free fatty acids and diglycerides can also affect the lubricity of Biodiesel, but not so much as monoglycerides.

Biodiesel is considered clean fuel it has no sulphur no aromatics and has about 10% built in oxygen, which helps it to burn fully its higher cetane number improves the ignition quality even when blended in the petroleum diesel.

It is a general property of hydrocarbons that the auto-ignition temperature is higher for more volatile hydrocarbons. Therefore, the less volatile middle distillate fractions of crude oil boiling in the range of 250–370 °C are suitable as diesel fuels. The hydrocarbons present in the diesel fuels include parafins, naphthenes, olefins and aromatics. Carbon numbers of these hydrocarbons ranges from 12 to 18.

5.3. Determination and measurement methods for oil/Biodiesel properties

The properties of the methyl esters were determined by methods specified in the Handbook of Analytical Methods for Fatty Acid Methyl Esters as Diesel Substitutes [147] or by equivalent standard methods, which given in Table 11.

A considerable amount of experience exists in the U.S. with a 20% blend of Biodiesel with 80% diesel fuel (B20). Although Biodiesel (B100) can be used, blends of over 20% Biodiesel with diesel fuel should be evaluated on a case-by-case basis until further experience is available [148]. Table 12 shows the Comparison of properties of diesel and Biodiesel Acid value, viscosity and density were determined according to ISO 660, 3104 and 3675, respectively. Ash content, cloud point and pour point were measured using BS 2000, cold filter plug point (CFPP) using BS 6188 and iodine value using DIN 53241. Total and free glycerine were
determined enzymatically [147]. Methanol content was measured by gas chromatography using a Porapak Q column (Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire), 900 mm × 3 mm at 90 °C, injector at 110 °C, 25 ml/min nitrogen flow, and flame ionization detector. Lubricating oils were screened for the presence of methyl esters by thin-layer chromatography [150,151]. If detected they were determined quantitatively by following the method: lubricating oil (5 g) was saponified [152] and the molar amount of methyl ester in the oil was calculated from the difference in titre volumes between the original and used oils. The percentage of methyl ester in the used oil was determined by dividing the molar amount in the used oil by the molar amount in 5 g methyl ester, also determined by saponification.

6. Performance of alternative fuel (oil and Biodiesel) as a fuel

6.1. Use of oils as fuel and their performance

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines [3,4]. During World War II Seddon [153] experimented with using several different vegetable oils in Perkins P-6 diesel engine with great success and concluded that vegetable oils could be used to power a vehicle under normal operating conditions. However it was noted that much more work was needed before vegetable oils used as a reliable substitute for diesel fuel. Bruwer et al. [154] studied the use of sunflower seed oil as a renewable energy source. When operating tractor with 100% sunflower oil instead of diesel fuel, an 8% power loss occurred after 1000 h of operation, which was corrected by replacing the fuel injector, and injector pump. Yarbrough et al. [155] reported that raw sunflower oils were found to be unsuitable fuel, while refined sunflower oil was found to be satisfactory. Tahir et al. [156] reported that oxidation of sunflower oil left heavy gum and wax deposits on tested tractor, which could lead to engine failure. Bettis et al. [157] and Engler et al. [158] reported that the sunflower seed oil is acceptable only for short-term use as a fuel source but long term durability test indicated severe problems due to carbonization of combustion chamber. Goering et al. [159] studied the characteristic properties of eleven vegetable oils to determine which oil would be best suited for use as an alternative fuel source. Bacon et al. [160] evaluated the use of several vegetable oils as potential fuel sources and reported that use of these oils caused carbon build up in the combustion chamber. Schoedder [161] used rapeseed oil as a diesel fuel replacement in Germany with mixed results. Short-term engine tests indicated similar energy outputs in both rapeseed oil and diesel fuel. Initial long-term engine tests showed that difficulties arose in engine operation after 100 h due to deposits on piston rings, valves and injectors. Auld et al. [162] analyze rapeseed oil and showed a relationship between viscosity and fatty acid chain length. Bettis et al. [157] reported that rapeseed oil contained 94–95% of the energy content of diesel fuel, and to be approximately 15 times viscous. Reid et al. [163] evaluated chemical and physical properties of 14 vegetable oils. They pointed out that the oils are very differently from petroleum-based fuel because of ‘high viscosity’. Engine test showed that carbon deposits in the engine were reduced if the oil was heated prior to combustion. It was also noted that carbon deposit levels differed from oils with similar viscosities because of oil composition.

6.2. Need of blending and its effect on performance

Engelman et al. [164] reported that 10–50% soybean oil fuel blends with diesel minimize the carbon deposition in combustion chamber. Quick [165] used over 30 different vegetable oils to operate compression engines and reported that the use of raw vegetable oil fuels can lead to premature engine failure. Blending vegetable oils with diesel fuel was found to be a method to reduce choking and extend engine life. Sims et al. [166] indicated that short-term engine tests with 50% vegetable oil fuel blend had no adverse effects. Carbon deposits on combustion chamber components was found to be approximately same as that found in engines operated on 100% diesel fuel. The similar results were reported by Bartholomew [167], Barsic and Humke [168], Fort et al. [169], Baranescu and Lusco [170], Worgetter [171], Wanger and Peterson.

Table 11

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Method</th>
<th>Limits</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash Point</td>
<td>D93</td>
<td>130 min</td>
<td>C</td>
</tr>
<tr>
<td>Water &amp; Sediment</td>
<td>D2709</td>
<td>0.050 max</td>
<td>%vol.</td>
</tr>
<tr>
<td>Kinematic Viscosity (40 °C)</td>
<td>D445</td>
<td>1.9–6.0</td>
<td>mm²/s</td>
</tr>
<tr>
<td>Sulfated Ash</td>
<td>D874</td>
<td>0.020 max.</td>
<td>%mass</td>
</tr>
<tr>
<td>Sulfur</td>
<td>D5453.</td>
<td>0.05 max</td>
<td>%mass</td>
</tr>
<tr>
<td>Copper Strip Corrosion</td>
<td>D130</td>
<td>No. 3 max.</td>
<td></td>
</tr>
<tr>
<td>Cetane</td>
<td>D613</td>
<td>47 min</td>
<td></td>
</tr>
<tr>
<td>Cloud Point</td>
<td>D2500</td>
<td>Report</td>
<td>C</td>
</tr>
<tr>
<td>Carbon Residue (100% Sample)</td>
<td>D4530*</td>
<td>0.050 max</td>
<td>% mass</td>
</tr>
<tr>
<td>Acid Number</td>
<td>D664</td>
<td>0.80 max</td>
<td>Mg KOH/g</td>
</tr>
<tr>
<td>Free Glycerin</td>
<td>D6584</td>
<td>0.020 max</td>
<td>%mass</td>
</tr>
<tr>
<td>Total Glycerin</td>
<td>D6584</td>
<td>0.240 max</td>
<td>%mass</td>
</tr>
<tr>
<td>Phosphorous Content</td>
<td>D4951</td>
<td>0.001 max</td>
<td>%mass</td>
</tr>
<tr>
<td>Distillation Temperature, Atmospheric Equivalent Temperature (90% Recovered)</td>
<td>D1160</td>
<td>360 max</td>
<td>C</td>
</tr>
</tbody>
</table>

*The carbon residue shall be run on the 100% sample.

**Table 12**

Comparison of fuel properties between diesel and Biodiesel.

<table>
<thead>
<tr>
<th>Fuel Property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Standard</td>
<td>ASTM D975</td>
<td>ASTM PS 121</td>
</tr>
<tr>
<td>Fuel composition</td>
<td>C10-C21 HC</td>
<td>C12-C22 FAME</td>
</tr>
<tr>
<td>Lower Heating Value (Btu/gal)</td>
<td>131.295</td>
<td>117.093</td>
</tr>
<tr>
<td>Kin, Viscosity, @ 40 °C</td>
<td>1.3–4.1</td>
<td>1.9–6.0</td>
</tr>
<tr>
<td>Specific Gravity kg/l @ 60 °F</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>Density, lb/gal @ 15 °C</td>
<td>7.079</td>
<td>7.328</td>
</tr>
<tr>
<td>Water, ppm by wt.</td>
<td>161</td>
<td>0.05% max</td>
</tr>
<tr>
<td>Carbon (wt.%)</td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen (wt.%)</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen, by dif. wt.%</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Sulfur (wt.%)</td>
<td>.05 max</td>
<td>0.0 - 0.0024</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>188–343</td>
<td>182–338</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>60–80</td>
<td>100–170</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>-15 to 5</td>
<td>-3 to 12</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-35 to -15</td>
<td>-15 to 10</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>40–55</td>
<td>48–65</td>
</tr>
<tr>
<td>Stoichiometric Air/Fuel Ratio (w/w)</td>
<td>15</td>
<td>13.8</td>
</tr>
<tr>
<td>BOCLE Scuff (g)</td>
<td>3.600</td>
<td>&gt;7.000</td>
</tr>
<tr>
<td>HFR (μm)</td>
<td>685</td>
<td>314</td>
</tr>
</tbody>
</table>

Source: [149].
[172] and Vander Walt and Hugo [173] working on different oils such as pea nut oil, cottonseed oil, sunflower oil, rapeseed oil, and sunflower oil respectively. German et al. [174] reported that carbon deposits on the internal engine components were greater for the tractor fueled with 50/50 sunflower oil/diesel than those fueled with a 25/75 sunflower/diesel fuel blend. Sapaun et al. [175] reported that power output was nearly the same for palm oil, blend of palm oil and diesel fuel, and 100% diesel fuel. Short-term using of palm oil fuel showed no adverse effects. Hofman et al. [176] and Peterson et al. [177] indicated that while vegetative oil fuel blends had encouraging results in short term testing, problems occurred in long term durability tests. Peses and Stanisloa (1984) [178] used a one to one blend of vegetable oil and diesel fuel to study the piston rings deposits. Premature piston ring sticking and carbon built up due to the use of the one to one fuel blend caused engine failure. These investigators suggested that to reduce piston ring deposits a fuel additive or a fuel blend with less vegetative oil was needed. The atomization and injection characteristic of vegetative oils were significantly different from that of diesel fuel due to the higher viscosity of the vegetative oils [179]. Engine performance tests showed that power output slightly decreased when using vegetable oil fuel blends. Nag et al. [180] showed that performance tests using fuel blend as great as 50–50 seed oil from the Indian Amla seed plant and diesel fuel exhibited no loss of power. Knock free performance with no observable carbon deposits on the functional parts of the combustion chamber were observed during these tests. McCutchen [181] compared engine performance of direct injection engine to indirect injection engines when fueled with 30% soybean oil 70% diesel fuel. The result showed that indirect injection could be operated on this fuel blend while the direct injection engine could not without catastrophic engine failure occurring. The direct injection engines showed injector coking and piston ring sticking as a result of using sunflower oil. McDonnell et al. [182] studied the use of a semi-refined rapeseed oil as a diesel fuel extender. Test results indicated that the rapeseed oil could serve as a fuel extender at inclusion rates up to 25%. As a result of using rapeseed oil as a fuel, injector life was shortened due to carbon build up.

6.3. Use of esters as fuel and their performance

Usta [54] showed that tobacco seed oil methyl ester can be partially substituted for the diesel fuel at most operating conditions in term of performance parameter and emissions without any engine modification and preheating of the blends. Frohlich and Rice [37] reported that in vehicle tests, the reduction in fuel economy with camellia methyl ester did not lead to a more rapid deterioration of the lubricating oil. Kallligeros et al. [183] reported that the engine was fueled with pure marine diesel fuel and blends containing two types of Biodiesel, at proportion up to 50%, the performance was satisfactory. Monyem and Van Gerpen [184] evaluated the impact of oxidized Biodiesel on engine performance and emission. A John Deere 4276 turbocharged DI diesel engine was fueled with oxidized and unoxidized Biodiesel and the performance and emission were compared with No. 2 diesel fuel. The engine performance of the neat Biodiesels and their blends was similar to that of No. 2 diesel fuel with the same thermal efficiency, but higher fuel consumption. Machacon et al. [185] studied the operation of the test engine with pure coconut oil and coconut oil diesel fuel blends for a wide range of engine load condition was shown to be successful even without engine modification. It was also shown that increasing the amount of coconut oil in the coconut oil–diesel fuel blend resulted in lower smoke and NOx emission. Tan [26] estimated reduction in net CO2 emission at 77–104 g/kWh of diesel replaced by Biodiesel. He predicted reduction in CO2 emission which are much greater than values reported in recent studied on Biodiesel derived from other vegetable oils, due to both the large amount of potential fuel in the residual biomass and to the lower energy input the traditional coconut farming techniques. Wang [186] shown that the heavy trucks fueled by B35 emitted significantly lower particulate matter (PM) and moderately lower carbon monoxide (CO) and hydrocarbon (HC) than the same trucks fueled by number 2 diesel (D2). Oxides of nitrogen (NOx) emission from B35 and D2, however, were generally in the same level. Clark et al. [187] reported that the derivatives particularly the methyl esters of rapeseed, soybean and other seed oils have been shown to be similar to diesel fuel in performance. Mittelbach et al. [188] examined that the exhaust from combustion of the vegetative oil esters is lower in carbon monoxide and particulate content but higher in nitrogen oxide than diesel fuel. Peterson et al. [112] used ethyl ester of rapeseed as a Biodiesel and reported that no problems or unusual events were encountered with the truck's operation. The truck was completely unmodified as to the engine and fuel system. However, the Biodiesels were considerably less volatile than the conventional diesel fuel. Peterson et al. [6] stated that the Biodiesel esters can be used directly or as blends with diesel fuel in a diesel engine.

Kalam and Masjuki [52] evaluate the effect of anticorrosion additive in Biodiesel isolated from palm as a palm ester on diesel engines performance, emission and wear characteristics. Cardone et al. [36] used the non-food use of *Brassica carinata* oil for Biodiesel production. The Biodiesel, produced by transesterification of the oil extracted from the *Brassica carinata* seeds, displayed physical-chemical properties suitable for the use as diesel car fuel. Raheman and Phadate [43] used the blend of the *Pongamia pinnata* methyl ester and diesel to evaluate the diesel engine emissions and performance and found reduction in exhaust emission together with increase in torque, brake power, brake thermal efficiency and reduction in brake-specific, fuel consumption. The blends of *Pongamia pinnata* esterfide oil is a suitable alternative fuel for diesel and could help in controlling air pollution. Carretetto et al. [189] checked the operation of a Biodiesel fueled boiler for some months and stated that the Biodiesel seems to be a promising solution for boilers with only minor adjustments and the performances are comparable with oil operation. Carbon monoxide emission is reduced but no NOx are increased. Shi et al. [190] prepared blend of 20% (v/v) ethanol/methyl soyate and observed that particulate matters decreased with increasing oxygenate content in the fuel but nitrogen oxide (NOx) emission increased. Spataru and Romig [191] and Schumacher and Bolgert [192] both studied several blends of No. 2 diesel and SME or canola methyl ester (CME) to determine and compare engine emission from the Detroit Diesel corporation (DDC) 6V92TA engine (a type of diesel engine widely used in transit buses and heavy trucks) operated on those fuels. Grabaski et al. [193] also employed a 1991 DDC series 60 engine to determine emission of NOx, CO, HC, and PM that result from blending Biodiesel (methyl soy ester) and conventional diesel. The test showed that as the percentage of Biodiesel blend in fuel increased, the NOx increased but HC, CO, and PM decreased. Schumacher and Peterson [191,194] both conducted about 100,000 mi of road test on Cummins B5 9L engine running on 100% Biodiesel in Dodge pickups. No fuel related problems were noted during the tests on the modification trucks. Both emission test results showed that CO, HC, and smoke exhaust emission from Biodiesel tend to be lower. Chang et al. [195] studied the effects of using blends of methyl and isopropyl ester of soybean oil with no 2 diesel at several steady state operational conditions in a four-cylinder turbocharged John Deer 4276T engine. Both methyl and isopropyl ester provided significant reductions in PM emission as compared with no. 2 diesel fuels. Emission of CO, and HC were also reduced significantly, but NOx increased by about 12%. The fatty acid methyl esters of seed oils and fats and have already been found
suitable for use as fuel in diesel engine [140] because transesterification provides a fuel viscosity that is close to that of diesel fuel. In India the prohibitive cost of edible oils prevent their use in Biodiesel, but non edible oils are affordable for Biodiesel production. The main commodity sources for Biodiesel in India can be non-edible oils obtained from plant species such as jatropha curcas (ratanjyot), Pongamia pinnata (Karanj), Calophyllum inophyllum (Nagchampa), Hevca brasiliensis (Rubber), etc. Biodiesel can be blended at any level with petroleum diesel to create a Biodiesel blend or can be use in its pure form just like petroleum diesel. The diesel engines operated by Biodiesel are required very little or low engine modification because Biodiesel has properties similar to petroleum diesel fuels. It can be stored just like a petroleum diesel fuel and hence does not require separate infrastructure.

7. Problems arises and their solution during the use of alternative fuels

7.1. Problem arises during the use of oil

There are many problems associated with direct use of oil in engine. A potential solution has been given to overcome from these problems caused by use of vegetative oil at the place of petroleum diesel (Table 13).

These effects can be reduced or eliminated using filtered, frying oil and the blend of 95% used cooking oil and 5% diesel fuel [196]. Due to their high viscosity (about 11–17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines [33]. Different ways have been considered to reduce the high viscosity of vegetable oils:

(a) dilution of 25 parts of vegetable oil with 75 parts of diesel fuel, (b) microemulsions with short chain alcohols such as ethanol or methanol, (c) thermal decomposition, which produces alkanes, alkenes, carboxylic acids, (d) catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes, and (e) transesterification with ethanol or methanol.

7.2. Problem arises during the use of Biodiesel

The technical disadvantages of Biodiesel/fossil diesel blends include problems with fuel freezing in cold weather, reduced energy density, and degradation of fuel under storage for prolonged periods. One additional problem is encountered when blends are first introduced into equipment that has a long history of pure hydrocarbon usage. Hydrocarbon fuels typically form a layer of deposits on the inside of tanks, hoses, etc. Biodiesel blends loosen these deposits, causing them to block fuel filters. However, this is a minor problem, easily remedied by proper filter maintenance during the period following introduction of the Biodiesel blend [200].

The disadvantages of Biodiesel are:

- Constraints on the availability of agricultural feedstock impose limits on the possible contribution of Biodiesels to transport.
- The kinematic viscosity is higher than diesel fuel. This affects fuel atomization during injection and requires modified fuel injection systems.
- Due to the high oxygen content, it produces relatively high NOx levels during combustion.
- Oxidation stability is lower than that of diesel so that under extended storage conditions it is possible to produce oxidation products that may be harmful to the vehicle components.
- Biodiesel is hygroscopic. Contact with humid air must be avoided.
- Production of Biodiesel is not sufficiently standardised. Biodiesel that is outside European or US standards can cause corrosion, fuel system blockage, seal failures, filter clogging and deposits at injection pumps.
- The lower volumetric energy density of Biodiesel means that more fuel needs to be transported for the same distance travelled.
- It can cause dilution of engine lubricant oil, requiring more frequent oil change than in standard diesel-fueled engines.
- A modified refuelling infrastructure is needed to handle Biodiesels, which adds to their total cost.

8. Economic viability of Biodiesel

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. The remaining challenges are its cost and limited availability of fat and oil resources. There are two aspects of the cost of Biodiesel, the costs of raw material (fats and oils) and the cost of processing. The cost of raw materials accounts for 60–75% of the total cost of Biodiesel fuel [98].

<table>
<thead>
<tr>
<th>Problem</th>
<th>Probable cause</th>
<th>Potential solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short-term Cold weather starting</td>
<td>High viscosity, low cetane, and low flash point of vegetable oils</td>
<td>Preheat fuel prior to injection. Chemically alter fuel to an ester</td>
</tr>
<tr>
<td>Plugging and gumming of filters, lines and injectors</td>
<td>Natural gums (phosphatides) in vegetable oil. Other ash</td>
<td>Partially refine the oil to remove gums. Filter to 4-μm</td>
</tr>
<tr>
<td>Engine knocking</td>
<td>Very low cetane of some oils. Improper injection timing</td>
<td>Adjust injection timing. Use higher compression engines.</td>
</tr>
<tr>
<td>Long-term Coking of injectors on Piston and head of engine</td>
<td>High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils</td>
<td>Preheat fuel prior to injection. Chemically alter fuel to an ester</td>
</tr>
<tr>
<td>Carbon deposits on Piston and head of engine</td>
<td>High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils</td>
<td>Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester</td>
</tr>
<tr>
<td>Excessive engine wear</td>
<td>High viscosity of oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubrication oil due to blow-by of vegetable oil</td>
<td>Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester</td>
</tr>
<tr>
<td>Failure of engine lubricating oil due to Polymerization</td>
<td>Collection of polyunsaturated Vegetable oil blow-by in crankcase to the point where polymerization Occurs vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation</td>
<td>Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester. Increase motor oil changes. Motor oil additives to inhibit oxidation</td>
</tr>
</tbody>
</table>
The use of used cooking oil can lower the cost significantly. However, the quality of used cooking oils can be bad [198]. Studies are needed to find a cheaper way to utilize used cooking oils to make Biodiesel fuel. There are several choices, first removing free fatty acids from used cooking oil before transesterification, using acid catalyzed transesterification, or using high pressure and temperature [199]. In terms of production cost, there also are two aspects, the transesterification process and by-product (glycerol) recovery. A continuous transesterification process is one choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Because little water is present in the system, the Biodiesel glycerol is more concentrated. Unlike the traditional soap glycerol recovery process, the energy required to recover Biodiesel glycerol is lower due to the elimination of the evaporation process. In addition, the process is also simpler than soap glycerol recovery since there is a negligible amount of soap in Biodiesel glycerol.

This implies that the cost of recovering high quality glycerol from Biodiesel glycerol is lower than that of soap glycerol and that the cost of Biodiesel fuel can be lowered if a Biodiesel plant has its own glycerol recovery facility. With the increase in global human population, more land may be needed to produce food for human consumption (indirectly via animal feed). So insufficient land may also increase the production cost of Biodiesel plants. The problem already exists in Asia where vegetable oil prices are relatively high. The same trend will eventually happen in the rest of the world. This is the potential challenge to Biodiesel production. Biodiesel can be used most effectively as a supplement to other energy forms. Biodiesel is particularly useful in mining and marine situations where lower pollution levels are important. Biodiesel also can lower US dependence on imported petroleum based fuel.

9. Conclusion

In recent years, Biodiesel has become more attractive as an alternative fuel for diesel engines because of its environmental benefits and the fact that it is made from renewable resources. Several methods available for producing Biodiesel, transesterification of natural oils and fats are currently the method of choice. The purpose of the process is to lower the viscosity of the oil or fat. Researchers focused mainly the edible oils to produce the Biodiesel because of easily availability and familiarity. Very few researchers concentrated on Non edible oil for the same purpose. Non-edible oils can also be utilized for making Biodiesel fuel. For the production of Biodiesel fuel, an alkali-catalysis process has been established that gives high conversion levels of oils to methyl esters. Enzymatic processes using both extra cellular and intracellular lipases have recently been developed. The cost of lipase production is the main hurdle to commercialization of the lipase-catalyzed process; several attempts have been made to develop cost-effective systems. In terms of production cost, there also are two aspects, the transesterification process and by-product (glycerol) recovery. A continuous transesterification process is one choice to lower the production cost. The foundations of this process are a shorter reaction time and greater production capacity. The recovery of high quality glycerol is another way to lower production cost. Land may be a cost increasing factor for Biodiesel production, because of more and more land required to live the growing population. To overcome the land problem, the high yielding Biodiesel plants (non edible producing plants) should be grown in marginal and waste land areas.

References


Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

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Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

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tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.

Anonymous. The wealth of India: raw materials, vol. VII. New Delhi: Publica-

tion & Information Directorate, Council of Scientific & Industrial Research; 1959.


Hofman, Kaufman JD, Helgeson D, Dinusson WE. Sunflower oil as power NDSU Cooperative Extension service circular AE-735. Fargo, ND; 1981.


[196] Anon.. Filtered used frying fat powers diesel feet. JAOCS 1982;59:780A–1A.


Biodiesel is a notable alternative to the widely used petroleum-derived diesel fuel since it can be generated by domestic natural sources such as soybeans, rapeseeds, coconuts, and even recycled cooking oil, and thus reduces dependence on diminishing petroleum fuel from foreign sources. The injection and atomization characteristics of the vegetable oils are significantly different than those of petroleum-derived diesel fuels, mainly as the result of their high viscosities. Modern diesel engines have fuel-injection system that is sensitive to viscosity change. One way to avoid these problems is to reduce fuel viscosity of vegetable oil in order to improve its performance. The conversion of vegetable oils into biodiesel is an effective way to overcome all the problems associated with the vegetable oils. Dilution, micro-emulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. Transesterification is the most common method and leads to monoalcohol esters of vegetable oils and fats, now called biodiesel when used for fuel purposes. The methyl ester produced by transesterification of vegetable oil has a high cetane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions.

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1. Introduction

During the past 25 years, worldwide petroleum consumption has steadily increased, resulting in higher standards of living, increased transportation and trucking, and increased use of plastics and other petrochemicals [1]. In 1985, total worldwide petroleum consumption was 2807 million tons, but in 2008, the figure reached 3928 million tons [2], with an average annual growth rate of almost 1.5%. However, the petroleum is a finite source for fuel that is rapidly becoming scarcer and more expensive [3]. At the end of 2008, according to BP’s annual Statistical Review of World Energy [2], the world proven oil reserves were estimated at 1.7 × 10¹¹ tons with a reserve-to-production (R/P) ratio of 42 years. In addition, petroleum-based products are one of the main causes of anthropogenic carbon dioxide (CO₂) emissions to the atmosphere. Today, the transportation sector worldwide is almost entirely dependent on petroleum-derived fuels. One-fifth of global CO₂ emissions are created by the transport sector [4], which accounts for some 60% of global oil consumption [5]. Around the world, there were about 806 million cars and light trucks on the road in 2007 [6]. These numbers are projected to increase to 1.3 billion by 2030 and to over 2 billion vehicles by 2050 [7]. This growth will affect the stability of ecosystems and global climate as well as global oil reserves [8,9]. There are active research programs to reduce reliance on fossil fuels by the use of alternative and sustainable fuel sources, and thus to increase the time over which fossil fuels will still be available [10]. As an alternative to petroleum-based transportation fuels, bio-fuels can help to reinforce energy security and reduce the emissions of both greenhouse gases (GHGs) and urban air pollutants.

The term bio-fuel is referred to as liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. A variety of fuels can be produced from biomass resources including liquid fuels, such as bioethanol, methanol, biodiesel, Fischer–Tropsch diesel, and gaseous fuels, such as hydrogen and methane [11]. Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. Biodiesel production is a very modern and technological area for testing and materials) and the European standard EN 14214. The biodiesel is characterized by determining its physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pour point, gross heat of combustion and volatility. In general, biodiesel compares well to petroleum-based diesel (Table 1) [13].

The advantages of biodiesel as diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number and higher biodegradability [14]. The main disadvantages of biodiesel as diesel fuel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide emission, lower engine speed and power, injector coking, engine compatibility, high price, and higher engine wear [15]. Biodiesel offers safety benefits over diesel fuel because it is much less combustible, with a flash point greater than 423 K compared to 350 K for petroleum-based diesel fuel [16]. Biodiesel has a higher cetane number (around 50) than diesel fuel [17], no aromatics, no sulfur, and contains 10–11% oxygen by weight [18]. The cetane number is a commonly used indicator for the determination of diesel fuel quality, especially the ignition quality. It measures the readiness of the fuel to auto-ignite when injected into the engine. Ignition quality is one of the properties of biodiesel that is determined by the structure of the fatty acid methyl ester (FAME) component [19]. Viscosity is the most important property of biodiesel since it affects the operation of the fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. Biodiesel has a viscosity close to that of diesel fuels. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors [20].

Elemental composition and relative amounts of compounds present in biodiesel and diesel fuel are given in Tables 2 and 3. Due to presence of electronegative element oxygen, biodiesel is slightly more polar than diesel fuel as a result viscosity of biodiesel is higher than diesel fuel. Presence of elemental oxygen lowers the heating value of biodiesel when compared to the diesel fuel [21].

The lower heating value (LHV) is the most common value used for engine applications. It is used as an indicator of the energy content of the fuel. Biodiesel generally has a LHV that is 12% less than

2. Fuel characteristics of biodiesel

2.1. Technical characteristics of biodiesel as a transportation fuel

Biodiesel is a cleaner burning alternative to petroleum-based diesel fuel. Just like petroleum-based diesel fuel, biodiesel operates in the compression ignition (diesel) engines. The successful introduction and commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN 14214. The biodiesel is characterized by determining its physical

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>ASTM D975</td>
<td>ASTM D6751</td>
</tr>
<tr>
<td>Composition</td>
<td>HC² (C10–C21)</td>
<td>FAME³ (C12–C22)</td>
</tr>
<tr>
<td>Kin. viscosity (mm²/s)</td>
<td>1.9–4.1</td>
<td>1.9–6.0</td>
</tr>
<tr>
<td>Specific gravity (g/mL)</td>
<td>0.85</td>
<td>0.88</td>
</tr>
<tr>
<td>Flash point (K)</td>
<td>333–353</td>
<td>373–443</td>
</tr>
<tr>
<td>Cloud point (K)</td>
<td>258–278</td>
<td>270–285</td>
</tr>
<tr>
<td>Pour point (K)</td>
<td>238–258</td>
<td>258–289</td>
</tr>
<tr>
<td>Water (vol.%)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon (wt.%)</td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>Hydrogen (wt.%)</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Oxygen (wt.%)</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Sulfur (wt.%)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cetane number</td>
<td>40–55</td>
<td>48–60</td>
</tr>
<tr>
<td>HHRR⁴ (μm)</td>
<td>685</td>
<td>314</td>
</tr>
<tr>
<td>BOCLE⁵ scuff (g)</td>
<td>3600</td>
<td>&gt;7000</td>
</tr>
</tbody>
</table>

¹ Hydrocarbons.
² Fatty acid methyl esters.
³ High frequency reciprocating rig.
⁴ Ball-on-cylinder lubricity evaluator.
No. 2 diesel fuel on a weight basis (16,000 Btu/lb compared with 18,300 Btu/lb). Since the biodiesel has a higher density, the LHV is only 8% less on a volume basis (118,170 Btu/gallon for biodiesel compared with 129,050 Btu/gallon for No. 2 diesel fuel) [22, 23].

Biodiesel can be used as pure fuel or blended at any level with petroleum-based diesel for use by diesel engines. The most common biodiesel blends are B2 (2% biodiesel and 98% petroleum diesel), B5 (5% biodiesel and 95% petroleum diesel), and B20 (20% biodiesel and 80% petroleum diesel). The technical disadvantages of biodiesel/petroleum diesel blends include problems with fuel freezing in cold weather, reduced energy density, and degradation of fuel under storage for prolonged periods [24]. Biodiesel blends up to B20 can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment. These low-level blends generally do not require any engine modifications. Higher blends and B100 (pure biodiesel) may be used in some engines with little or no modification, although the transportation and storage of B100 requires special management [25].

### 2.2. Characteristics of biodiesel as a renewable fuel

#### 2.2.1. The impact of biodiesel fuels on air quality

Air pollution is one of the most serious environmental problems all over the world. The combustion of petroleum-based diesel fuel is a major source of GHG emissions. Apart from these emissions, petroleum-based diesel fuel is also major source of other air contaminants including carbon monoxide (CO), nitrogen oxides (NOx), sulfur oxides (SOx), particulate matter (PM), and volatile organic compounds (VOCs). Biodiesel, a fuel that can be made from renewable biological sources, such as vegetable oils, animal fats and waste cooking oils, may have the potential to reduce the reliance on imported oil and reduce air pollutant emissions from diesel engines [26]. Using biodiesel in a conventional diesel engine substantially reduces emissions of HCs, CO, PM, sulfates, polycyclic aromatic hydrocarbons and nitrated polycyclic aromatic hydrocarbons. These reductions increase as the amount of biodiesel blended into diesel fuel increases. The best emissions reductions are seen with B100 (Table 4). NOx emissions increase with the concentration of biodiesel in the fuel. In October 2002, the Environmental Protection Agency (EPA) [27] assessed the impact of biodiesel fuel on emissions and published a draft report summarizing the results. According to the report soybean-based B20 fuel results in a reduction of 10.1 in total PM, 21.1% in HC, and 11% in CO emissions. These are offset by a 2% increase in NOx emissions.

Biodiesel from virgin vegetable oil reduces CO2 emissions when used in place of petroleum diesel. This conclusion is based on a life cycle analysis of biodiesel and petroleum diesel, accounting for emissions for all steps in the production and use of the fuel [28]. The use of pure biodiesel in the transport sector lowers the emissions of CO2 by 80% [29].

#### 2.2.2. The net energy balance

The energy balance measures the units of energy yielded for each unit of energy required to produce the fuel. The net energy balance of various ethanol and biodiesel feedstock has been a center of debate within scientific and policy circles [30]. The energy balance for a bio-fuel production system can be defined as the relation between the energy produced (output/kg biodiesel) and the energy consumed (input/kg biodiesel) for each unit of product and that is an important index for the economic and environmental feasibility of a bio-fuel project [31].

Biodiesel has the highest energy balance ratio of any liquid fuel. It has been reported that the growth of energy crops for biodiesel production produces a positive energy balance of 2.5–3.2 as output of energy from the use of biodiesel exceeds that of the energy input for manufacturing the fuel [30]. The Sheehan et al. study left out many of the fossil energy inputs to achieve an energy balance of 3.2 [32]. Most fossil fuels have a negative energy balance meaning it takes more units of energy to recover, transport and process the fuel than it returns in units of fuel energy. Every unit of fossil fuel energy used to extract and refine crude oil into petroleum diesel yields only 0.83 units of energy – a negative energy balance [33].

### 3. Review of biodiesel feedstocks

In general, biodiesel feedstock can be categorized into three groups: vegetable oils (edible or non-edible oils), animal fats, and used waste cooking oil including triglycerides. The study by Johnston and Holloway [34] evaluated production volumes and prices across 226 countries and territories and estimated current worldwide production potential at 51 billion liters from 119 countries. Table 5 depicts the list of top ten countries in terms of absolute biodiesel production. These ten countries collectively account for more than 80% of the total. Among these countries, the average feedstock dependence is: 28% for soybean oil, 22% for palm oil, 20% for animal fats, 11% for coconut oil, and 5% each for rapeseed, sunflower and olive oils [35].

#### 3.1. Vegetable oils as diesel fuels

The concept of using vegetable oil as a transportation fuel dates back to 1893 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Vegetable oil is one of the renewable fuels. Vegetable oils have become more attractive recently because of its environmental benefits and the fact that it is made...
from renewable resources. Vegetable oils have the potential to substitute a fraction of petroleum distillates and petroleum-based petrochemicals in the near future [20,24]. The basic constituent of vegetable oils is triglyceride. Vegetable oils comprise 90 to 98% triacylglycerides and small amounts of mono- and diglycerides [35]. These usually contain free fatty acids (FFAs), water, sterols, phospholipids, odorants and other impurities [15]. Different types of vegetable oils have different types of fatty acids. The fatty acids found in the vegetable oils are summarized in Table 6 [15,18,36–40].

The advantages of vegetable oils as diesel fuel are their portability, ready availability, renewability, higher heat content (about 88% of D2 fuel), lower sulfur content, lower aromatic content, and biodegradability. The main disadvantages of vegetable oils as diesel fuel are higher viscosity, lower volatility, and the reactivity of unsaturated hydrocarbon chains [41].

The injection and atomization characteristics of the vegetable oils are significantly different than those of petroleum-derived diesel fuels, mainly as the result of their high viscosities [42]. The vegetable oils, as alternative engine fuels, are all extremely viscous with viscosities ranging from 9 to 17 times greater than that of petroleum-derived diesel fuel [43]. Modern diesel engines have fuel-injection system that is sensitive to viscosity change. One way to avoid these problems is to reduce fuel viscosity of vegetable oil in order to improve its performance. The vegetable oils may be blended to reduce the viscosity with diesel in presence of some additives to improve its properties. Heating and blending of vegetable oils may reduce the viscosity and improve volatility of vegetable oils but its molecular structure remains unchanged hence polyunsaturated character remains. Blending of vegetable oils with diesel, however, reduces the viscosity drastically and the fuel handling system of the engine can handle vegetable oil–diesel blends without any problems [44,45]. The conversion of vegetable oils into FAME is an effective way to overcome all the problems associated with the vegetable oils.

The most common way of producing biodiesel is the transesterification of vegetable oils [46]. The methyl ester produced by transesterification of vegetable oil has a high cetane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions. Its use results in the minimization of carbon deposits on injector nozzles [47].

### 3.2. Vegetable oils as biodiesel feedstock

#### 3.2.1. Edible vegetable oils

Biodiesel has been mainly produced from edible vegetable oils all over the world. More than 95% of global biodiesel production is made from edible vegetable oils [48]. Global use of edible oils increased faster, between marketing years 2004 and 2007, than its production. The estimated increase in edible oil use for biodiesel production was 6.6 million tons from 2004 to 2007, which would attribute 34% of the increase in global consumption to biodiesel [49]. Between 2005 and 2017, biodiesel use of edible oils is projected to account for more than a third of the expected growth in edible oil use [50]. The largest biodiesel producers were the European Union (EU), the United States, Brazil, Indonesia, with a combined use of edible oil for biodiesel production of about 8.6 million tons in 2007 compared to global edible oil production of 132 million tons [49,51]. The combined use of edible oils for biodiesel in the EU was 6.1 million tons in 2007 compared with about 1.0 million tons in 2001 [49].

A rough estimate suggests that about 7.8 Mha were used to provide biodiesel feedstocks in the four major producing countries in 2007 (Table 7) [52]. Biodiesel production uses around 4.4 Mha of

### Table 5

Top ten countries in terms of absolute biodiesel potential [34].

<table>
<thead>
<tr>
<th>Country</th>
<th>Volume potential (Ml)</th>
<th>Production cost (US$ per liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malaysia</td>
<td>14,540</td>
<td>0.53</td>
</tr>
<tr>
<td>Indonesia</td>
<td>7595</td>
<td>0.49</td>
</tr>
<tr>
<td>Argentina</td>
<td>5255</td>
<td>0.62</td>
</tr>
<tr>
<td>USA</td>
<td>3212</td>
<td>0.7</td>
</tr>
<tr>
<td>Brazil</td>
<td>2567</td>
<td>0.62</td>
</tr>
<tr>
<td>Netherlands</td>
<td>2946</td>
<td>0.75</td>
</tr>
<tr>
<td>Germany</td>
<td>2024</td>
<td>0.79</td>
</tr>
<tr>
<td>Philippines</td>
<td>1234</td>
<td>0.53</td>
</tr>
<tr>
<td>Belgium</td>
<td>1213</td>
<td>0.78</td>
</tr>
<tr>
<td>Spain</td>
<td>1073</td>
<td>1.71</td>
</tr>
</tbody>
</table>

### Table 6

Percentage of fatty acid type for different oils.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Palmitic (C16:0)</th>
<th>Palmitoleic (C16:1)</th>
<th>Stearic (C18:0)</th>
<th>Oleic (C18:1)</th>
<th>Linoleic (C18:2)</th>
<th>Linolenic (C18:3)</th>
<th>Other acids</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>6.0</td>
<td>–</td>
<td>2.0</td>
<td>44.0</td>
<td>48.0</td>
<td>–</td>
<td>–</td>
<td>[36]</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>28.3</td>
<td>–</td>
<td>0.9</td>
<td>13.3</td>
<td>57.5</td>
<td>–</td>
<td>–</td>
<td>[37]</td>
</tr>
<tr>
<td>Olive</td>
<td>14.6</td>
<td>–</td>
<td>–</td>
<td>75.4</td>
<td>10</td>
<td>–</td>
<td>–</td>
<td>[36]</td>
</tr>
<tr>
<td>Palm</td>
<td>42.6</td>
<td>0.3</td>
<td>4.4</td>
<td>40.5</td>
<td>10.1</td>
<td>0.2</td>
<td>1.1</td>
<td>[15,38]</td>
</tr>
<tr>
<td>Peanut</td>
<td>11.4</td>
<td>–</td>
<td>2.4</td>
<td>48.3</td>
<td>32.0</td>
<td>0.9</td>
<td>9.1</td>
<td>[37]</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>3.5</td>
<td>0.1</td>
<td>0.9</td>
<td>54.1</td>
<td>22.3</td>
<td>–</td>
<td>0.2</td>
<td>[36]</td>
</tr>
<tr>
<td>Safflower</td>
<td>7.3</td>
<td>0.1</td>
<td>1.9</td>
<td>13.5</td>
<td>77</td>
<td>–</td>
<td>–</td>
<td>[36]</td>
</tr>
<tr>
<td>Soybean</td>
<td>11.9</td>
<td>0.3</td>
<td>4.1</td>
<td>23.2</td>
<td>54.2</td>
<td>6.3</td>
<td>–</td>
<td>[15]</td>
</tr>
<tr>
<td>Sunflower</td>
<td>6.4</td>
<td>0.1</td>
<td>2.9</td>
<td>17.7</td>
<td>72.9</td>
<td>–</td>
<td>–</td>
<td>[15,38]</td>
</tr>
<tr>
<td>Tallow</td>
<td>29.0</td>
<td>–</td>
<td>24.5</td>
<td>44.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[36]</td>
</tr>
<tr>
<td>J. curcas</td>
<td>14.2</td>
<td>0.7</td>
<td>7.0</td>
<td>44.7</td>
<td>32.8</td>
<td>0.2</td>
<td>–</td>
<td>[39]</td>
</tr>
<tr>
<td>P. pinnata</td>
<td>10.2</td>
<td>–</td>
<td>7.0</td>
<td>51.8</td>
<td>17.7</td>
<td>3.6</td>
<td>–</td>
<td>[37]</td>
</tr>
<tr>
<td>M. indica</td>
<td>24.5</td>
<td>–</td>
<td>22.7</td>
<td>37.0</td>
<td>14.3</td>
<td>–</td>
<td>–</td>
<td>[40]</td>
</tr>
<tr>
<td>WCO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>20.4</td>
<td>4.6</td>
<td>4.8</td>
<td>52.9</td>
<td>13.5</td>
<td>0.8</td>
<td>–</td>
<td>[18]</td>
</tr>
</tbody>
</table>

<sup>a</sup> WCO-waste cooking oil.

#### Table 7

Biodiesel production and land use by major producing countries, 2006/2007.

<table>
<thead>
<tr>
<th>Country</th>
<th>Biodiesel feedstocks</th>
<th>Implied feedstock area (Mha)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Country total (Mha)</th>
<th>Arable land (Mha)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Biodiesel share (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentina</td>
<td>Soybean (100%)</td>
<td>0.73</td>
<td>0.73</td>
<td>28.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Brazil</td>
<td>Soybean (66%)</td>
<td>0.45</td>
<td>0.45</td>
<td>59.1</td>
<td>0.8</td>
</tr>
<tr>
<td>EU-27</td>
<td>Rapeseed (64%)</td>
<td>2.75</td>
<td>4.33</td>
<td>113.8</td>
<td>3.8</td>
</tr>
<tr>
<td>USA</td>
<td>Soybean (74%)</td>
<td>2.31</td>
<td>2.31</td>
<td>174.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Total</td>
<td>7.82</td>
<td>7.82</td>
<td>357.7</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Million hectares.
arable land in the EU [52]. Replacing 10% of EU diesel with biodiesel would account for around 19% of world edible oil production in 2020 which means more land will be planted with crops and more land somewhere in the world will be converted into farmland, thereby releasing GHG emissions [53]. Industrialized countries with bio-fuels targets, such as the United States and the EU countries, are unlikely to have the agricultural land base needed to meet their growing demand for current production of bio-fuels. Currently, biodiesel is mainly prepared from conventionally grown edible oils such as rapeseed, soybean, sunflower and palm thus leading to alleviate food versus fuel issue [54]. Serious problems face the world food supply today. The rapidly growing world population and rising consumption of bio-fuels are increasing demand for both food and bio-fuels. This exagerates both food and fuel shortages. The human population faces serious food shortages and malnutrition [55]. Nearly 60% of humans in the world are currently malnourished, so the need for grains and other basic foods is critical. Growing crops for fuel squanders land, water, and energy resources vital for the production of food for people [56].

Rapeseed and sunflower oils are used in the EU, palm oil predominates in biodiesel production in tropical countries, and soybean oil is the major feedstock in the United States [57]. According to Pahl [58], rapeseed oil has 5% of total global biodiesel raw material sources, followed by soybean (25%), palm oil (10%), sunflower oil (5%), and other (1%).

Rapeseed used for biodiesel is the EU’s dominant bio-fuel crop with a share of about 80% of the feedstock [59]. Total EU rapeseed production was 15.3 million tons in 2006/2007 [60]. About 65% of rapeseed oil supply is used for biodiesel production [49]. The EU is now a net importer of rapeseed oil (0.57 million tons in 2006/2007) [61]. China, a major producer of rapeseed, is also starting to produce biodiesel from this source. Chinese production of rapeseed biodiesel, which currently totals about 114 Ml per year, is limited because of less advanced technology, but scientists are working at improving technologies in China to increase their biodiesel production from rapeseed oil [27]. Rapeseed (known in North America as canola) produces 1 ton of oil per hectare [62], giving it the highest yield of any conventional oilseed field crop. Comparison of some sources of biodiesel is given in Table 8.

Soybean is the most common feedstock in the United States and it represents 25% of total global biodiesel raw material sources, according to Pahl [58]. Soybean oil accounts for approximately 90% of the biodiesel produced in the United States [63]. The United States is the world leader in soybean production with about 87 million tons produced in 2006/2007 crop year [64]. Based on current US diesel consumption of 227 billion liters per year, this would require more than 500 Mha of land in soybeans or more than half the total US planted just for soybeans [56]. Soybeans only produce about 0.52 tons of oil per hectare [62]. Typically, oil derived from commercial soybean varieties is composed of approximately 12% palmitic acid (C16:0), 4% stearic acid (C18:0), 23% oleic acid (C18:1), 54% linoleic acid (C18:2), and 6% linolenic acid (C18:3) (Table 6). High levels of oleic acid make the oil more resistant to oxidation and hence more suitable for processes requiring high oxidative stability at high temperatures as in biodiesel and biolubricants applications. On the other hand, high linoleic acid content (less stable to oxidation) makes the oil to have excellent drying properties, which is a desirable property for applications in paints, inks and varnishes [65]. Of importance are the combustion and flow properties of biodiesel fuel which are determined primarily by FFA content of the vegetable oil. Properties of selected vegetable oils and biodiesel fuels are depicted in Table 9 [14,66–70] and Table 10 [14,66,72–75].

Palm oil is produced from the fruit of the oil palm, or Elaeis Guineesis tree, which originated in West Guinea. The tree was introduced into other parts of Africa, South East Asia and Latin America during the 15th century [76]. After almost 100 years palm oil is now increasingly being produced on large-scale plantations in tropical lowland regions especially in Indonesia and Malaysia as well as on the Philippines, in Myanmar and Thailand. Today the world market consists of 38.13 million tons annually, and Indonesia and Malaysia as largest and second-largest producer of palm oil in the world account together for more than 85% of exports [77]. China is the largest consumers of palm oil in the world with total domestic consumption in 2006/2007 forecast to reach 5.1 million

### Table 8
Comparison of some sources of biodiesel.

<table>
<thead>
<tr>
<th>Energy crop</th>
<th>Oil yield (tons per hectare)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapeseed</td>
<td>1</td>
</tr>
<tr>
<td>Soybean</td>
<td>0.52</td>
</tr>
<tr>
<td>Palm</td>
<td>5</td>
</tr>
<tr>
<td>Jatropha*</td>
<td>0.5</td>
</tr>
<tr>
<td>Microalgae</td>
<td>12</td>
</tr>
</tbody>
</table>

* Under arid conditions.

### Table 9
Fuel-related properties of selected vegetable oils.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oil</th>
<th>Iodine value</th>
<th>CN*</th>
<th>CPa (K)</th>
<th>PFb (K)</th>
<th>BPc (K)</th>
<th>Viscosityd (mm²/s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cottonseed</td>
<td>90–119</td>
<td>41.8</td>
<td>274.7</td>
<td>258.0</td>
<td>507</td>
<td>33.5</td>
<td>[66]</td>
</tr>
<tr>
<td>2</td>
<td>Rapseed</td>
<td>94–120</td>
<td>37.6</td>
<td>269.1</td>
<td>241.3</td>
<td>519</td>
<td>37.0</td>
<td>[66]</td>
</tr>
<tr>
<td>3</td>
<td>Safflower</td>
<td>126–152</td>
<td>41.3</td>
<td>291.3</td>
<td>266.3</td>
<td>533</td>
<td>31.3</td>
<td>[66]</td>
</tr>
<tr>
<td>4</td>
<td>Soybean</td>
<td>117–143</td>
<td>37.9</td>
<td>269.1</td>
<td>260.8</td>
<td>527</td>
<td>32.6</td>
<td>[66]</td>
</tr>
<tr>
<td>5</td>
<td>Sunflower</td>
<td>110–143</td>
<td>37.1</td>
<td>280.2</td>
<td>258.0</td>
<td>547</td>
<td>37.1</td>
<td>[66]</td>
</tr>
<tr>
<td>6</td>
<td>Karanja</td>
<td>–</td>
<td>29.9</td>
<td>–</td>
<td>278.0</td>
<td>488</td>
<td>43.63</td>
<td>[67]</td>
</tr>
<tr>
<td>7</td>
<td>Jatropha</td>
<td>101</td>
<td>23</td>
<td>–</td>
<td>267.0</td>
<td>459</td>
<td>35.4</td>
<td>[68]</td>
</tr>
<tr>
<td>8</td>
<td>Palm</td>
<td>35–61a</td>
<td>42e</td>
<td>–</td>
<td>577b</td>
<td>42.66</td>
<td>–</td>
<td>[66,69]</td>
</tr>
<tr>
<td>9</td>
<td>Palm kernel</td>
<td>14–331</td>
<td>–</td>
<td>–</td>
<td>295.0d</td>
<td>515d</td>
<td>115.55</td>
<td>[70]</td>
</tr>
<tr>
<td>10</td>
<td>WCOd</td>
<td>141.5</td>
<td>49</td>
<td>–</td>
<td>284.0</td>
<td>485.0</td>
<td>36.4</td>
<td>[14]</td>
</tr>
</tbody>
</table>

* CN – cetane number.

a CP – cloud point.

b PP – pour point.

c BP – flash point.

d WCO – waste cooking oil.

f Measured at 313 K (entries 1–5) and at 313 K (entries 6–10).

i Iodine value and cetane number combined from Ref. [66].

j Flash point and viscosity combined from Ref. [69].

k Iodine value combined from Ref. [70].

l Pour point, flash point and viscosity combined from Ref. [71].
tons [78]. Other large scale consumers of palm oil include Indonesia, India, Malaysia and the EU. These five major consumers account for 55% of global palm oil consumption. Even allowing for increasing biodiesel usage it is expected that by 2010 no more than 2% of global palm oil is likely to be used in biodiesel in the EU [79]. The palm oil system generates more biodiesel per hectare than the rapeseed system, and has less parasitic demand [80]. Palm, which can produce an astounding 4000 l of oil per hectare, has the highest oil yield of plants grown for biodiesel feedstock. There are great differences between palm oil and palm kernel oil with respect to their physical and chemical characteristics. The major difference between palm oil and palm kernel oil (PKO) is in their fatty acid content. Palm oil contains mainly palmitic and oleic acids, the two common fatty acids, and about 50% saturated fatty acids [14], while PKO contains mainly lauric acid and more than 80% saturated fatty acids [81].

### 3.2.2. Non-edible vegetable oils

Currently, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry [48]. However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials – the food versus fuel dispute. There are concerns that biodiesel feedstock may continue up to 60 years. The kernel constitutes about 70% of the seed and contains about 20% FFAs and a procedure for converting this mahua residue soybean and maize. The comparatively high price of Jatropha is also still a drawback [99]. Karanja (P. pinnata) is native to a number of countries including India, Malaysia, Indonesia, Taiwan, Bangladesh, Sri Lanka and Myanmar. P. pinnata can grow in humid as well as subtropical environments with annual rainfall ranging between 500 and 2500 mm [100]. It is a fast-growing leguminous tree with the potential for high oil seed production and the added benefit of the ability to grow on marginal land. These properties support the suitability of this plant for large-scale vegetable oil production required by a sustainable biodiesel industry [101]. The seeds of P. pinnata contain around 30–40% of oil [101–103], which has been identified as a source of biodiesel. The fatty acid composition of P. pinnata oil has been reported Akoh et al. [37]. The predominant fatty acid is oleic acid (51.8%) with linoleic acid (17.7%), palmitic acid (10.2%), stearic acid (7.0%), and linolenic acid (3.6%).

The two major species of genus mahua found in India are M. indica and Madhuca longifolia [14]. M. indica is one of the forest based tree-borne non-edible oils with large production potential of about 60 million tons per annum in India [104]. The yield of M. indica seeds varies (5–200 kg/tree) depending upon size and age of the tree [105]. The mahua tree starts producing seeds after 10 years and continues up to 60 years. The kernel constitutes about 70% of the seed and contains 50% oil [25]. The mahua oil generally contains about 20% FFAs and a procedure for converting this mahua oil to biodiesel is very much required [93]. Rice bran oil is an underutilized non-edible vegetable oil, which is available in large quantities in rice cultivating countries, and very little research has been done to utilize this oil as a replacement for mineral diesel [91].

Biodiesel from oil crops is being produced in increasing amounts as a clean-burning alternative fuel, but its production in large quantities is not sustainable. Extensive use of vegetable oils may cause other significant problems such as starvation in developing countries. With nearly 60% of humans in the world now currently malnourished, the need for grains and other basic food crops continues to be critical [106]. Microalgae have long been recognized as potentially good sources for bio-fuel production because of their high oil content and rapid biomass production. In recent years, use of microalgae as an alternative biodiesel feedstock has gained renewed interest from researchers, entrepreneurs, and the

### Table 10

Properties of selected biodiesel fuels.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Biodiesel*</th>
<th>CNb</th>
<th>CPb (K)</th>
<th>PPb (K)</th>
<th>FPb (K)</th>
<th>Viscosityc (mm²/s)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cottonseed</td>
<td>51.2</td>
<td>–</td>
<td>269</td>
<td>383</td>
<td>6.8</td>
<td>[66]</td>
</tr>
<tr>
<td>2</td>
<td>WCOd</td>
<td>54</td>
<td>–</td>
<td>262</td>
<td>469</td>
<td>5.3</td>
<td>[14]</td>
</tr>
<tr>
<td>3</td>
<td>Rapseed</td>
<td>54.4</td>
<td>271</td>
<td>264</td>
<td>357</td>
<td>6.7</td>
<td>[66]</td>
</tr>
<tr>
<td>4</td>
<td>Safflower</td>
<td>49.8</td>
<td>–</td>
<td>267</td>
<td>453</td>
<td>–</td>
<td>[66]</td>
</tr>
<tr>
<td>5</td>
<td>Soybean</td>
<td>46.2</td>
<td>275</td>
<td>272</td>
<td>444</td>
<td>4.08</td>
<td>[66]</td>
</tr>
<tr>
<td>6</td>
<td>Sunflower</td>
<td>46.6</td>
<td>273</td>
<td>269</td>
<td>456</td>
<td>4.22</td>
<td>[66]</td>
</tr>
<tr>
<td>7</td>
<td>Karanja</td>
<td>55</td>
<td>280</td>
<td>277</td>
<td>456</td>
<td>4.66</td>
<td>[72]</td>
</tr>
<tr>
<td>8</td>
<td>Jatropha</td>
<td>48</td>
<td>–</td>
<td>272</td>
<td>366</td>
<td>5.38</td>
<td>[73]</td>
</tr>
<tr>
<td>9</td>
<td>PMEc</td>
<td>65</td>
<td>289</td>
<td>289</td>
<td>447</td>
<td>4.5</td>
<td>[74]</td>
</tr>
<tr>
<td>10</td>
<td>PEEe</td>
<td>56.2</td>
<td>281</td>
<td>279</td>
<td>292</td>
<td>4.5</td>
<td>[66]</td>
</tr>
<tr>
<td>11</td>
<td>Palm kernel</td>
<td>–</td>
<td>279</td>
<td>275</td>
<td>440</td>
<td>4.84</td>
<td>[75]</td>
</tr>
</tbody>
</table>

* Methyl esters (entries 1–9) and ethyl esters (entries 10 and 11).

b Explanations as in Table 9.

c PME – palm oil methyl ester.

d PEE – palm oil ethyl ester.

e Measured at 294 K (entry 1), at 310.8 K (entry 2) and at 313 K (entries 3–11).
general public [107]. Microalgae are classified as diatoms (bacillarophyceae), green algae (chlorophyceae), goldenbrown (chrysophyceae) and blue-green algae (cyanophyceae) [108]. Microalgae are the untapped resource with more than 25,000 species of which only 15 are in use [109]. According to Benemann [110] total world commercial microalgal biomass production is about 10,000 tons per year. Microalgae are photosynthetic microorganisms that convert sunlight, water and carbon dioxide to algal biomass [111]. Microalgae contain lipids and fatty acids as membrane components, storage products, metabolites and sources of energy. Algae present an exciting possibility as a feedstock for biodiesel, and when you realize that oil was originally formed from algae. As could be seen from Table 11, algae contain anywhere between 2% and 40% of lipids/oils by weight [112]. The oil contents of some microalgae are given in Table 12 [113]. They have much higher growth rates and productivity when compared to conventional forestry, agricultural crops, and other aquatic plants, requiring much less land area than other biodiesel feedstocks of agricultural origin, up to 49 or 132 times less when compared to rapeseed or soybean crops, for a 30% (w/w) of oil content in algae biomass [114]. The production of algae to harvest oil for biodiesel has not been undertaken on a commercial scale, but working feasibility studies have been conducted to arrive at the above number. Specially bred mustard varieties can produce reasonably high oil yields and have the added benefit that the meal left over after the oil has been pressed out can act as an effective and biodegradable pesticide [14].

3.3. Animal fats as biodiesel feedstock

Another group of feedstock for biodiesel production is fats derived from animals. Animal fats used to produce biodiesel include tallow [115,116], choice white grease or lard [117], chicken fat [118] and yellow grease [119]. Compared to plant crops, these fats frequently offer an economic advantage because they are often priced favorably for conversion into biodiesel [107]. Animal fat methyl ester has some advantages such as high cetane number, non-corrosive, clean and renewable properties [120]. Animal fats tend to be low in FFAs and water, but there is a limited amount of these oils available, meaning these would never be able to meet the fuel needs of the world [121].

3.4. Waste cooking oil as biodiesel feedstock

Waste cooking oil (WCO) is a promising alternative to vegetable oil for biodiesel production. In order to reduce the cost of production, WCO would be a good choice as raw material since it is cheaper than virgin vegetable oils [122]. Its price is 2–3 times cheaper than virgin vegetable oils [123]. The conversion of WCO into methyl esters through the transesterification process approximately reduces the molecular weight to one-third, reduces the viscosity by about one-seventh, reduces the flash point slightly and increases the volatility marginally, and reduces pour point considerably [14,124]. The production of biodiesel from WCO is challenging due to the presence of undesirable components such as FFAs and water [125].

The amount of WCO generated in each country is huge and varies depending on the use of vegetable oil. Management of WCOs poses a significant challenge because of its disposal problems and possible contamination of the water and land resources. Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. As large amounts of WCO are illegally dumped into rivers and landfills, causing environmental pollution, the use of waste cooking oil to produce biodiesel as petroleum-based diesel fuel substitute offers significant advantages because of the reduction in environmental pollution [18]. Therefore, biodiesel derived from WCO has taken a commercial patent as an alternative fuel to petroleum-based diesel fuel for diesel engines in the markets of Europe and the United States [126]. Every year many millions of tons of WCO are collected and used in a variety of ways throughout the world. This is a virtually inexhaustible source of energy which might also prove an additional line of production for “green” companies [127]. An estimate of the potential amount of WCO from the collection in the EU is approximately 0.7–1.0 million tons per year [125]. US restaurants, including all the fast-food chains, produce an estimated 3 billion gallons of WCO per year [128]. According to Chhetri et al. [18], approximately 135,000 tons per year of WCO is produced in Canada. Turkey produces over 350,000 tons of WCO per year [28]. According to a report by the USDA Foreign Agricultural Service [129], WCO accounts about 80,000 tons of China’s biodiesel production.

4. Derivatives of triglycerides as diesel fuels

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon-based diesel fuels. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character [35]. Dilution/blending, micro-emulsification, pyrolysis, and transesterification are the four techniques applied to solve the problems encountered with the high fuel viscosity. Among all these techniques, the transesterification seems to be the best.
choice, as the physical characteristics of fatty acid esters are very close to those of diesel fuel and the process is relatively simple.

4.1. Dilution with diesel fuel

Vegetable oils may be used with dilution modification technique as an alternative diesel fuel [130]. The problems posed by the high viscosity of vegetable oil can be minimized by blending it with diesel. The vegetable oil–diesel fuel blend is a simple way to reduce the viscosity of neat vegetable oil. This method does not require any chemical process [131]. The use of blends of conventional diesel fuel with sunflower oil [132], soybean oil [133], cottonseed oil [134], rapeseed oil [135], J.-curcas oil [84], P. pinnnata oil [89], and WCO [136] has been described.

Caterpillar Brazil, in 1980, used pre-combustion chamber engines with the mixture of 10% vegetable oil to maintain total power without any alteration or adjustment to the engine. At that point it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50:50 ratio [137].

Ziejewski et al. [132] investigated the effects of the fuel blend of 25% sunflower oil with 75% diesel fuel (25/75 fuel) in a direct-injection diesel engine. The viscosity of this blend was 4.88 cSt at 313 K (maximum specified ASTM value is 4.0 cSt at 313 K). This blend was considered not suitable for long-term use in a direct-injection engine.

The effect of temperature on viscosities of J. curcas oil and various blends in the range 298–348 K has been investigated by Pramanik [84]. Results of the study show that the viscosity of J. curcas oil is higher than diesel oil at any temperature. Viscosity values of 50:50 J. curcas oil/diesel fuel and 40:60 J. curcas oil/diesel fuel are close to diesel in the range of 328–333 K and at about 318 K, respectively, whereas the blend containing 30:70 J. curcas oil/diesel fuel has viscosity close to diesel at the range of 308–313 K.

4.2. Micro-emulsification of oils

Micro-emulsification is the formation of microemulsions (co-solvency) which is a potential solution for solving the problem of vegetable oil viscosity. Microemulsions are defined as transparent, thermodynamically stable colloidal dispersions in which the diameter of the dispersed-phase particles is less than one-fourth the wavelength of visible light. Microemulsion-based fuels are sometimes also termed “hybrid fuels”, although blends of conventional diesel fuel with vegetable oils have also been called hybrid fuels [66].

To solve the problem of the high viscosity of vegetable oils, microemulsions with immiscible liquids, such as methanol, ethanol and ionic or non-ionic amphiphiles have been studied. It has been demonstrated that short-term performances of both ionic and non-ionic microemulsions of aqueous ethanol in soybean oil are nearly as well as that of No. 2 diesel fuel [138]. Ziejewski et al. [139] prepared a microemulsion containing 53% (v/v) alkali-redefined and winterized sunflower oil, 13.3% (v/v) 190-proof ethanol and 33.4% (v/v) 1-butanol. This non-ionic microemulsion had a viscosity of 6.31 cSt at 313 K, a cetane number of 25, and an ash content of less than 0.01%. Lower viscosities and better spray patterns (more even) were observed with an increase of 1-butanol.

4.3. Pyrolysis

The goal of pyrolysis is the optimization of high-value fuel products from biomass by thermal and catalytic means [140]. The pyrolyzed material can be any type of biomass, such as vegetable oils, animal fats, wood, bio-waste, etc. Conversion of vegetable oils and animal fats composed predominantly of triglycerides using pyrolysis type reactions represents a promising option for the production of biodiesel [141]. Many investigators have reported the pyrolysis of triglycerides to obtain products suitable for diesel engines [142–147].

Thermal decomposition of triglycerides produces the compounds of classes including alkanes, alkenes, alkadienes, aromatics and carboxylic acids. Different types of vegetable oils produce large differences in the composition of the thermally decomposed oil [35]. The mechanism of thermal decomposition of triglycerides in Fig. 1 was proposed by Schwab et al. [142]. Mechanisms for the thermal decomposition of triglycerides are likely to be complex because of the many structures and multiplicity of possible reactions of mixed triglycerides. Generally, thermal decomposition of these structures proceeds through either a free-radical or carbonium ion mechanism. The formation of aromatics is supported by a Diels–Alder addition of ethylene to a conjugated diene formed in the pyrolysis reaction. Carboxylic acids formed during the pyrolysis of vegetable oils probably result from cleavage of the glycerol moiety [35,142]. The compositions of pyrolyzed oils are listed in Table 13. The main components were alkanes and alkenes, which accounted for approximately 60% of the total weight. Carboxylic acids accounted for another 9.6–16.1% [137].

The fuel properties of the liquid product fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Pyrolyzed soybean oil, for instance, contains 79% carbon and 11.88% hydrogen [35]. It has low viscosity and a high cetane number compared to pure vegetable oils. Soybean oil pyrolyzed distillate, which consisted mainly of alkanes, alkenes and carboxylic acids had a cetane number of 43, exceeding that of soybean oil (37.9) and the ASTM minimum value of 40. The viscosity of the distillate was 10.2 mm²/s at 311 K, which is higher than the ASTM specification for No. 2 diesel fuel (1.9–4.1 mm²/s) but considerably below that of soybean oil (32.6 mm²/s) [66].

The HHV of pyrolysis oil from vegetable oil is pretty high. The HHV of pyrolysis oil from rapeseed oil (38.4 MJ/kg) is slightly lower than that of gasoline (47 MJ/kg), diesel fuel (43 MJ/kg), or petroleum (42 MJ/kg) but higher than coal (32–37 MJ/kg) [15].

Table 13

<table>
<thead>
<tr>
<th></th>
<th>High oleic safflower</th>
<th>Soybean oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂ sparge</td>
<td>Air</td>
</tr>
<tr>
<td>Alkanes</td>
<td>37.5</td>
<td>40.9</td>
</tr>
<tr>
<td>Alkenes</td>
<td>22.2</td>
<td>22.0</td>
</tr>
<tr>
<td>Alkadienes</td>
<td>8.1</td>
<td>13.0</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td>11.5</td>
<td>16.1</td>
</tr>
<tr>
<td>Unresolved unsaturates</td>
<td>9.7</td>
<td>10.1</td>
</tr>
<tr>
<td>Aromatics</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Unidentified</td>
<td>8.7</td>
<td>12.7</td>
</tr>
</tbody>
</table>

![Fig. 1. The mechanism of thermal decomposition of triglycerides [142].](image-url)
The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products [146–148]. The saponification and pyrolysis of sodium soap of vegetable oil proceed as follows [146]:

**Saponification:**

Vegetable oils or fats + NaOH → RCOONa + Glycerin

(1)

**Pyrolysis of sodium soaps:**

4RCOONa + (1/2)O₂ → R-R + Na₂CO₃ + CO₂

(2)

The soaps obtained from the vegetable oils can be pyrolyzed into hydrocarbon-rich products according to Eq. (2) with higher yields at lower temperatures. Demirbas [146] investigated the yields of decarboxylation products by pyrolysis from sodium soaps of four vegetable oils. The maximum decarboxylation products were obtained from pyrolysis of sunflower oil (97.5%), corn oil (97.1%), cottonseed oil (97.5%), and soybean oil (97.8%) at 610 K. Fig. 2. shows distillation curves for sunflower oil and methyl ester and sodium soap of sunflower oil.

The production of bio-fuels (especially bio-gasoline) from vegetable oils by catalytic cracking is a promising alternative. Several vegetable oils (e.g. palm, canola, soybean) have been employed in the process that involves conversion of the oils into bio-fuels suitable for gasoline engines using acid catalysts such as transition metal catalysts (that yield bio-fuels enriched in diesel fraction – over 50% by weight) and zeolites and mesoporous materials that give bio-fuels with higher gasoline fractions – over 40% – with higher aromatic content [149]. The reaction is normally performed at moderate to high temperatures (573–773 K) using different oils to catalyst ratios depending on the oil and the catalyst [149]. Catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline: this process involves carbocations and yields alkanes and alkenes with the highly branched structures desirable in gasoline [147].

Certain petroleum fractions are converted into other kinds of chemical compounds. Catalytic isomerization changes straight-chain alkanes into branched-chain ones. The cracking process converts higher alkanes and alkenes, and thus increases the gasoline yield. The process of catalytic reforming converts alkanes and cycloalkanes into aromatic hydrocarbons and thus increases the gasoline yield. The process of catalytic reforming converts alkanes and cycloalkanes into aromatic hydrocarbons and thus provides the chief raw material for the large-scale synthesis of another broad class of compounds [15].

4.4. Transesterification of triglycerides to biodiesel

Amongst the four techniques, chemical conversion (transesterification) of the oil to its corresponding fatty ester is the most promising solution to the high viscosity problem. Sometimes, it is more convenient to convert the alkyl group of an ester to another alkyl group. This process is known as ester exchange or transesterification. Fig. 3 shows the transesterification reaction of triglycerides [150]. Transesterification is the reversible reaction of a fat or oil with an alcohol (methanol or ethanol) to form fatty acid alkyl esters and glycerol. It can be alkali-, acid-, or enzyme-catalyzed; however, currently the majority of the commercialized technology resides in transesterification using alkali-catalyzed reaction [137]. Mostly, biodiesel is derived from the vegetable oils using sodium or potassium hydroxide catalytic transesterification (m)ethanol process [151].

The transesterification reaction proceeds with catalyst or without any catalyst by using primary or secondary monohydric aliphatic alcohols having 1–8 carbon atoms [124]. The alcohols employed in the transesterification are generally short chain alcohols such as methanol, ethanol, propanol, and butanol [152]. Transesterification reaction is an equilibrium reaction. In this reaction, however, a larger amount of methanol is used to shift reaction equilibrium to right side and produce more methyl esters as...
proposed product [153]. Ethanol is a preferred alcohol in transesterification reaction compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however, methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol).

Generally, the reaction temperature near the boiling point of the alcohol is recommended. Nevertheless, the reaction may be carried out at room temperature [126]. The reactions take place at low temperatures (~338 K) and at modest pressures (2 atm, 1 atm = 101.325 kPa). Biodiesel is further purified by washing and evaporation to remove any remaining methanol. The oil (87%), alcohol (9%), and catalyst (1%) are the inputs in the production of biodiesel (86%), the main output [154]. Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (~513 K), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 333 to 353 K at a molar ratio of 6:1 [155]. Inputs and mass requirements for the transesterification process are given in Table 14.

For a complete reaction, an FFA value of lower than 3% is needed and the other materials should be substantially anhydrous [150]. Ideally, it should be kept below 1% [150]. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. Soap formation reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult [156].

The physical properties of the primary chemical products of transesterification are given in Tables 15 and 16. The physical properties of these products indicate that the boiling points and melting points of the fatty acids, methyl esters, mono, di and triglycerides increase as the number of carbon atoms in the carbon chain increase, but decrease with increases in the number of double bonds. The melting points increase in the order of tri, di and monoglycerides due to the polarity of the molecules and hydrogen bonding [137].

### 4.4.1. Catalytic transesterification methods

Transesterification reactions can be catalyzed by alkalis [54,157,158], acids [97,159,160] or enzymes [161–163]. The catalytic transesterification of vegetable oils with methanol is an important industrial method used in biodiesel synthesis. Also known as methanolysis, this reaction is well studied and established using acids or alkalis, such as sulfuric acid or sodium hydroxide as catalysts. However, these catalytic systems are less active or completely inactive for long chain alcohols. Usually, industries use sodium or potassium hydroxide or sodium or potassium methoxide as catalyst, since they are relatively cheap and quite active for this reaction [164]. Enzymes-catalyzed procedures, using lipase as catalyst, do not produce side reactions, but the lipases are very expensive for industrial scale production and a three-step process was required to achieve a 95% conversion [165].

#### 4.4.1.1. Acid-catalytic transesterification methods

Biodiesel produced by transesterification reaction can be catalyzed by sulfuric, phosphoric, hydrochloric and organic sulfonic acids. Currently, the catalysts more used in biodiesel production are the organic acids, such as the derivates of toluenesulfonic acid and, more often, mineral acids such as sulfuric acid [166]. Although transesterification using acid catalysts is much slower than that obtained from alkali catalysis, typically 4000 times, if high contents of water and FFAs are present in the vegetable oil, acid-catalyzed transesterification can be used [167]. The acid-catalyzed reaction commonly requires temperatures above 373 K and reaction times of 3–48 h have been reported, except when reactions were conducted under high temperature and pressure [168]. These catalysts give very high yields in the transesterification process. Acid-catalyzed reactions require the use of high alcohol-to-oil molar ratios in order to obtain good product yields in practical reaction times. However, ester yields do not proportionally increase with molar ratio. For instance, for soybean methanolysis using sulfuric acid, ester

### Table 14

Inputs and mass requirements for the transesterification process.

<table>
<thead>
<tr>
<th>Input</th>
<th>Requirement/ton biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>1000 kg vegetable oil</td>
</tr>
<tr>
<td>Steam requirement</td>
<td>415 kg</td>
</tr>
<tr>
<td>Electricity</td>
<td>12 kWh</td>
</tr>
<tr>
<td>Methanol</td>
<td>96 kg</td>
</tr>
<tr>
<td>Catalyst</td>
<td>5 kg</td>
</tr>
<tr>
<td>Hydrochloric acid (37%)</td>
<td>10 kg</td>
</tr>
<tr>
<td>Caustic soda (50%)</td>
<td>1.5 kg</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1 Nm³</td>
</tr>
<tr>
<td>Process water</td>
<td>20 kg</td>
</tr>
</tbody>
</table>

### Table 15

Physical properties of chemicals related to transesterification [137].

<table>
<thead>
<tr>
<th>Name</th>
<th>Specific gravity (g/ml)</th>
<th>Melting point (K)</th>
<th>Boiling point (K)</th>
<th>Solubility (&gt;10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl myristate</td>
<td>0.875</td>
<td>291.0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Methyl palmitate</td>
<td>0.825</td>
<td>303.8</td>
<td>469.2</td>
<td>Acids, benzene, ETOH, Et₂O</td>
</tr>
<tr>
<td>Methyl stearate</td>
<td>0.85</td>
<td>311.2</td>
<td>488.2</td>
<td>Et₂O, chloroform</td>
</tr>
<tr>
<td>Methyl oleate</td>
<td>0.875</td>
<td>253.4</td>
<td>463.2</td>
<td>ETOH, Et₂O</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.792</td>
<td>176.2</td>
<td>337.9</td>
<td>H₂O, ether</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.789</td>
<td>161.2</td>
<td>351.6</td>
<td>H₂O, ether</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1.26</td>
<td>255.3</td>
<td>563.2</td>
<td>H₂O, ether</td>
</tr>
</tbody>
</table>

### Table 16

Melting points of fatty acids, methyl esters and mono-, di-, and triglycerides [137].

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Carbons</th>
<th>Melting point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>Acid</td>
</tr>
<tr>
<td>Myristic</td>
<td>14</td>
<td>327.6</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16</td>
<td>292.0</td>
</tr>
<tr>
<td>Stearic</td>
<td>18</td>
<td>343.7</td>
</tr>
<tr>
<td>Oleic</td>
<td>18:1</td>
<td>340.0</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:2</td>
<td>330.2</td>
</tr>
</tbody>
</table>

*a Melting point of highest melting, most stable polymorphic form.
formation was sharply improved from 77% using a methanol-to-oil ratio of 3.3:1–87.8% with a ratio of 6:1. Higher molar ratios showed only moderate improvement until reaching a maximum value at a 30:1 ratio (98.4%) [13]. Despite its insensitivity to FFAs in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate [169].

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Fig. 4. It can be extended to di- and triglycerides. The protonation of carbonyl group of the ester leads to the carbocation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst [170].

Acid-catalyzed transesterification reactions have been extensively reported in the literature. Reaction conditions reported in the literature using acid catalysts are summarized in Table 17 [168,171–173]. Rachmaniah et al. [171] studied the transesterification of refined soybean oil (>99% triglycerides) and low grade high FFA (C10/C18/C20/C24/C60%) rice bran oil with methanol using 10% hydrochloric acid as a catalyst (weight percent of oil) at a temperature of 343 K. In the study, all the reactions were carried out with a methanol molar ratio of 20:1. The highest FAME content of 90% was obtained from transesterification of low grade high FFA rice bran oil with a reaction time of 6 h.

4.4.1.2. Alkali-catalytic transesterification methods. The transesterification process is catalyzed by alkaline metal alkoxides, and hydroxides, as well as sodium or potassium carbonates. Sodium methoxide is the most widely used biodiesel catalyst with over 60% of industrial plants using this catalyst [174]. Alkaline catalysts have the advantages, e.g. short reaction time and relatively low temperature can be used with only a small amount for catalyst and with little or no darkening of colour of the oil [68]. They show high performance for obtaining vegetable oils with high quality, but a question often arises; that is, the oils contain significant amounts of FFAs which cannot be converted into biodiesels but to a lot of soap [175]. These FFAs react with the alkaline catalyst to produce soaps that inhibit the separation of the biodiesel, glycerin, and wash water [176].

In the alkali catalytic methanol transesterification method, the catalyst is dissolved into methanol by vigorous stirring in a small reactor. The oil is transferred into a biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil. The final mixture is stirred vigorously for 2 h at 340 K in ambient pressure. A successful transesterification reaction produces two liquid phases: ester and crude glycerol [14].

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps [137]. The alkali-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. The mechanism of the alkali-catalyzed transesterification of vegetable oils is shown in Fig. 5. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Fig. 5, Step 1), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Fig. 5, Step 2). The latter deprotonates the catalyst, thus regenerating the active species (Fig. 5, Step 3), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol [14,177,178].

In general, alkali-catalyzed transesterification processes are carried out at low temperatures and pressures (333–338 K and 1.4–4.2 bar) with low catalyst concentrations (0.5–2 wt.%) [13]. Table 18 shows typical reaction conditions for alkali-catalyzed transesterification processes in biodiesel synthesis. Alkaline metal alkoxides (as CH3ONa for the methanolysis) are the most active catalysts, since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water, which makes them inappropriate for typical industrial processes [14,177]. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Oil</th>
<th>Catalyst (wt.%)</th>
<th>Temp. (K)</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2SO4</td>
<td>Soybean</td>
<td>1</td>
<td>338</td>
<td>69</td>
<td>&gt;90</td>
<td>[168]</td>
</tr>
<tr>
<td>HCl</td>
<td>Soybean</td>
<td>10</td>
<td>343</td>
<td>45</td>
<td>65</td>
<td>[171]</td>
</tr>
<tr>
<td>HCl</td>
<td>Rice bran</td>
<td>10</td>
<td>343</td>
<td>6</td>
<td>&gt;90</td>
<td>[171]</td>
</tr>
<tr>
<td>p-TsOH*</td>
<td>Corn</td>
<td>4</td>
<td>353</td>
<td>2</td>
<td>97.1</td>
<td>[172]</td>
</tr>
<tr>
<td>AlCl3</td>
<td>Canola</td>
<td>5</td>
<td>383</td>
<td>18</td>
<td>98</td>
<td>[173]</td>
</tr>
</tbody>
</table>

*a* p-TsOH – p-toluenesulfonic acid (CH3C6H4SO3H).
alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol% [177]. Extensive studies have been carried out on the alkaline-catalyzed transesterification of vegetable oils [179–185]. Reaction conditions reported in the literature using alkaline catalysts are summarized in Table 19.

Most of the biodiesel is currently made from edible oils by using methanol and alkaline catalyst. However, there are large amounts of low cost oils and animal fats that could be converted into biodiesel. The problems with processing these low cost oils and animal fats are that they often contain large amounts of FFAs that cannot be converted to biodiesel using alkaline catalyst [186–188].

4.4.1.3. Enzyme-catalyzed transesterification methods. Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding fatty acid alkyl esters in short reaction times, it suffers from several drawbacks: it is energy intensive, the recovery of glycerol is difficult, the acid or alkaline catalyst has to be removed from the product, alkaline wastewater requires treatment, and FFAs and water interfere with the reaction. Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems [170,189,190]. As shown in Table 20, enzymatic transesterification methods can overcome the problems mentioned above. In particular, it should be noted that the byproduct, glycerol, can be easily recovered with simple separation processes. Nevertheless, enzymatic catalysts are often more expensive than chemical catalysts, so recycling and reusing them is often a must for commercial viability. Though at present the high cost of enzyme production may be the major obstacle to the commercialization of enzyme-catalyzed processes, recent

<table>
<thead>
<tr>
<th>Table 18</th>
<th>Typical reaction conditions for biodiesel synthesis using homogeneous alkali catalysis [13].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstocks</td>
<td>Triglyceride mixtures with low free fatty acid contents (&lt;0.5%) e.g., refined vegetable oils + anhydrous short chain alcohol (generally, methanol)</td>
</tr>
<tr>
<td>Alcohol-to-oil molar ratio (recommended)</td>
<td>6:1</td>
</tr>
<tr>
<td>Temperature</td>
<td>333–338 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.4–4.1 bar</td>
</tr>
<tr>
<td>Catalyst</td>
<td>NaOH (most common)</td>
</tr>
<tr>
<td>Catalyst concentration (by weight of lipid feedstock)</td>
<td>0.5–2 wt.%</td>
</tr>
<tr>
<td>Conversions</td>
<td>&gt;95% can be expected after 1 h reaction</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 19</th>
<th>Summary of some studies using alkaline catalysts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Oil</td>
</tr>
<tr>
<td>KOH</td>
<td>Soybean</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sunflower</td>
</tr>
<tr>
<td>NaOCH3</td>
<td>Cottonseed</td>
</tr>
<tr>
<td>NaOCH3</td>
<td>Rice bran</td>
</tr>
<tr>
<td>NaOH</td>
<td>Palm</td>
</tr>
<tr>
<td>KOH</td>
<td>Palm kernel</td>
</tr>
<tr>
<td>KOH</td>
<td>Jatropha</td>
</tr>
<tr>
<td>KOH</td>
<td>Waste frying</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 20</th>
<th>Comparison between alkali catalysis and lipase-catalysis methods for biodiesel fuel production [189].</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkali-catalysis process</td>
</tr>
<tr>
<td>reaction temperature (K)</td>
<td>333–338</td>
</tr>
<tr>
<td>Free fatty acids in raw materials</td>
<td>Saponified products</td>
</tr>
<tr>
<td>Water in raw materials</td>
<td>Interference with the reaction</td>
</tr>
<tr>
<td>Yield of methyl esters</td>
<td>Normal</td>
</tr>
<tr>
<td>Recovery of glycerol</td>
<td>Difficult</td>
</tr>
<tr>
<td>Purification of methyl esters</td>
<td>Repeated washing</td>
</tr>
<tr>
<td>Production of catalyst</td>
<td>Cheap</td>
</tr>
</tbody>
</table>

Fig. 5. Mechanism of the alkali-catalyzed transesterification of vegetable oils (B: base) [177,178].
advances in enzyme technology, such as the use of solvent-tolerant lipases and immobilized lipases - making catalyst re-utilization possible, have been made to develop cost-effective systems [167,191,192]. Furthermore, the possibility of using non-commercial lipases obtained from relatively low cost and renewable raw materials renders additional importance towards conducting studies on enzyme-catalyzed production of biodiesel [193].

Enzyme-catalyzed reactions have the advantage of reacting at room temperature without producing spent catalysts [194]. However, enzyme-catalyzed system requires a much longer reaction time than the other two systems. Alcoholysis of triacylglycerols with a lipase is considered to be one of the most effective reactions for production of biodiesel. Lipases catalyze the hydrolysis of triacylglycerols into fatty acids and glycerol, as well as the reactions that involve synthesis [195]. The two main categories in which lipase-catalyzed reactions may occur are as follows [196]:

(i) Hydrolysis

\[ R_1\text{COOR}_2 + H_2\text{O} \rightarrow R_1\text{COOH} + R_2\text{OH} \quad (3) \]

(i) Synthesis: Reactions under this category can be further divided:

- Esterification

\[ R_1\text{COOH} + R_2\text{OH} \rightarrow R_1\text{COOR}_2 + H_2\text{O} \quad (4) \]

- Transesterification: Under certain circumstances, lipases catalyze a number of transesterification reactions. These reactions can be illustrated by Eqs. (5) and (6) as follows:

- Alcoholysis

\[ R_1\text{COOR}_2 + R_2\text{OH} \rightarrow R_1\text{COOR}_3 + R_2\text{OH} \quad (5) \]

- Acidolysis

\[ R_1\text{COOR}_2 + R_3\text{COOH} \rightarrow R_1\text{COOR}_3 + R_3\text{COOH} \quad (6) \]

The enzyme reactions are highly specific and chemically clean. The excess alcohol is reported to be inhibitory to some enzymes and hence a typical strategy is to feed the alcohol into the reactor in three steps of 1:1 molar ratio each. Generally, these reactions are very slow, with a three step sequence requiring from 4 to 40 h, or more [194,197,198]. The reaction conditions are modest, from 303 to 313 K (Table 20).

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in the literature. These studies consist mainly in optimizing the reaction conditions (temperature, solvent, PH, alcohol/oil molar ratio, type of microorganism which generates the enzyme, etc.) in order to establish suitable characteristics for an industrial application. Synthesis of biodiesel using enzymes such as Candida antarctica [199–202], Candida rugosa [203,204], Candida sp. [205], Pseudomonas cepacia [206], Rhizomucor miehei (Lipozyme RMIM) [207], Pseudomonas fluorescens [208], Pseudomonas sp. [209], and Thermomyces lanuginosus [210] is well reported in the literature. Reaction conditions reported in the literature using enzymes are summarized in Table 21. Ognjanovic et al. [201] used methanol as an acyl acceptor for biodiesel production from sunflower oil by a commercial immobilized C. antarctica lipase (Novozyme 435)-catalyzed alcoholysis reaction. The authors used 3% by weight of the enzyme, an alcohol/oil ratio of 3:1, and obtained a high yield (>99%) at 318 K after 50 h of reaction. Bernardes et al. [207] investigated the enzymatic alcoholysis of soybean oil with methanol and ethanol using a commercial, immobilized lipase (Lipozyme RMIM). In that study, the best conditions were obtained in a solvent-free system with ethanol/oil molar ratio of 3.0, temperature of 323 K, and enzyme concentration of 7.0% (w/w). Under these conditions, the yield of ethyl ester was obtained about 60% after 4 h of reaction. In another study, Shah and Gupta [206] obtained a high yield (98%) by using P. cepacia lipase immobilized on celite at 323 K in the presence of 4–5% (w/w) water in 8 h.

4.4.2. Non-catalytic transesterification methods

There are two basic routes to produce biodiesel by non-catalyzed transesterification, namely, (i) BIXO co-solvent process and (ii) the supercritical alcohol process.

4.4.2.1. BIXO co-solvent process. Co-solvent options are designed to overcome slow reaction time caused by the extremely low solubility of the alcohol in the triglyceride phase. One approach that is nearing commercialization is the BIXO process [211]. This process uses either tetrahydrofuran (THF) or methyl tert-butyl ether (MTBE) as a co-solvent to generate a one-phase system. The result is a fast reaction, on the order of 5–0 min, and no catalyst residues in either the ester or the glycerol phase [14,17]. The THF co-solvent is chosen, in part, because it has a boiling point very close to that of methanol. This system requires a rather low operating temperature, 303 K [190,211].

4.4.2.2. Supercritical alcohol transesterification. The transesterification of triglycerides by supercritical methanol, ethanol, propanol and butanol has proved to be the most promising process. Saka and Kusdiana [212] and Demirbas [213] first proposed that biodiesel fuels may be prepared from vegetable oil via non-catalytic transesterification with supercritical methanol. Saka and Kusdiana [212] have proposed that the reactions of rapeseed oil were complete within 240 s at 623 K, 19 MPa, and molar ratio of methanol to oil at 42. To achieve more moderate reaction conditions, further effort through the two-step preparation was made Kusdiana and Saka [214]. In this method, oils/fats are, first, treated in subcritical water for hydrolysis reaction to produce fatty acids. After hydrolysis, the reaction mixture is separated into oil phase and water phase by decantation. The oil phase (upper portion) is mainly fatty acids, while the water phase (lower portion) contains glycerol in water. The separated oil phase is then mixed with methanol and treated at supercritical condition to produce methyl esters thoroughly esterification. After removing unreacted methanol and water produced in reaction, FAME can be obtained as biodiesel [215]. Methyl esterification of fatty acids is a major reaction to produce FAME in the two-step supercritical methanol method, whereas transesterification of triglycerides is a major one in the conventional alkali- and acid-catalyzed methods. This esterification reac-

### Table 21
Summary of some studies using enzyme catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Oil</th>
<th>Catalyst (wt.%)</th>
<th>Temp. (K)</th>
<th>Reaction time (h)</th>
<th>Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candida antarctica</td>
<td>Soybean</td>
<td>4</td>
<td>303</td>
<td>48</td>
<td>93.8</td>
<td>[198]</td>
</tr>
<tr>
<td>Candida antarctica</td>
<td>Sunflower</td>
<td>3</td>
<td>318</td>
<td>50</td>
<td>&gt;99</td>
<td>[199]</td>
</tr>
<tr>
<td>Candida antarctica</td>
<td>Rapeseed</td>
<td>5</td>
<td>313</td>
<td>24</td>
<td>76.1</td>
<td>[200]</td>
</tr>
<tr>
<td>Pseudomonas cepacia</td>
<td>Jatropha 5-April</td>
<td>323</td>
<td>8</td>
<td>98</td>
<td></td>
<td>[204]</td>
</tr>
<tr>
<td>Lipozyme RMIM</td>
<td>Soybean</td>
<td>7</td>
<td>323</td>
<td>4</td>
<td>60</td>
<td>[205]</td>
</tr>
</tbody>
</table>
tion is, therefore, an important step for high quality biodiesel fuel production [216].

Demirbas [213] studied the transesterification reaction under supercritical methanol employing six potential vegetable oils at varying molar ratios of alcohol to vegetable oil and reaction temperature. It was found that at molar ratio of methanol to oil of 24, 523 K, and 300 s reaction time, the best methyl ester yield was 95%. Balat [217] investigated the yields of ethyl esters from vegetable oils via transesterification in supercritical ethanol. The critical temperature and the critical pressure of ethanol were 516.2 K and 6.4 MPa, respectively. It was observed that increasing reaction temperature, especially supercritical temperatures had a favorable influence on ester conversion (Fig. 6). The critical temperatures and critical pressures of the various alcohols are shown in Table 22.

According to the current literature, non-catalytic transesterification reactions at high temperature and pressure conditions provide improved phase solubility, decrease mass-transfer limitations, provide higher reaction rates and make easier separation and purification steps. Besides, the supercritical transesterification method is more tolerant to the presence of water and FFAs than the conventional alkali-catalyzed technique, and hence more tolerant to various types of vegetable oils, even for fried and waste oils. Comparison of the yields in alkaline-catalyzed, acid-catalyzed and supercritical methanol is given in Table 23 [218].

4.4.3. Effect of different reaction parameters on the biodiesel yield

The main factors affecting transesterification are the molar ratio of glycerides to alcohol, catalyst, reaction temperature and pressure, reaction time and the contents of FFAs and water in oils.

4.4.3.1. Effect of molar ratio and alcohol type. The molar ratio of alcohol to oil is one of the most important variables influencing the conversion into esters. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1, higher molar ratios are used to enhance the solubility and to increase the contact between the triglyceride and alcohol molecules [219]. A higher molar ratio is required to drive the reaction to completion at a faster rate [94]. The molar ratio of 6:1 or higher generally gives the maximum yield (higher than 98 wt.%) [220]. Lower molar ratios require a longer time to complete the reaction. With higher molar ratios production is increased but recovery is decreased due to poor separation of glycerol. At optimum molar ratio only the process gives higher yield and easier separation of the glycerol. The optimum molar ratios depend on the type and quality of the vegetable oil used [220].

The vegetable oils are transesterified 1:6–1:40 vegetable oil–alcohol molar ratios in catalytic and supercritical alcohol conditions [14]. The sunflower seed oil was transesterified 1:1, 1:3, 1:9, 1:20, and 1:40 vegetable oil–ethanol molar ratios in supercritical ethanol conditions [217]. It was observed that increasing molar ratio had a favorable influence on ester conversion. Fig. 7 shows the effect of molar ratio of sunflower seed oil to ethanol on yield of ethyl ester at 517 K.

Acid-catalyzed reactions require the use of high alcohol-to-oil molar ratios in order to obtain good product yields in practical reaction times. However, ester yields do not proportionally increase with molar ratio. For instance, for soybean methanolysis using sulfuric acid, ester formation sharply improved from 77% using a methanol-to-oil ratio of 3.3:1–87.8% with a ratio of 6:1. Higher molar ratios showed only moderate improvement until reaching a maximum value at a 30:1 ratio (98.4%) [13].

Another important variable affecting the yield of ester is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields. Canakci and Van Gerpen [221] investigated the effect of different alcohol types on acid-catalyzed transesterification of pure soybean oil. Results of this study are summarized in Table 24.

4.4.3.2. Effect of water and FFA contents. The water and FFA content are key parameters for determining the viability of the vegetable oil transesterification process. In the base-catalyzed transesterification process, the acid value of the vegetable oil should be less than 1 and all materials should be substantially anhydrous [14]. If acid value is greater than 1, more alkali is injected to neutralize the FFAs. The presence water has a greater negative effect than that

Table 22

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Critical temperature (K)</th>
<th>Critical pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>312</td>
<td>1.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>516</td>
<td>6.4</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>537</td>
<td>5.1</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>560</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 23

<table>
<thead>
<tr>
<th>Raw material</th>
<th>FFA content (wt.%)</th>
<th>Water content (wt.%)</th>
<th>Yields of methyl esters (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Alkaline-catalyzed</td>
</tr>
<tr>
<td>Rapeseed oil</td>
<td>2.0</td>
<td>0.02</td>
<td>97.0</td>
</tr>
<tr>
<td>Palm oil</td>
<td>5.3</td>
<td>2.1</td>
<td>94.4</td>
</tr>
<tr>
<td>Frying oil</td>
<td>5.6</td>
<td>0.2</td>
<td>94.1</td>
</tr>
<tr>
<td>Waste palm oil</td>
<td>&gt;20.0</td>
<td>&gt;61.0</td>
<td>–</td>
</tr>
</tbody>
</table>

* FFA – free fatty acid.

* SCM – supercritical methanol.
of the FFAs [126]. Water can cause soap formation and frothing. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and made the separation of glycerol difficult [14,178].

In the conventional transesterification of fats and vegetable oils for biodiesel production, free fatty acids and water always produce negative effects since the presence of free fatty acids and water causes soap formation consumes catalyst and reduces catalyst effectiveness. In catalyzed methods, the presence of water has negative effects on the yields of methyl esters [14]. However, the presence of water affected positively the formation of methyl esters in supercritical methanol method. Recently, Kusdiana and Saka [218] studied the effect of water on the yield of methyl esters by the supercritical methanol treatment (623 K, 43 MPa, 4 min of treatment with a methanol to oil molar ratio of 42:1) compared with those from alkaline- and acid-catalyzed method. In the supercritical methanol method the amount of water added into the reaction system did not have a significant effect on the conversion. Effect of water and FFA contents on the alkaline- and acid-catalyzed and supercritical transesterification of triglycerides are shown in Figs. 8 and 9.

### 4.4.3.3. Effect of reaction temperature and time

The reaction temperature influences the reaction rate and yield of ester. Therefore, generally the reaction is conducted close to the boiling point of methanol, 318–338 K at atmospheric pressure [14,100]. Further increase in temperature is reported to have a negative effect on the conversion [222–224]. Iso et al. [222] examined the effect of reaction temperature on production of propyl oleate at the temperature range from 313 K to 343 K with free P. fluorescens lipase. In this study, the conversion ratio to propyl oleate was observed highest at 333 K, whereas the activity highly decreased at 343 K. Foon et al. [223] studied the effect of temperature on the transesterification of palm oil using a molar ratio of oil to methanol of 1:10, catalyzed by NaOMe and NaOH, and at 323 K, 333 K and 343 K, respectively. For reactions using NaOH, the effect of temperature was more significant. For the NaOH catalyzed reactions, it is best to carry them out at 333 K. Darnoko et al. [224] studied transesterification of palm oil with methanol (6:1) and 1% KOH at different reaction temperatures. According to study results, the best yield was obtained at 338 K (82%). Effect of temperature on the ethyl esters production from soybean oil in propane medium with lipase from Yarrowia lipolytica was investigated by Hildebrand et al. [193]. The experiments were performed in the temperature range of 308–338 K at 50 bar, enzyme concentration of 5 wt.%, oil to ethanol molar ratio of 1:6, and solvent to substrates mass ratio of 2:1. Fig. 10 presents the results of these experiments.

The methyl ester conversion rate increases with the reaction time. Different researchers have reported different reaction times for the transesterification process. Kim et al. [225] studied the transesterification reaction, with methanol (6:1), of vegetable oils using NaOH and Na/NaOH/γ-Al2O3 as catalysts at 333 K. They reached the maximum biodiesel yield within 1 h both for the case of homogeneous and heterogeneous catalyst system. For the homogeneous catalyst system, the maximum biodiesel production yield was higher by 20% than that of the heterogeneous catalyst system. Results of this study are shown in Fig. 11. Demirbas [213] investigated the changes in yield percentage of methyl esters

### Table 24

The effect of alcohol type on conversion and specific gravity of ester [221].

<table>
<thead>
<tr>
<th>Alcohol type</th>
<th>Boiling point (K)</th>
<th>Reaction temperature (K)</th>
<th>Conversion (%)</th>
<th>Specific gravity of biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>338</td>
<td>333</td>
<td>87.8</td>
<td>0.8876</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>355.4</td>
<td>348</td>
<td>92.9</td>
<td>0.8786</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>390</td>
<td>383</td>
<td>92.1</td>
<td>0.8782</td>
</tr>
<tr>
<td>Ethanol</td>
<td>351.5</td>
<td>348</td>
<td>95.8</td>
<td>0.8814</td>
</tr>
</tbody>
</table>
as treated with subcritical and supercritical methanol at different temperatures as a function of reaction time. Molar ratio of vegetable oil to methyl alcohol: 1:41. Sample: hazelnut kernel oil [213].

4.4.3.4. Effect of catalyst content and type. Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [137]. Stavarache et al. [165] investigated the effect of different catalyst concentrations on base-catalyzed transesterification during biodiesel production from vegetable oil by means of ultrasonic energy. The best yields were obtained when the catalyst was used in small concentration, i.e. 0.5% wt/wt of oil.

The effect of different catalysts types on methanolysis of RBD palm oil with a low FFA content of <0.1% was examined by May [226]. In that study, it was concluded that Na, NaOH and KOH are effective catalysts. Results of this study are shown in Table 25.

Meneghetti et al. [227] investigated the effect of different catalyst types at different temperatures during the production of free and bound ethyl ester from castor oil. Results of this study showed that HCl is much more effective than NaOH at higher reaction temperatures (Fig. 13).

4.4.4. Downstream processing

The ASTM standards ensure that the following important factors in the fuel production process by transesterification are satisfied: (i) complete transesterification reaction, (ii) removal of glycerin, (iii) removal of catalyst, (iv) removal of alcohol, and (v) complete esterification of FFAs. Lower value of the specific gravity of the final product is an indication of completion of reaction and removal of heavy glycerin [100]. As a rule of thumb difference, in specific gravity of 0.1 in a mixture of compounds will result in phase separation by gravity [228]. Gravity separation is suitable to recover biodiesel from the process byproducts (glycerin and alcohol), as can be seen in Table 15.

The chemical reaction products are an alkyl ester, commonly referred to as a biodiesel and crude glycerol. Crude glycerol, the heavier liquid will collect at the bottom after several hours of settling. Phase separation can be observed within 10 min and can be complete within 2 h after stirring has stopped. After the phases separate, the biodiesel

![Fig. 10. Effect of temperature on the ethyl esters production from soybean oil in propane medium with lipase from Yarrowia lipolytica [193].](image1)

![Fig. 11. Effect of reaction time on the biodiesel production yield. Methanol/VO molar ratio 6:1, reaction temperature 333 K, stirring speed 300 rpm, without cosolvent [225].](image2)

![Fig. 12. Changes in yield percentage of methyl esters as treated with subcritical and supercritical methanol at different temperatures as a function of reaction time. Molar ratio of vegetable oil to methyl alcohol: 1:41. Sample: hazelnut kernel oil [213].](image3)

![Fig. 13. The effect of different catalyst types at different temperatures during the production of free and bound ethyl ester (FAEE) from castor oil [227].](image4)

Table 25

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount (wt.% based on oil)</th>
<th>Reaction time (min)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.1</td>
<td>16–32</td>
<td>99% yield</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.2</td>
<td>16–32</td>
<td>98% yield</td>
</tr>
<tr>
<td>KOH</td>
<td>1</td>
<td>16–32</td>
<td>98% yield</td>
</tr>
<tr>
<td>H₂SO₄ (conc.)</td>
<td>1</td>
<td>&gt;300</td>
<td>50% yield</td>
</tr>
<tr>
<td>HCl (conc.)</td>
<td>1</td>
<td>&gt;300</td>
<td>30% yield</td>
</tr>
<tr>
<td>Ion exchange resin (H⁺)</td>
<td>2</td>
<td>&gt;300</td>
<td>Too slow</td>
</tr>
<tr>
<td>Dowex 50 (Na⁺)</td>
<td>1</td>
<td>&gt;300</td>
<td>Too slow</td>
</tr>
<tr>
<td>Acid treated Florisil</td>
<td>2</td>
<td>&gt;300</td>
<td>Too slow</td>
</tr>
<tr>
<td>Activated silica gel</td>
<td>1</td>
<td>&gt;300</td>
<td>Not suitable</td>
</tr>
</tbody>
</table>

4 The following conditions were used: type of oil = RBD palm oil (FFA = 0.05%); ratio of oil-to-solvent (methanol) = 1:15.6; temperature = reflux temperature.
separate, water is added at the rate of 5.5% by volume of the feedstock and then stirred for 5 min and the glycerol allowed to settle again. After settling is complete the glycerol is drained and the ester layer remains [15].

An excess of alcohol is normally used in biodiesel production, to be sure that the oil or fat used will be fully converted to esters. But the amount of alcohol in the system has to be minimized for good phase separation. Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream [211, 229].

5. Conclusion

With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines. Vegetable oils have the potential to substitute a fraction of petroleum distillates and petroleum-based petrochemicals in the near future. Fundamentally, high viscosity appears to be a property at the root of many problems associated with direct use of vegetable oils as engine fuel. Vegetable oils can be converted into to avoid these viscosity-related problems. Different ways have been considered to reduce the high viscosity of vegetable oils.

The transesterification of vegetable oils by methanol, ethanol, propanol, and butanol has proved to be the most promising process. Biodiesel from transesterification of the vegetable oils is better than diesel fuel in terms of sulfur content, flash point, aromatic content and biodegradability. Ethanol is a preferred alcohol in transesterification reaction compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however, methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol).

The catalytic transesterification of vegetable oils with methanol is an important industrial method used in biodiesel synthesis. Although transesterification using acid catalysts is much slower than that obtained from alkali catalysis, typically 4000 times, if high contents of water and FFAs are present in the vegetable oil, acid-catalyzed transesterification can be used. Alkaline catalysts have the advantages, e.g., short reaction time and relatively low temperature can be used with only a small amount for catalyst and with little or no darkening of colour of the oil. They show high performance for obtaining vegetable oils with high quality. However, alkaline catalyzed transesterification has several drawbacks: it is energy intensive, the recovery of glycerol is difficult, the acid or alkaline catalyst has to be removed from the product, alkaline wastewater requires treatment, and FFAs and water interfere with the reaction. Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems. In particular, it should be noted that the byproduct, glycerol, can be easily recovered with simple separation processes. Nevertheless, enzymatic catalysts are often more expensive than chemical catalysts, so recycling and reusing them is often a must for commercial viability.

Recently, there have been some reports on the non-catalytic transesterification reaction employing supercritical methanol conditions. Transesterification of vegetable oils in supercritical methanol are carried out without using any catalyst. Supercritical methanol has a high potential for transesterification of triglycerides to methyl esters for diesel fuel substitute. Besides, the supercritical transesterification method is more tolerant to the presence of water and FFAs than the conventional alkali-catalyzed technique, and hence more tolerant to various types of vegetable oils, even for fried and waste oils. Compared with transesterification, pyrolysis process has more advantages. The fuel properties of the liquid product fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. The higher heating value of pyrolysis oil from a vegetable oil is slightly lower than that of gasoline, diesel fuel or petroleum, but higher than coal.

References


[51] Lustig N. The curse of volatile food prices: policy dilemmas in the developing world. Tenth annual conference on “natural resources and development” global development network, Kuwait City (Kuwait), February 1–5; 2009.


Novel highly integrated biodiesel production technology in a centrifugal contactor separator device

G.N. Kraai, B. Schuur, F. van Zwol, H.H. van de Bovenkamp, H.J. Heeres* 

Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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The base catalyzed production of biodiesel (FAME) from sunflower oil and methanol in a continuous centrifugal contactor separator (CCS) with integrated reaction and phase separation was studied. The effect of catalyst loading (sodium methoxide), temperature, rotational frequency and flow rates of the feed streams was investigated. An optimized and reproducible FAME yield of 96% was achieved at a feed rate of 12.6 mL min\(^{-1}\) sunflower oil and a sixfold molar excess of MeOH containing the catalyst (1 wt% with respect to the oil). A jacket temperature of 75 °C and a rotational frequency of 30 Hz were applied. The productivity under those conditions (61 kg FAME m\(^{-3}\) min\(^{-1}\)) was slightly higher than for a conventional batch process. The main advantage is the combined reaction–separation in the CCS, eliminating the necessity of a subsequent liquid–liquid separation step.

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1. Introduction

Concerns for the environment combined with the current high crude oil prices have stimulated the interest in biofuels from renewable resources [1–3]. In January 2007 the European Commission published the New Energy Policy for Europe, targeting a 10% share of biofuels in the transportation sector and raising the share of renewable energy to 20% by 2020 [1]. This has stimulated the production of biofuels in Europe considerably, with biodiesel being the most important example. The projected biodiesel consumption for 2007 was 3.8 MTOE, a 70% increase compared to 2006 [4].

Typically, biodiesel, also known as FAME (fatty acid methyl ester) is produced from plant or vegetable oils and fats by transesterification with an alcohol (Fig. 1) [5,6]. A wide variety of different oils and alcohols can be used for the production of biodiesel. Most frequently methanol is the alcohol of choice, although higher alcohols like ethanol, 2-propanol and 1-butanol may be applied as well [7]. Glycerol is a byproduct from the transesterification and has to be separated from the FAME after the reaction [8]. FAME production may either be catalyzed by acidic or basic catalysts. Typical examples of homogeneous base catalysts are sodium hydroxide, potassium hydroxide and sodium methoxide [9], well known examples of homogeneous acidic catalysts are sulfuric acid, phosphoric acid and hydrochloric acid [10]. Both types of catalyzed reactions have been extensively studied [11–13]. Besides homogeneous acidic and basic catalysts, enzymes [14] and heterogeneous catalysts have been explored as well [11,15].

FAME production is most commonly performed in batch operation, although continuous processes are emerging [11,16–21]. New catalyst, reactor and process concepts for biodiesel production have been reported the last decade. An interesting example is the use of supercritical methanol [22]. In this medium, complete conversion is obtained within 5 min of reaction time without the need of a catalyst.

We here report the use of highly intensified centrifugal contactor separator (CCS) equipment (CINC V02 [23]) for biodiesel synthesis. In the CCS device reaction and separation are combined in a single apparatus, thus making it a good example of process intensification (PI). PI is currently one of the most significant trends in process engineering and aims at replacing large, energy consuming processes (PI). PI is currently one of the most significant trends in process engineering and aims at replacing large, energy consuming processes [24] by small, highly integrated processes to reduce the size and energy consumption of process plants. Some well known examples of PI are reactive distillation, reactive extraction and the application of micro-reactors [24,25].

The CINC V02 (Fig. 2) is basically a rotating centrifuge in a static reactor housing. The immiscible liquids are fed to the CCS where they are dispersed in the annular zone between the static housing and the rotating centrifuge. The dispersion is then transferred into the hollow centrifuge, through a hole in the bottom plate, where the phases are separated by centrifugal forces of up to 900 × g, making it possible to separate fluids with densities that differ only 10 kg m\(^{-3}\). Both liquid phases are collected individually, making use of a weir system.

The CCS was originally designed for waste water cleaning in the nuclear industry [26] and has been used successfully for oil–water
separation [27] (e.g. for cleaning oils spills [28]), for extraction of fermentation broths [29] and several other extraction processes [30–33]. We recently demonstrated the use of the CCS for enantioselective extractions of amino acid derivatives [34] and reported process integration in the CCS by combining biphasic (bio)catalytic conversions with the separation of the catalyst and the reaction products in the device [35]. These examples clearly illustrate the potential of the CCS equipment for the combined reaction and separation for liquid–liquid systems. The use of the CCS for biodiesel synthesis was also mentioned in this communication. We here report the results of an in depth experimental study to optimize the biodiesel yield in a CCS. The effects of process variables like the temperature, the flow rates and the rotational frequency on the biodiesel yield will be provided and rationalized and the potential of the CCS for biodiesel manufacture will be discussed.

2. Methods

2.1. Materials

Methanol (99.8%) was obtained from Labscan, sodium methoxide solution 30% in methanol (5.4 M) was obtained from Fluka. D$_2$O (99.9%) and CDCl$_3$ (99.8%) were obtained from Sigma–Aldrich. Hydrochloric acid (37%) was obtained from Merck and the sunflower oil was purchased from Albert Heijn, the Netherlands.

2.2. Equipment and conditions

The experiments were performed in a CCS of the type CINC V02 (CINC stands for Costner Industries Nevada Corporation) equipped with a heating/cooling jacket, a high-mix bottom plate and a 0.925 in. weir. The CCS was operated at ambient pressure and jacket temperatures ranging from 60 to 75 °C using a Julabo MV basis temperature controlled water bath (accuracy ±0.01 °C) connected to the jacket. Two Watson-Marlow 101U/R MK2 peristaltic tube pumps were used to feed the CCS. The temperature was monitored at each of the two CCS outlets using CMA B016BT temperature sensors connected to a PC via a Coachlab II (CMA) interface. The system was operated at atmospheric pressure by positioning air inlets in the liquid in and outlets. A schematic illustration of the set-up is shown in Fig. 3. The impeller in the annular zone is for illustrative purposes only. In a CINC, mixing in the annular zone is the result of rotation of the centrifuge.

2.3. Experimental procedure

The CCS was operated in a once-through mode for both liquids without recycle of the exit streams. The supply vessels containing the pure sunflower oil and the methanol with sodium methoxide, respectively were preheated to 60 °C and the water bath was set to the pre-determined temperature (60–75 °C). The centrifuge was started (20–90 Hz) and the CCS was fed with pure sunflower oil (12.6–40 mL min$^{-1}$). The molar ratio of methanol to oil was set at 6:1 in all experiments. As soon as the oil started flowing out of the heavy phase outlet, the reaction was started by feeding the methanol and sodium methoxide solution (1% (w/w) with regard to sunflower oil) at 3.15–10 mL min$^{-1}$. After steady operation was achieved (typically 10–35 min), a glycerol stream with some unreacted methanol exited the CCS through the heavy phase exit. FAME with unreacted oil left the CCS through the light phase exit. The dissolved catalyst is present in both outlet phases. Samples were taken at regular intervals from the light phase outlet and analyzed using $^1$H NMR.

2.4. Analytical methods

The FAME yield was determined using $^1$H NMR. Hereto, a 1 mL sample of the light phase was directly quenched by adding 1 mL of 0.1 M HCl in water to neutralize the remaining sodium methoxide. The mixture was vigorously shaken and centrifuged for 10 min. A few drops were taken from the top layer and dissolved in CDCl$_3$. The samples were analyzed using a 200 MHz Varian NMR. To determine the FAME yield [36], the intensity of the characteristic signal of the

---

**Fig. 1.** The transesterification of a plant or vegetable oil or fat with methanol.

**Fig. 2.** Schematic cross-sectional view of the CINC (courtesy of Auxill, the Netherlands).
ester (2.3 ppm) was compared with that of the characteristic signal of the methyl end group (0.9 ppm) present in both sunflower oil and FAME.

3. Results and discussion

3.1. Exploratory experiments

The experiments were carried out with sunflower oil and NaOMe as the catalyst. Sunflower oil is readily available in high purity with a low free fatty acid number (FFA). The latter is important as a high FFA number renders the base catalyzed biodiesel synthesis cumbersome due to the formation of the sodium salts of free fatty acids (soap). The FFA number of the sunflower oil applied in this study was below 1 wt%. The molar ratio of methanol to oil was set at 6:1 in all experiments, in line with batch studies in the literature for sunflower oil and methanol [37].

In an exploratory experiment the CCS was fed with sunflower oil (40 mL min\(^{-1}\)) and a solution of NaOMe in MeOH (10 mL min\(^{-1}\), 1% (w/w) with regard to sunflower oil). The reaction was performed with a jacket temperature of 60 °C and a rotational frequency (N) of 50 Hz. The profile of the FAME yield in time is shown in Fig. 4. It takes about 15 min to reach the steady-state FAME yield of about 65%. The liquid residence time in the CCS is estimated to be about 3.5 min, based on a total liquid hold-up of 180 mL [38] and a total liquid flow rate of 50 mL min\(^{-1}\). Thus, steady-state is reached in just over 3 residence times. After reaching steady-state, the FAME with residual sunflower oil exited the CCS as the light phase, whereas the heavy phase consisted of glycerol in MeOH. To gain insights in the reproducibility, a second run was performed under identical conditions. The results are shown in Fig. 4 as well and imply that reproducibility is good.

These exploratory experiments clearly indicate the proof of principle of biodiesel synthesis in a CCS. In the following part of this paper, the effect of process conditions (temperature, catalyst loading, flow rates, rotational speed of centrifuge) on the biodiesel yield will be described, with the objective to obtain 95+% yield in a single run.

3.2. Effect of reaction temperature

The effect of the reaction temperature on the FAME yield was studied by adjusting the jacket temperature in the range 60–75 °C, while keeping all the other variables constant (N: 30 Hz, F\(_{\text{oil}}\): 12.6 mL min\(^{-1}\), F\(_{\text{MeOH/NaOMe}}\): 3.15 mL min\(^{-1}\) (6:1 molar ratio of methanol to oil), and NaOMe: 1% (w/w) with regard to sunflower oil). The reaction was performed with a jacket temperature of 60 °C and a rotational frequency (N) of 50 Hz. The profile of the FAME yield in time is shown in Fig. 4. It takes about 15 min to reach the steady-state FAME yield of about 65%. The liquid residence time in the CCS is estimated to be about 3.5 min, based on a total liquid hold-up of 180 mL [38] and a total liquid flow rate of 50 mL min\(^{-1}\). Thus, steady-state is reached in just over 3 residence times. After reaching steady-state, the FAME with residual sunflower oil exited the CCS as the light phase, whereas the heavy phase consisted of glycerol in MeOH. To gain insights in the reproducibility, a second run was performed under identical conditions. The results are shown in Fig. 4 as well and imply that reproducibility is good.

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3.3. Effect of catalyst loading

The amount of catalyst has a profound effect on the rate of biodiesel formation. Typically 1 wt% of catalyst on the oil is applied. This loading was also used in the exploratory experiments described above. A number of experiments were performed at higher catalyst loadings (1–1.3% (w/w) with regard to sunflower oil) with all other conditions at constant value (N: 30 Hz, F\(_{\text{oil}}\): 12.6 mL min\(^{-1}\), F\(_{\text{MeOH/NaOMe}}\): 3.15 mL min\(^{-1}\), and NaOMe: 1% (w/w) with regard to sunflower oil).

The steady-state FAME yield at the lowest temperature in the range (60 °C) was 87%. At 75 °C, the yield increased to 96%, see Fig. 5 for details. It is well known that the FAME yield is a strong function of the temperature, with higher temperatures leading to higher yields for a given reaction time [35]. Higher jacket temperatures to further enhance the yield could not be applied due to excessive methanol evaporation.

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The effect of the reaction temperature on the FAME yield was studied by adjusting the jacket temperature in the range 60–75 °C, while keeping all the other variables constant (N: 30 Hz, F\(_{\text{oil}}\): 12.6 mL min\(^{-1}\), F\(_{\text{MeOH/NaOMe}}\): 3.15 mL min\(^{-1}\), and NaOMe: 1% (w/w) with regard to sunflower oil).

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of the triglyceride and reaction of the remaining free fatty acids with NaOMe. Thus, yield enhancement by the application of higher intakes of catalyst is not possible due to solid soap formation in the centrifuge.

3.4. Effect of liquid flow rates

The effect of the liquid flow rates on the FAME yield was studied in the range 12.6–40 mL min$^{-1}$ for sunflower oil. In all cases, the methanol flow rate was 25% of the sunflower flow rate to ensure a fixed sixfold molar excess of methanol over sunflower oil [37].

The FAME yield drops when increasing the sunflower flow rate from 12 to 40 mL min$^{-1}$, see Fig. 6 for details. The prime reason is likely a reduction of the mean residence times of both phases in the CINC when increasing the flow rates, leading to lower conversions. Recent work by Schuur et al. [39] have shown that the liquid hold-ups at these relatively low feed rates (<100 mL min$^{-1}$) are essentially independent of the flow rates, implying that the mean residence time is a function of the flow rate. Further reduction of the sunflower flow rates below 12 mL min$^{-1}$ to increase the FAME yield is not possible due to incomplete phase separation of both outlet streams.

3.5. Effect of rotational frequency

The rotational frequency was varied from 20 to 90 Hz for two jacket temperatures (60 and 70 °C) while keeping the other parameters constant ($F_{\text{oil}}$: 12.6 mL min$^{-1}$, $F_{\text{MeOH/NaOMe}}$: 3.15 mL min$^{-1}$, and NaOMe: 1% (w/w) with regard to sunflower oil).

The FAME yield is a strong function of $N$ and varied between 60 and 94% (Fig. 7). At low rotational frequencies ($N < 30$ Hz), a strong increase of the yield was found with increasing $N$. The yield reaches a maximum between 30 and 40 Hz. A further increase leads to a lowering of the yield. Similar trends were observed for the biphasic esterification of oleic acid with 1-butanol catalyzed by a Rhizomucor miehei lipase [35], where a maximum at 40 Hz was observed.

The overall sunflower conversion in this biphasic system is expected to be determined by the intrinsic kinetics of sunflower formation as well as by mass transfer effects. The trends in Fig. 7 may be rationalized by taking these two factors into account. At low rotational speed ($N < 30$ Hz), the overall conversion is likely mainly determined by mass transfer effects (mass transfer limited regime). The power input is rather limited, leading to relatively large droplets in the annular zone and thus to a relatively low value of the volumetric mass transfer coefficient ($k_{\text{L}}a$) [40–43].

Based on this rationalize, the overall conversion rate for $N > 40$ Hz is determined solely by the intrinsic kinetics of biodiesel synthesis and the FAME yield is expected to be independent of the value of $N$ (kinetic regime). However, this is not the case and the yield is lowered at higher $N$ values. It is well possible that this reduction is related to the changes in the volume of the reactive phase in the CINC as a function of the value of $N$. For a biphasic reaction with relatively fast kinetics, the reaction only takes place in a dispersion consisting of a continuous and a dispersed phase of small droplets. In the CCS, this dispersion is found in the annular zone as well as in parts of the centrifuge. The volume of the dispersed phase in the annular zone is about constant at these low flow rates and independent of $N$ [39]. However, the volume of the dispersed phase in the centrifuge is expected to be a function of the rate of rotation $N$.

This may be rationalized by considering the settling velocity of individual drops in the centrifuge. In a centrifugal settler the settling velocity for individual drops is given by Eq. (1) [44]:

$$v_{S, CCS} = \frac{d^{2} \rho_{d} (\rho_{d} - \rho_{c}) \omega^{2} R}{18 \mu_{c}} \tag{1}$$

The settling velocity of the droplets in the dispersed zone is thus proportional to the difference in density, the angular momentum and the squared drop diameter.

Due to the proportionality of the settling velocity with the angular momentum, we can expect that the dispersed phase volume in the centrifuge will be reduced considerably at high rotational speeds, see Fig. 8 for details. Thus, the observed reduction of the FAME yield in the kinetic regime at $N > 40$ Hz, is likely due to a strong reduction of the volume of the reactive, dispersed phase in the centrifuge of the CCS.
are shown in Fig. 9. Reproducibility is good, see Fig. 9 for details.

The yield of FAME in time, duplicate run. (N = 30 Hz, catalyst load of 1% (w/w), jacket temperature 75 °C, flow of the oil and of the methanol/methoxide feed of 12.6 and 3.15 mL min⁻¹, respectively). The results for two duplicate runs are shown in Fig. 9. After about 30 min, steady-state is reached and the FAME yield was on average 96%. Reproducibility is good, see Fig. 9 for details.

3.6. FAME synthesis at optimum settings

With the effects of the most important process variables on the FAME yield established, experiments at optimum settings were performed (N = 30 Hz, catalyst load of 1% (w/w), jacket temperature 75 °C, flow of the oil and of the methanol/methoxide feed of 12.6 and 3.15 mL min⁻¹, respectively). The results for two duplicate runs are shown in Fig. 9. Thus, it appears that the productivity in the CINC V02 is at least comparable and likely higher than state of the art batch processes. However, compared to batch the CCS has other advantages, the main being that a liquid–liquid separator after reaction is not required as this function is already integrated in the CCS. From the literature [46] it is known that it may take up to 2 h to obtain complete phase separation. Furthermore, the obvious advantages of continuous processes compared to batch are also valid in this case (e.g. product consistency and operator effort).

4. Conclusions and outlook

In this study, the proof of principle for the continuous biodiesel manufacture in a highly integrated CCS of the type CINC V02 is provided. As such, it demonstrates the potential of CCS equipment to be used for combined reactions and separation for biphasic (catalytic) systems. At optimum conditions a reproducible FAME yield of 96% was achieved. The volumetric production rates are at least comparable to state of the art batch processes. Further improvements are likely by hardware modifications, and particularly by modifications of the annular zone to allow for higher flow rates while maintaining a high conversion level. These studies as well as reactor engineering studies including detailed kinetics and hydrodynamics features are in progress at the moment.

Due to the compact size and flexibility in operation, the CCS equipment is likely very suitable for biodiesel production in mobile units in developing countries. A cascade of two CINCs in series, one for biodiesel production and one for a subsequent aqueous wash to remove remaining glycerol and catalyst, followed by a methanol stripper, may be a very attractive process option for further exploration and demonstration.

3.7. Volumetric production rate in the CCS

The volumetric production rate of FAME production in the CINC V02 at optimized settings were calculated to be 61 kgs⁻¹ FAME m⁻³ liquid min⁻¹. This corresponds with an annual production rate of about 5.6 ton/year. The largest CCS of the CINC type available is the CINC V20 with a maximum flow through put of 757 L min⁻¹. When assuming that the same volumetric production rate can be achieved in this CCS and taking a volumetric ratio of both devices of about 400, the productivity in the large CINC V20 is estimated to be about 2.2 kton/year.

It is of interest to compare the volumetric production rate in the CINC V02 with that for a typical batch process. Literature data imply that 98% yield is typically obtained in 20 min reaction time [45]. This corresponds with a productivity of about 40 kgs⁻¹ FAME m⁻³ liquid min⁻¹.

Fig. 9. The yield of FAME in time, duplicate run. (N = 30 Hz, catalyst load of 1% (w/w), jacket temperature 75 °C, flow of the oil and of the methanol/methoxide feed of 12.6 and 3.15 mL min⁻¹, respectively (6:1 molar ratio of methanol to oil), yield is the average steady-state yield for at least 2 h runtime.)

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References

Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions

T. Eevera*, K. Rajendran, S. Saradha

Department of Biotechnology, Periyar Maniammai University, Periyar Nagar, Vallam, Thanjavur, Tamilnadu 613 403, India

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Abstract

In this study, both edible (coconut oil, palm oil, groundnut oil, and rice bran oil) and non-edible oils (pongamia, neem and cotton seed oil) were used to optimize the biodiesel production process variables like catalyst concentration, amount of methanol required for reaction, reaction time and reaction temperature. The fuel properties like specific gravity, moisture content, refractive index, acid value, iodine number, saponification value and peroxide value were estimated. Based on the cetane number and iodine value, the methyl esters obtained from palm and coconut oils were not suitable to use as biodiesel in cold weather conditions, but for hot climate condition biodiesel obtained from the remaining oil sources is suitable.

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1. Introduction

The increased use of diesel fuel resulted in depletion of its fossil reserves. This triggers for many initiatives to search for alternate fuel, which can supplement or replace such fossil fuel. In recent years, research has been directed to explore plant-based fuels and plant oils and fats as fuels have bright future [1]. The most common that is being developed and used at present is biodiesel, which is fatty acid methyl esters of seed oils and fats and have already been found suitable for use as fuel in diesel engine. Biodiesel is found to be environmentally safe, non-toxic and biodegradable [2].

The raw material being exploited commercially by the developed countries constitutes the edible fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, linseed, etc. [3]. Use of such edible oil to produce biodiesel in India is not feasible in view of a big gap in demand and supply of such oils in the country. Increased pressure to augment production of edible oil has also put limitation on the use of these oils for production of biodiesel. Under such conditions, those crops that produce non-edible oil in appreciable quantities can be grown in large scale in non-cropped marginal lands and wastelands only considered for biodiesel production [4].

Long list of trees, shrubs and herbs is available plenty in India, which can be exploited for fuel production. In this study we have utilized both edible and non-edible oils for the biodiesel production process optimization and fuel property characterization to assess the suitability of the different methyl esters to the varied environmental conditions.

2. Materials and methods

Edible (coconut oil, palm oil, groundnut oil, rice bran oil, and gingelly oil) and non-edible (pongamia, cotton seed oil and neem oil) oils were used in this experiment.

All the oils were first filtered by cloth mainly to remove the dirt and other inert materials from the oil and then placed in a conical flask equipped with magnetic stirrer, thermometer and condenser. Under agitation the raw oil was heated up to nearer to the boiling point to remove the water contaminant present in the oil. After that oil is allowed to cool down under room temperature, and the treated oil alone was taken for biodiesel production purpose. Again, under agitation, the above treated oil was heated up to a desired temperature on a hot plate. A fixed amount of freshly prepared sodium hydroxide–methanol solution was added into the oils, taking this moment as the starting time of the reaction. When the reaction reached the preset reaction time, heating and stirring were stopped. The products of reaction were allowed to settle overnight. During settling two distinct liquid phases were formed: crude ester phase at the top and glycerol phase at the bottom. The crude ester phase separated from the bottom glycerol phase was then washed by cold or warm de-ionized water several times until the washed water became clear. The excess methanol and water in ester phase were then removed by evaporation under atmospheric condition.
After that weight of the ester was taken for product yield calculation.

The reaction was investigated step by step. The optimal value of each parameter involved in the process was determined while the rest of the parameters were kept constant. After each optimal value was attained, this value was adopted for the optimization of the next parameter.

Physical and chemical properties of methyl esters were estimated [5,6] under laboratory conditions. The cetane number (CN) and higher heating values (HHVs) were calculated [4,6] from the following equation by using the estimated saponification value (SV) and iodine value (IV).

\[
CN = 46.3 + \frac{5458}{SV} - 0.225IV \tag{1}
\]

\[
HHV = 49.43 - [0.041(SV) + 0.015(IV)] \tag{2}
\]

3. Result and discussion

3.1. Effect of catalyst concentration

The effect of sodium hydroxide concentration on the transesterification of the edible and non-edible oils was investigated with its concentration varying from 0.5 to 2.5 wt.% (based on the weight of raw oil). The operation conditions during the whole reaction process were fixed at the optimal level: reaction temperature of 55°C, reaction time of 90 min. and 180 and 210 ml of methanol for edible and non-edible oils, respectively.

Experimental results showed changes in ester yield content with varied catalyst concentration. As the sodium hydroxide concentration increased, the conversion of triglyceride as well as the ester content also increased. Insufficient amount of sodium hydroxide resulted in incomplete conversion of triglycerides into the esters as indicated from its lower ester content. The ester content reached an optimal value when the sodium hydroxide concentration reached 1.5 wt.%, and further increase in catalyst concentration in all the cases, ester production amount decreased as shown in Fig. 1. Large amount of soap was observed in excess amount of sodium hydroxide added experiments. This is because addition of excess alkaline catalyst caused more triglycerides’ participation in the saponification reaction with sodium hydroxide, resulting in the production of more amount of soap and reduction of the ester yield [7].

3.2. Effect of reaction time

The reaction time of the transesterification reaction conducted at 55°C was optimized with the highest achievable mixing degree, an excess amount of alcohol (220 ml per liter of oil) and optimal sodium hydroxide concentration of 1.5 wt.% for all the oils.

The changes in product composition with reaction time during the transesterification of the oils and the distribution of various components in the reaction system can be clearly seen. When the reaction time reached 90 min, no triglyceride was left in the product mixture, indicating complete conversion. In this experiment, glycerol started to separate within 15 min. The ester content increased with reaction time from 15 min onwards and reached a maximum at a reaction time of 90 min at 55°C, and then remained relatively constant with increasing further the reaction time (Fig. 2). The results indicated that an extension of the reaction time from 90 to 150 min had no significant effect on the conversion of triglycerides but leads to a reduction in the product yield. This is because longer reaction enhanced the hydrolysis of esters (reverse reaction of transesterification), resulted in loss of esters as well as causing more fatty acids to form soap.

3.3. Effects of methanol amount

The effect of alcohol amount on yield of the transesterification experiments was conducted with different amounts of methanol to oil in the range of 120–240 ml. The optimized catalyst concentration and reaction time as obtained in the above sections were adopted. Maximum ester content was obtained at a methanol amount of 180 ml for edible oil and 210 ml for non-edible oils.

With further increase in the methanol to oil amount above 210 ml, a very little effect on the biodiesel yield was observed.
Moreover, it was observed that for high alcohol amount added the set up required longer time for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier that enhances emulsion. Therefore, increasing the alcohol amount to oil is another important parameter affecting the biodiesel yield and biodiesel purity, apart from catalyst concentration and reaction time. This result is in line with the report of many investigations based on neat vegetable oils [7–9]. However the non-edible like pongamia and neem require 210 ml of methanol to give maximum ester yield, possibly due to higher viscosity of non-edible oil than edible oils. In this case more amount of methanol is required to increase the solubility of the oil in the methanol. This leads to maximize the ester yield at high methanol concentration level. However, when compared to edible oil ester content yield was minimal in non-edible oil but glycerol yield was found to be more in non-edible oil when compared to edible oil.

### 3.4. Effect of reaction temperature

To study the effect of reaction temperature on methyl esters’ formation, the transesterification reaction was carried out under the optimal conditions obtained in the previous section (i.e. 180 and 210 ml of methanol for edible and non-edible oils, and 1.5 wt.% sodium hydroxide). The experiments were conducted at temperature ranging from 40 to 60 °C at 5 °C interval. The effect of reaction time was shown in Fig. 4.

Experimental results showed that the transesterification reaction could proceed within the temperature range studied but the reaction time to complete the reaction varied significantly with reaction temperature. It can be seen that a high product yield could be achieved at 50 °C. With the temperature increase above 55 °C, the product yield started to decrease. The reason for this is that higher temperature accelerates the side saponification reaction of triglycerides.

### 3.5. Methyl ester chemical and physical property

Fuel properties like specific gravity, moisture content, refractive index, acid value (AV), iodine value (IV), saponification value (SV) and peroxide value (PV) were estimated. The cetane number (CN) and higher heating values (HHVs) of methyl ester were calculated based on the estimated SV and IV (Tables 1 and 2).

The estimated SV and IV range from 188 to 259 and 9 to 113, respectively. The CN value among the oils varied from 49.91 to 65.34; the HHV ranges in between 38.68 and 40.33 among the different methyl esters.

CN is the ability of fuel to ignite quickly after being injected. Better ignition quality of the fuel is always associated with higher CN value. This is one of the important parameter, which is considered during the selection of methyl esters for use as biodiesel. For this different countries/organization have specified different minimum values. Biodiesel standards of USA (ASTM D 6751), Germany (DIN V51606) and European Organization (EN 14214) have set this value as 47, 49, and 51, respectively [10]. In our experiment all the different methyl esters have CN value of higher than 51 except methyl esters obtained from gingelly (49.91) and groundnut (50.51) oils.

Another important criterion for selection of methyl esters is its degree of unsaturation, which is measured as IV. To an extent, the
presence of unsaturated fatty acid component in methyl esters is required as it restricts the methyl esters from solidification. However, with higher degree of unsaturation, methyl esters are not suitable for biodiesel as the unsaturated molecules react with atmospheric oxygen and are converted to peroxide, cross-linking at the unsaturation site can occur and the material may get polymerized into a plastic like body. At high temperature, commonly found in an internal combustion engine, the process can get accelerated and the engine can quickly become gummed up with the polymerized methyl esters. To avoid this kind of situation, biodiesel standards have set a minimum limit of IV in their specifications. All of the eight species, which qualify the specification of CN, also meet the requirement as it restricts the methyl esters from solidification. However, with increase of CN, IV decreases which means degree of unsaturation decreases. This situation will lead to the solidification of methyl esters at higher temperature. To avoid this situation, the upper limit of CN (65) has been specified in US biodiesel standards (ASTM D 6751-99 & ASTM PS 121-99) [10c,10d]. Among the eight methyl esters, which already met the specification of CN and IV of biodiesel standards, two of them like palm and coconut esters have low IV (<57.0) and exceed the upper limit of CN. So these two methyl esters are not suitable to use as a biodiesel in the cold weather conditions. The oils from remaining, as mentioned in the respective sources, are liquids under laboratory conditions, can be used both in cold and hot climates.

4. Conclusion

The study on the biodiesel production process optimization of edible and non-edible oils showed that the quantity of catalyst, amount of methanol, reaction temperature and reaction time are the main factors affecting the production of methyl esters. The optimal values of these parameters for achieving maximum conversion of oil to esters depended on the chemical and physical properties of these oils. The following conclusions are drawn from the study:

- Addition of excess catalyst causes more triglycerides’ participation in the saponification reaction leading to a marked reduction in the ester yield.
- Biodiesel production process is incomplete when the methanol amount is less than the optimal value. Operating beyond the optimal value, the ester yield would not be increased but will result in additional cost for methanol recovery.
- Higher reaction temperature decreases the viscosities of the oils and resulted in increased rate of transesterification and shortening of the reaction time. When the temperature increases beyond the optimum level it induces a negative impact on the ester yield due to acceleration of the saponification of triglycerides.
- Sufficient reaction time should be allowed to ensure complete conversion of triglycerides into esters. However, excess reaction time did not promote the conversion but favors the reverse reaction of transesterification which resulted in a reduction in the ester yield.
- The optimal reaction conditions for production of methyl esters from edible oil sources are established as follows: the reaction time of 90 min at 50 °C, 180 ml of methanol for 1000 ml of oil and 1.5 wt.% of NaOH catalyst. For non-edible oil based methyl esters’ production except the amount of methanol (210 ml/1000 ml of oil) requirement, the remaining optimal parameters are similar to edible oil based methyl esters’ production.
- Based on CN and IV, the palm and coconut oil based methyl esters are not suitable to use as a biodiesel in cold weather conditions. In hot climate conditions, however, all the methyl esters produced in this experiment including coconut and palm oil based esters are suitable to use as a fuel.

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References


### Table 2

<table>
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<th>SV</th>
<th>IV</th>
<th>PV</th>
<th>Moisture content (wt.%)</th>
<th>HHV (kJ/g)</th>
<th>CN</th>
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Activity of solid catalysts for biodiesel production: A review

Masoud Zabeti, Wan Mohd Ashri Wan Daud *, Mohamed Kheireddine Aroua

Chemical Engineering Department, Faculty of Engineering, University Malaya, 50603, Kuala Lumpur, Malaysia

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A B S T R A C T

Heterogeneous catalysts are promising for the transesterification reaction of vegetable oils to produce biodiesel. Unlike homogeneous, heterogeneous catalysts are environmentally benign and could be operated in continuous processes. Moreover they can be reused and regenerated. However, a high molar ratio of alcohol to oil, large amount of catalyst and high temperature and pressure are required when utilizing heterogeneous catalysts to produce biodiesel. In this paper, the catalytic activity of several solid base and acid catalysts, particularly metal oxides and supported metal oxides, was reviewed. Solid acid catalysts were able to do transesterification and esterification reactions simultaneously and convert oils with high amount of FFA (Free Fatty Acids). However, the reaction rate in the presence of solid base catalysts was faster. The catalyst efficiency depended on several factors such as specific surface area, pore size, pore volume and active site concentration.

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1. Introduction

Finding an alternative fuel has attracted considerable attraction in recent years due to limitation of traditional fossil resources and increasing of crude oil prices as well as concern over greenhouse gas emissions. Biodiesel, a biodegradable and renewable form of energy, consisting of mono alkyl esters of fatty acids derived from sources such as vegetable oils and animal fats, has cardinal potential as the engines could be fed with vegetable oils [2]. Recently, there has been renewed interest on vegetable oils and animal fats to produce biodiesel engine invented by Rudolph Diesel and it was concluded that the engines could be fed with vegetable oils [2]. Recently, there has been renewed interest on vegetable oils and animal fats to produce biodiesel since it offers many advantages such as high flash point, high cetane number, low viscosity, high lubricity, biodegradability, environmentally friendly due to less carbon monoxide emissions, as well as fewer emission profiles compared to conventional fossil fuels [3]. It can also be used in conventional compression-ignition engines without the need for engine modifications [4]. In addition, the fuel either used as pure or blend can reduce the particulate emissions from engine [5].

Different varieties of vegetable oils such as, canola [6], palm [7], jatropha [8], palm kernel [9], sunflower [10], and coconut [11] have been studied as precursors for biodiesel production. The main concern about biodiesel production is the high price of vegetable oils compared to that of fossil based diesel fuel. As a result, in some countries, non-edible oils such as jatropha or waste cooking oils [12] are preferred due to their low price. Blending of biodiesel with diesel fuel is another option to mitigate the high price of biodiesel and in this case, the blended product is designated as Bxx (B30, 30% biodiesel in 70% diesel fuel) [13].

There are several methods to produce biofuels from renewable sources and among the earliest is based on pyrolysis process whereby heavy molecules such as vegetable oils or animal fats are converted to smaller one by means of heat or heat and catalyst. The fuel obtained through this process was called “diesel-like fuels” since there were variety of components such as olefins and paraffin which are similar to the petroleum-based diesel. However, this process requires high temperatures between 300 and 500 °C and products characterization is difficult due to the variety of reaction products [14]. Lima et al. [15] pyrolyzed soybean oil using zeolite as the catalyst, at reaction temperature of 400 °C in a nitrogen flow and olefins, paraffin, carboxylic acids and aldehydes were observed in the products. Ensöz et al. [16] investigated the influence of particle size on the pyrolysis of rapeseed by varying the particle size of rapeseed in the range of 0.224–1.8 mm and found that the yields of products are largely independent of particle size. More than 30 compounds were detected from pyrolysis of Macauba fruit and was concluded that the amount of main products decreases by increasing the pyrolysis temperature [17].

Transesterification is one of the most commercially useable methods to produce biodiesel and the process involves a reaction between ester (here triglyceride) and alcohol to form new ester and alcohol. Different types of alcohols such as, methanol, ethanol, propanol and butanol have been used. However, methanol and ethanol are the most widely used, particularly methanol owing to its low price and availability [18].
the transesterification of triglyceride to fatty acid alkyl esters three reversible reactions take place consecutively in which diglycerides and monoglycerides are major intermediate products (Fig. 1) [19]. A review by Ma and Hanna [20] summarized the parameters that significantly affect on the rate of transesterification reaction which include reaction temperature, alcohol to oil molar ratio, catalyst concentration and type of catalyst. Transesterification can be performed at different temperatures, and the methyl ester yields increase by rising the reaction temperature. However, if the temperature reaches to the boiling point of methanol, a lot of methanol’s bubbles are formed hence inhibit the mass transfer on the phase’s interface [21]. In transesterification reaction the stoichiometric ratio of alcohol to oil is three moles of alcohol to one mole of oil. Therefore by using alcohol in excess it favors the formation of methyl esters. The alcohol oil molar ratio is dependent on the type of oil. Therefore by using alcohol in excess it favors the formation of methyl esters. The alcohol oil molar ratio required is approximately 6:1. Nevertheless, when acid catalysts are used more alcohol/oil molar ratio is required [22]. Transesterification reaction can be either carried out via non-catalytic or catalytic processes. Base catalysts, acid catalysts and enzymes are three categories of catalysts which have been studied for biodiesel production. Enzymatic base production of biodiesel has attracted many attention in recent years since enzymes tolerate free fatty acid and water contents in the oil to avoid soap formation and thus purification of biodiesel and glycerol is easier [23,24]. However, enzymes are expensive to be used in a commercial production of biodiesel.

Non-catalytic transesterification reaction is slow and normally needs high pressures and temperatures to be completed. Kusdiana and Saka [25] subjected rapeseed oil into transesterification process in the absence of catalyst and in the supercritical methanol and found that the amount of water in the reaction does not affect the conversion of oil. Conversely, the presence of certain amount of water increases the formation of methyl esters and esterification of free fatty acids takes place simultaneously in one stage. Although the products can be easily separated since there is no base or acid catalyst, the supercritical process needs to be carried out at high temperatures (250–400 °C) and pressure (35–60 MPa).

Significant amounts of work have been carried out on homogeneous acid and base catalysis transesterification of vegetable oils. Sulphuric acid and hydrochloric acid are normally used as acid catalysts especially when the oil contains high amount of free fatty acids and water since these catalysts are capable to handle esterification and transesterification of triglyceride simultaneously. Nonetheless, the process requires a high molar ratio of alcohol to oil and long reaction time [26]. Besides that, under these conditions all the equipment need to withstand against corrosion due to an acidity environment [27]. Sodium hydroxide and potassium hydroxide are examples of homogeneous base catalysts which are usually used in industry [28,29]. The transesterification can be performed in a shorter reaction time and relatively modest operation conditions [4]. In spite of this, the water and free fatty acids content in the oil need to be very low because of the probability of soap formation which can consume catalyst thus reducing the methyl ester yields. One of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is consumed in the reaction and separation of catalyst from products is difficult and requires more equipment which could result in higher production costs [26]. Besides, the process is not environmentally friendly because a large amount of waste water is produced in the separation step [30].

Based on the above premises, developing a new solid catalyst seems to be an appropriate solution to overcome problems associated with homogeneous catalysts. Metal hydroxides [6], metal complexes [31], metal oxides such as calcium oxide [32], magnesium oxide [33], zirconium oxide [34] and supported catalysts [35] have been investigated as solid catalysts. The catalysts are not consumed or dissolved in the reaction and therefore can be easily separated from the products. As a result, the products do not contain impurities of the catalyst and the cost of final separation could be reduced. The catalysts can also be readily regenerated and reused and is more environmentally benign because there is no need for acid or water treatment in the separation step [36]. Nevertheless, one of the major problems associated with heterogeneous catalysts is the formation of three phases with alcohol and oil which leads to diffusion limitations thus lowering the rate of the reaction [37]. One way of overcoming mass transfer problem in heterogeneous catalysts is using certain amount of co-solvent to promote miscibility of oil and methanol and accordingly accelerate the reaction rate. Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), n-hexane and ethanol were used more frequently as co-solvent in transesterification of vegetable oils with methanol and solid catalysts. Gryglewicz [38] used CaO as a solid base catalyst for transesterification of rapeseed oil with methanol and after 170 min of reaction time methyl ester yields of 93% were obtained. However, by adding certain amount of THF into rapeseed oil/methanol mixture the same yields of 93% were observed after 120 min of reaction time. Another way to promote mass transfer problems associated with heterogeneous catalysts is using structure promoters or catalyst supports which can provide more specific surface area and pores for active species where they can anchor and react with large triglyceride molecules.

Studies have been carried out to synthesize and develop new solid catalysts for transesterification reaction in order to overcome disadvantages of use of homogeneous catalyst and more likely to reduce the cost of biodiesel production. Bournay et al. [39] invented a new commercial continuous biodiesel production process, where a solid catalyst consists of zinc oxide and alumina was used and results showed that the process does not require any post treatment to remove the catalyst from biodiesel and methyl ester yields, close to theoretical value, were achieved at high pressure and temperature. Moreover, glycerol obtained through this process had a purity of approximately 98%.

Applications of heterogeneous catalysts for biodiesel production have been reviewed by some researchers such as reviews by Di Serio et al. [40] and Lotero et al. [41] and the mechanism of solid acid and base catalysts and their kinetics for transesterification reaction were mainly focused. However, in this article the application of different types of solid catalysts, particularly metal oxides and supported metal oxides, in transesterification of vegetable oils to produce biodiesel was reviewed in order to find the most suitable base and acid catalysts, supports, and the most effective parameters on the catalyst activity.

2. Catalysts

2.1. Metal oxides

Many metal oxides include alkali earth metal oxides and transition metal oxides have been studied for transesterification process of oils. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acid and negative oxygen ions (anions) which possess Bronsted base. In methanolysis of oils, it provides sufficient adsorptive sites for methanol, in which the O–H bonds readily break into methoxide anions and hydrogen cations (Fig. 2). Thus methoxide anions then react with triglyceride molecules to form corresponding fatty acid

![Fig. 1. Transesterification reaction of vegetable oil with alcohol to esters and glycerol.](image-url)
methyl esters [42]. There are several metal oxides which have been studied and among them are discussed below:

2.1.1. Alkali earth metal oxides

2.1.1.1. Magnesium oxide. Magnesium oxide which is produced by direct heating of magnesium carbonate or magnesium hydroxide has the weakest basic strength and solubility in methanol among group II oxides and has been rarely used for biodiesel production. Nano magnesium oxide has been used in transesterification of soybean oil and yields of 99% were obtained in 10 min under supercritical temperature of 523 °C and high pressure of 24 MPa [33]. The results showed that this catalyst has more activity at higher pressures and temperatures.

2.1.1.2. Calcium oxide. Among alkali earth metal oxides, calcium oxide has attracted many attentions for transesterification reaction since it possess relatively high basic strength and less environmental impacts due to its low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide. Calcium oxide has also been used as a catalyst for reactions involved in organic compounds such as isomerization of 5-vinylbicycle [2.2.1] hept-2-ene (VBH) to 5-ethylidenebicyclo [2.2.1] hept-2-ene (ENB) [43] and synthesis of 1,3-dialklyurea from ethylene carbonate and amine [44] and showed a high activity for organic reactions. In case of biodiesel production, Granados et al. [32] used the activated calcium oxide as a solid base catalyst in the methanalysis of sunflower oil to investigate the role of water and carbon dioxide on the deterioration of the catalytic performance by contact with air for different periods of time. The study showed that CaO is rapidly hydrated and carbonated in air. No calcium oxide peaks were detected in the samples exposed to air for more than 20 days. This means that active surface sites of CaO were poisoned with CO2 and covered with H2O. As a result, in order to avoid reduction of CaO catalytic activity, the catalyst was thermally treated at 700 °C in order to chemically desorb CO2 before being used in the reaction. After 100 min of reaction time, 94% conversion was obtained at 60 °C with alcohol/oil molar ratio of 13:1 and catalyst content of 3 wt.% based on the weight of oil. Leaching of active species was observed in the reaction media when the catalyst was activated at high temperature. However, the amount of leaching did not result in catalyst activity reduction and the catalyst was reusable for 8 cycles.

It was also found that small amounts of water can improve catalytic activity of CaO and biodiesel yields because in the presence of water, O\(^2^-\) on the surface of the catalyst extracts H\(^+\) from water molecules to form OH\(^-\) which subsequently extracts H\(^+\) of methanol to form methoxide anions, which are the real catalyst of transesterification reaction [45]. By adding 2.03 wt.% water into the reaction medium of 12:1 alcohol/oil molar ratio and 8 wt.% catalysts, the methyl ester yields exceeded 95% within 3 h of reaction time compare to 80% under anhydrous conditions. No leaching of the active species into the reaction media was observed and the activity of the catalyst was stable after 20 cycles of the reaction.

On the other hand, Demirbas [46] described the effect of the supercritical conditions on the catalytic transesterification of sunflower oil in the presence of 3 wt.% CaO 60–120 mesh, 40:1 alcohol/oil molar ratio, at 252 °C and pressure of 24 MPa. And found that after 26 min of reaction time 98.5% methyl ester yields were obtained. Unlike Granados et al. [32] and Liu et al. [45], Demirbas [46] believes that the calcium oxide catalytic performance is quite weak at low temperatures since only 5% methyl ester yields were obtained at 60 °C after 3 h.

2.1.1.3. Strontium oxide. Not much works have been carried out using this catalyst. Strontium oxide is a highly active metal oxide and seems to be soluble in the reaction medium. Transesterification of soybean oil with SrO as a solid base catalyst showed that although the specific surface area of the catalyst is as low as 1.05 m\(^2\)/g, 90% yields of methyl esters were achieved after 30 min of reaction time at 65 °C with alcohol/oil molar ratio of 12 and 3 wt.% catalyst [21]. The catalyst was stable even after 10 reaction cycles.

2.1.2. Transition metal oxides

Zirconium oxide, titanium oxide and zinc oxide are among the transition metal oxides that have attracted attention for biodiesel production due to their acidic properties. Zirconia has been used in variety of reactions, for example alkylation of isobutane [47] and isomerization of N-butane [48] and showed high activity correlated with acidity. Titanium oxide has been also used in reactions, including dehydration [42]. There have been several reports on the usage of zirconia as a solid acid catalyst for transesterification of different oils rather than other transition metal oxides due to its strong acidity and was found that the acidity is promoted when the surface of these metal oxides contains anions like sulfate and tungstate. Jitputti et al. [34] assessed the catalytic performance of zinc oxide and zirconium oxide as solid acid catalysts in transesterification reaction of palm kernel oil at supercritical methanol and found that after 1 h of reaction time, using 3 wt.% catalyst and 6:1 molar ratio of alcohol/oil, 86.1% methyl ester yields were obtained for zinc oxide while only 64.5% for zirconium oxide. However, using sulfated zirconia, the yields considerably increased to 90.3% which might be due to high acidic strength of sulfate anions on the surface of zirconia.

Catalytic activity of ZrO\(_2\)/SO\(_4^2-\) and ZrO\(_2\)/WO\(_3\) as super acid catalysts in the methanalysis of triacetin was compared by López et al. [49] and the results are shown in Table 1. The results indicate that the specific surface area and active site concentration play an important role in the catalyst activity. Sulfated zirconia showed more activity toward conversion of triacetin than tungstated zirconia owing to its higher specific surface area and active phase concentration under the same conditions of 60 °C and 8 h of reaction time.

Comparing activity of TiO\(_2\)/SO\(_4^2-\) and ZrO\(_2\)/SO\(_4^2-\) as solid strong acid catalysts in the transesterification of cotton seed oil to methyl esters, both catalysts showed high activity. However, higher methyl ester yields were obtained for sulfated titanium oxide due to its higher specific surface area of 99.5 m\(^2\)/g compare to 91.5 m\(^2\)/g for sulfated zirconia [50]. It was found that after the introduction of sulfate anions new Bronsted acid sites were formed on the catalyst surface. By introducing 2 wt.% catalyst and 12:1 alcohol/oil molar ratio, after 8 h of reaction time the methyl ester yields in the presence of TiO\(_2\)/SO\(_4^2-\) and ZrO\(_2\)/SO\(_4^2-\) were 90% and 85% respectively.

The activity of zirconium oxide functionalized with tungsten oxide was also studied by López et al. [51] to investigate the effect of calcination temperatures on the catalytic properties of ZrO\(_2\)/WO\(_3\) as a solid strong acid for transesterification of triacetin. The most active catalyst was obtained after calcination of 800 °C with the formation of Bronsted acid sites concentration of 161 μmol/g. The catalyst was active for both transesterification and esterification reactions although the reaction time was relatively long.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m(^2)/g)</th>
<th>Active site concentration (μmol/g)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO(_2)/SO(_4^2-)</td>
<td>134</td>
<td>94</td>
<td>57</td>
</tr>
<tr>
<td>ZrO(_2)/WO(_3)</td>
<td>89</td>
<td>54</td>
<td>10</td>
</tr>
</tbody>
</table>
On the other hand, Ramu et al. [52] evaluated the effect of calcination temperature on the catalytic performance of ZrO$_2$/WO$_3$ as well as the effect of amount of WO$_3$ loading on the zirconium oxide for the esterification of palmitic acid with methanol and discovered that the catalyst which was calcined at 500 °C had the most activity. This activity was attributed to the formation of tetragonal phase of ZrO$_2$. Beyond 500 °C the tetragonal phase transferred to the monoclinic phase which caused a decrease in the activity from 98% conversion of palmitic acid to 8% for the catalyst which was calcined at 900 °C. With 5 wt.% loading of WO$_3$ the acid site concentration of 1.04 mmol/g was achieved. The acidity which is correlated to the activity decreased by increasing the amount of WO$_3$ as a result of excess coverage of WO$_3$ species on ZrO$_2$.

Furuta et al. [53] studied conversion of soybean oil over tungstated zirconia and found that the catalyst activity remained stable up to 100 h of use. After reaction time of 8 h at 300 °C, 94% of oil was converted with alcohol/oil molar ratio of 40:1. He also compared activity of sulfated tin oxide and zirconium oxide under the same reaction conditions and found that WZ0 showed the highest activity for conversion of soybean oil whereas 70% and 80% conversions were reached over SZO and STO respectively.

Vanadium phosphate solid acid catalyst was also studied for transesterification reaction [54]. Although the specific surface area of the catalyst was low (2–4 m$^2$/g), the catalyst was active for the transesterification of soybean oil with methanol since the methyl ester yields reached 80% at 150 °C after 1 h of reaction. Furthermore, only 0.2 wt.% of the catalyst and 1:100 alcohol/oil molar ratio was used in the reaction. A slow deactivation of the catalyst was observed at high reaction temperatures due to the reduction of vanadium species form V$^5+$ to V$^3+$ with methanol. However, the catalyst could be readily regenerated.

Fe–Zn double metal cyanide complex has been tested as a solid acid catalyst for methanolysis of sunflower oil [55]. The catalyst was prepared by mixing three solutions: aqueous solution of K$_2$Fe(CN)$_6$·3H$_2$O, a solution of ZnCl$_2$ in mixture of distilled water and tert-butanol and a solution of tri-block copolymer, poly ethylene glycol-block-poly propylene glycol-block-poly ethylene glycol, in mixture of water and tert-butanol with subsequent calcination at 180 °C. The specific surface area of the catalyst was 51.6 m$^2$/g. When the transesterification reaction was performed at 170 °C, with oil/alcohol molar ratio of 1:15 and 3 wt.% of catalyst, the oil conversion reached 97% after 8 h of reaction. The catalyst activity was attributed to the Lewis acid active sites of probably Zn$^{2+}$ on the surface of catalyst. Moreover, the catalyst converted the oil with up to 20% of water content which implies the surface hydrophobicity of the catalyst. The activity of catalyst was successfully tested for esterification of high amount of FFA in the oil. In addition, the catalyst was stable after many cycles since no significant loss of activity was detected.

Siano et al. [56] patented the application of Mg–Al hydrotalcite for biodiesel production from soybean oil and found that the activity of the catalyst was affected by the ratio of Mg/Al and the most active catalyst was obtained with Mg/Al ratio of 3 to 8. The catalyst was suitable for oils with high amount of water content (10,000 ppm) and a conversion of 92% obtained after 1 h of reaction time using catalyst content of 5 wt.% and alcohol/oil weight ratio of 0.45 at reaction temperature of 180 °C.

Mg–Al hydrotalcite has been reported as solid base catalyst for the transesterification of soybean oil with methanol to produce biodiesel [57]. The hydrotalcite was synthesized by co-precipitation method of aqueous solution of Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, NaOH and Na$_2$CO$_3$ under vigorous stirring. The precipitate was then calcined at different temperatures to examine the effect of calcination temperatures on the catalyst performance. The results indicated that by enhancing calcination temperature the catalyst activity and basicity improved since the optimum catalyst for the reaction obtained after calcination at 500 °C. However, this catalyst represented quite low activity with only 67% conversion of oil after 9 h of reaction time with alcohol/oil molar ratio of 15:1 and 7.5 wt.% of catalyst content at temperature of 65 °C. On the other hand, Georgogianni et al. [58] compared the catalyst activities of Mg–Al hydrotalcite base catalysts and MgO supported on MCM-41 for transesterification of soybean frying oil with methanol and after 24 h of reaction time and under identical operation conditions conversion of oil achieved 97% and 85% respectively. The greater activity of the hydrotalcite was correlated to its higher basicity although the specific surface area of Mg–Al hydrotalcite (82 m$^2$/g).

Di Serio et al. [59] also investigated the catalytic activity of Mg–Al hydrotalcite for biodiesel production from soybean oil. The catalyst was prepared by co-mixing of 0.8 M solution of Mg(NO$_3$)$_2$, 0.2 solution of Al(NO$_3$)$_3$, NaOH and Na$_2$CO$_3$ followed by calcination at 500 °C and based on the results of TPD analysis four different basic sites including weak basic sites related to OH$^-$ surface groups, medium basic sites related to oxygen atoms in both Mg$^{2+}$−O$^-$ and Al$^{3+}$−O$^-$, strong basic sites and super-basic sites attributed to isolated O$^-$ anions were found to be responsible for the basicity and accordingly the activity of the catalyst. Moreover, the activity of the catalyst was also correlated to porosity of the catalyst since Mg–Al hydrotalcite with larger pore size showed more activity than MgO with micropores structure towards transesterification reaction. The Mg–Al hydrotalcite showed high performance at higher reaction temperatures and when the reaction was performed at 215–225 °C using catalyst content of 1 wt.% and methanol/oil weight ratio of 0.45 the biodiesel yields of 94% were obtained.

3. Catalyst supports

One of the ways to minimize the mass transfer limitation for heterogeneous catalysts in liquid phase reactions is using catalyst supports. Supports can provide higher surface area through the existence of pores where metal particles can be anchored [42]. Supports such as: alumina, silica, zinc oxide and zirconium oxide have been used in biodiesel production.

3.1. Alumina

Alumina oxide exists in forms of porous γ-alumina and α-alumina and nonporous crystalline α-alumina has been widely used as a support in catalysis processes, such as polymerization, reforming, steam reforming, dehydration and hydrogenation owing to its extremely thermal and mechanical stability, high specific surface area, large pore size and pore volume and. This also includes in the synthesis of biodiesel. Catalytic activity of titanium oxide–zinc oxide supported by alumina (ATZ) and titanium oxide–bismuth oxide supported by alumina (ATB) for transesterification of colza oil with methanol was studied [60]. Both catalysts were prepared by co-mixing method and followed by calcination at 600 °C for 3 h. The specific surface areas of ATZ and ATB were 62 m$^2$/g and 54 m$^2$/g respectively. Although the specific surface area of both catalysts was high, a long reaction time of 8 h was required to reach 94% of methyl ester yields. The reaction took place at temperature of 200 °C and pressure of 50 bar. Both catalysts were reusable and showed almost the same activity in the second cycle.

Al$_2$O$_3$/ZrO$_2$/WO$_3$ solid acid catalyst was prepared by co-precipitation method and was investigated in the methanolysis of soybean oil [61]. The catalyst was compatible for both esterification and transesterification reaction and under reaction conditions of temperature of 250 °C and alcohol/oil molar ratio of 40:1 methyl ester yields of 90% were obtained. This catalyst was also compared to Al$_2$O$_3$/ZrO$_2$; however, the yields were 80%.

Xie et al. [62] evaluated the catalytic efficiency of potassium supported by alumina as a solid base catalyst in the transesterification of soybean oil to biodiesel. The catalyst was prepared by an impregnation method of aqueous solution of potassium nitrate on...
alumina. The results demonstrated that the catalyst calcined at 500 °C and loaded by 35 wt.% of KNO3 was the most active. From Hammett indicator method, the basicity was 6.75 mmol/g and a correlation between catalyst performance and basic sites on the surface of catalyst, probably K2O and Al–O–K, was detected. The highest conversion of oil reached 87%, after the reaction time of 8 h with molar ratio of methanol to soybean oil of 15:1 and 6.5 wt.% of catalyst.

In another work, Xie and Li [63] used potassium iodide supported by alumina as a solid base catalyst for methanolysis of the same oil to study the effect of loading amount of KI on the support and calcination temperature on the conversion. The optimum catalyst was obtained by loading 35 wt.% of KI on the support and calcined at 500 °C for 3 h and from Hammett indicator method the basicity recorded was 1.57 mmol/g. These results were directly correlated with the conversion of oil since the maximum conversion reached 96%. The reaction was performed with oil to methanol molar ratio of 1:15, catalyst content of 2.5 wt.% and 8 h of reaction time. Table 2 represents the effect of catalyst precursor by comparing the activity of Al2O3/KI synthesized by two different potassium precursors. Both reactions have been carried out with alcohol/oil molar ratio of 15:1, catalyst content of 2.5 wt.% and 8 h of reaction time. As can be seen from the table, although the basicity of Al2O3/KI is less than the basicity of Al2O3/KNO3, more conversion was obtained using Al2O3/KI which implies the effect of precursor type on the catalyst activity.

Kim et al. [64] utilized alumina loaded with sodium and sodium hydroxide as a solid base catalyst for transesterification of soybean oil with a mixture of hexane and methanol to biodiesel. The specific surface area of γ-alumina decreased from 143.1 m²/g to 83.2 m²/g when Na and NaOH were loaded onto the support. However, the biodiesel yields reached 83% using Al2O3/Na/NaOH while it was only 1% when γ-alumina was used without any modification. The activity was closely correlated to basic active sites which determined by temperature programmed desorption of carbon dioxide (TPD-CO2). The catalyst activity was also compared to NaOH homogeneous catalyst and nearly the same activity was detected.

Kaita et al. [65] patented aluminum phosphate solid acid catalyst for transesterification of palm kernel oil with methanol. Two catalysts were prepared by a co-precipitating method of aluminum nitrate and orthophosphoric acid. One calcined at temperature of 400 °C for 3 h and another one used as amorphous. The reaction was carried out at 200 °C for 5 h and 69% methyl ester yields were obtained in the presence of crystalline catalyst compared to 63% yields when amorphous one was used. Then the crystalline catalyst was molded into cylindrical form with 3 mm diameter to study the effect of catalyst shapes on catalyst efficiency and as a result, methyl ester yields increased to 90.1%.

3.2. Zinc oxide

Yang and Xie [66] compared the catalyst performance of alkali earth metals loaded on different catalyst supports for soybean oil conversion to biodiesel and discovered a correlation between loading amount of catalyst precursor on support and the conversion of oil. They also found that the catalyst performance is depending upon concentration of basic sites on the surface of the catalyst. Different catalysts were prepared by impregnation method of water solution of an alkali earth metal nitrate with specified concentration and calcined at 600 °C for 5 h and among them ZnO/Sr (NO3)2 showed the best catalytic activity. In this case the most active catalyst was obtained by loading 2.5 mmol of strontium nitrate on zinc oxide which resulted in basicity of 10.8 mmol/g. After 5 h of reaction time, at 65 °C, with 12:1 molar ratio of alcohol/oil and 5 wt.% of catalyst content, the maximum conversion achieved was 93.7%. In order to study the effect of co-solvent on the conversion of soybean oil to biodiesel, Yang and Xie [66] applied different co-solvents such as THF, DMSO and n-hexane and THF was found as the most effective co-solvent since the conversion of soybean oil increased to 96.8%.

Xie and Huang [35] also applied potassium supported by zinc oxide as a solid base catalyst and the catalyst was prepared by an impregnation method of aqueous solution of potassium fluoride followed by calcination at 600 °C for 5 h. Based on Hammett titration method the concentration of basic sites reached 1.47 mmol/g when 15 wt.% of KF was loaded on ZnO. The reaction was performed with alcohol/oil molar ratio of 10:1 and catalyst content of 3 wt.% and after 9 h of the reaction time 87% of soybean oil was converted. The result is quite similar to that of Al2O3/KNO3 which was previously described [62].

A mixture of Zn/I2 was used as a heterogeneous catalyst for transesterification of soybean oil with methanol [9]. The metal was treated with distilled water and diluted HCL and iodine was treated by sublimation. A mixture of 5 wt.% Zn and 2.5 wt.% I2 was applied in the reaction. After 26 h, by using alcohol/oil molar ratio of 42:1, the conversion of oil reached 86%. The influence of co-solvent on the reaction rate was also investigated by introducing co-solvents such as THF and DMSO into the reaction and a 10% increase in conversion of soybean oil was observed after adding a certain amount of DMSO into the reaction mixture.

3.3. Silicate

Catalyst properties of CaO supported on different types of mesoporous silica were studied and results from XRD characterization showed that after impregnation of CaO, the hexagonal structure of SBA-15 remained stable while this structure of MCM-41 and fumed silica was collapsed indicated that only SBA-15 can stabilize calcium oxide species on its surface [67]. The optimum catalyst was obtained by loading 15 wt.% of calcium oxide on SBA-15 followed by calcination at 900 °C and using this catalyst the maximum conversion of sunflower oil achieved 95% within 5 h. Transesterification reaction was carried out at 60 °C, with 1 wt.% catalyst and methanol to sunflower oil molar ratio of 12.

Lin and Radu [68] patented the application of sulfonic acid supported by mesoporous silica as a strong solid acid for transesterification reaction. The method of catalyst synthesis was relatively complicated, whereby Tetraethoxysilane (TEOS) was used as a precursor of silica. Mesoporous silica was synthesized by cetyldimethylammonium bromide functionalized group denoted as CDAB, while those prepared by using tri-block Pluronic L64 and Pluronic P123 copolymers denoted as SBA-15. The textural properties of the catalysts are summarized in Table 3. As can be seen from the table, SBA-15-SO3H-P123 bears the most surface acidity. Consequently, the maximum biodiesel yields achieved were 85% within 20 h of reaction over SBA-15-SO3H-P123 while CDAB-SO3H with 0.6 meq/g of surface acidity showed the least

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading amount of active material (wt.%)</th>
<th>Active site concentration (mmol/g)</th>
<th>Catalyst content in the reaction (wt.%)</th>
<th>Conversion (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3/KNO3</td>
<td>35</td>
<td>6.75</td>
<td>2.5</td>
<td>37</td>
<td>[62]</td>
</tr>
<tr>
<td>Al2O3/KI</td>
<td>35</td>
<td>1.57</td>
<td>2.5</td>
<td>96</td>
<td>[63]</td>
</tr>
</tbody>
</table>

Both catalysts were activated at 500 °C for 3 h.

Table 3

Textural properties of functionalized mesoporous silicate [68].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surfactant</th>
<th>S BET (m²/g)</th>
<th>V P (cm³/g)</th>
<th>D p (Å)</th>
<th>H+ (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDAB-SO3H-C12</td>
<td>CDAB</td>
<td>778</td>
<td>0.39</td>
<td>28</td>
<td>0.60</td>
</tr>
<tr>
<td>SBA-15-SO3H-L64</td>
<td>Pluronic L64</td>
<td>820</td>
<td>0.58</td>
<td>27</td>
<td>0.84</td>
</tr>
<tr>
<td>SBA-15-SO3H-P123</td>
<td>Pluronic P123</td>
<td>735</td>
<td>0.67</td>
<td>35</td>
<td>1.44</td>
</tr>
<tr>
<td>SBA-15-ph-SO3H-P123</td>
<td>Pluronic P123</td>
<td>540</td>
<td>0.71</td>
<td>50</td>
<td>0.92</td>
</tr>
</tbody>
</table>
### Table 4

Summary of the activity of metal oxides and supported catalysts as heterogeneous catalysts for biodiesel production.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst characterizations</th>
<th>Catalyst preparation</th>
<th>Feedstock</th>
<th>Operation conditions</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano MgO solid base</td>
<td>Particle size = 60 nm</td>
<td>Not reported</td>
<td>Soybean oil</td>
<td>Methanol/oil = 10:1, Alcohol/oil = 1:1, catalyst content = 3%</td>
<td>Conversion = 98%</td>
<td>[35]</td>
</tr>
<tr>
<td>CaO solid base</td>
<td>SSA = 32 m²/g, MPS = 25–30 nm</td>
<td>CaO powder was calcined at 1000 °C.</td>
<td>Sunflower oil</td>
<td>Methanol/oil = 12:1, catalyst content = 6%</td>
<td>Conversion = 93%</td>
<td>[66]</td>
</tr>
<tr>
<td>CaO solid base</td>
<td>SSA = 56 m²/g</td>
<td>Not reported</td>
<td>Soybean oil</td>
<td>Methanol/oil = 1:1, catalyst content = 2%</td>
<td>Conversion = 95%</td>
<td>[21]</td>
</tr>
<tr>
<td>Ca(C2H3O2)2/SBA-15</td>
<td>SSA = 7.4 m²/g, pore volume = 0.019 cm²/g</td>
<td>The catalyst was prepared by an impregnation method of aqueous solution of calcium acetate on the support followed by calcination at 500 °C for 4 h.</td>
<td>Sunflower oil</td>
<td>Methanol/oil = 12:1, catalyst content = 5%</td>
<td>Conversion = 95%</td>
<td>[18]</td>
</tr>
<tr>
<td>Ca(OH)2 solid base</td>
<td>SSA = 19 m²/g, pore size = 40 nm</td>
<td>Calcium methoxide was synthesized by a direct reaction of calcium and methanol at 65 °C for 4 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 1:1, catalyst content = 6%</td>
<td>Conversion = 98%</td>
<td>[71]</td>
</tr>
<tr>
<td>SrO solid base</td>
<td>SSA = 1.05 m²/g</td>
<td>SrO was prepared from calcination of strontium carbonate in a muffle furnace at 1200 °C for 5 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 10:1, catalyst content = 3%</td>
<td>Conversion = 87%</td>
<td>[35]</td>
</tr>
<tr>
<td>ZnO/Sr(NO3)2 solid base</td>
<td>Basicity = 10.8 mmol/g</td>
<td>The aqueous solution of Sr(NO3)2 was loaded on ZnO by impregnation method and calcined at 600 °C for 5 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 12:1, catalyst content = 1%</td>
<td>Conversion = 93%</td>
<td>[66]</td>
</tr>
<tr>
<td>ZnO/Ba solid base</td>
<td>Basicity = 14.54 mmol/g</td>
<td>The catalyst was prepared by an impregnation method using barium nitrate as precursor on ZnO. Dried overnight and calcined at 600 °C in air for 5 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 12:1, catalyst content = 6%</td>
<td>Conversion = 95%</td>
<td>[18]</td>
</tr>
<tr>
<td>ZnO/KF solid base</td>
<td>Basicity = 1.62 mmol/g</td>
<td>The supported catalyst was prepared by impregnation method with an aqueous solution of KF. Afterward was dried at 393 K and calcined at 600 °C in air for 5 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 10:1, catalyst content = 3%</td>
<td>Conversion = 87%</td>
<td>[35]</td>
</tr>
<tr>
<td>Al2O3/KI solid base</td>
<td>Basicity = 1.57 mmol/g</td>
<td>The catalyst was prepared by an impregnation method from aqueous solution of potassium iodide, dried at 120 °C and activated at 500 °C for 3 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 12:1, catalyst content = 3%</td>
<td>Methyl ester yields = 83%.</td>
<td>[64]</td>
</tr>
<tr>
<td>Al2O3/KNO3 solid base</td>
<td>Basicity = 6.67 mmol/g</td>
<td>KNO3 was added to alumina by an impregnation method from aqueous solution, dried at 393 K for 16 h and finally calcined at 500 °C for 5 h.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 1:1, catalyst content = 7%</td>
<td>Methyl ester yields = 87%.</td>
<td>[62]</td>
</tr>
<tr>
<td>Al2O3/Na/NaOH solid base</td>
<td>SSA = 83.2 m²/g</td>
<td>The catalyst was prepared by mixing of γ-Al2O3, NaOH and metal sodium in a stainless steel reactor at 320 °C.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 9:1, catalyst content = 1 g</td>
<td>Methyl ester yields = 83%.</td>
<td>[64]</td>
</tr>
<tr>
<td>VOPO4·2H2O solid acid</td>
<td>SSA = 2–4 m²/g</td>
<td>Vanadyl phosphate was obtained from the suspension of V2O5 in diluted phosphoric acid. Then activated at 500 °C.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 1:1, catalyst content = 2%</td>
<td>Methyl ester yields = 80%.</td>
<td>[54]</td>
</tr>
<tr>
<td>ZnO solid acid</td>
<td>Not reported</td>
<td>Pure metal oxide was used.</td>
<td>1-palm kernel oil</td>
<td>Methanol/oil = 12:1, catalyst content = 3%</td>
<td>1-methyl ester yields = 77.5%</td>
<td>[34]</td>
</tr>
<tr>
<td>ZnO/I2 solid acid</td>
<td>Not reported</td>
<td>The metal was prepared just by some treatment with distilled water and dilute HCl. Iodine was treated by sublimation.</td>
<td>Soybean oil</td>
<td>Methanol/oil = 20:1, catalyst content = 15%</td>
<td>Conversion = 97%</td>
<td>[52]</td>
</tr>
<tr>
<td>ZrO2/WO3 δ− solid acid</td>
<td>Not reported</td>
<td>The isopoly tungstated zirconia was prepared by suspending a known amount of zirconium oxyhydroxide powder in an aqueous solution of ammonium metatungstate, finally calcined at 750 °C.</td>
<td>Sunflower oil</td>
<td>Methanol/oil = 20:1, catalyst content = 1%</td>
<td>1-methyl ester yields = 90.3%</td>
<td>[34]</td>
</tr>
<tr>
<td>ZrO2/Al2O3 δ− solid acid</td>
<td>Not reported</td>
<td>Zirconia powder was immersed in sulfuric acid solution, filtered, dried and calcined at 500 °C for 2 h.</td>
<td>1-palm kernel oil</td>
<td>Methanol/oil = 10:1, catalyst content = 1%</td>
<td>Methyl ester yields = 86.3%</td>
<td>[65]</td>
</tr>
<tr>
<td>TiO2/Al2O3 δ− solid acid</td>
<td>SSA = 99.5 m²/g</td>
<td>TiO2·nH2O was prepared from precipitation of TiCl4 using aqueous ammonia. Then immersed to sulfuric acid and finally calcined at 550 °C for 3 h to give TiO2·SO4 ·10H2O.</td>
<td>Cottonseed oil</td>
<td>Methanol/oil = 12:1, catalyst content = 2%</td>
<td>Methyl ester yields = 90%.</td>
<td>[50]</td>
</tr>
<tr>
<td>Al2O3/SiO2 δ− solid acid</td>
<td>Not reported</td>
<td>Aluminium nitrate hydrated with nine moles of water dissolved in water and 85% orthophosphoric acid was added. The PH was controlled at 7 by aqueous solution of ammonia. The final precipitation was filtered out, washed, and dried at 383 K for 12 h, finally calcined at 400 °C for 3 h.</td>
<td>Palm kernel oil</td>
<td>Methanol/oil = 5:1, catalyst content = 10 g</td>
<td>Methyl ester yields = 69%.</td>
<td>[65]</td>
</tr>
<tr>
<td>Al2O3/TiO2/ZnO solid acid</td>
<td>SSA = 62 m²/g</td>
<td>The catalyst was prepared by co-mixing of boehmite, titanium gel and zinc oxide in the presence of nitric acid and water. Calcined at 600 °C for 3 h.</td>
<td>Colza oil</td>
<td>Methanol/oil = 1:1, catalyst content = 6%</td>
<td>Methyl ester yields = 94%</td>
<td>[60]</td>
</tr>
</tbody>
</table>

(continued on next page)
activity with less than 55% methyl ester yields. MCM-41 also was subjected to the transesterification of soybean oil and yields of 60% were obtained. All the reactions were carried out at 75 °C, 10 wt.% of catalyst and methanol/oil molar ratio of 20:1.

Siano et al. [69] studied the effect of loading amount of the catalyst precursor on the support and the effect of the support shaping on the activity of TiO2 supported by amorphous silica and found that by increasing the loading amount of the precursor (titanium tetraisopropoxide) the activity of the catalyst is increased. Moreover, they used powder form and pellet form of the support to prepare the catalyst and under the same operating conditions more conversion of soybean oil obtained using the catalyst which was prepared by powder form of silica. They also tested the effect of the reaction temperature and found that conversion of oil was increased by the reaction temperature. Using TiO2 supported on the powder form of silica the conversion of 88% obtained after 5 1/2 h when the reaction was performed at temperature of 225 °C using the catalyst content of 2.5 wt.% and methanol/oil weight ratio of 0.45.

Silica supported phosphoric acid was also investigated for transesterification of triacetin with methanol [49]. The catalyst activity was extremely low with less than 10% conversion of triacetin, consistent with the small specific surface area of 2.6 m²/g and weak acid site concentration about 986 μmol/g.

3.4. Zirconium oxide

Zirconia-supported heteropoly and isopoly tungsten acids were applied in biodiesel synthesis from sunflower oil and the result indicated that isopoly tungsten was more active than heteropoly tungsten since it possesses more Bronsted acid sites[70]. Oil conversion of 97% was reached after 5 h of reaction time under reaction conditions of temperature of 200 °C with catalyst content of 15 wt.% and alcohol/oil molar ratio 15:1.

The catalytic activity of some metal oxides and catalyst supports for the biodiesel production is summarized in Table 4. From this table it can be concluded that, generally solid catalysts need a longer reaction time than homogeneous catalysts. Solid acid catalysts either supported or unsupported require higher temperature to give more methyl esters yields, even though solid acid catalysts are active for both transesterification and esterification reactions are able to convert oils with high amount of FFA. All alkali earth metal oxides except MgO produced high concentration of methyl esters at lower temperature of 65 °C at a moderate reaction time. Furthermore, from the table it can be observed that alumina was more preferred as a support than other supports for transesterification reaction. Therefore modification and optimization of these catalysts in order to obtain the most active catalyst for transesterification reaction or producing a supported catalyst contain basic and acidic species are optimistic ways to find a new heterogeneous catalyst to be substituted by homogeneous catalysts for biodiesel production.

<table>
<thead>
<tr>
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<tr>
<td>Al2O3/ZrO2/WO3 solid acid</td>
<td>Not reported</td>
<td>The catalyst was prepared from mixture of hydrated zirconia, hydrated alumina and ammonium metatungstate and deionized water. Calcinated at 900 °C for 1 h. Tetrathoxysilane (TETS) was used as silica source. 3-(mercaptotripropyl)-trimethoxysilane was used as mesoporous silica modifier. Pluronic P123 (tri-block copolymer) used as surfactant. A co-condensation method was applied.</td>
<td>Soybean oil</td>
<td>T = 250 °C, t = 20 h, methanol/oil = 40:1, catalyst content = 4 g</td>
<td>Methyl ester yields = 90%</td>
<td>[61]</td>
</tr>
<tr>
<td>SBA-15-SO3H-P123</td>
<td>SSA = 735 m²/g, pore volume = 0.67 cm³/g</td>
<td>Solid acid</td>
<td>Soybean oil</td>
<td>T = 75 °C, t = 20 h, methanol/oil = 20:1, catalyst content = 10%</td>
<td>Methyl ester yields = 85%</td>
<td>[68]</td>
</tr>
</tbody>
</table>

4. Conclusion

Effective factors on catalytic activity of solid catalysts are specific surface area, pore size, pore volume and active site concentration on the surface of catalyst. Moreover type of precursor of active materials has significant effect on the catalytic activity of supported catalysts. However active site concentration was found to be the most important factor for solid catalyst performance. The use of catalyst supports such as alumina, silica and zinc oxide could improve the mass transfer limitation of the three phase reaction. Furthermore, by anchoring metal oxides inside pores, catalyst supports could prevent active phases from sintering in the reaction medium. The amount of methyl ester yields and conversion of oils depend on not only catalyst activity but also the type of oils and the applied operation conditions. By modifying the catalyst activity and synthesis cost, heterogeneous catalyst could be replaced by homogeneous catalyst for the biodiesel production.

Acknowledgement

This study was carried out with the aid of a research grant from University Malaya Research Fund.

References

[13] K. Ropkins, R. Quinn, J. Beebe, H. Li, B. Daham, J. Tate, M. Bell, G. Andrews, Real-world cation and optimization of these catalysts in order to obtain the most active catalyst for transesterification reaction or producing a supported catalyst contain basic and acidic species are optimistic ways to find a new heterogeneous catalyst to be substituted by homogeneous catalysts for biodiesel production.

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</table>
1. Introduction

The majority of commercial biodiesel is made by transesterification of vegetable oils and animal fats with methanol or ethanol in stirred tank reactors in the presence of base or acids catalysts. There are some challenges related to this process as follows:

a. Reaction rate can be limited by mass transfer between the oils and alcohol because they are immiscible;

b. Transesterification itself is a reversible reaction and therefore there is an upper limit to conversion in the absence of product removal;

c. Most commercial processes are run in a batch mode and thus do not gain some of the advantages of continuous operation.

In order to overcome these problems, current conventional techniques involve long reaction time, high molar ratio of alcohol to oil and catalyst concentration. High operating cost and energy consumption are required to purify biodiesel and recover excess amount of alcohol and catalysts during downstream processing. Significant amounts of toxic waste water may also be produced during downstream purification. Long residence times and down-
stream processing time incur low production efficiency. Hence, some process intensification technologies have been developed and applied to improve mixing and mass/heat transfer between the two liquid phases in recent years. These technologies either utilize novel reactors or coupled reaction/separation processes. Reaction rate is greatly enhanced and thus residence time may be reduced. Some of the technologies have been applied successfully in commercial production. We do not specifically review intensification technologies involving advanced materials such as new heterogenous catalysts in packed or fluidized bed reactors. The goal of this review is to give an overall summary of process intensification technologies which enhance physical processes including heat, mass, and momentum transfer in the context of biodiesel synthesis.

2. Novel reactors

2.1. Static mixers

Static mixers consist of specially designed motionless geometric elements enclosed within a pipe or a column and create effective radial mixing of two immiscible liquids as they flow through the mixer. Recently, they have been used in continuous biodiesel synthesis in combination with other equipment [1,2].

Thompson and He [3] used a stand-alone closed-loop static mixer system as a continuous-flow reactor to produce biodiesel from canola oil with methanol when sodium hydroxide was used as catalyst. The experimental setup is shown in Fig. 1. The system is composed of two stainless steel static reactors (4.9 mm ID × 300 mm long) including 34 fixed right- and left-hand helical mixing elements. High quality biodiesel which met the ASTM D6584 specification was obtained after optimization of experimental conditions. The most favorable conditions for completeness of reaction included operation at a temperature of 60°C and using a concentration of 1.5% sodium hydroxide catalyst and a reaction time of 30 min. The total glyceride content was lower than 0.24 wt% when the molar ratio of methanol to oil is 6:1. Boucher et al. [4] also reported a reactor/separater design involving a static mixer for continuous biodiesel production and product separation as shown in Fig. 2. Pretreated waste canola oil and the solution of potassium hydroxide in methanol flow into a static mixer, which was exploited as an injector into a reaction chamber with no moving parts. Emulsified reactants were released into the chamber from the mixer with decreasing bulk velocity and separated into two phases under laminar flow conditions in the main body of the reactor. The less dense biodiesel phase separated as an upper layer. The glycerol phase, which had a higher density, settled as the lower layer. This required that the bulk flow velocity be set to a value which was lower than the settling velocity of glycerol. The new reactor system obtained conversions greater than 95% with simultaneous removal of 70–99% of the glycerol after 6 h continuous running. This was achieved at slightly elevated temperatures (40–50 °C), using an overall feed rate of 1.2 L/min, a 6:1 molar ratio of methanol to vegetable oil triglycerides, and a 1.3 wt% catalyst. Static mixers present the advantage of low maintenance and operating cost and low space requirement because they have no moving parts. However, the mixing process relies mainly on slow, unforced molecular inter-diffusion in the laminar regime and therefore reactions are still slow.

2.2. Micro-channel reactors

Micro-channel reactors achieve rapid reaction rates by improving the efficiency of heat and mass transfer and utilizing high surface area/volume ratio and short diffusion distance [5]. Canter [6] reported that biodiesel could be produced in a microreactor at mild conditions. Yields of greater than 90% biodiesel after a residence time of 4 min were reported. Sun et al. [7] studied KOH-catalyzed transesterification of unrefined rapeseed oil and cottonseed oil with methanol in capillary microreactors with inner diameters of 0.25 mm. At a 5.89 min residence time, they obtained a 99.4% yield of methyl esters at a catalyst concentration of 1 wt% KOH and using a 6:1 molar ratio of methanol to oil and at a temperature of 60 °C. Finally, Wen et al. [8] investigated zigzag micro-channel reactors for continuous alkali-based biodiesel synthesis. The configuration of zigzag micro-channel reactors with narrower channel size and more turns is shown in Fig. 3. This type of reactor was
shown to intensify the biodiesel production process by obtaining smaller droplets compared to those micro-channel reactors with T- or Y-flow structures. At a residence time of 28 s and a temperature of 56 °C, the yield of methyl ester reached 99.5% in an optimized zigzag micro-channel reactor using a 9:1 molar ratio of methanol to oil and a catalyst concentration of 1.2 wt% sodium hydroxide. Under these conditions it was reported that less energy consumption was needed for the same amount of biodiesel than in the case of a conventional stirred reactor. This was attributed to the high heat transfer rates achieved in the micro-channel reactor. The micro-channel reactor is smaller in size offering reductions in footprint requirements, construction and operating costs. Another advantage of micro-channel reactors is ease of scale-up which may be readily achieved by adding more reactors of the same proven dimensions in parallel. This approach can reduce the risks associated with scaling up of conventional reactors.

2.3. Oscillatory flow reactors

Oscillatory flow reactors are tubular reactors in which orifice plate baffles are equally spaced and produce oscillatory flow using a piston drive as shown in Fig. 4. When a bulk fluid is introduced into the reactor, an oscillatory motion interacts with it and intensifies radial mixing, with enhancements in mass and heat transfer whilst maintaining plug flow. The reactor can achieve long residence times because the degree of mixing is not directly dependent upon the Reynolds number of the bulk flow through it, but is mainly related to the oscillatory conditions. Hence the oscillatory flow reactor can be designed with a short length-to-diameter ratio and improves the economy of biodiesel production due to smaller “footprint”, lower capital and pumping cost, and easier control. Harvey et al. [9] developed a continuous oscillatory flow reactor (OFR) to produce saleable biodiesel from rapeseed oil in a pilot-scale plant shown in Fig. 5. The reactor is composed of two vertically positioned jacketed QVF tubes of 1.5 m length and 25 mm internal diameter. Conversions of biodiesel up to 99% were achieved after 30 min at 50 °C using a molar ratio of methanol to rapeseed oil of 1.5 and in the presence of a sodium hydroxide catalyst. Another biodiesel pilot plant using an oscillatory flow reactor was demonstrated by the Polymer Fluids Group in the University of Cambridge [10]. It has been in operation since 2004 and producing at a rate of 25 l/h.

One of the advantages of this technology is the very low molar ratio of methanol to oil they applied. It is lower than the stoichiometric ratio (3:1) required and reduces significantly the operating cost. The short length-to-diameter of this reactor decreases capital cost and allows it to be scaleable.

2.4. Cavitational reactors

Cavitational reactors use acoustic energy or flow energy to generate cavitation phenomena, which results in process intensification. During the process of cavitation, the violent collapse of the cavities produced by the pressure changes from sound and flow energy releases large magnitude of energy over a small location, and brings about very high temperatures and pressures [11]. A picture of hydrodynamic cavitation is shown in Fig. 6. Cavitation also intensifies the mass transfer rate by generation of local turbulence and liquid micro-circulation in the reactor [13,14]. All of them contribute to the intensification of processes which under other conditions are limited by mass transfer and heat transfer. Kelkar et al. [15] investigated two different reactors based on acoustic and hydrodynamic cavitation and compared their performance in biodiesel synthesis from vegetable oils. At a reaction time of 15 min, more than 90% yield of biodiesel was obtained during transesterification of vegetable oils with methanol in the presence of sodium hydroxide in these two reactors. From the point of view of energy efficiency of mixing, hydrodynamic cavitation (1 × 10⁻⁴ to 2 × 10⁻⁴ g/l) is about 40 times more efficient than acoustic cavitation (5 × 10⁻⁶ to 2 × 10⁻⁵ g/l) and 160–400 times more efficient than conventional mixing methods [15]. Moreover, it is difficult for sonochemical reactors to be scaled up because acoustic cavitation relies on a source of vibrations. The scale-up of the hydrodynamic cavitation reactors is relatively easier and thus they provide potential for commercial scale applications because extensive information about the fluid dynamics downstream of the constriction is readily available [16,17].

Arisdyne System, Inc. [18] used controlled flow cavitation (CFC) technology to produce higher grade ASTM 6751 B100 biodiesel as shown in Fig. 7. The reactor consisted of one or more controlled flow cavitation zones or flow constrictions achieved by a diaphragm with one or more orifices. The pressure drop across the constrictions is controlled by the size of orifices, the flow rate of reaction mixture and, by a localized hydraulic resistance downstream of the constriction. Precise process control ensures a tightly controlled, repeatable droplet size distribution by cavitation during the process. The conversion of fatty acids to fatty acid alkyl esters reached 99% after passing through four cavitation constrictions in series with 1:6 molar ratio of fatty acids to methanol at 60 °C only in residence time of microseconds.

Another reactor design which uses the principle of cavitational mixing is described by Hydro Dynamics, Inc. [19]. Here a Shock-Wave Power Reactor (SPR) based on “controlled cavitation” is described for process intensification of the transesterification reaction in biodiesel production. A commercial SPR is shown in Fig. 8. One difference between the SPR and above the controlled flow cavitation reactor is the mechanism of producing flow cavitation. The ShockWave Power Reactor works by taking a feedstock, methanol and catalyst, into the machine housing, where it is passed through the generator’s spinning cylinder. The specific geometry of cavities in the cylinder and rotational speed creates pressure differences within the liquids where tiny bubbles form and collapse. The cavitation is controlled so that the bubbles collapse only inside the cavities and away from the metal surfaces and therefore reduce the risk of damaging the material of construction. The shock waves increase the surface area of the compounds being mixed so that a higher mass transfer rate occurs. It takes only several seconds to complete transesterification of vegetable oils or animal fats. Hence, the reactor allows the use of a variety of feedstocks with a broader range of free fatty acid concentrations because short reaction time leads to less saponification and emulsification.
2.5. Rotating/spinning tube reactors

The rotating, or spinning tube reactor is a shear reactor consisting of two tubes. A scheme of the rotating tube reactor is shown in Fig. 9. One inner tube rotates rapidly within another concentric stationary outer tube. There is a very narrow annular gap between the outer tube and the inner tube. Once reactants are introduced into the gap, Couette flow is induced and the two liquids are mixed instantaneously and move through the gap as a coherent thin film due to the high shear rate. Couette flow leads to high mass transfer rate and very short mixing time. The thin film presents a very large interfacial contact area. Hence, the rate of reaction between reactants is enhanced. Less reaction time and mixing power input are required compared to conventional reactors.

Four Rivers BioEnergy Company, Inc. [22] utilized the technology and developed a commercial Spinning Tube in a Tube (STT) system for biodiesel production as shown in Fig. 10. The STT reactor accelerates the rates of chemical reactions by up to three orders of magnitude. The transesterification reaction of soybean oil and methanol for biodiesel production is conducted at a residence time of 0.5 s.

Lodha and Jachuck [23] investigated a rotating tube reactor to produce biodiesel from canola oil with sodium hydroxide as catalyst. Within 40 s, conversions to biodiesel greater than 98% were attained under mild operating temperatures in the range 40–60 °C, and at atmospheric pressure.
The short residence time allows this reactor to handle feedstocks with high free fatty acid content. The size of the reactor is relatively small and it is easy to scale up.

### 2.6. Microwave reactors

Microwave reactors are units that utilize microwave irradiation to transfer energy directly into reactants and thus accelerate the rate of chemical reaction. Thus conversions are achieved in less time compared with similar reactors using conventional thermal heating. Recently, microwave reactors have been developed for biodiesel synthesis. Because the mixture of vegetable oil, methanol, and alcohol contains both polar and ionic components, microwave irradiation can play an active role in heating reactants to the required temperature quickly and efficiently [24]. Breccia et al. [25] studied the transesterification of commercial seed oils with methanol under microwave irradiation. In the presence of a variety of catalysts, yields greater than 97% were achieved with reaction times of less than 2 min. Leadbeater and Stencel [26] used microwave irradiation to enhance production of biodiesel in a batch reactor. They made biodiesel with a quantitative conversion obtained after heating vegetable oil, methanol (1:6 molar ratio) and potassium hydroxide (1 wt%) to 50°C in a microwave apparatus called MARS and maintaining this temperature for 1 min. Finally, they [24] achieved continuous-flow preparation of biodiesel in the apparatus. The apparatus could produce approximately 6.1 L of biodiesel per minute with attainment of 99% conversion. Rudimentary energy consumption studies showed that the continuous-flow preparation of biodiesel using microwave heating proved to be more energy efficient than the conventional synthesis of biodiesel in large tank reactors. Leadbeater et al. [27] also used this apparatus to make biodiesel from vegetable oils and 1-butanol at flow rates up to 2.3 L/min with sulfuric acid or potassium hydroxide as catalyst. Azcan and Danisman [28] reported that reaction times of transesterification of cottonseed oil with methanol by microwave irradiation were reduced to 7 min while conventional heating typically required reaction times of 30 min to obtain similar conversion at 60°C. In experiments to study microwave-assisted transesterification of rapeseed oil in the presence of 1.0% KOH, 93.7% of biodiesel yield and 97.8% of biodiesel purity were obtained at 50°C using a 5 min reaction time [29].

All above novel reactors intensify biodiesel production process by improving the mixing of oil and methanol except the microwave reactor. The mixing intensity of static mixers depends on the flow rate of the reactants or superficial velocity besides the geometric configuration of mixers. The mean droplet size was 63 μm in a static mixer when the superficial velocity was 1.3 m/s [30]. In the micro-channel reactor, the droplet size of emulsion decreases and the specific interfacial area increases and hence reaction rate is enhanced greatly compared to the batch stirred reactors. Mean droplet sizes of down to 1.93 μm were reported in a zigzag micro-channel reactor at a residence time of 28 s, approximately one third that observed in a batch stirred reactor at the residence time of 1 h [8]. The degree of mixing is also dependent on the oscillatory motion or the oscillatory frequency and is not related to the bulk flow. The oscillatory Reynolds number of typically 700 is required to achieve good mixing [9]. Cavitational reactors utilizing ultrasonic mixing produced the minimum droplet size of about 140 nm, which is three times smaller than the droplets obtained with impeller at 1000 rpm at the same input energies [31]. In spinning tube reactors, high mixing intensity is achieved through the high shear forces created in the narrow gap between the stator and the rapidly spinning rotor. The droplet sizes from cavitational reactors and spinning tube reactor are relatively smaller than other reactors.

### 3. Reaction/separation coupled technologies

#### 3.1. Membrane reactors

Membrane reactors integrate reaction and membrane-based separation into a single process. They can increase the conversion of equilibrium-limited reactions by removing some products from the reactants stream via membranes. Dubé et al. [32] exploited the possibility of biodiesel production from canola oil and methanol using a two-phase tubular membrane reactor as shown in Fig. 11. The pore size of the carbon membrane used in the reactor was 0.05 μm. The inner and outer diameters were 6 and 8 mm, respectively. Its length was 1200 mm giving 0.022 m² surface area. The transesterification of canola oil was performed via both acid- or base-catalysis in the 300 ml membrane reactor in semi-batch mode at 60, 65 and 70°C and at different catalyst concentrations and feed flow rates. At high flow rate of methanol/acid catalyst, they obtained 65% conversion. When base was used as catalyst, conversions of greater than 95% were attained at different flow rates. They found that the microporous carbon membrane selectively permeates FAME, methanol and glycerol while excluding bound glycerides (TG, DG, MG) from passing through. Hence, there are almost no bound glycerides in the permeate stream thus yielding high purity biodiesel. The reactor was also used to handle feedstock with high FFA content because the membrane retained soap from the side reaction and also retained other unreactable components. Cao et al. [33] investigated the effects of the pore size of the membrane on
the performance of a semicontinuous reactor. The analysis results show that no oil was found in the permeate stream and all permeate samples obtained were biodiesel of high purity at 65 °C. It also indicated that the oil droplets size in the membrane reactor were greater than the pore sizes tested. The kinetics of canola oil trans-esterification in a membrane reactor was also reported [34]. The study showed that the membrane reactor could enhance reaction rate by the excellent mixing in the membrane reactor loop and the continuous removal of product from the reaction medium.

3.2. Reactive distillation

Reactive distillation (RD) is a technique which combines chemical reactions and product separations in one unit. Currently reactive distillation has attracted more and more attention and been used widely [35–38] due to its many advantages over conventional sequential processes, such as a fixed-bed-reactor followed by a distillation column. One of the most important advantages of reactive distillation is that conversion limitation is avoided by continuous in situ product removal for equilibrium-controlled reactions. Integration of reaction and separation reduces capital investment and operating costs.

For reversible (trans)esterification reaction of vegetable oils with alcohol, usually an excess amount of alcohol (6:1 or higher alcohol: oil molar ratio) is used to drive the equilibrium to the product side in order to obtain high conversion rates and high final equilibrium conversion. Since recovery of excess alcohol from the esters and glycerol streams involves additional operating cost, application of reactive distillation to biodiesel production may lead to a more efficient process. He et al. [39,40] reported a novel reactor system using RD for biodiesel production from canola oil and methanol using KOH as catalyst. In this system, reaction at methanol: oil molar ratio of 4:1 yielded 95% conversion rate in about 3 min at 65 °C column temperature. The experimental conditions of a continuous-flow reactive distillation reactor were optimized for biodiesel production [41,42]. The upward-flowing methanol vapor served as an agitator in the reactant mixture, providing uniform mixing while it was bubbling through the liquid phase on each plate. This process has several advantages over conventional biodiesel production processes.

1. Short reaction time and high unit productivity, 2. no excess alcohol requirement, 3. lower capital costs due to the small size of RD and no need for additional separation units. Fig. 12 shows the FAME production process based on reactive distillation.


3.3. Centrifugal contactors

The centrifugal contactor is another process intensification technology because it integrates reaction and centrifugal separation into a unit. It consists of a mixing zone and a separating zone as shown in Fig. 13. As the rotor in the contactor is rapidly rotating within a stationary cylinder, it can achieve intense mixing and good mass transfer by high shear stress and quick phase separation by high centrifugal force simultaneously. However, the residence time in a conventional centrifugal contactor is as low as about 10 s and cannot allow reaction to reach equilibrium. The researchers [46] at Oak Ridge National Laboratory modified the design of a centrifugal contactor and achieved the control of residence time in mixing zone. They used the updated centrifugal contactor to continuously produce biodiesel via base-catalyzed production. Fig. 14 presents the experimental setup for biodiesel production using the modified centrifugal contactor. At 60 °C more than 99% conversion was achieved after about 1 min using a volumetric phase ratio of 5:1 oil to methoxide and potassium hydroxide as catalyst when rotor was spinning in 3600 rpm. Good product separation was realized after 3 min. The technology has been commercialized with Nu-Energie, LLC [47].

Kraai et al. [45] tested the performance of a centrifugal contact separator for the continuous production of biodiesel from sunflower oil. At an elevated temperature of 60 °C, a yield of 96% of FAME was achieved after about 40 min using a 6:1 molar ratio of methanol to oil and 1% NaOMe as catalyst at 30 Hz (1800 rpm).
The study showed that the flow rate of two phases affected the conversion due to the change of residence time.

4. Summary

Biodiesel production can be enhanced by process intensification technologies. Each technology has the potential to improve production efficiency and thus reduce operating cost of the process. Table 1 summarizes the advantages of these technologies used in continuous biodiesel production over traditional stirred tank reactors. A rudimentary assessment of reaction time, energy efficiency, operating/capital cost, the difficulty of temperature control, and current status is presented in the table. Most of these reactors or process technologies increase the rate of reaction by intensifying transport process and mixing between alcohol and oil. In summary, the static mixers can accomplish effective radial mixing as fluids pass through it. Micro-channel reactors improve heat and mass transfer efficiency due to short diffusion distance and high volume/surface area. Oscillatory reactors enhance radial mixing and transport process by independent and controlled oscillatory motion. In cavitational reactors, the collapse of cavity or bubbles produces high temperature and pressure and turbulence locally resulting in rapid reaction rate. Couette flow from high shear rate in spinning tube reactor with fine gap leads to high mass transfer rate and intensive mixing. Microwave reactors increase reaction rate through direct and efficient heating by microwave irradiation replacing conventional thermal heating. Membrane reactors achieve high reaction rate by selective removal of bound glycerin from products via a membrane. Reactive distillation improves biodiesel production efficiency via in situ separation of productions by distillation. Rates of transesterification can be intensified due to uniform mixing by exploiting high shear forces which may produced in reactor geometries involving for example narrow flow field between a rotating surface and stationary surface. High reaction rate means less reaction time to reach high equilibrium yield of biodiesel or complete the conversion of oil, and high selectivity due to less side reactions allowed. High conversion can be reached at several minutes or even several seconds of reaction time. Potentially, biodiesel can be made continuously which increases process throughput.

Another common characteristic of process intensification technologies is the small “footprint” required compared to conventional equipment. In micro-channel reactors the diameter of channel is only several hundred micrometers. Oscillatory flow reactors can be designed in shorter length-diameter ratio. The coupled reaction/separation technologies reduce downstream processing procedures. Reactive distillation systems can realize recovery of alcohol from products simultaneously. Centrifugal contactors may obviate the need for a separate separation process for recovery of the glycerol from biodiesel product. Hence, small size of reactors and less processing processes reduce the cost of construction and maintenance. Another advantage from enhanced reaction rate allows less molar ratio of alcohol to oil. The oscillatory flow reactor achieved high conversion with a 1.5:1 molar ratio of oil to methanol. These process intensification technologies also improve the flexibility of biodiesel production. Cavitational reactors and spinning tube in tube reactors are able to handle different feedstocks with a wider range of free fatty acid concentration due to less reaction time. Efficient heat transfer along with high mass transfer rate brings about less energy consumption in mixing than conventional stirred reactors and good temperature control. Cavitational reactors and microwave reactors have very high energy efficiency. Finally, these technologies can realize easy scale-up and commercialization due to small size. As a result, some technologies have been scaled-up and commercialized successfully.

The quality of biodiesel is a crucial issue in commercial production. Biodiesel quality depends on not only reaction process but also downstream processing like product separation, water washing, and methanol recovery. However, the PI technologies for biodiesel production discussed here focus on reaction or/and product separation. These novel reactors can achieve low total glycerin (<0.24 wt%) in shorter residence times because reaction is intensified by improving mass and heat transfer rate and mixing intensity, but the quality of biodiesel may be still affected by other downstream processing steps. In addition, reaction/separation coupled technologies can require less downstream processing steps than the novel reactors. Membrane reactors can realize high quality biodiesel because membranes selectively permeate products while retaining bound glycerides and soaps. Reactive distillation can realize methanol recovery when obtaining high conversion. Centrifugal contactors can effect good product separation of biodiesel and glycerol following reaction. All of these further help improve biodiesel quality.

Table 1

<table>
<thead>
<tr>
<th>Residence time</th>
<th>Energy efficiency (g/J)</th>
<th>Operating and capital cost</th>
<th>Temperature control</th>
<th>Current status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static mixer</td>
<td>∼30 min</td>
<td>14.9–384 [30]</td>
<td>Low</td>
<td>Lab scale</td>
</tr>
<tr>
<td>Micro-channel reactor</td>
<td>28 s–several minutes</td>
<td>0.018 [8]</td>
<td>Low</td>
<td>Lab scale</td>
</tr>
<tr>
<td>Oscillatory flow reactor</td>
<td>30 min</td>
<td>N/A</td>
<td>Low</td>
<td>Pilot plant</td>
</tr>
<tr>
<td>Cavitationary reactor</td>
<td>Microseconds–several seconds</td>
<td>1 x 10⁻⁴ to 2 x 10⁻⁴ (hydrodynamic cavitation), 5 x 10⁻⁶ to 2 x 10⁻⁵ (acoustic cavitation)</td>
<td>Low</td>
<td>Commercial scale</td>
</tr>
<tr>
<td>Spinning tube in tube reactor</td>
<td>&lt;1 min</td>
<td>N/A</td>
<td>Low</td>
<td>Commercial scale</td>
</tr>
<tr>
<td>Microwave reactor</td>
<td>Several minutes</td>
<td>∼0.038 L/kg [24]</td>
<td>Low</td>
<td>Lab scale</td>
</tr>
<tr>
<td>Membrane reactor</td>
<td>1–3 h</td>
<td>N/A</td>
<td>Lower</td>
<td>Pilot plant</td>
</tr>
<tr>
<td>Reactive distillation</td>
<td>Several minutes</td>
<td>∼1.6 x 10⁻⁶ [43]</td>
<td>Lower</td>
<td>Pilot plant</td>
</tr>
<tr>
<td>Centrifugal contactor</td>
<td>∼1 min</td>
<td>N/A</td>
<td>Lower</td>
<td>Commercial scale</td>
</tr>
</tbody>
</table>

Fig. 14. Experimental setup for biodiesel synthesis using centrifugal contactor [47] (Courtesy of American Institute of Chemical Engineers).
5. Conclusions

Process intensification technologies have significant potential for enhancement of biodiesel production. Enhancement in transport processes and higher reaction rates provide the scope for continuous production. Hence higher conversion yields are possible, under milder conditions and involving reduced molar ratios of alcohol to oil, lower reaction temperature and catalyst concentration than conventional stirred reactors. Some process intensification technologies offer the flexibility to process a variety of feedstocks. Compared to conventional tank systems, these technologies are proved more energy efficient because of enhanced heat transfer. Their small “footprint” allows them to be scaled up easily and reduces the capital and operating cost and thus increases profit.

References

A review on biodiesel production using catalyzed transesterification

Dennis Y.C. Leung *, Xuan Wu, M.K.H. Leung

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China

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A B S T R A C T

Biodiesel is a low-emissions diesel substitute fuel made from renewable resources and waste lipid. The most common way to produce biodiesel is through transesterification, especially alkali-catalyzed transesterification. When the raw materials (oils or fats) have a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps. The water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. Both of the above reactions are undesirable and reduce the yield of the biodiesel product. In this situation, the acidic materials should be pre-treated to inhibit the saponification reaction. This paper reviews the different approaches of reducing free fatty acids in the raw oil and refinement of crude biodiesel that are adopted in the industry. The main factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature and catalyst concentration, are discussed. This paper also described other new processes of biodiesel production. For instance, the Biox co-solvent process converts triglycerides to esters through the selection of inert co-solvents that generates a one-phase oil-rich system. The non-catalytic supercritical methanol process is advantageous in terms of shorter reaction time and lesser purification steps but requires high temperature and pressure. For the in situ biodiesel process, the oilseeds are treated directly with methanol in which the catalyst has been previously dissolved at ambient temperatures and pressure to perform the transesterification of oils in the oilseeds. This process, however, cannot handle waste cooking oils and animal fats.

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1. Introduction

Due to the depletion of the world’s petroleum reserves and the increasing environmental concerns, there is a great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels. Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification [1]. Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids and is typically made from nontoxic, biological resources such as vegetable oils [2–24], animal fats [16,17,23,24], or even used cooking oils (UFO) [10]. Table 1 shows some feedstocks of biodiesel and their physicochemical properties. Vegetable oils are promising feedstocks for biodiesel production since they are renewable in nature, and can be produced on a large scale and environmentally friendly [25]. Vegetable oils include edible and non-edible oils. More than 95% of biodiesel production feeds come from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute [26]. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [11]. Moreover, it will cause deforestation in some countries because more and more forests have been felled for plantation purposes. In order to overcome these disadvantages, many researchers are interested in non-edible oils which are not suitable for human consumption because of the presence of some toxic components in the oils. Furthermore, non-edible oil crops can be grown in waste lands that are not suitable for food crops and the cost of cultivation is much lower because these crops can still sustain reasonably high yield without intensive care [12,26]. However, most non-edible oils contain high free fatty acids. Thus they may require multiple chemical steps or alternate approaches to produce biodiesel, which will increase the production cost, and may lower the ester yield of biodiesel below the standards [14,25,27]. Animal fats contain higher saturated fatty acids and normally exist in solid form at room temperature that may cause problems in the production process. Its cost is also higher than vegetable oils [18]. UFO is not suitable for human consumption but is a feedstock for biodiesel production. Its usage significantly reduces the cost of biodiesel production. However, the quality of UFO may cause concern because its physical and chemical properties depend on the contents of fresh cooking oil and UFO may contain lots of undesired impurity, such as water, free fatty acids [18,26,28,29]. Since the cost of raw materials accounts about 60–80% of the total cost of biodiesel production, choosing a right feedstock is very important [18,26]. Also, the yield and properties of biodiesel products produced from different feedstocks would be quite different from each other. Table 2 shows some physicochemical properties of biodiesel from different feedstocks and their yields under different production conditions [7,9,11,14,16,18,20,22,25–28,30–38]. Although at present biodiesel

<table>
<thead>
<tr>
<th>Type of oil</th>
<th>Species</th>
<th>Main chemical composition (fatty acid composition wt%)</th>
<th>Density (g/cm³)</th>
<th>Flash point (°C)</th>
<th>Kinematic viscosity (cst, at 40 °C)</th>
<th>Acid value (mg KOH/g)</th>
<th>Heating value (MJ/kg)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable oil</td>
<td>Edible oil</td>
<td>Soybean</td>
<td>C16:0, C18:1, C18:2</td>
<td>0.91</td>
<td>254</td>
<td>32.9</td>
<td>0.2</td>
<td>39.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Rapessed</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.91</td>
<td>246</td>
<td>35.1</td>
<td>2.92</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sunflower</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.92</td>
<td>274</td>
<td>32.6</td>
<td>–</td>
<td>36.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Palm</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.92</td>
<td>267</td>
<td>39.6a</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Peanut</td>
<td>C16:0, C18:0, C18:1, C18:2, C20:0, C22:0</td>
<td>0.90</td>
<td>271</td>
<td>22.72</td>
<td>3</td>
<td>39.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corn</td>
<td>C16:0, C18:0, C18:1, C18:2, C18:3</td>
<td>0.91</td>
<td>277</td>
<td>34.9a</td>
<td>–</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Camelina</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.91</td>
<td>–</td>
<td>–</td>
<td>0.76</td>
<td>42.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Canola</td>
<td>C16:0, C18:0, C18:1, C18:2, C18:3</td>
<td>0.91</td>
<td>–</td>
<td>–</td>
<td>0.1</td>
<td>35.2</td>
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<tr>
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<td></td>
<td>Cotton</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.91</td>
<td>234</td>
<td>18.2</td>
<td>–</td>
<td>39.5</td>
</tr>
<tr>
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<td></td>
<td>Pumpkin</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.92</td>
<td>&gt;230</td>
<td>35.6</td>
<td>0.55</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jatropha curcas</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.92</td>
<td>225</td>
<td>29.4</td>
<td>28</td>
<td>38.5</td>
</tr>
<tr>
<td>Non- edible oil</td>
<td>Pongamina pinnata</td>
<td>C16:0, C18:0, C18:1, C18:2, C18:3</td>
<td>0.91</td>
<td>205</td>
<td>27.8</td>
<td>5.06</td>
<td>34</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>Sea mango</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.92</td>
<td>–</td>
<td>29.6</td>
<td>0.24</td>
<td>40.86</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>Palanga</td>
<td>C16:0, C18:0, C18:1, C18:2</td>
<td>0.90</td>
<td>221</td>
<td>72.0</td>
<td>44</td>
<td>39.25</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>Tallow</td>
<td>C14:0, C16:0, C16:1, C17:0, C18:0, C18:1, C18:2</td>
<td>0.92</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>40.05</td>
<td>[17,23]</td>
</tr>
<tr>
<td></td>
<td>Nile tilapia</td>
<td>C16:0, C18:1, C20:5, C22:6, other acids</td>
<td>0.91</td>
<td>–</td>
<td>32.1b</td>
<td>2.81</td>
<td>–</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>Poultry</td>
<td>C16:0, C16:1, C18:0, C18:1, C18:2, C18:3</td>
<td>0.90</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>39.4</td>
<td>[23,24]</td>
</tr>
<tr>
<td></td>
<td>Used cooking oil</td>
<td>Depends on fresh cooking oil</td>
<td>0.90</td>
<td>–</td>
<td>44.7</td>
<td>2.5</td>
<td>–</td>
<td>[10]</td>
</tr>
</tbody>
</table>

a Kinematic viscosity at 38 °C, mm²/s.
b Kinematic viscosity at 37 °C, mm²/s.
cannot entirely replace petroleum-based diesel fuel, there are several distinct advantages of biodiesel over diesel fuel. Biodiesel has higher combustion efficiency, cetane number than diesel fuel [39]. It is biodegradable and more than 90% biodiesel can be biodegraded within 21 days [40,41]. Biodiesel has lower sulfur and aromatic content than diesel fuel and that means it will not emit lots of toxic gas [42,43]. Moreover, it reduces most exhaust emissions except NOx, such as monoxide, unburned hydrocarbons, and particulate matter [44–48].

A number of methods are currently available and have been adopted for the production of biodiesel fuel. There are four primary ways to produce biodiesel ([Table 3]): direct use and blending of raw oils [49–53], micro-emulsions [54], thermal cracking [55–60], and transesterification [61]. The most commonly used method for converting oils to biodiesel is through the transesterification of animal fats or vegetable oils, which forms the basis of the present paper. The objective of this paper is to give an overview on the technological advancement of producing biodiesel through transesterification. The main factors affecting the yield of biodiesel and other types of transesterification will also be discussed.

2. Biodiesel production with catalyzed transesterification

2.1. Basic chemical reactions

Common vegetable oils or animal fats are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters are called triglycerides, which can react with alcohol in the presence of a catalyst, a process known as transesterification. The simplified form of its chemical reaction is presented in equation

\[
CH_2-O-CO-R_1 + CH_2-OH + R-O-CO-R_2 \rightarrow CH_2-O-CO-R_3 + 3ROH
\]

where \( R_1, R_2, R_3 \) are long-chain hydrocarbons, sometimes called fatty acid chains. Normally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. When the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally to glycerol, 1 mol of fatty ester is liberated at each step [61]. Usually, methanol is the preferred alcohol for producing biodiesel because of its low cost.

Vegetable oils and fats may contain small amounts of water and free fatty acids (FFA). For an alkali-catalyzed transesterification, the alkali catalyst that is used will react with the FFA to form soap. Eq. (2) shows the saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water.

\[
R_1-\text{COOH} + \text{NaOH (sodium hydroxide)} \rightarrow R_1\text{COONa} + H_2O \text{ (water)}
\]

This reaction is undesirable because the soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve a higher

\[ \text{Feedstock} \quad \text{Kinematic viscosity (cst, at 40 °C)} \quad \text{Density (g/cm}^3) \quad \text{Saponification number} \quad \text{Iodine value} \quad \text{Acid value (mg KOH/g)} \quad \text{Cetane number} \quad \text{Heating value (MJ/kg)} \quad \text{Production conditions}^2 \quad \text{Yield (%) \quad References} \]

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Kinematic viscosity (cst, at 40 °C)</th>
<th>Density (g/cm³)</th>
<th>Saponification number</th>
<th>Iodine value</th>
<th>Acid value (mg KOH/g)</th>
<th>Cetane number</th>
<th>Heating value (MJ/kg)</th>
<th>Production conditions^2</th>
<th>Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean</td>
<td>4.08</td>
<td>0.885</td>
<td>201</td>
<td>138.7</td>
<td>0.15</td>
<td>52</td>
<td>40</td>
<td>65</td>
<td>90 1:12</td>
<td>[18,20,27,33,35]</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>4.3–5.83</td>
<td>0.88–0.886</td>
<td>–</td>
<td>–</td>
<td>0.25–0.45</td>
<td>49–50</td>
<td>45</td>
<td>65</td>
<td>120 1:6</td>
<td>[36]</td>
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<tr>
<td>Sunflower</td>
<td>4.9</td>
<td>0.88</td>
<td>200</td>
<td>142.7</td>
<td>0.24</td>
<td>49</td>
<td>45.3</td>
<td>60</td>
<td>120 1:6</td>
<td>[20,38]</td>
</tr>
<tr>
<td>Palm</td>
<td>4.42</td>
<td>0.86–0.9</td>
<td>207</td>
<td>60.07</td>
<td>0.08</td>
<td>62</td>
<td>34</td>
<td>Room 584 1:11</td>
<td>89.23</td>
<td>[18,20,32]</td>
</tr>
<tr>
<td>Peanut</td>
<td>4.42</td>
<td>0.88–0.82</td>
<td>200</td>
<td>67.45</td>
<td>–</td>
<td>54</td>
<td>40.1</td>
<td>40</td>
<td>60 1:6</td>
<td>[9,18,20]</td>
</tr>
<tr>
<td>Corn</td>
<td>3.39</td>
<td>0.88–0.89</td>
<td>202</td>
<td>120.3</td>
<td>–</td>
<td>58–59</td>
<td>45</td>
<td>60</td>
<td>120 1:6</td>
<td>[89]</td>
</tr>
<tr>
<td>Camelina</td>
<td>6.12–7</td>
<td>0.882–0.888</td>
<td>–</td>
<td>152–157</td>
<td>0.08–0.52</td>
<td>–</td>
<td>–</td>
<td>Room 60 1:6</td>
<td>KOH1.5</td>
<td>[97.9]</td>
</tr>
<tr>
<td>Canola</td>
<td>3.53</td>
<td>0.88–0.9</td>
<td>182</td>
<td>103.8</td>
<td>–</td>
<td>56</td>
<td>45</td>
<td>60</td>
<td>120 1:6</td>
<td>[20,25]</td>
</tr>
<tr>
<td>Cotton</td>
<td>4.07</td>
<td>0.875</td>
<td>204</td>
<td>104.7</td>
<td>0.16</td>
<td>54</td>
<td>45</td>
<td>65</td>
<td>90 1:6</td>
<td>[20,37]</td>
</tr>
<tr>
<td>Pumpkin</td>
<td>4.41</td>
<td>0.8837</td>
<td>202</td>
<td>115</td>
<td>0.48</td>
<td>–</td>
<td>38</td>
<td>60</td>
<td>60 1:6</td>
<td>[97.5]</td>
</tr>
<tr>
<td>Jatropha</td>
<td>4.78</td>
<td>0.8636</td>
<td>202</td>
<td>108.4</td>
<td>0.496</td>
<td>61–63</td>
<td>40–42</td>
<td>60</td>
<td>120 1:6</td>
<td>[98]</td>
</tr>
<tr>
<td>Pongamia</td>
<td>4.8</td>
<td>0.883</td>
<td>–</td>
<td>–</td>
<td>0.62</td>
<td>60–61</td>
<td>42</td>
<td>65</td>
<td>180 1:6</td>
<td>[14,25–26,34]</td>
</tr>
<tr>
<td>Sea mango</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>180 1:6</td>
<td>83.8</td>
<td>[11]</td>
</tr>
<tr>
<td>Palanga</td>
<td>3.99</td>
<td>0.869</td>
<td>–</td>
<td>41</td>
<td>66</td>
<td>4</td>
<td>1:12b</td>
<td>85</td>
<td>98</td>
<td>[14]</td>
</tr>
<tr>
<td>Tallow</td>
<td>–</td>
<td>0.856</td>
<td>244.5</td>
<td>126</td>
<td>0.65</td>
<td>59</td>
<td>–</td>
<td>60</td>
<td>1440 1:30</td>
<td>98.28</td>
</tr>
<tr>
<td>Nile tilapia</td>
<td>–</td>
<td>0.856</td>
<td>251.23</td>
<td>130</td>
<td>0.25</td>
<td>61</td>
<td>–</td>
<td>50</td>
<td>1440 1:30</td>
<td>99.72</td>
</tr>
<tr>
<td>Poultry</td>
<td>–</td>
<td>0.856</td>
<td>251.23</td>
<td>130</td>
<td>0.25</td>
<td>61</td>
<td>–</td>
<td>50</td>
<td>1440 1:30</td>
<td>99.72</td>
</tr>
<tr>
<td>Used cooking oil</td>
<td>–</td>
<td>0.856</td>
<td>251.23</td>
<td>130</td>
<td>0.25</td>
<td>61</td>
<td>–</td>
<td>50</td>
<td>1440 1:30</td>
<td>99.72</td>
</tr>
</tbody>
</table>

1. \( T = \) reaction temperature (°C); \( P = \) transesterification reaction period (min); \( M = \) molecular ratio of oil/methanol; \( C = \) amount of catalyst (wt.%).

2. Kinematic viscosity at 20 °C.

b. Volumetric ratio of oil/methanol.
2.2. Biodiesel production processes

2.2.1. Process flow chart

Today, most of the biodiesel is produced by the alkali-catalyzed process. Fig. 1 shows a simplified flow chart of the alkali-catalyst process. As described earlier, feedstocks with high free fatty acid will react undesirably with the alkali catalyst thereby forming soap. The maximum amount of free fatty acids acceptable in an alkali-catalyzed system is below 2.5 wt.% FFA. If the oil or fat feedstock has a FFA content over 2.5 wt.%, a pretreatment step is necessary before the transesterification process [64] (see Section 2.2.3).

2.2.2. Raw materials treatment

The raw materials, which can be vegetable oils, animal fats, or recycled greases, used in the production of biodiesel contain triglycerides, free fatty acids, water, and other contaminants in various proportions. Some crude vegetable oils contain phospholipids that need to be removed in a degumming step. Phospholipids can produce lecithin, a commercial emulsifier [65]. Liu et al. compared the different degumming methods, such as membrane filtration, hydration, acid micelles degumming, supercritical extraction, etc. The characteristics of the raw oils should be investigated before choosing the suitable degumming method because different degumming methods have their advantages and disadvantages [66]. The oil can be separated through membrane filtration according to the average molecular weight or the particle size of phospholipids. Although degumming method can solve the problem,
its process involves two steps with the use of an organic solvent. Therefore, this method has no superiority on cost because of its complicated processing [67,68]. In the hydration process, because of phospholipids hydrophilicity, hot water can be added into the oil with stirring. The phospholipids solubility will be significantly reduced, so it could be separated from the oil by natural settlement. The hydration method features a simple process, easy operation, and high yields refining, but non-hydratable phospholipids cannot be removed by this method, as reported by Verleyen et al. [69]. For removing non-hydratable phospholipids, critic acid or phosphoric acid can be added into the oil which is heated to 70 °C, this is called the special micelles degumming method. Pan et al. [70] found that the reaction time for this method is about 5 min, followed by neutralization through dilute lye. The supercritical extraction method is employed to separate the phospholipids. Moreover, by refining with supercritical CO2 extraction, it can effectively remove the free fatty acids and the peroxidation products that are in the crude oil. However, the high pressure required in this process will be the biggest challenge in its industrial application [71,72].

The free fatty acids are removed in a refining step and excess free fatty acids can be removed as soaps in a later pretreatment step. In addition, deodorization is another important step in the raw material treatment. During this step, steam, at 1–6 mm Hg pressure, is injected into the oil at 490–550 K in order to eliminate free fatty acids, aldehydes, unsaturated hydrocarbons, and ketones, all of which cause undesirable odors and flavors in the oil [73]. Next, in order to determine the percentage of FFA in the oils or fats, titration is performed. As described above, if the percentage of FFA is over 2.5 wt.%, pretreatment is necessary to reduce the content of FFA. This step also determines the amount of caustic soda required in the neutralization step.

2.2.3. Pretreatment of acidic feedstocks

Many pretreatment methods have been proposed for reducing the high free fatty acid content of the oils, including steam distillation [74], extraction by alcohol [75], and esterification by acid-catalysis [76]. However, steam distillation for reducing high free fatty acids requires a high temperature and has low efficiency. Because of the limited solubility of free fatty acids in alcohol, extraction by alcohol method needs a large amount of solvent and the process is complicated. Compared with the two former methods, esterification by acid-catalysis makes the best use of the free fatty acids in the oil and transforms it into biodiesel [75,77]. The common pretreatment is esterification of the FFA with methanol in the presence of acidic catalysts (usually sulphuric acid). The catalysts can be homogeneous acid-catalysts or solid acid-catalysts [78]. Compared with the former one, solid acid-catalysts offer some advantages for eliminating separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower [76]. As described earlier, free fatty acids will be converted to biodiesel by direct acid esterification and the water needs to be removed. If the acid value of the oils or fats is very high, one-step esterification pretreatment may not reduce the FFA efficiently because of the high content of water produced during the reaction. In this case, a mixture of alcohol and sulphuric acid can be added into the oils or fats three times (three-step pre-esterification). The time required for this process is about 2 h and water must be removed by a separation funnel before adding the mixture into the oils or fats for esterification again [79]. Moreover, some researchers reduce the percent of FFA by using acidic ion exchange resins in a packed bed. Strong commercial acidic ion exchange resins can be used for the esterification of FFA in waste cooking oils but the loss of the catalytic activity maybe a problem [80–84].

An alternative approach to reduce the FFA is to use iodine as a catalyst to convert free fatty acids into biodiesel. An obvious advantage of this approach is that the catalyst (iodine) can be recycled after the esterification reaction. Li et al. [85] found through orthogonal tests, under the optimal conditions (i.e. iodine amount: 1.3 wt.% of oils; reaction temperature: 80 °C; ratio of methanol to oils: 1.75:1; reaction time: 3 h) that the FFA content can be reduced to <2% [85].

Another new method of pretreatment is to add glycerol into the acidic feedstock and heat it to a high temperature of about 200 °C, normally with a catalyst such as zinc chloride. The glycerol will react with the FFA to form monoglycerides and diglycerides. Then the FFA level will become low and biodiesel can be produced using the traditional alkali-catalyzed transesterification method. The advantage of this approach is that no alcohol is needed during the pretreatment and the water formed from the reaction can be immediately vaporized and vented from the mixture. However, the drawbacks of this method are its high temperature requirement and relatively slow reaction rate [86].

2.2.4. Catalyst and alcohol

In general, there are three categories of catalysts used for biodiesel production: alkalis, acids, and enzymes [87–89]. Enzyme catalysts have become more attractive recently since it can avoid soap formation and the purification process is simple to accomplish. However, they are less often used commercially because of the longer reaction times and higher cost. To reduce the cost, some researchers developed new biocatalysts in recent years. An example is so called whole cell biocatalysts which are immobilized within biomass support particles. An advantage is that no purification is necessary for using these biocatalysts [90–93]. Compare with enzyme catalysts, the alkali and acid catalysts are more commonly used in biodiesel production [61]. The alkali and acid catalysts include homogeneous and heterogeneous catalysts. Due to the low cost of raw materials, sodium hydroxide and potassium hydroxide are usually used as alkali homogeneous catalysts and alkali-catalyzed transesterification is most commonly used commercially [36,38,94–99]. These materials are the most economic because the alkali-catalyzed transesterification process is carried out under a low temperature and pressure environment, and the conversion rate is high with no intermediate steps. However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the yield [28]. Therefore, they should be properly handled. On the other hand, some heterogeneous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement. In addition, solid heterogeneous catalysts can stimulatingly catalyze the transesterification and esterification reaction that can avoid the pre-esterification step, thus these catalysts are particularly useful for those feedstocks with high free fatty acid content [100]. However, using a solid catalyst, the reaction proceeds at a slower rate due to low diffusion rate and this reaction mixture constitutes a three-phase system, which, due to diffusion reasons, inhibits the reaction [33,101]. Table 4 classifies the three categories of catalysts with their advantages and disadvantages [27,33,82,102–109].

The alcohol materials that can be used in the transesterification process include methanol, ethanol, propanol, butanol, and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently. Methanol is especially used because of its lower cost and its physical and chemical advantages. Ma and Hanna [61] reported that methanol can react with triglycerides quickly and the alkali catalyst is easily dissolved in it. However, due to its low boiling point, there is a large explosion risk associated with methanol vapors which are colorless and odorless. Both methanol and methoxide are extremely hazardous materials that should be handled carefully. It should be ensured that one is not exposed to these chemicals during biodiesel production.
of alcohol, and excess alcohol is used to ensure total conversion of the oil to its esters. As previously mentioned, if the free fatty acid level or water level is too high, it may cause problems downstream with the saponification and the separation of the glycerol by-product. Therefore, the amount of water and free fatty acids in the feedstock oil should be monitored during the reaction.

Once the transesterification reaction is completed, two major products exist: esters (biodiesel) and glycerol. The glycerol phase is much denser than the biodiesel phase and settles at the bottom of the reaction vessel, allowing it to be separated from the biodiesel phase. Phase separation can be observed within 10 min and can be completed within several hours of settling. The reaction mixture is allowed to settle in the reaction vessel in order to allow the initial separation of biodiesel and glycerol, or the mixture is pumped into a settling vessel. In some cases, a centrifuge may be used to separate the two phases [86].

Both the biodiesel and glycerol are contaminated with an unreacted catalyst, alcohol, and oil during the transesterification step. Soap that may be generated during the process also contaminates the biodiesel and glycerol phase. Schumacher [114] suggested that although the glycerol phase tends to contain a higher percentage of contaminants than the biodiesel, a significant amount of contaminants is also present in the biodiesel. Therefore, crude biodiesel needs to be purified before use.

2.2.7. Refining crude glycerol

Although biodiesel is the desired product from the reactions, the refining of glycerol is also important due to its numerous applications in different industrial products such as moisturizers, soaps, cosmetics, medicines, and other glycerol products [115–117]. It is one of the few products that has a good reactivity on sump oil, and is extremely effective for washing shearing shed floor, so it can be used as a heavy duty detergent and degreaser. Whittington [118] reported that glycerol can even be fermented to produce ethanol, which means more biofuel can be produced.

According to the statements of Van Gerpen et al. [86], typically produced glycerol is about 50% glycerol or less in composition and mainly contains water, salts, unreacted alcohol, and unused catalyst. The unused alkali catalyst is usually neutralized by an acid. In some cases, hydrochloric or sulphuric acids are added into the glycerol phase during the re-neutralization step and produce salts such as sodium chloride or potassium sulphate, the latter can be
recovered for use as a fertilizer [119]. Generally, water and alcohol are removed to produce 80–88% pure glycerol that can be sold as crude glycerol. In more sophisticated operations, the glycerol is distilled to 99% or higher purity and sold in different markets [120].

After the re-neutralization step, the alcohol in the glycerol phase can be removed through a vacuum flash process or by other types of evaporators. Usually, the alcohol vapor is condensed back into liquid and reused in the process. However, the alcohol may contain water that should be removed in a distillation column before the alcohol is returned to the process. The alcohol recovery step is more difficult when the alcohol that is used, such as ethanol or isopropyl alcohol, forms an azetrop with the water. Gerpen [121] proposed the use of a molecular sieve to remove the water generated.

### 2.2.8. Purification of crude biodiesel

After separation from the glycerol phase, crude biodiesel is mainly contaminated with residual catalyst, water, unreacted alcohol, free glycerol, and soaps that were generated during the transesterification reaction [114]. Normally, crude biodiesel enters a neutralization step and then passes through an alcohol stripper before the washing step. In some cases, acid is added to crude biodiesel to neutralize any remaining catalyst and to split any soap. Soaps react with the acid to form water soluble salts and free fatty acids. Gerpen [121] stated that neutralization before the washing step reduces the materials required for the washing step and minimizes the potential for emulsions being formed during the washing step. Unreacted alcohol should be removed with distillation equipment before the washing step to prevent excess alcohol from entering the wastewater effluent [86]. The primary purpose of this step is to wash out the remnants of the catalyst, soaps, salts, residual alcohol, and free glycerol from the crude biodiesel. Generally, three main approaches are adopted for purifying biodiesel: water washing, dry washing [122], and membrane extraction [123,124]. These approaches are briefly shown in Table 5 and discussed in detail as follows.

#### 2.2.8.1. Water washing

Since both glycerol and alcohol are highly soluble in water, water washing is very effective for removing both contaminants. It also can remove any residual sodium salts and soaps. The primary material for water washing is distilled warm water or softened water (slightly acidic) [72,73]. Warm water prevents the precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. Softened water (slightly acidic) eliminates calcium and magnesium contamination and neutralizes any remaining alkali catalysts [86]. After washing several times, the water phase becomes clear, meaning that the contaminants have been completely removed. Then, the biodiesel and water phases are separated by a separation funnel or centrifuge [125]. Moreover, because of the immiscibility of water and biodiesel, molecular sieves and silica gels, etc., can also be used to remove water from the biodiesel [86]. The remaining water can be removed from the biodiesel by passing the product over heated Na₂SO₄ (25 wt.% of the amount of the ester product) overnight and then be removed by filtration [126]. However, there are many disadvantages to this method, including an increased cost and production time, polluting liquid effluent, product loss, etc. Moreover, emulsions can form when washing the biodiesel made from waste cooking oils or acidic feedstocks because of the soap formation [127].

#### 2.2.8.2. Dry washing

Cooke et al. [122] used dry washing by replacing the water with an ion exchange resin or a magnesium silicate powder in order to remove impurities. These two dry washing methods can bring the free glycerol level down and is reasonably effective for removing soaps. Both the ion exchange process and the magnesol process have the advantage of being waterless and thus eliminate many of the problems outlined above. Although the magnesol process has a better effect on the removal of methanol than the ion resins, none of the products from this process fulfill the limits specified in the EN Standard [128,129].

#### 2.2.8.3. Membrane extraction

Gabelman and Hwang [123] proved that the contaminants can be removed by using a hollow fiber membrane extraction, such as polysulfone. In this method, a hollow fiber membrane (1 m long, 1 mm diameter) filled with distilled water is immersed into the reactor (20°C). The crude biodiesel is pumped into the hollow fiber membrane (flow rate: 0.5 ml/min; operating pressure: 0.1 MPa). Following this step, biodiesel is passed over heated Na₂SO₄ and then filtered to remove any remaining water [124]. This approach effectively avoids emulsification during the washing step and decreases the loss during the refining process. The purity of the biodiesel obtained is about 90% and the other properties conform to the ASTM standards [130]. It is a very promising method for purifying biodiesel.

#### 2.2.9. Quality control

For commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets inter-

<table>
<thead>
<tr>
<th>Approaches</th>
<th>Primary material used</th>
<th>Function</th>
<th>Phases separation</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water washing</td>
<td>Distilled warm water</td>
<td>Prevents precipitation of saturated fatty acid esters</td>
<td>Separation funnel, centrifuge, molecular sieves, silica gels, etc.</td>
<td>Very effective in removing contaminants</td>
<td>Increased cost and production time, liquid effluent, product loss, emulsions formation</td>
<td>[46,72–74]</td>
</tr>
<tr>
<td></td>
<td>Softened water</td>
<td>Retards the emulsion formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry washing</td>
<td>Ion exchange resin</td>
<td>Eliminates calcium and magnesium contamination</td>
<td>Brings the free glycerol level down and removing soaps</td>
<td>Waterless</td>
<td>Overruns the limit in the EN Standard</td>
<td>[69,75,76]</td>
</tr>
<tr>
<td></td>
<td>Magnesium silicate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane extraction</td>
<td>Polysulfone</td>
<td>Remove the contaminants</td>
<td>–</td>
<td>Avoids the emulsion formation and decreases the refining loss</td>
<td>Probably high cost and low throughput due to contaminants existed</td>
<td>[70,71]</td>
</tr>
</tbody>
</table>

- Cooke et al. [122] used dry washing by replacing the water with an ion exchange resin or a magnesium silicate powder in order to remove impurities. These two dry washing methods can bring the free glycerol level down and is reasonably effective for removing soaps. Both the ion exchange process and the magnesol process have the advantage of being waterless and thus eliminate many of the problems outlined above. Although the magnesol process has a better effect on the removal of methanol than the ion resins, none of the products from this process fulfill the limits specified in the EN Standard [128,129].

- Gabelman and Hwang [123] proved that the contaminants can be removed by using a hollow fiber membrane extraction, such as polysulfone. In this method, a hollow fiber membrane (1 m long, 1 mm diameter) filled with distilled water is immersed into the reactor (20°C). The crude biodiesel is pumped into the hollow fiber membrane (flow rate: 0.5 ml/min; operating pressure: 0.1 MPa). Following this step, biodiesel is passed over heated Na₂SO₄ and then filtered to remove any remaining water [124]. This approach effectively avoids emulsification during the washing step and decreases the loss during the refining process. The purity of the biodiesel obtained is about 90% and the other properties conform to the ASTM standards [130]. It is a very promising method for purifying biodiesel.
national standards. A few specifications have been set but the ASTM D 6751 and EN 14214 standards are the most commonly used standards. Even in blends with conventional diesel fuel, Mettelbach [131] stated that most people in the industry expect the biodiesel blending stock to meet the relevant standard before being blended. Some properties in the standard, such as the cetane number or density, can reflect the properties of the chemical compounds that make up the biodiesel, and other properties provide an indication of the quality of the production process [54]. Generally, biodiesel standards identify the parameters that pure biodiesel must meet before being used as a pure fuel or being blended with distillate fuels [120,129,130].

To ensure safe operation in diesel engines, the most important aspects of the biodiesel product are the completion of the reaction, the removal of the free glycerol, residual catalyst and alcohol, and the absence of free fatty acids [39,41,42,132]. As mentioned before, if the transesterification reaction is not complete then triglycerides, diglycerides, or monoglycerides may be left in the final product. Chemically, each of these compounds contains a glycerol molecule. Fuel with excessive free glycerol may plug the fuel filters and cause combustion problems in the diesel engine. Therefore, the ASTM standard requires the total glycerol to be <0.24% of the final biodiesel product [54,130]. On the other hand, since residual methanol, even as little as 1%, can lower the flashpoint of the final biodiesel product from 170 °C to <40 °C, the EN 14214 standard limits the amount of alcohol to a very low level [86,129]. Finally, although a specific value for the residual catalyst is not included in the ASTM standard, it is limited by the specification on levels of sulfated ash, which may lead to engine deposits and high abrasive wear levels [42,130].

Because the European specification for sulfur content (i.e. EN 14214) is much tighter than the US requirement, Ali et al. [133] reported that a number of producers in Europe are resorting to the use of vacuum distillation for the removal of sulfur compounds from the final biodiesel product. In addition, some vegetable oils, yellow greases, and brown greases leave an objectionable color in the biodiesel. Although there is no color specification in the ASTM standard, in some cases, an activated carbon bed, which is an effective method for the removal of excessive color, is used to produce a colorless biodiesel [120].

### 2.3. Storage of biodiesel product

Biodiesel is safe to store and the properties of biodiesel should conform to respective standards after it has been stored for a long time. Table 6 shows the ASTM D 6751 and EN 14214 standards.

There are several key factors that need to be considered for the storage of biodiesel, including exposure temperature, oxidative stability, fuel solvency, and material compatibility [40,134]. Lee et al. [135] stated that the temperature of stored biodiesel should be controlled so as to avoid the formation of crystals which can plug fuel lines and fuel filters. For this reason, the storage temperature of most pure biodiesel is generally kept between 7 and 10 °C. Even in extremely cold climates, underground storage of pure biodiesel usually provides the storage temperature necessary for preventing crystal formation [86].

Bondioli et al. [136] noted that the stability of biodiesel is an important property when it is to be stored for a prolonged period. Poor stability can lead to an increased acid value and fuel viscosity and to the formation of gums and sediments. Therefore, if the duration of storing biodiesel or biodiesel blends is more than 6 months, it should be treated with an antioxidant additive [86]. Moreover, because water contamination will lead to biological growth in the fuel, it should be minimized in the stored fuel by using biocides. Biodiesel storage tanks made of aluminum, steel, Teflon, and fluorinated polyethylene or polypropylene should be selected.

Table 6 Specifications and test methods of ASTM D6751 and EN 14214 standards [129,130].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Limits</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ASTM D6751</td>
<td>EN 14214</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>130.0 min</td>
<td>101.0 min</td>
</tr>
<tr>
<td>Kinematic viscosity at 40 °C</td>
<td>mm²/s</td>
<td>1.9–6.0</td>
<td>3.5–5.0</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>47 min</td>
<td>51 min</td>
</tr>
<tr>
<td>Sulphated ash content</td>
<td>% (m/m)</td>
<td>0.020 max</td>
<td>D874</td>
</tr>
<tr>
<td>Copper strip corrosion</td>
<td></td>
<td>No. 3 max</td>
<td>Class 1</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg KOH/g</td>
<td>0.80 max</td>
<td>0.5 max</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>% (m/m)</td>
<td>0.020 max</td>
<td>D8684</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>% (m/m)</td>
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<td>0.25 max</td>
</tr>
<tr>
<td>Phosphorous content</td>
<td>% (m/m)</td>
<td>0.001 max</td>
<td>0.01 max</td>
</tr>
<tr>
<td>Carbon residue</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D6751 (100% sample)</td>
<td>% (m/m)</td>
<td>0.050 max</td>
<td>–</td>
</tr>
<tr>
<td>EN 14214 (10% bottoms)</td>
<td></td>
<td>–</td>
<td>0.3 max</td>
</tr>
<tr>
<td>Cloud point</td>
<td>°C</td>
<td>360 max</td>
<td>–</td>
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<tr>
<td>Distillation T90 AET</td>
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</tr>
<tr>
<td>Sulfur (5 Grade)</td>
<td>ppm</td>
<td>0.05 max</td>
<td>–</td>
</tr>
<tr>
<td>Sulfur (500 Grade)</td>
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<td>10 max</td>
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</tr>
<tr>
<td>Water and sediment</td>
<td>%vol.</td>
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</tr>
<tr>
<td>Water content</td>
<td>mg/kg</td>
<td>500 max</td>
<td>–</td>
</tr>
<tr>
<td>Total contamination</td>
<td>mg/kg</td>
<td>24 max</td>
<td>–</td>
</tr>
<tr>
<td>Oxidation stability at 110 °C</td>
<td>h</td>
<td>6 min</td>
<td>–</td>
</tr>
<tr>
<td>Iodine value</td>
<td></td>
<td>120 max</td>
<td>–</td>
</tr>
<tr>
<td>Linolenic acid methyl ester</td>
<td>% (m/m)</td>
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</tr>
<tr>
<td>Polyunsaturated (&gt;4 double bonds) methyl esters</td>
<td>% (m/m)</td>
<td>1 max</td>
<td>–</td>
</tr>
<tr>
<td>Ester content</td>
<td>% (m/m)</td>
<td>96.5 min</td>
<td>–</td>
</tr>
<tr>
<td>Methanol content</td>
<td>% (m/m)</td>
<td>0.2 max</td>
<td>–</td>
</tr>
<tr>
<td>Monoglyceride content</td>
<td>% (m/m)</td>
<td>0.8 max</td>
<td>–</td>
</tr>
<tr>
<td>Diglyceride content</td>
<td>% (m/m)</td>
<td>0.2 max</td>
<td>–</td>
</tr>
<tr>
<td>Triglyceride content</td>
<td>% (m/m)</td>
<td>0.2 max</td>
<td>–</td>
</tr>
<tr>
<td>Alkaline metals (Na + K)</td>
<td>mg/kg</td>
<td>5 max</td>
<td>–</td>
</tr>
</tbody>
</table>
The tanks should minimize the possibility of water contamination and should be cleaned prior to use for biodiesel storage [137].

2.4. Main factors affecting the yield of biodiesel

2.4.1. Alcohol quantity

Many researchers recognized that one of the main factors affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride [28,47,61,138]. Theoretically, the ratio for transesterification reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in a greater ester conversion in a shorter time. The yield of biodiesel is increased when the alcohol triglyceride ratio is raised beyond 3 and reaches a maximum. Further increasing the alcohol amount beyond the optimal ratio will not increase the yield but will increase cost for alcohol recovery [28]. In addition, the molar ratio is associated with the type of catalyst used and the molar ratio of alcohol to triglycerides in most investigations is 6:1, with the use of an alkali catalyst [47,138]. When the percentage of fatty free acids in the oils or fats is high, such as in the case of waste cooking oil, a molar ratio as high as 15:1 is needed when using acid-catalyzed transesterification [28,133,139,140].

2.4.2. Reaction time

Freedman et al. [141] found that the conversion rate of fatty acid esters increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of <90 min, and then remains relatively constant with a further increase in the reaction time [28,142]. Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps [143,144].

2.4.3. Reaction temperature

Temperature clearly influences the reaction and yield of the biodiesel product. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, Leung and Guo [28] and Eevera et al. [143] found that when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides. The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization. Depending on the oil used, the optimal temperature ranges from 50°C to 60°C [28,61,141].

2.4.4. Catalyst concentration

Catalyst concentration can affect the yield of the biodiesel product. As mentioned before, the most commonly used catalyst for the reaction is sodium hydroxide. However, Freedman et al. [141] found that sodium methoxide was more effective than sodium hydroxide because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will affect the product yield because of the hydrolysis reaction [145]. This is the reason why the catalyst should be added into the methanol first and then mixed with the oil. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters [28,145]. Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt.% and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap [28,143].

3. Other processes of biodiesel production

3.1. Biox co-solvent process

The Biox co-solvent process was developed by Boocock et al. in 1996 [146]. In this process, triglycerides are converted to esters through the selection of inert co-solvents that generate a one-phase oil-rich system [86,94,146]. Co-solvent options are available to overcome slow reaction times caused by the extremely low solubility of the alcohol in the triglyceride phase. Demirbas [94] uses tetrahydrofuran (THF) as a co-solvent to make the methanol soluble. After the completion of the reaction, the biodiesel–glycerol phase separation is clean and both the excess alcohol and the tetrahydrofuran co-solvent can be recovered in a single step [94]. However, because of the possible hazard and toxicity of the co-solvents, they must be completely removed from the glycerol phase as well as the biodiesel phase and the final products should be water-free [146]. The unique advantage of the Biox co-solvent process is that it uses inert, reclaimable co-solvents in a single-pass reaction that takes only seconds at ambient temperature and pressure, and no catalyst residues appear in either the biodiesel phase or the glycerol phase [86]. This process can handle not only grain-based feedstocks but also waste cooking oils and animal fats. Van Gerpen et al. [62] found, however, that the recovery of excess alcohol is difficult when using this process because the boiling point of the THF co-solvent is very close to that of methanol.

3.2. Supercritical alcohol process

As is known, when a fluid or gas is subjected to temperatures and pressures in excess of its critical point, a number of unusual properties are exhibited. Under such conditions, a distinct liquid and vapor phase no longer exist. Instead, a single fluid phase is formed [86]. Therefore, a process for biodiesel production has been developed by a non-catalytic supercritical methanol method [147,148]. Because of the lower value of the dielectric constant of methanol in the supercritical state, this approach is believed to be able to solve the problems associated with the two-phase nature of normal methanol/triglyceride mixtures by forming a single phase, and the reaction is completed in a very short time [149]. Supercritical transesterification is carried out in a high pressure reactor, with heat supplied from an external heater. Reaction occurs during the heating period. After the reaction is complete, the gas is vented and the product in the reactor is poured into a collecting vessel. The remaining contents are removed from the reactor by washing it with methanol [150,151]. During the whole process, several variables (i.e. reaction pressure and temperature) affect the yield of the biodiesel product and the highest yield can be obtained under the optimal conditions. In contrast to the common alkali-catalyzed method, this process has advantages in terms of reaction time and purification but requires a high temperature and pressure, hence requiring a high amount of energy [94,147,148].

3.3. In situ biodiesel process

The in situ biodiesel production is a novel approach for converting oil to biodiesel which was developed by Harrington and D’Arcy-Evans in 1985 [152]. In this method, to achieve transesterification
of its acyglycerols, the oilseeds are directly treated at ambient temperature and pressure with a methanol solution in which the catalyst has been previously dissolved. That means that the oil in the oilseeds is not isolated prior to transesterification to fatty acid esters [152–154]. To reduce the alcohol requirement for high efficiency during in situ transesterification, the oilseeds need to be dried before the reaction takes place [155]. Milled oilseeds are mixed with alcohol in which the catalyst had been dissolved and the mixture is heated under reflux for 1–5 h. Two layers are formed around the time of the completion of the reaction. The lower layer is the alcohol phase and can be recovered. The upper layer, including the crude biodiesel, is washed with water to remove the contaminants until the washing solution is neutral. After the washing step, the upper layer is dried over anhydrous sodium sulfate, then filtered, and the residual product is biodiesel [156]. Haas and Scott [155] found that the final biodiesel product can conform to the ASTM standard and the conversion of the oilseed is very high (about 98%). Since this method eliminates the need for the isolation of, and possibly for the refining of, the oilseed lipid, the process could reduce biodiesel production costs, reduce the long size of the production system associated with the pre-extraction, degumming, and maximize the yield of the biodiesel production. However, this process cannot handle waste cooking oils and animal fats, which can reduce the cost of feedstock [156,157].

4. Conclusions

Biodiesel is a clean-burning diesel fuel with a chemical structure of fatty acid alkyl esters. Of the various methods available for producing biodiesel, the alkali-catalyzed transesterification of vegetable oils and animal fats is currently the most commonly adopted method. Transesterification is basically a sequential reaction. However, when the raw materials (oils or fats) contain a high percentage of free fatty acids or water, the alkali catalyst will react with the free fatty acids to form soaps and the water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. These are undesirable reactions which reduce the yield of the biodiesel product. Therefore, after refining the raw materials, the acidic feedstocks should be pre-treated to inhibit the saponification reaction. There are three primary approaches for reducing the amount of free fatty acids: esterification of free fatty acids with methanol, in the presence of acidic catalysts; using iodine as a catalyst; adding glycerol into the acidic feedstock with a catalyst like methanol, in the presence of acidic catalysts; using iodine as a reactant and a catalyst. The most commonly used catalyst has been previously dissolved. That means that the oil in the oilseed is needed and the water (formed from the reaction) can be immediately vaporized and vented from the mixture. The transesterification reaction requires an alcohol as a reactant and a catalyst. The most commonly used alcohol is methanol while sodium hydroxide and potassium hydroxide are the most commonly used catalysts. During the reaction, glycerol will be produced as a by-product. Because of its numerous industrial applications, the crude glycerol should be refined with purity higher than 99% to make it usable. For refining the crude biodiesel produced, the product should first be neutralized and then put through an alcohol stripper before cleaning by either one of the following approaches: water washing, membrane extraction, and dry washing. A very promising method for washing biodiesel is the hollow fiber membrane extraction, which effectively avoids emulsification during the washing step and decreases the refining loss. As a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure that it meets international standards even if it has been stored for a long time.

There are four primary factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature, and catalyst concentration. To ensure a complete transesterification reaction, the molar ratio of alcohol to triglycerides should be increased to 6:1 with the use of an alkali catalyst. For used cooking oils or for oils with a high percentage of free fatty acids, a higher molar ratio is needed for acid-catalyzed transesterification. Because the conversion rate of fatty acid esters increases with reaction time but the yield of the biodiesel product reaches a maximum at an optimal reaction time. Higher reaction temperature can decrease the viscosity of oils, enhancing the reaction rate. The optimal temperature ranged between 50 °C and 60 °C, depending on the oil used. The optimal condition of catalyst concentration is about 1.5 wt.% for NaOH which is the most commonly used catalyst. With increasing concern over global warming, it is foreseeable that biodiesel usage would continue to grow at a fast pace. This will trigger the development of more sophisticated methods of biodiesel production and refining to cope with the increasing market demand.

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References


One-pot process combining transesterification and selective hydrogenation for biodiesel production from starting material of high degree of unsaturation

Ru Yang\textsuperscript{a,∗}, Mengxing Su\textsuperscript{a}, Min Li\textsuperscript{a}, Jianchun Zhang\textsuperscript{b}, Xinmin Hao\textsuperscript{b}, Hua Zhang\textsuperscript{b}

\textsuperscript{a}State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
\textsuperscript{b}The Quartermaster Institute of General Logistics, Department of CPLA, Beijing 100088, PR China

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\textbf{A B S T R A C T}

A one-pot process combining transesterification and selective hydrogenation was established to produce biodiesel from hemp (Cannabis sativa L.) seed oil which is eliminated as a potential feedstock by a specification of iodine value (IV; 120 g I\textsubscript{2}/100 g maximum) contained in EN 14214. A series of alkaline earth metal oxides and alkaline earth metal supported copper oxide were prepared and tested as catalysts. SrO supported 10 wt.% CuO showed the superior catalytic activity for transesterification with a biodiesel yield of 96% and hydrogenation with a reduced iodine value of 113 and also exhibited a promising selectivity for eliminating methyl linolenate and increasing methyl oleate without rising methyl stearate in the selective hydrogenation. The fuel properties of the selective hydrogenated methyl esters are within biodiesel specifications. Furthermore, cetane numbers and iodine values were well correlated with the compositions of the hydrogenated methyl esters according to degrees of unsaturation.

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1. Introduction

Biodiesel has lately emerged as an alternative fuel with wide acceptance because of its reduction of most exhaust emissions, improved lubricity, higher flash point, improved biodegradability and reduced toxicity over conventional diesel fuel (CDF) (Christos et al., 2010; Knothe, 2006; Moser et al., 2007). It is usually produced by the transesterification of vegetable oil or animal fat with short-chain alcohols (Su et al., 2010). The vegetable oils being exploited commercially constitute the edible fatty oils derived from rape-seed, soybean, palm, sunflower, etc. Owning to the high price and a big gap in demand and supply of such oils, it is not feasible to produce biodiesel in developing countries such as China and India. This highlights the need for the development of technologies allowing the use of non-edible vegetable oils. More than 350 oil-bearing crops have been identified (Dorado et al., 2004); oils from 75 plant species have been converted to biodiesel and iodine value (IV) and cetane number (CN) varied from 4.8 to 212 and 20.56 to 67.47, respectively (Azam et al., 2005). However, regardless of the raw materials used, biodiesel marketed for consumption must comply with specifications mandating biodiesel quality, most notably EN 14214, which contains a specification for iodine value (IV: 120 g I\textsubscript{2}/100 g maximum) and cetane number (CN: 51 minimum), which eliminates the highly poly-unsaturated oil as a potential feedstock.

Biodiesel properties included as specifications in standards were determined by the nature of the biodiesel components. As biodiesel consists of fatty acids esters, not only the structure of the fatty acids but also that of the ester moiety derived from the alcohol can influence the fuel properties of biodiesel. These structural features include degree of unsaturation, chain length, and branching of the chain (Knothe, 2005), and degree of unsaturation of the fatty acids is the most important factor. The properties of a biodiesel fuel, including iodine value, oxidative stability, cetane number, cold-flow properties, viscosity and lubricity, are directly determined by the degree of unsaturation of its component fatty esters (Knothe, 2008). Iodine value and cold-flow properties increase as the number of double bonds in the fatty acid molecular increases (Moraes et al., 2008; Imahara et al., 2006), while cetane number and the oxidative stability decrease with an increasing degree of unsaturation in the fatty acid chain (Knothe, 2005). Thus, only through modifying and keeping a proper degree of unsaturation can biodiesel obtained from starting materials of high degree of unsaturation can meet the specifications. Several approaches are possible to modify the fatty acid composition of biodiesel. A first approach is the use of oils with inherently modified fatty acid profile by genetic modification giving advantageous fuel properties (Knothe, 2008). A second approach is the fraction distillation obtaining biodiesels with different fatty acid compositions of fatty acids esters (Falk and Meyer-Pittroff, 2004). However, when the good distillates were selected for biodiesel fuel, the problem of application of the left ones occurs. A third approach is the catalytic hydrogenation of the feedstock and/or the fatty acids esters. In
order to use fatty substances having iodine values greater than 120 g I₂/100 g, more preferably greater than 150 g I₂/100 g, for the production of biodiesel, selective hydrogenation is essential and practical, which reduces the degree of unsaturation without increasing the stearic acid content and limiting cis–trans and positional isomerisation as much as possible (Federico et al., 2006). Past attempts to reduce the degree of unsaturation of the fatty acids in the highly ploy-unsaturated fatty substances using partial hydrogenation over conventional catalysts, lead to derivatives that were unsuited to the manufacture of biodiesel. In deed, the selectivity for biodiesel production in partial hydrogenation is difficult to achieve with the nickel (Moser et al., 2007) and noble metal-based catalysts like platinum (Nohair et al., 2005), rhodium (Nicolau et al., 2009) and palladium (Fernandez et al., 2005; Pérez-Cadenas et al., 2006), resulted in the formation of significant quantities of high melting point saturated fatty acids, which prejudice the cold-weather behavior of the product obtained (Federico et al., 2006). On the contrary, copper catalysts were found to have good catalytic activity and selectivity in the selective hydrogenation of highly unsaturated vegetable oils. Cu/Al₂O₃ (Federico et al., 2006) and Cu/SiO₂ (Nicoletta et al., 2002) possess high selectivity for hydrogenating linolenate C₁₈:₃ to oleate C₁₈:₁ with oleate C₁₈:₁ unreduced, therefore, the percentage of saturated is scarcely changed during the hydrogenation process. However, it should be pointed out that these previous researches applied two separate processes, i.e., the hydrogenation of triglycerides or esters and transesterification for biodiesel production. The employment of different catalysts and equipments for the separate processes could increase the cost for large-scale biodiesel production.

Hemp (Cannabis sativa L.), an annual herbaceous plant, has been grown agriculturally for many centuries for its bast fiber and hempseed oil. (Oomaha et al., 2002). Due to the increasing demand of hempseed oil were analyzed in our laboratory through transesterification at 65 °C for 3 h with methanol using 1 wt.% NaOH. According to GC analysis, the fatty acid consisted of palmitic acid 6.64%, stearic acid 2.76%, oleic acid 10.12%, linoleic acid 54.31%, linolenic acid (C₁₈:₃) 23.76%, and traces of other acids. All chemicals used were of analytical grade, which were purchased from Beijing Chemical Co., Ltd., China.

2.2. Catalyst preparation

MgO, CaO, SrO, BaO, and CuO catalysts were prepared by the conventional precipitation method from Mg(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, Sr(NO₃)₂, Ba(NO₃)₂, and Cu(NO₃)₂·3H₂O using ammonium bicarbonate as precipitate. The catalyst preparation was attempted into a three neck flask equipped with mechanical stirrer and a dropping funnel. Two aqueous solutions were first prepared. For a typical catalyst preparation, the first was a solution of 25.6 g Mg(NO₃)₂·6H₂O (0.10 mol) in 100 ml distilled water. The second was a solution of 9.6 g ammonium bicarbonate (anhydrous, 0.10 mol) in 100 ml distilled water. The first solution was put into the flask where the second one was added under vigorous stirring at ambient temperature. After that, the mixture was stirred for 4 h to form precipitate. The precipitate was washed with distilled water, dried under vacuum at 120 °C, and then calcinated at 1000 °C in vacuum for 5 h.

Alkaline earth oxides loaded with copper oxide were prepared by the chemisorption–hydrolysis (CH) method (Nicoletta et al., 2002). The support was added to a Cu(NH₃)₄(NO₃)₂ solution prepared by adding NH₄OH to a Cu(NO₃)₂·3H₂O solution until pH was 9. After 20 min under stirring, the slurry was slowly diluted in order to allow hydrolysis of the copper complex and deposition of the finely dispersed product to occur. After that, the solids were separated by filtration, dried overnight at 120 °C. Prior to each reaction, the as-prepared catalysts were calcined at 1000 °C in vacuum for 5 h. The loading amounts of copper oxide were calculated on the basis of the amounts of the initial materials.

2.3. Base strength determination

Basic strengths of the catalysts (H⁺) were determined using Hammett indicators (Kawashima et al., 2009). About 25 mg of the catalyst sample was shaken with 5 ml of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 h. After the equilibration, the color of the catalyst was noted. The following Hammett indicators were used: neutral red (pK₉BH⁺ = 6.8), phenolphthalein (pK₉BH⁺ = 9.3), 2,4-dinitroaniline (pK₉BH⁺ = 15.0), 4-nitroaniline (pK₉BH⁺ = 18.4) and 4-chloroaniline (pK₉BH⁺ = 26.5). The base strength is quoted as being stronger than the weakest indicator which exhibits a color change, but weaker than the strongest indicator that produces no change.

2.4. Reaction procedure

The catalytic performance of alkaline earth metal oxides and alkaline earth metal oxides supported copper oxide were evaluated in the one-pot process combining transesterification of hempseed oil with methanol and selective hydrogenation of methyl esters. For a typical reaction, 100 ± 0.01 g of hempseed oil and 50 ± 0.1 ml of anhydrous methanol (molar ratio of methanol to hempseed oil = 12:1) with 3 ± 0.01 g of catalyst immersed (weight ratio of catalyst to hempseed oil = 3%) was charged into a 500 ml stainless steal autoclave, which equipped with a stirrer and a cooling jacket surrounded by a heating mantle controlled by a proportional Integra derivative (PID) temperature controller. The autoclave was purged with nitrogen, and the last traces of N₂/air were removed by a number of pressurizing/depressurizing cycles with H₂ before the reaction and then the autoclave was pressured.
and the contents were heated to 180 ± 1 °C with a rate of 5 °C/min, constant in all the experiments with constant stirring at 1000 rpm. The one-pot process was carried out at 3.0 ± 0.01 MPa for 3 h. At the end of reaction, the autoclave was cooled to room temperature, vented of H₂ and the product mixture was removed. The catalyst was separated from the reaction solution by filtration. The alcohol phase (glycerin and methanol in excess) was separated from the organic phase (methyl esters) by decantation, and finally the residual methanol in the methyl ester phase was eliminated by distillation.

2.5. Product analysis

The products collected were immediately analyzed by a SP-3420A gas chromatograph from Beijing Beifen–Ruili Analytical Instrument (Group) Co. Ltd., equipped with a flame ionization detector (FID) and a BFSP-0677-02 capillary column (2 m × 0.32 mm × 0.25 μm). Methyl heptadecanoate was used as the internal standard to determine the amounts of products. The injector temperature was 240 °C and the detector temperature was 250 °C. The analysis of biodiesel for each sample was carried out by dissolving 1 mL of biodiesel sample into 5 mL of acetone and injecting 1 μL of this solution in GC. The yield of biodiesel (FAME) with respect to hempseed oil was calculated from the content of methyl esters analyzed by GC with the following equation:

\[
\text{Yield} = \frac{\text{Amount of biodiesel(mol)}}{5 \times \text{Charge amount of oil(mol)}} \times 100(\%)
\]

Cetane numbers of biodiesel samples were determined in the Waukesha A111462B, which was calibrated with hexadecane and 2,2,4,4,6,8-heptamethylnonane (HMN) as primary reference fuels, according to GB/T386 method (China-GB/T386, 1991). Iodine values of biodiesel samples were determined by AOLS Official methods Cd 1-25 (AOCs, 1089). Density, kinematic viscosity at 40 °C, flash point in open vase, and pour point were evaluated according to American Society for Testing and Materials standard methods: ASTM D1298, ASTM D445, ASTM D92, ASTM D97, respectively. The acid value was determined according to the International Organization for Standardization ISO 660.

3. Results and discussion

3.1. Catalytic activities of transesterification and hydrogenation in the one-pot process

Alkaline earth metal oxides, including MgO, CaO, SrO, and BaO, used as heterogeneous basic catalysts for the transesterification of triglycerides with methanol have been published. The obtained results revealed that alkaline earth metal oxides became active for transesterification after a thermal pretreatment and the catalytic activities were predominant upon their alkalinitis (Helwani et al., 2009; Patil and Deng, 2009; Singh and Fernando, 2007). As the basic strength increased in the order of MgO < CaO < SrO < BaO, which was attributed to the decrease of electro-negativity of the conjugated metal cation of alkaline earth metal oxides, the catalytic activities of transesterification exhibited in the same sequence. SrO had basic sites stronger than H⁺ = 26.5 and gave a biodiesel yield in excess of 95% at 65 °C within 30 min in the transesterification of soybean oil to biodiesel (Liu et al., 2007). MgO, CaO, SrO, and BaO were also reported to show catalytic activity for hydrogenation of olefins. The alkaline earth metal oxides became active on evacuating above 600 °C and showed maximum activities in the order of MgO < CaO < BaO < SrO when evacuated around 1000 °C (Hattori et al., 1975). It is suggested that alkaline earth metal oxides evacuated at high temperature showed catalytic activity for transesterification of triglycerides with methanol or hydrogenation of olefins. In this paper, therefore, alkaline earth metal oxides were investigated for a one-pot process combining transesterification of hempseed oil with methanol and hydrogenation of hempseed oil methyl esters. Basic strengths and catalytic activities in terms of biodiesel yields and the compositions of biodiesels of alkaline earth metal oxides were listed in Table 1. As shown in Table 1, the basic strength of alkaline earth metal oxides, which were determined using Hammett indicators, increased in the order Mg < Ca < Sr = Ba. The SrO and BaO samples owned the highest basic strength with H⁺ > 26.5 and gave high activities for transesterification, whereas the MgO and CaO samples possessed weaker basic sites with H⁺ < 26.5 and performed lower biodiesel yields. It seems that such catalytic activities for transesterification of hempseed oil with methanol at a hydrogen pressure are dependent upon the basic strengths of alkaline earth metal oxides which are consistent with those reported by Patil and Deng (2009). Compared with the biodiesel obtained through transesterification by NaOH at 65 °C (see Table 1), the biodiesels obtained by alkaline earth metal oxides showed no obvious differences of iodine value and the amount of un-saturates such as linolenate (C18:3), linoleate (C18: 2), and oleate (C18:1), indicated that alkaline earth metal oxides gave poor activity for hydrogenation. It is likely that alkaline earth metal oxides are effective catalysts for transesterification of hempseed oil with methanol but can not efficiently catalyze the hydrogenation of fatty acid esters.

Alkaline earth metal oxides are active catalysts for the transesterification of hempseed oil with methanol at a hydrogen pressure, as discussed above, while copper catalysts were reported to be active in the hydrogenation of fatty acid methyl esters and triglyceride and selective for the reduction of linolenate (C18:3) to oleate (C18:1) leaving stearate (C18:0) unaffected (Federico et al., 2006; Nicoletta et al., 2002). A series of alkaline earth metal oxides loaded with 10 wt.% CuO were prepared and tested in the one-pot process to examine the influence of the support on the catalytic performances of transesterification and hydrogenation. Basic strengths and catalytic activities in terms of biodiesel yields and the compositions as well as iodine values were also listed in Table 1. As can be seen, MgO loaded with copper oxide exhibited the same basic strength as MgO with H⁺ in the range of 9.3–15, whereas CaO, SrO, and BaO loaded with copper oxide showed a lower basic strength with H⁺ in the range of 15–18.4 compared to those of the pure alkaline earth metal oxides. It suggested that the loading of copper oxide led to decreases of basic strengths of alkaline earth metal oxides. With the reduction of basic strength, thereafter, the biodiesel yields decreased slightly. The as-synthesized biodiesels by alkaline earth metal oxides loaded with copper oxide showed lower amounts of methyl linolenate (C18:3) and methyl linoleate (C18:2), and higher amount of methyl oleate (C18:1), resulting in lower iodine values, which indicated that alkaline earth metal oxides loaded with copper oxide showed higher activities toward hydrogenation and higher selectivity for increasing methyl oleate (C18:1) than alkaline earth metal oxides. Among the catalysts tested, SrO loaded with copper oxide gave the highest decrease of iodine value from 164 g I₂/100 g to 113 g I₂/100 g and presented the lowest methyl linolenate (18:3) and methyl linoleate (18:2) contents and the highest amount of methyl oleate (C18:1) with the methyl stearate (C18:0) and methyl palmitate (C16:0) unchanged. It seems that alkaline earth metal oxides loaded with copper oxide were both active for the transesterification of hempseed oil with methanol and selective hydrogenation of methyl esters and Cu/SrO catalysts exhibited the best catalytic performance of transesterification of hempseed oil with methanol and selective hydrogenation of methyl esters under the experimental conditions used.

The influence of the copper oxide loading in Cu/SrO catalysts on the activities for transesterification and selective hydrogenation...
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Basic strength (H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;)</th>
<th>Biodiesel yield (%)</th>
<th>C16:0 (%)</th>
<th>C18:0 (%)</th>
<th>C18:1 (%)</th>
<th>C18:2 (%)</th>
<th>C18:3 (%)</th>
<th>Total saturates (%)</th>
<th>Total unsaturates (%)</th>
<th>Total PUFA&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>IV (g I&lt;sub&gt;2&lt;/sub&gt;/100 g)</th>
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</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>NaOH</td>
<td>15 &lt; H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>98 (±1.1)</td>
<td>6.64(±0.1)</td>
<td>2.76(±0.1)</td>
<td>10.12(±0.5)</td>
<td>54.31(±0.5)</td>
<td>23.76(±0.4)</td>
<td>9.4</td>
<td>88.19</td>
<td>78.07</td>
<td>164 (±1.0)</td>
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<tr>
<td>2</td>
<td>MgO</td>
<td>9.3 &lt; H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>79 (±2.2)</td>
<td>6.58(±0.1)</td>
<td>2.78(±0.1)</td>
<td>16.21(±0.9)</td>
<td>50.34(±1.1)</td>
<td>21.67(±1.4)</td>
<td>9.36</td>
<td>88.22</td>
<td>71.01</td>
<td>158 (±1.1)</td>
</tr>
<tr>
<td>3</td>
<td>CaO</td>
<td>18.4 &lt; H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>84 (±1.3)</td>
<td>6.60(±0.1)</td>
<td>2.78(±0.1)</td>
<td>12.45(±0.8)</td>
<td>52.07(±0.9)</td>
<td>23.03(±1.2)</td>
<td>9.38</td>
<td>87.55</td>
<td>75.1</td>
<td>160 (±1.2)</td>
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<tr>
<td>4</td>
<td>SrO</td>
<td>26.5 &lt; H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>96 (±1.5)</td>
<td>6.59(±0.1)</td>
<td>2.77(±0.1)</td>
<td>14.17(±0.9)</td>
<td>51.31(±1.3)</td>
<td>22.52(±0.9)</td>
<td>9.36</td>
<td>88.20</td>
<td>73.83</td>
<td>159 (±1.2)</td>
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<td>5</td>
<td>BaO</td>
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<td>95 (±2.3)</td>
<td>6.61(±0.1)</td>
<td>2.80(±0.1)</td>
<td>12.54(±1.1)</td>
<td>51.74(±1.7)</td>
<td>23.82(±1.5)</td>
<td>9.41</td>
<td>88.10</td>
<td>75.56</td>
<td>162 (±1.2)</td>
</tr>
<tr>
<td>6</td>
<td>CuO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>71(±2.1)</td>
<td>6.71(±0.1)</td>
<td>2.79(±0.1)</td>
<td>18.72(±1.0)</td>
<td>52.84(±1.8)</td>
<td>16.54(±2.1)</td>
<td>9.46</td>
<td>88.10</td>
<td>69.38</td>
<td>150 (±1.1)</td>
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<tr>
<td>7</td>
<td>10% Cu/MgO</td>
<td>9.3 &lt; H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>73 (±3.1)</td>
<td>6.71(±0.1)</td>
<td>2.75(±0.1)</td>
<td>17.65(±1.2)</td>
<td>47.51(±1.4)</td>
<td>3.28(±1.5)</td>
<td>9.46</td>
<td>98.44</td>
<td>50.79</td>
<td>131 (±1.1)</td>
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<td>8</td>
<td>10% Cu/CaO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>77 (±2.5)</td>
<td>6.72(±0.1)</td>
<td>2.76(±0.1)</td>
<td>39.23(±1.1)</td>
<td>44.35(±1.4)</td>
<td>4.47(±1.3)</td>
<td>9.48</td>
<td>88.05</td>
<td>48.82</td>
<td>121 (±1.3)</td>
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<tr>
<td>9</td>
<td>10% Cu/BaO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>90 (±2.3)</td>
<td>6.65(±0.1)</td>
<td>2.76(±0.1)</td>
<td>17.82(±1.3)</td>
<td>52.34(±0.6)</td>
<td>18.29(±2.1)</td>
<td>9.41</td>
<td>88.45</td>
<td>70.63</td>
<td>153 (±1.2)</td>
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<td>10</td>
<td>1% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>90 (±1.2)</td>
<td>6.63(±0.1)</td>
<td>2.74(±0.1)</td>
<td>16.34(±1.2)</td>
<td>52.19(±1.3)</td>
<td>19.16(±1.3)</td>
<td>9.37</td>
<td>87.69</td>
<td>71.35</td>
<td>154 (±1.2)</td>
</tr>
<tr>
<td>11</td>
<td>3% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>92 (±2.4)</td>
<td>6.62(±0.1)</td>
<td>2.75(±0.1)</td>
<td>21.65(±1.1)</td>
<td>50.42(±1.1)</td>
<td>16.06(±1.2)</td>
<td>9.37</td>
<td>88.13</td>
<td>66.48</td>
<td>147 (±1.1)</td>
</tr>
<tr>
<td>12</td>
<td>5% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>92 (±2.4)</td>
<td>6.68(±0.1)</td>
<td>2.78(±0.1)</td>
<td>24.96(±1.1)</td>
<td>49.07(±1.2)</td>
<td>14.07(±1.3)</td>
<td>9.46</td>
<td>88.10</td>
<td>63.14</td>
<td>142 (±1.3)</td>
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<tr>
<td>13</td>
<td>7% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>94 (±2.3)</td>
<td>6.62(±0.1)</td>
<td>2.75(±0.1)</td>
<td>28.85(±1.2)</td>
<td>49.03(±0.9)</td>
<td>10.05(±1.1)</td>
<td>9.37</td>
<td>87.93</td>
<td>59.08</td>
<td>135 (±1.3)</td>
</tr>
<tr>
<td>14</td>
<td>10% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>96 (±2.0)</td>
<td>6.64(±0.1)</td>
<td>2.76(±0.1)</td>
<td>46.65(±1.0)</td>
<td>41.73(±1.2)</td>
<td>0.49(±1.0)</td>
<td>9.4</td>
<td>88.87</td>
<td>42.22</td>
<td>113 (±1.3)</td>
</tr>
<tr>
<td>15</td>
<td>20% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>94 (±1.9)</td>
<td>6.67(±0.1)</td>
<td>2.71(±0.1)</td>
<td>42.17(±1.2)</td>
<td>41.61(±1.1)</td>
<td>3.16(±0.9)</td>
<td>9.38</td>
<td>86.94</td>
<td>44.77</td>
<td>116 (±1.1)</td>
</tr>
<tr>
<td>16</td>
<td>30% Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>91 (±2.3)</td>
<td>6.68(±0.1)</td>
<td>2.74(±0.1)</td>
<td>42.87(±1.3)</td>
<td>41.03(±1.4)</td>
<td>3.88(±1.1)</td>
<td>9.42</td>
<td>87.78</td>
<td>44.91</td>
<td>117 (±1.1)</td>
</tr>
<tr>
<td>17</td>
<td>10% Ni/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>94 (±2.1)</td>
<td>6.64(±0.1)</td>
<td>16.75(±0.1)</td>
<td>18.68(±1.6)</td>
<td>44.98(±2.1)</td>
<td>10.51(±1.3)</td>
<td>23.39</td>
<td>74.17</td>
<td>55.49</td>
<td>121 (±1.3)</td>
</tr>
<tr>
<td>18</td>
<td>10% Ni–10%Cu/SrO</td>
<td>H&lt;sub&gt;C0&lt;/sub&gt;/C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>95 (±2.5)</td>
<td>6.68(±0.1)</td>
<td>5.86(±0.1)</td>
<td>33.69(±1.8)</td>
<td>46.34(±1.5)</td>
<td>4.99(±1.4)</td>
<td>12.54</td>
<td>85.02</td>
<td>51.33</td>
<td>122 (±1.3)</td>
</tr>
</tbody>
</table>

<sup>a</sup> One-pot process combining transesterification and selective hydrogenation from hempseed oil with methanol was performed at a hydrogen pressure of 3.0 MPa with molar ratio of methanol to oil = 12:1, and catalyst/oil = 3 wt.% for 3 h for all the reactions except for Entry 1.

<sup>b</sup> Metal oxide loadings (wt.%) are referred to nominal value of CuO or NiO loading on the support.

<sup>c</sup> PUFA means poly-un-saturate fatty acid methyl esters.

<sup>d</sup> The initial composition and iodine value of starting hempseed oil are shown in the first row though a typical transesterification reaction by NaOH at 65 °C for 3 h with molar ratio of methanol to oil = 6:1, and catalyst/oil = 1.0 wt.%. Triplicate runs (standard deviations given in parentheses).
was further investigated and the results are also listed in Table 1. As shown in this table, SrO with copper oxide loadings ranged from 1% to 30% showed the same strength of basic sites with H+ in the range of 15.0–18.4 and exhibited high activities for transesterification with biodiesel yields >90%. When the CuO loading increased from 1% to 10%, methyl linolenate (18:3) and methyl linoleate (C18:2) decreased gradually and methyl oleate (C18:1) increased considerably. A further increase of the CuO loading, from 10% to 30%, resulted in increases of methyl linolenate (18:3) and methyl linoleate (C18:2) and a decrease of methyl oleate (C18:1). As a result, the copper oxide loading amount of 10% is the optimum loading for Cu/SrO catalyst for the selective hydrogenation under conditions employed in our study. Actually, the amount of methyl linolenate (18:3) has been lowered to less than 0.5%. The total amount of poly-un-saturate fatty acid methyl esters (PUFA) was reduced to 42.22%, which was lower than that of hempseed oil methyl esters (HSME) (78.07%). The overall amount of saturates vs. un-saturates was essentially unchanged from hempseed oil methyl esters (HSME) to selective hydrogenated hempseed oil methyl esters (SHHSME) because the amount of mono-un-saturates has increased from HSME (10.12%, 18:1) to SHSME (46.65%, 18:1). Those results of hydrogenation selectivity are in perfect agreement with those obtained by Nicoletta et al. (2002) who performed the selective hydrogenation of soybean oil methyl esters using CuO/SiO2 as catalyst. The high selectivity towards the methyl linolenate and non-existing formation of saturates of Cu/SrO catalysts are in accordance with the mechanism proposed by Dijkstra (2002). Copper catalysts only hydrogenate double bonds in methylene interrupted poly-unsaturated fatty acid derivatives. And thus the copper-catalyzed reaction stops when the fatty acid derivatives present in the reaction mixture are only monounsaturated fatty acids and poly-unsaturated fatty acids in which the double bonds are separated by more than one methylene group, allowing copper catalysts to exhibit very high oleic acid selectivity (Dijkstra, 2002). It is noticed that the amount of methyl linoleate (C18:2) was only reduced from 54.31% to 41.73% and the remaining di-un-saturates may be further hydrogenated to mono-un-saturates by increasing hydrogen pressure or extending reaction time or using a pre-reduced copper catalyst (Nicoletta et al., 2002). This optimum loading for Cu/SrO catalysts would originate predominantly from the evolution of the morphology and structures of Cu/SrO catalysts with the increase of the loading of copper oxide, which were suggested for further work and to be a part of a future full paper.

Comparatively, 10%Ni/SrO and 10%Ni–10%Cu/SrO catalysts were also performed in a one-pot process combining transesterification of hempseed oil with methanol and hydrogenation of hempseed oil methyl esters. Their basic strengths and catalytic activities in terms of biodiesel yields and the compositions of as-synthesized biodiesels as well as iodine values were also showed in Table 1. It can be seen that Ni/SrO and Ni–Cu/SrO catalysts presented basic strengths with H+ in the range of 15.1–18.4 and exhibited biodiesel yields higher than 94%. The biodiesel obtained by Ni/SrO showed a lower iodine value of 121 g I2/100 g, suggesting that Ni/SrO were also active for the hydrogenation of hempseed oil methyl esters. However, the observation of a large amount of methyl stearate confirmed the poor selectivity for limiting saturates of biodiesels, which are similar to those already reported by authors Moser et al. (2007); Karabulut et al. (2003) who found that Ni catalysts showed rather low diene: monoene selectivity and gave early formation of saturated compounds in the oil hydrogenation. In contrast to Ni/SrO, Ni–Cu/SrO presented lower content of C18:0 and higher content of C18:1, suggesting the addition of Cu promoted the selectivity for methyl oleate and prevailed over the selectivity for methyl stearate. Ni-based catalysts presented a significant amount of methyl stearate, which has a much higher melting point than unsaturated fatty acid methyl esters, thereafter, the obtained biodiesels could suffer from bad cold-flow properties (Imahara et al., 2006; Knöthe, 2005).

Copper-based catalysts have long been known in edible oils hydrogenation as the most selective ones for the reduction of linolenate C18:3 to oleate C18:1 without increasing of stearate C18:0, thus, the degree of saturation is scarcely changed during the hydrogenation process (Federico et al., 2006). Copper catalysts were usually charged into the oil as divalent oxidic compounds, which were partly reduced to metal during use (Johansson and Lundin, 1979). Thus the active phases of copper catalysts must consist of Cu+ compounds and/or Cu0 (Johansson and Lundin, 1979; Nicoletta et al., 2002). It can be speculated that the catalytic activity for hydrogenation was first obtained from the catalyst subjected to reduction and then eventually from the metal-reduced form of catalyst. When the experimental Cu/SrO catalysts prepared by the chemisorption–hydrolysis (CH) method were charged into the oil in the oxidized form, the Cu/SrO catalysts was first reduced and showed high catalytic activity for transesterification and hydrogenation and hydrogenation selectivity toward the methyl linolenate without rising of methyl stearate (C18:0) in the one-pot process under the employed conditions. Compared with a reaction time of about 0.5 h for completing the transesterification over SrO (Liu et al., 2007), the hydrogenation of fatty acid methyl esters over copper catalysts required much longer time (Nicoletta et al., 2002) since the copper catalysts should be reduced by hydrogen gas and the H2 molecular adsorbed by the copper site required to dissociate as well. Moreover, CuO also showed catalytic activity for transesterification of hempseed oil with methanol in the hydrogen atmosphere (see Table 1). So the catalytic actions of one-pot process combining the transesterification of hempseed oil with methanol and hydrogenation of hempseed oil for Cu/SrO may be rationalized in the following manner. The transesterification of the hempseed oils firstly took place on the mixed oxides of strontium and copper, producing methyl esters of hempseed oil, thereafter the selective hydrogenation of methyl esters occurred on the reduced copper species, obtaining selective hydrogenated hempseed oil methyl esters.

3.2. Fuel properties of hydrogenated methyl esters

Biodiesel properties were largely determined by the composition of biodiesel, mainly including oleate (C18:1), linolenate (C18:2), linolenate (C18:3), stearate (C18:0) and palmitate (C16:0) (Knöthe, 2008). The relative rates of oxidation of oleate (C18:1), linoleate (C18:2), linolenate (C18:3) are 1:40:100, thus the decrease of linoleate (C18:2), linolenate (C18:3) and the increase of oleate (C18:1) will lead to a significant improvement of oxidative stability. Cetane number increases and NOx emissions decrease with decreasing degree of unsaturation (McCormick et al., 2001; Frankel, 2005). On the other hand, a high content of fully saturated compounds (stearate (C18:0) and palmitate (C16:0)) has a very negative impact on the cold properties of the fuel (cloud point, pour point and low-temperature filterability) (Knöthe, 2008). So the decreases of poly-un-saturates such as linolenate (C18:3) and linoleate (C18:2) and the increase of oleate (C18:1) by the above selective hydrogenation will inevitably change the properties of biodiesel. Before and after selective hydrogenation, the fuel properties of hempseed oil methyl esters were determined with standard methods and compared to ASTM D 6751, EN 14214 and GB/T20828-2007 biodiesel standards, and the results are listed in Table 2. The methyl esters and hydrogenated methyl esters showed a density of 0.872 and 0.876 g/cm3, which are within the specification limits. The kinematic viscosity of methyl ester and hydrogenated methyl esters were found to be 4.23 and 4.31 mm2/g at 40 °C which met the requirements of biodiesel standards. The flash points of the biodiesel and hydroge-
The correlation between the iodine value, cetane number and the degree of unsaturation of the experimental hydrogenated hempseed oil methyl esters obtained over Cu/SrO catalysts was demonstrated to be an effective bi-functional catalyst for the transesterification and selective hydrogenation of hempseed oil which is a typical oil of high degree of unsaturation. The biodiesel from hempseed oil could be a competitive alternative to conventional diesel fuel.

4. Conclusions

A one-pot process combining transesterification and selective hydrogenation was developed for biodiesel production using hempseed oil having iodine values greater than 150 g I₂/100 g as starting material. Strontium oxide supported copper oxide was demonstrated to be an effective bi-functional catalyst for the transesterification and selective hydrogenation to produce selective hydrogenated methyl esters as biodiesels meeting EN 14214 as far as IV and CN are concerned. This one-pot process gives the competitive alternative to conventional diesel fuel.

Table 2

<table>
<thead>
<tr>
<th>Property (units)</th>
<th>Biodiesel</th>
<th>Hydrogenated biodiesel</th>
<th>ASTM D 6751</th>
<th>EN 14214</th>
<th>GB/T20828-2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.872 (±0.011)</td>
<td>0.876 (±0.012)</td>
<td>0.87–0.90</td>
<td>0.86–0.900</td>
<td>0.86–0.90</td>
</tr>
<tr>
<td>Kinematic viscosity (mm²/g)</td>
<td>4.23 (±0.05)</td>
<td>4.31 (±0.04)</td>
<td>2.5–6.0</td>
<td>3.5–5.0</td>
<td>3.0–8.0</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>131 (±0.9)</td>
<td>137 (±1.2)</td>
<td>Min. 130</td>
<td>Min. 120</td>
<td>Min. 130</td>
</tr>
<tr>
<td>Cetane number</td>
<td>44.0 (±2.3)</td>
<td>55.8 (±2.1)</td>
<td>Min. 47</td>
<td>Min. 51</td>
<td>Min. 49</td>
</tr>
<tr>
<td>Iodine value (g I₂/100 g)</td>
<td>164 (±1.3)</td>
<td>113 (±9)</td>
<td>-</td>
<td>Max. 120</td>
<td>-</td>
</tr>
<tr>
<td>Acid number (mg NaOH/g)</td>
<td>0.01 (±0.01)</td>
<td>0.01 (±0.01)</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>15 (±1)</td>
<td>12 (±1)</td>
<td>-</td>
<td>15 to 10</td>
<td>-</td>
</tr>
</tbody>
</table>

*Values at 40 °C. Triplicate runs (standard deviations given in parentheses).
opportunity to extend the high un-saturate materials for biodiesel production, thus making a wide portfolio of raw materials available without interfering with the food market.

References


Jie, J. 2009. This is the moment of China’s hemp. China Fiber Inspection 6, 46–47.


Biodiesel production from acid oils and ethanol using a solid basic resin as catalyst

J.M. Marchetti*, A.F. Errazu

Planta Piloto de Ingeniería Química, UNS-CONICET, Camino La Carrindanga km 7, (8000) Bahía Blanca, Argentina

Abstract

In the search of an alternative fuel to substitute diesel fuel, biodiesel appears as one of the most promising sources of energy for diesel engines because of its environmental advantages and also due to the evolution of the petroleum market. Refined oil is the conventional raw material for the production of this biofuel; however, its major disadvantage is the high cost of its production. Therefore, frying oils, waste oils, crude oils and/or acid oils are being tested as alternative raw materials; nevertheless, there will be some problems if a homogeneous basic catalyst (NaOH) is employed due to the high amount of free fatty acid present in the raw oil.

In this work, the transesterification reaction of acid oil using solid resin, Dowex monosphere 550 A, was studied as an alternative process. Ethanol was employed to have a natural and sustainable final product. The reaction temperature’s effects, the initial amount of free fatty acid, the molar ratio of alcohol/oil and the type of catalyst (homogeneous or heterogeneous) over the main reaction are analyzed and their effects compared.

The results obtained show that the solid resin is an alternative catalyst to be used to produce fatty acid ethyl esters (FAEEs) by a transesterification reaction with a final conversion over 90%. On the other hand, the time required to achieve this conversion is bigger than the one required using conventional technology which employs a homogeneous basic catalyst. This reaction time needs to be optimized.

1. Introduction

Over the last few years, as well as projecting for the following 15–20 years, the consumption of petroleum based fuels will have increased from 11.52 millions of tonnes per day in 2005 to an estimate of 15.7 millions of tonnes per day in 2030. Simultaneously to this grow it will be associated a decreasing on the fossil fuels’ reserves, producing a net increase on its selling price, reaching historical values over US$ 100 per 0.1388 tonnes [1]. Because of this, researches have been done in order to find an alternative substitute for diesel fuels, being biodiesel, defined by ASTM as the mono alkyl ester produced from vegetable oils or animal fats, one of the most promising alternatives.

Some of the major advantages of this biofuel are that it is biodegradable, produced from a renewable source and that it does not produce carbon monoxide or any sulfur residues [2–6]. Despite all these advantages, one of the mayor drawbacks on the biodiesel production process is its cost, mainly associated with the price of the oil used related to its quality [7]. Due to this economic restriction, alternative raw materials of a lower price/cost, like frying oils, soap stocks, acid oils, and waste oils, have been studied [8–13].
Acid oils present high amounts of free fatty acids (FFAs), varying from 3% to 40% [2,4,9], which make non-recom-
mendable its usage with the conventional technology that
employs a basic homogeneous catalyst such as sodium or
potassium hydroxides. The basic catalyst and the FFA will
interact to produce soap, according to Equation (1). This
makes the amount of available catalyst for the trans-
esterification reaction to be reduced and also complicates the
downstream separation and the biodiesel purification.

\[
\text{R-COOH} + \text{NaOH} \leftrightarrow \text{H}_2\text{O} + \text{R-COO-\text{Na}} \tag{1}
\]

Alternative processes for FAEE production have been under
development in order to employ different catalysts: homoge-
nous ones (sulfuric acid for example), as well as heteroge-
nous ones such as enzymes or solid resin. Solid catalysts
have been useful to carry out the transesterification reaction
of refine oil achieving conversion around 79.6%, 91.07%, 95.1%
and 95% in 3, 2, 7 and 3 h respectively for each research work
[14–18]. On the other hand, several research works showed
that the esterification reaction can be carried out in the
presence of triglycerides using different catalysts [19–22].

Biodiesel is generally produced by transesterification of
triglyceride, but it might also be generated by direct esterifi-
cation of free fatty acid; both reactions could be summarized
as follows

\[
\begin{align*}
\text{CH}_2\text{OOC-R}_1 & + 3\text{R’OH} \leftrightarrow \text{R}_1\text{-COO-R’} + \text{CH}_2\text{-OH} \\
\text{CH-OOC-R}_2 & + \text{R}_2\text{-COO-R’} + \text{CH}_2\text{-OH} \\
\text{CH}_2\text{OOC-R}_3 & + \text{R}_3\text{-COO-R’} + \text{CH}_2\text{-OH} \\
\text{Triglycerides} & \text{Alcohol} \hspace{1cm} \text{Esters} \hspace{1cm} \text{Glycerin}
\end{align*}
\]

\[
\text{R-COOH} + \text{R’OH} \leftrightarrow \text{H}_2\text{O} + \text{R-COO-R’} \tag{3}
\]

where R_1, R_2, R_3 and R’ denote any hydrocarbon chain.

The employment of a homogeneous catalyst, such as
sulfuric acid, has some drawbacks associated with the
process itself. The down-stream separation and purifica-
tion are more complicated than when a solid catalyst is
used.

In Marchetti et al. [23] it has been prepared as a mixture
of TG (triglycerides) and FFA (free fatty acid). In that work, it
has been tested this mixture to see how FFAs are converted
into FAME by the esterification reaction, with the aim of
using this catalyst as a pretreatment; therefore, no study
was done on the triglycerides. In this work, the same
mixture was used and the same reaction conditions were
used, but the conversion of triglycerides was studied to see if
this catalyst could be used to produce biodiesel (not only as
a pretreatment). The reactant and the reaction studied in
Marchetti et al. [23] are the FFA and the esterification reac-
tion, while for this work the reactant is the triglycerides and
the reaction is the transesterification reaction, both reaction
and reactants are different and this work is a complemen-
tary studied for the previous work [23].

It has been studied and compared the effects of the main
variables of the whole process: reaction temperature, molar
ratio of alcohol/oil and initial amount of free fatty acid. It has
been also compared this alternative with sulfuric acid under
similar operational conditions.

2. Materials and methods

Refined sunflower oil from a commercial brand was employed
to carry out this study; also, oleic acid provided by Anedra and
ethanol anhydrous provided by either Anedra or Cicarelli were
employed.

The acid oil used as raw material was made in the labo-
ratory by mixing measured amounts of refined oil and oleic
acid. Once the mixture was made, a small sample was
analyzed to reassure the initial amount of free fatty acid; this
was done by titration [23]. It was employed a lab scale reactor
with a volume of 500 ml. The system contains a warmer jacket
that allows us to set the reaction temperature with a margin of
error of ±0.1 °C. Since the reaction was carried out in
a temperature range between 30 °C and 55 °C, water was
employed as heating stream.

The mixture (TG + FFA) was fed into the reactor to be pre-
heated, when reaching the reaction temperature, the solid
catalyst as well as the ethanol was added to the reaction
medium in order to start the reaction, making a pseudoho-
ogeneous reaction environment. All these experiments
have been done with 200 rpm to have a good mix of the
compounds and eliminate possible mass transfer problems.
At specified times, samples were withdrawn from the
reaction mixture and washed with water to separate the
alcohol from the mixture and to assure that the reaction was stopped. Each sample was centrifuged for 15–20 min to have a better separation between the water phase and the oil phase. From the oil phase, a small amount was taken and prepared for a gas chromatography (GC) analysis. It was employed a GC Varian 3700 with a high temperature column DB-5HT&W Scientific (15 m long, 0.32 mm I.D. and 0.1 µm for the film) to quantify triglycerides, diglycerides, monoglycerides and esters. This technique allows us to analyze the total amount of FAEE produced, not only from the TG but also from the FFA.

The reproducibility of the analysis has been tested for random amount of samples at random time in order to assure that it was a verifiable value the one obtained from the GC.

3. Results and discussion

The transesterification reaction is a series of consecutive reactions, in which from triglycerides, diglycerides are produced; the latter one is transformed into monoglycerides which, in a following step, are modified into glycerol. In all these steps FAEE is produced. Fig. 1 shows the main compounds involved on this reaction when the reaction temperature was 45 °C, an initial amount of free fatty acids of 19.49% w/w, 2.5% w/w of catalyst, 200 rpm of agitation and a molar ratio alcohol/mixture of 6.1:1. In Fig. 1 it can be seen that while esters are produced, triglycerides are consumed. Diglycerides and monoglycerides go through a maximum because they are produced and consumed during the reaction.

In order to assure that the catalyst will not interact with the medium in any other way that to carry out the desirable reaction, a simple experiment was done by mixing the solid resin and fatty acid and measuring the acidity of the medium. It was not measured any modification in the acidity of the medium, showing that no soaps have been produced and no catalyst has been consumed.

3.1. Effect of the reaction temperature

Variations over the reaction temperature have been analyzed, three temperatures, 30, 45 and 55 °C, have been tested while the remains of the operation conditions were set at 200 rpm, molar ratio alcohol/mixture 6.1:1, 2.2 w/w % of catalyst, 9.9% w/w of initial free fatty acids. A higher temperature could not be tested since this catalyst has a maximum operational temperature of 60 °C.

Fig. 2 shows that when the temperature increases the final conversion increases as well. Nevertheless, at short reaction times, the initial reaction rate follows a non-common behavior producing a slower reaction while the reaction temperature increases. These results might be due to a partial deactivation of the catalyst as a result of been working close to the maximum allowed temperature (60°). A similar effect was seen when the esterification reaction was studied [23]; as a result, certain deactivation of the catalyst, due to an operation close to the maximum allowed temperature, was confirmed.

A similar work was done by Hamad et al. [17] where they reached similar final conversion using an acid catalyst. They have used ethanol as well but with rapeseed oil as raw material. The reaction reached the desirable conversion in 3 h., being a much better performance than from our base catalyst. While Noiroj et al. [15] reached slightly lower conversion in 6 h of reaction. The authors used a KOH/NaY catalyst.

3.2. Effect of the molar ratio alcohol/mixture

Variations on the amount of alcohol have been done (N = 4.2:1, 5.01:1 and 6.1:1) to study the effect of increasing one of the raw materials with respect to the other. The reaction was carried out at a constant temperature of 45 °C, an agitation speed of 200 rpm, 2.2% w/w of the catalyst was employed, as well as an initial amount of FFA of 9.9% w/w.

Fig. 3 shows that the final conversion into esters increases when the amount of ethanol is increased. However, the initial
reaction rate is slower when higher concentration of alcohol is present in the reaction mixture. This outcome is the result of two effects that take place simultaneously, the reaction kinetics and a dissolution effect.

When small amounts of alcohol are used kinetics effects are more pronounced and relevant; consequently, its initial reaction rate is higher. When the amount of alcohol increases, the presence of a large quantity of this raw material has a more dissolving effect over the mixture and, therefore, the initial reaction rate is slow. Nevertheless, the high concentration of alcohols gives higher final conversions. This result is in good accuracy with the results presented by Noiroj et al. [15], where molar ratios from 6 to 21 were used. When using a molar ratio of 6 the conversion achieved is lower than 30% meaning that more reaction time was required to achieve full conversion.

3.3. Effect of the amount of initial free fatty acid

To study the effect of the presence of free fatty acids in acid oil, three different concentrations of free fatty acid in the reaction mixtures have been made, 2.8%, 9.9% and 19.5% w/w of free fatty acids. These fatty acid initial concentrations are only with the purpose of having a less pure raw material and not to see the effect of this increase in the FAEE production, this result has been published previously elsewhere [23].

The reaction temperature was set at 45 °C, the agitation was 200 rpm, the molar ratio was 6.1:1, and the amount of catalyst was 2.2% w/w, all these operational variables were kept constant during the experiments.

As expected, Fig. 4 shows that when the initial amount of free fatty acid increases the final conversion increases as well. This could be due to the fact that under similar conditions high amounts of free fatty acids give higher final conversion, as showed by Marchetti et al. [23]. Therefore, this effect could also be seen on the total FAEE production since the final amount of biofuel will be produced from the triglycerides as well as from the fatty acids present in the reaction mixture.

3.4. Comparison of technologies

Conventional technology employs a basic homogenous catalyst to perform the transesterification reaction; normally NaOH and methanol [24,25] are used. Other alternative catalyst which continues to be a homogeneous one is sulfuric acid. It has the advantage of allowing the use of raw material with high amounts of free fatty acids and the drawbacks that the reaction is slower than with NaOH.

It has been compared the production of esters using sulfuric acid and a base solid resin with ethanol anhydrous under similar operational conditions, such as T = 55 °C, initial amount of FFA = 9.9% w/w, 2.2% w/w of each catalyst, 200 rpm of agitation speed and a molar ratio of alcohol/mixture of 6.1:1.

Fig. 5 shows that under the same operational conditions, sulfuric acid reaches its final conversion in about 3 days time, which is similar to the results showed by Canacky and Van Gerpen [26,27]. Even thought the time required for the heterogeneous technology to reach a good final is much higher than

![Fig. 3 - Influence of different amounts of alcohol. (■) N = 4.1, (▲) N = 5.01, (●) N = 6.1.](image)

![Fig. 4 - Influence of different amounts of FFA. (■) FFA₀ = 2.8%, (●) FFA₀ = 9.9%, (▲) FFA₀ = 19.5%.](image)

![Fig. 5 - Variations of esters for both catalysts sulfuric acid (■) and solid resin (●).](image)
when using sulfuric acid, the down streaming separation and purification are much simpler and requires less equipment.

It is important to know that the reactions’ time showed in this work was established with the goal of producing FAEE that satisfy international standards and have low concentrations of triglycerides, diglycerides, monoglycerides and glycerin. It should also be noticed that the reactions’ time has not been improved or optimized at this point; this is because this work is mainly done within the scope of a comparative analysis between the acid catalyst and the behavior of the reaction when a base solid resin is used.

The catalyst has not been reused for this reaction due to the fact that this kind of catalyst has previously showed that need to be regenerated in order to recover its activity properties. Despite the fact that it could be possible to carry out the reaction with out regeneration of the catalyst, due to the fact that it might still remain some activity in it, the reaction time is so high as it is that it will not provided with any improvement to the system that has showed that is suitable to produce FAEE form a technical point of view but need optimization in the reaction time.

4. Conclusions

The use of Dowex monosphere 550A for FAEE production appears as an alternative catalyst when an acid oil and ethanol are employed.

This catalyst shows high final conversion for several operational conditions. If the amount of initial free fatty acid is increased, a higher final conversion will be reached, also given a faster initial reaction rate. When the amount of alcohol is increased the initial reaction rate gets slower; on the contrary, the final conversion follows the expected behavior by reaching higher values for higher amounts of alcohol.

Comparatively with an acid homogeneous catalyst, this alternative is slower, but it reaches high final conversions. Nevertheless, when sulfuric acid is used, even though the final conversion is achieved in shorter time, the down streaming purification and separation in order to produce FAEE that could be employed in engines are more complicated, less environmental friendly, and more expensive; while for the heterogeneous catalyst, there is no need either of catalyst regeneration or neutralization, after the reaction step. Moreover, the purity of the secondary product, glycerin, is much higher when solid resins are used.

Respectively to the reaction time, the time required for complete conversion is far from competitive or industrial time; however, this work was thought of aiming at having a comparison between the acid catalyst and an alternative heterogeneous catalyst that could treat high impure oils (high amount of free fatty acid raw materials). However, this reaction time could be optimized in order to have a more competitive process.

Acknowledgements

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References


Supercritical biodiesel production and power cogeneration: Technical and economic feasibilities

A. Deshpande, G. Anitescu, P.A. Rice, L.L. Tavlarides *

Dept. of Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY 13244, United States

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ABSTRACT
An integrated supercritical fluid technology with power cogeneration to produce biodiesel fuels, with no need for the costly separations involved with the conventional technology, is proposed, documented for technical and economic feasibility, and preliminarily designed. The core of the integrated system consists of the transesterification of various triglyceride sources (e.g., vegetable oils and animal fats) with supercritical methanol/ethanol. Part of the reaction products can be combusted by a diesel power generator integrated in the system which, in turn, provides the power needed to pressurize the system and the heat of the exhaust gases necessary in the transesterification step. The latter energy demand can also be satisfied by a fired heater, especially for higher plant capacities. Different versions of this system can be implemented based on the main target of the technology: biodiesel production or diesel engine applications, including power generation. The process options considered for biodiesel fuel production estimate break-even processing costs of biodiesel as low as $0.26/gal ($0.07/L) with a diesel power generator and $0.35/gal ($0.09/L) with a fired heater for a plant capacity of 15,000 gal/day (56,775 L/day). Both are significantly lower than the current processing costs of approximately $0.51/gal ($0.13/L) of biodiesel produced by conventional catalytic methods. A retail cost of biodiesel produced by the proposed method is likely to be competitive with the prices of diesel fuels.

1. Introduction

Significant investments in biofuels, both in research and development (R&D) and in the construction of new commercial plants, emphasize a continued commitment to alternative energy as availability, volatility, security and environmental impact of the fossil fuels drive the need for new and renewable energy sources. Biodiesel (BD), a mixture of fatty acid alkyl esters, derived from plant and animal triglycerides (TG) through transesterification (TE) reactions with an alcohol, is one such fuel that is under a great deal of consideration. While worldwide the TG sources are diverse, over 90% of BD current production in the United States is based on soybean oil (SO) (Collins, 2006). It has been estimated that BD yields 93% more energy than that invested in its production and, relative to fossil fuels, greenhouse gas emissions are reduced 41% by the BD production and combustion while less air pollutants are released per net energy gain (Hill et al., 2006). Unfortunately, there are concerns that BD cannot replace much petrodiesel without impacting food supplies by the extension of the areas of oilseed cultivation. Yet, there is significant feedstock of waste cooking oil, animal fats (e.g., yellow grease and tallow), non-edible and potentially large excess of edible oils which do not negatively impact the alimentary TG supply. Also, by increasing, for example, the production of soybeans, there is a positive feedback on agriculture through higher quantity of soybean meals made available as animal feedstock after SO extraction (Biodiesel, 2008). This also means more meat for food and more TG supply for BD production.

Although these benefits are very attractive, the final cost of BD produced by conventional means is still prohibitively high without governmental subsidies (Radich, 2004; USA Biodiesel Prices, 2009). Compared with conventional acid/base catalytic methods, relatively new supercritical (SC) methods were found not only being capable to reduce TE time from several hours to a few minutes through a continuous TE process, but also to require no TG feed pretreatment for the FFA and water (Kusdiana and Saka, 2004). Without any significant pretreatment, nearly all of the TG content, even from low-quality feedstock, could be turned into high-quality BD fuels.

Despite these advantages, given the high number of the competitive process parameters affecting SC TE conversions, it is difficult to successfully control their effects. Indeed, there are not even two reported sets of data gathered by SC methods with the claimed optimum TE conditions being similar (Table 1). Although high-quality BD fuels have been eventually obtained at laboratory-scale through often sophisticated processing and purification steps, the
market price of these fuels from the industrial production facilities being competitive with that of diesel fuel is the ultimate criterion in the acceptance of any of the proposed methods. Unfortunately, technical and economic feasibility studies of creating a modern alternative to conventional BD industry are scarce (D’Ippolito et al., 2007; Kasteren and Nisworo, 2007; Lim et al., 2009).

We conceptually designed an integrated two-step SC technology to produce both vegetable oils and BD fuels by extracting the oils with SC CO2 followed by SC TE with methanol/ethanol in a continuous tubular reactor (Fig. 1). The small amount of CO2 remaining in the oil in the flash tank exhibits a positive effect as cosolvent to increase the mutual oil–alcohol solubility. The mechanical and electrical power as well as the necessary heat for these processes is provided by a diesel power generator which will consume a fraction of the produced fuel. Optionally, the required TE heat can be supplied by a fired heater. In this paper only the TE step will be discussed. The overall goal of this study was to develop a simplified process for continuous and cost-effective BD production based on our laboratory-scale screening experiments (Anitescu et al., 2008). Special emphasis was on technical and economic analyses performed for the proposed process in order to compare the processing costs at commercial scale with those of the current methods.

The proposed SC TE technology to produce BD fuels consists of a simple, non-catalytic process with no need for the costly BD–alcohol–catalyst–glycerol separations required for the acid/base conventional TE. This simplification is made possible by using a close to stoichiometric proportion of oil and alcohol and by decomposing the glycerol byproduct in smaller molecular fuel components at high reaction temperatures (Anitescu et al., 2008). When this SC TE method (Fig. 2) is compared with a conventional catalytic technology (Fig. 3), the simplicity of the former is apparent. The method will use a diesel power generator to provide power and heat for the upstream processes or a highly efficient fired heater which will consume a fraction of the produced fuel.

The proposed integrated system has a potentially wide range of applications. First, it is very attractive for farmers since it reduces their dependency on high petrodiesel prices. Many farmers use the oil from soybeans (18–20% oil content) as a fuel. However, SO alone is not an acceptable fuel because of its very high viscosity, combustion emissions and damage it renders to the engines, especially on long-term usage. Alternatively, further processing the oil to BD with associated power generation, is a suitable solution especially for remote farms. Also, as large biofuel plants encounter residential resistance, smaller and process-contained modules certainly will have a much better environmental fit. Secondly, this

![Table 1](https://example.com/table1.png)

Table 1

Reported optimum conditions and yield for batch (B) and continuous (C) SC TE processes.

<table>
<thead>
<tr>
<th>Oil/cosolvent</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>TG/MeOH</th>
<th>t (min)</th>
<th>B/C</th>
<th>Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean/CO2(^a)</td>
<td>280</td>
<td>143</td>
<td>24</td>
<td>10</td>
<td>B</td>
<td>98</td>
<td>Han et al. (2005)</td>
</tr>
<tr>
<td>Canola</td>
<td>450</td>
<td>400</td>
<td>45</td>
<td>4</td>
<td>C</td>
<td>Near 100</td>
<td>Iijima et al. (2004)</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>350</td>
<td>450</td>
<td>42</td>
<td>4</td>
<td>B</td>
<td>95</td>
<td>Saka and Kusdiana (2001); Kusdiana and Saka (2001)</td>
</tr>
<tr>
<td>Coconut and palm</td>
<td>310</td>
<td>350</td>
<td>40</td>
<td>25</td>
<td>C</td>
<td>96</td>
<td>Bunyakiat et al. (2006)</td>
</tr>
<tr>
<td>Soybean</td>
<td>235</td>
<td>62</td>
<td>27</td>
<td>600</td>
<td>B</td>
<td>85</td>
<td>He et al. (2007); Diasakou et al. (1998)</td>
</tr>
<tr>
<td>Soybean/C(_3)H(_8)(^b)</td>
<td>280</td>
<td>128</td>
<td>24</td>
<td>10</td>
<td>B</td>
<td>98</td>
<td>Cao et al. (2005)</td>
</tr>
<tr>
<td>Sunflower</td>
<td>350</td>
<td>200</td>
<td>40</td>
<td>40</td>
<td>B</td>
<td>96</td>
<td>Madras et al. (2004)</td>
</tr>
<tr>
<td>Castor and linseed</td>
<td>350</td>
<td>200</td>
<td>40</td>
<td>40</td>
<td>B</td>
<td>98</td>
<td>Varma and Madras (2007)</td>
</tr>
<tr>
<td>Soybean/C(_3)H(_8)(^b)</td>
<td>288</td>
<td>96</td>
<td>64</td>
<td>10</td>
<td>B</td>
<td>99</td>
<td>Hegel et al. (2007)</td>
</tr>
<tr>
<td>Soybean</td>
<td>290</td>
<td>110</td>
<td>12</td>
<td>40</td>
<td>B</td>
<td>Near 100</td>
<td>D’Ippolito et al. (2007)</td>
</tr>
<tr>
<td>Waste oil/C(_3)H(_8)(^b)</td>
<td>280</td>
<td>128</td>
<td>24</td>
<td>17</td>
<td>C</td>
<td>95</td>
<td>Kasteren and Nisworo (2007)</td>
</tr>
<tr>
<td>Soybean</td>
<td>400</td>
<td>100</td>
<td>3</td>
<td>3</td>
<td>C</td>
<td>Near 100</td>
<td>This study</td>
</tr>
</tbody>
</table>

\(^a\) CO\(_2\)/MeOH = 0.1.
\(^b\) C\(_3\)H\(_8\)/MeOH = 0.05.
\(^c\) Molar ratio.

![Fig. 1](https://example.com/fig1.png)

Fig. 1. Schematic of the Integrated Multistage Supercritical Technology System to produce vegetable oils and biofuels.
system should have great potential to be implemented on transportation vehicles since only minor retrofits of the diesel engines are required to produce on site the necessary fuel.

2. Selection of optimum TE conditions

Experiments with both continuous and batch reactors (Hastelloy coiled pipes and 316 stainless steel, respectively) have been conducted at laboratory-scale to select ranges of P–T conditions, feedstock composition and residence time under which the highest yield of BD is obtained without requiring costly separation/purification steps (Anitescu et al., 2008). The conditions at which glycerol decomposed in our reaction system without adversely affecting the FAME composition of BD fuel have been determined as 350–400 °C and 100–300 bar. It is noted that the temperature effect on TG conversion dominates that of the pressure for SC TE and shortens the residence time to very attractive ranges for commercial applications.
The SC TE global reaction, used for the process design, is given below for a generic composition of TG and lumped glycerol decomposition products (GDP):

\[
\begin{align*}
\text{CH}_2\text{-OOCR}_1 + & \text{R}_2\text{COOCH}_3 & \rightarrow \text{R}_1\text{COOCH}_3 \\
\text{CH}_2\text{-OOCR}_2 + & 3\text{CH}_3\text{OH} & \rightarrow \text{R}_2\text{COOCH}_3 + \text{GDP} \\
\text{CH}_2\text{-OOCR}_3 & \rightarrow \text{R}_1\text{COOCH}_3 
\end{align*}
\]

In this global reaction, \(R_1\), \(R_2\), and \(R_3\) are the hydrocarbon chains of the major SO fatty acids (e.g., palmitic, oleic, and linoleic) employed in the BD composition calculations. It is well established that the steps of these TE reactions include TG conversion to diglycerides (DG), then to monoglycerides (MG), and finally to fatty acid methyl esters (FAME) and glycerol (Diasakou et al., 1998). Our GC–MSD chromatograms (for example, Fig. 4a) revealed negligible amounts of both DG and MG intermediate TE byproducts. Although the glycerol decomposition products were not fully analyzed, they mainly included ethers and carbonylic compounds. It was estimated that these byproducts are smaller molecular organic compounds than the main FAME components and can be included in the BD fuel as described elsewhere (Iijima et al., 2004; Aimaretti et al., 2009; Marulanda et al., 2009).

Experiments carried out in our laboratory have shown that reacting stoichiometric quantities of alcohol and oil at 350–400 °C, 100–300 bar for about three minutes gives nearly complete oil conversion to FAME and GDP. In these SC states, in contrast to the BD production at conventional conditions (1 atm, 60–80 °C, with base catalysts), the reaction rate is about two orders of magnitude faster, BD components are formed using near stoichiometric quantities of alcohol, and negligible alcohol and glycerol are left in the final reaction products. This situation would simplify the BD production process greatly since these byproducts no longer have to be separated from the FAME and additional fuel will be produced. Furthermore, the presence of small molecular components in BD such as C8–C14 methyl esters, some linear alkanes and glycerol decomposition products positively affects the viscosity and the cloud/pour point of the fuel. For example, at 5 °C, commercial samples of BD (composition given in Fig. 4b), which are richer in saturated FAME, are solids while our samples only reach the cloud point. This property change can also be attributed to the smaller molecular compounds which exhibit lower melting points. In addition, because the alcohol can be used only in slight excess of the TE stoichiometric amounts, essentially all of the alcohol reacts, eliminating the need for alcohol separation and recycling at significant pumping costs.

3. Economic analysis

3.1. Process design

The aim of this economic assessment was to investigate the feasibility of BD production coupled or not with power cogeneration (i.e., to determine the BD production and processing costs). The scope of this study does not include the retail cost of BD and other measures of process profitability such as rate of return, payback period and net present value. Economic estimates for two different system configurations were performed to select the most desirable architecture based on maximum benefits. We targeted a system to exhibit lower melting points. In addition, because the alcohol can be used only in slight excess of the TE stoichiometric amounts, essentially all of the alcohol reacts, eliminating the need for alcohol separation and recycling at significant pumping costs.

3.1.3. Design assumptions

For the process design of equipment the following assumptions were made: (1) the reverse reactions are considered to be negligible (due to high T–P conditions and glycerol decomposition the reaction equilibrium is shifted to product side); (2) glycerol decomposition products are soluble in methyl esters and would not adversely affect the combustion of methyl esters; (3) disappearing conversion of SO was taken as 99.5%; (4) pressure drop across any equipment was neglected; (5) diesel engine efficiency (BD energy to shaft power) was taken as 40%, and the efficiency of the power generator (shaft power to electricity) was taken as 95%; and (6) temperature and pressure of the reaction were selected as 400 °C and 100 bar, respectively.

Mass flow rates and compositions of the process input and output streams were quantified using component, mass, and energy balances, stoichiometric relations, and established process param-
The process conditions and the flow rates of each stream in the process flow diagram are given in Table 2.

3.1.4. Process simulation

CHEMCAD was used to design all of the process units except the soybean oil preheater, SC TE reactor, diesel engine/generator set, and fired heater. While the overall results of process simulation from CHEMCAD seemed to be appropriate, the results for steady state simulation for heat exchangers appeared to be less reliable. To exercise caution, hand calculations were also performed in this case and the best of the results were taken into consideration for finalizing the design. The reactor was sized based on the residence

Fig. 4. Main TE products of: (a) soybean oil with methanol and (b) a commercial sample. Main peaks are the methyl esters of: palmitic (51.4/51.6); linoleic (57.2/57.4); oleic (57.6/57.9); linolenic (57.7); and stearic (58.7/58.8) acids. (Analytical GC–MSD method used: cross-linked methyl syloxane column of 30 m × 0.25 mm I.D. × 0.25 μm film thickness with helium as carrier gas; the temperature program started at 60 °C hold for 2 min and continued with a subsequent ramp of 3 °C/min to 270 °C; the temperatures of the injector and GC–MSD interface were 250 °C and 270 °C, respectively).
time used in the laboratory experiments and was extended to 3.79 min to account for scaling-up factors. Furthermore, an extra volume of 20% was considered to provide sufficient heat transfer area for heating the reactant mixture from 308 to 400 °C with the exhaust gas. The diesel engine and fired heater were sized to provide sufficient heat for the TE reactions by consuming part of the produced BD (4.53 and 6.05 vol.%, respectively) as fuel. The electricity from the engine is used locally or is to be sold to the local grid for $0.10/kWh.

3.2. Economic evaluation

3.2.1. Cost of manufacturing (COM)

BD production costs were calculated with the chemical engineering methods available in the literature (Peters and Timmerhaus, 1991; Turton et al., 2003; Ulrich, 1984; Haas et al., 2006; Lim et al., 2009). The base-case design to be scaled up by a factor of approximately 6 for a BD plant with a capacity of 15,000 gal/day (56,775 L/day) was the TE of 2100 gal/day (7,949 L/day) of SO with 269 gal/day (1,018 L/day) of methanol to produce 2424 gal/day (56,775 L/day) was the TE of 2100 gal/day (7,949 L/day) of SO. The plant was assumed to operate 24 h/day for 346 days/year. The capital cost and COM for BD production with 269 gal/day (1,018 L/day) of methanol to produce 2424 gal/day (56,775 L/day) was the TE of 2100 gal/day (7,949 L/day) of SO.

First, COM was estimated from the equation:

$$\text{COM} = 0.2536 \cdot \text{FCI} + 2.2835 \cdot \text{COL} + 1.0309 \cdot (\text{CUT} + \text{CWT} + \text{CRM})$$

(2)

FCI is the fixed capital investment and COL, CUT, CWT, and CRM are the costs for operating labor, utilities, waste treatment, and raw materials, respectively. Although R&D costs are generally included in estimating COM, for those companies which are not interested in replacing the existing technology for a certain period of time, the R&D costs can be excluded from COM. Accordingly, these costs were not considered in the COM equation. Also, the retail cost of BD was not considered in this economic assessment, this cost structure being similar with the conventional BD cost and highly fluctuating in time. Van Gerpen (2007) provided the economics for BD production for conventional base catalyzed method for 5 × 10⁶ gal/year (18.925 × 10⁶ L/year). In this analysis selling and distribution costs were not considered in estimating COM. To make a comparison between the COM costs of BD for SC method and for a traditional method, we also neglected the selling and distribution costs in estimating COM. Various other items in the COM (e.g., maintenance, supervisory and clerical labor, depreciation of the FCI, and administrative costs) were estimated as fractions of the FCI and of operating labor, utilities, or raw material costs.

3.2.2. Capital cost

The costs of major pieces of equipment, their bare module costs in US dollars (2007) and the total module cost or FCI are given in Table 3. These costs were calculated based on CAPCOST software of Turton et al. (2003) and available information from manufacturers of the industrial equipment. Although the estimated prices for these equipments do not affect the COM costs significantly, when cost information was not available, we always considered a conservative approach in estimating these costs. The storage tanks were sized to have 14 days storage capacity. The costs of the power generator and fired heater have been evaluated from Ulrich (1984). The bare module cost for each piece of equipment includes consideration on high-pressure exposure and direct project expenses such as the purchased cost of equipment, cost of piping, instrumentation, structural supports, etc., associated with the equipment as well as the labor cost for installation and indirect costs such as freight, insurance, engineering fees, and overhead. An additional 18% was added for contingency and for the contractor’s fee. Carbon steel was specified for equipment exposed to temperatures less than 100 °C and stainless steel was specified for equipment exposed to temperatures above 100 °C.

### Table 3

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol storage tank</td>
<td>46,060</td>
<td>46,060</td>
<td></td>
</tr>
<tr>
<td>Soybean oil storage tank</td>
<td>63,000</td>
<td>63,000</td>
<td></td>
</tr>
<tr>
<td>Biofuel storage tank</td>
<td>63,600</td>
<td>63,600</td>
<td></td>
</tr>
<tr>
<td>Methanol feed pump</td>
<td>33,609</td>
<td>33,609</td>
<td></td>
</tr>
<tr>
<td>Soybean oil feed pump</td>
<td>64,508</td>
<td>64,508</td>
<td></td>
</tr>
<tr>
<td>Reactor</td>
<td>78,300</td>
<td>78,300</td>
<td></td>
</tr>
<tr>
<td>Soybean oil preheater</td>
<td>55,600</td>
<td>55,600</td>
<td></td>
</tr>
<tr>
<td>Methanol preheater</td>
<td>31,800</td>
<td>31,800</td>
<td></td>
</tr>
<tr>
<td>Pressure regulating valves</td>
<td>1,000</td>
<td>1,000</td>
<td></td>
</tr>
<tr>
<td>Power generator/fired heater</td>
<td>10,000</td>
<td>10,000</td>
<td></td>
</tr>
<tr>
<td>Dowtherm fluid</td>
<td>2000</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Total equipment cost</td>
<td>447,477</td>
<td>505,477</td>
<td></td>
</tr>
<tr>
<td>Contingency and fees</td>
<td>80,546</td>
<td>90,586</td>
<td></td>
</tr>
<tr>
<td>Total F.C.I.</td>
<td>528,023</td>
<td>596,463</td>
<td></td>
</tr>
</tbody>
</table>
than 250 °C and stainless steel was specified for equipment exposed to higher temperatures.

The capital cost for 5 × 10^6 gal/year (18.925 × 10^6 L/year) of BD production was estimated by scaling up the capital costs for the base-case unit using six-tenths rule. Peters and Timmerhaus (1991) suggested scaling up plant capacities up to 10 times the base-capacity. According with this rule, the BD plant capacity could have been scaled up to a capacity of 8.3 × 10^6 gal/year (31.4 × 10^6 L/year), but for easier economic comparison between conventional and SC methods and other considerations, we chose to analyze the SC BD process economics for 5 × 10^6 gal/year (18.925 × 10^6 L/year).

### 3.2.3. Utility cost

The components for the cost of utilities for BD production were taken from Turton et al. (2003) and are shown in Table 4. Due to energy cogeneration in the process, the utilities cost for the processes of the proposed SC TE technology are very low. More efficient use of high energy exhaust gas stream with other process streams can further reduce the energy requirement. The utilities costs were scaled linearly when the plant capacity was increased to 5 × 10^6 gal/year (18.925 × 10^6 L/year).

#### 3.2.4. Labor cost

The labor cost was calculated considering the number of operators per shift (N_{OL}) for BD production and the adjusting factor for 24/7 operations (Tables 5 and 6). The plant was assumed to run continuously with 3 shifts/day for 346 days/year (for the remaining days the plant was considered to be in shut down and maintenance mode). The annual operator salary in the rural area was considered to be $30,000 ($15/h). Hence, the operating labor costs (2007) were evaluated to be $270,000/year. Since the process is continuous and fully automated it requires less supervision and the labor costs were considered to be the same when the plant capacity was increased to 5 × 10^6 gal/year (18.925 × 10^6 L/year).

#### 3.2.5. Raw material costs

The raw material costs are for SO and methanol. The oil at the time of this analysis was available for $2.91/gal or $0.77/L (CME Group, 2007) while the price of petrodiesel fuel was approximately $3.00/gal or $0.79/L (Energy Information Agency, 2007). The total raw material costs as of August 2007 for 2424 gal/day (9,175 L/day) of BD production was approximately $3,333,000/year.

#### 3.2.6. Total COM

The total COM is given in Table 8 along with revenues from the sale of electricity, and the break-even cost of the net BD available for sale. The total COM per year includes the annual freight charges and the annual interest on the FCI. For the base-case design of 2424 gal/day (9,175 L/day) of BD production with power generation, COM was estimated to be approximately $3,333,000/year. The total electricity produced by the power generator is approximately 526 MWh/year, but 18 MWh/year are used to drive the methanol and oil feed pumps, leaving approximately 508 MWh/year available for sale. Assuming that the selling price of electricity to commercial or industrial sector is $0.10/kWh, the revenues obtained from electricity would be $51,000. Hence, the net COM was estimated to be $3,282,000/year. The total amount of BD fuel produced is 839,000 gal/year (3.2 × 10^6 L/year). From this amount, 4.53 vol.% is used for generation of electricity by the diesel-generator and the remaining 95.47% of BD fuel available for sale is 800,000 gal/year (3 × 10^6 L/year). The break-even cost of BD fuel is ($3,282,000/year)/800,000 gal/year or $4.10/gal ($1.08/L) with a processing cost of $1.02/gal ($0.27/L).

### Table 4

Utility costs (C_U) for biodiesel production.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Utility</th>
<th>Power (W)</th>
<th>Utility usage</th>
<th>Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Power generator</td>
<td>Fired heater</td>
</tr>
<tr>
<td>Reactor</td>
<td>EG/DFa</td>
<td>25,427</td>
<td>5.373 kg/min</td>
<td>8.94 kg/min</td>
</tr>
<tr>
<td>Methanol feed pump</td>
<td>Electricity</td>
<td>246</td>
<td>2043 kWh/year</td>
<td>2043 kWh/year</td>
</tr>
<tr>
<td>Soybean oil feed pump</td>
<td>Electricity</td>
<td>1926</td>
<td>15994 kWh/year</td>
<td>15994 kWh/year</td>
</tr>
<tr>
<td>Methanol preheater</td>
<td>Biofuel</td>
<td>9965</td>
<td>5.62 kg/min</td>
<td>5.62 kg/min</td>
</tr>
<tr>
<td>Soybean oil preheater</td>
<td>Biofuel</td>
<td>66,429</td>
<td>5.62 kg/min</td>
<td>5.62 kg/min</td>
</tr>
<tr>
<td>Fired heater</td>
<td>Biofuel</td>
<td>25,427</td>
<td>0.434 kg/min</td>
<td>0</td>
</tr>
<tr>
<td>Total (C_U)</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

a EG stands for exhaust gases and DF for Dowtherm fluid.
b DF cost is not considered as utility cost but as FCI as it is recycled and can be used in the process for a period of 4–5 years.

### Table 5

Operators per shift (N_{OL}).

<table>
<thead>
<tr>
<th>Equipment type</th>
<th>Number of equipment</th>
<th>Operators per shift per equipment</th>
<th>Operators per shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil preheater</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Methanol preheater</td>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Reactor</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Power generator/\ fired heater</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Total</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Operators per shift were rounded to nearest whole number, N_{OL} = 2.

### Table 6

Operating labor cost (C_{OL}).

<table>
<thead>
<tr>
<th>Operators/shift (N_{OL})</th>
<th>Factor for 24/7 week operation</th>
<th>Annual operator salary (AOS) ($)</th>
<th>Total cost ($/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4,236</td>
<td>30,000</td>
<td>270,000</td>
</tr>
</tbody>
</table>

C_{OL} = N_{OL} × adjusting factor × AOS (the N_{OL} × adjusting factor = 8.47 = 9).

### Table 7

Raw materials cost (C_{RM}).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Requirement (gal/year)</th>
<th>Cost (2007 US $/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>93,000</td>
<td>86,490</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>770,000</td>
<td>2,240,700</td>
</tr>
<tr>
<td>Freight charges</td>
<td>54,830</td>
<td></td>
</tr>
<tr>
<td>Total C_{RM}</td>
<td>2,382,020</td>
<td></td>
</tr>
</tbody>
</table>
3.2.7. Comparison with conventional TE processes

A comparison of the production and processing costs of BD fuels by conventional and SC methods for 5 × 10^6 gal/year (18.925 × 10^6 L/year) capacity as well as the costs for the base-capacity of 0.84 × 10^6 gal/year (3.18 × 10^6 L/year) is provided in Table 9. For the latter capacity, these costs are reported for only the SC method. Oil and methanol costs (August 2007) were updated for each column and freight charges were added to these costs. Various cost items reported in this table were calculated by using Turton et al. (2003). Interest on capital investment was additionally considered in the first column of Table 9.

Table 9
Comparative production and processing costs (in US $/gal) of biodiesel fuels for conventional and SC methods.

<table>
<thead>
<tr>
<th>Cost components</th>
<th>Van Gerpen (2007)</th>
<th>This study a</th>
<th>This study b</th>
<th>This study a</th>
<th>This study b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 × 10^6 gal/year</td>
<td>0.84 × 10^6 gal/year</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil</td>
<td>3.23 c</td>
<td>2.95 c</td>
<td>3.00 c</td>
<td>2.95 c</td>
<td>3.01 c</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.13 c</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>NaOCH3 catalyst</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutralizer</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Utilities</td>
<td>0.02</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Labor</td>
<td>0.10 c</td>
<td>0.066</td>
<td>0.065</td>
<td>0.065</td>
<td>0.065</td>
</tr>
<tr>
<td>Depreciation</td>
<td>0.15</td>
<td>0.033</td>
<td>0.038</td>
<td>0.038</td>
<td>0.038</td>
</tr>
<tr>
<td>Interest</td>
<td>0.02</td>
<td>0.025</td>
<td>0.029</td>
<td>0.029</td>
<td>0.029</td>
</tr>
<tr>
<td>Administration + overhead</td>
<td>0.020</td>
<td>0.064</td>
<td>0.066</td>
<td>0.066</td>
<td>0.066</td>
</tr>
<tr>
<td>Maintenance</td>
<td>0.040</td>
<td>0.020</td>
<td>0.023</td>
<td>0.023</td>
<td>0.023</td>
</tr>
<tr>
<td>Laboratory charges</td>
<td>0.011 e</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>Operating supplies</td>
<td>0.011 e</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Local taxes + insurance</td>
<td>0.040 d</td>
<td>0.010</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>Patents + royalties</td>
<td>0.12 d</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Total production cost</td>
<td>3.96</td>
<td>3.41</td>
<td>3.47</td>
<td>4.16</td>
<td>4.28</td>
</tr>
<tr>
<td>Electricity revenue</td>
<td>0.00</td>
<td>0.064</td>
<td>0.00</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Net production cost</td>
<td>3.96</td>
<td>3.34</td>
<td>3.47</td>
<td>4.16</td>
<td>4.28</td>
</tr>
<tr>
<td>Processing cost</td>
<td>0.51</td>
<td>0.26</td>
<td>0.35</td>
<td>1.02</td>
<td>1.14</td>
</tr>
</tbody>
</table>

a Process with power generator.
b Process with fired heater.
c Updated costs to August, 2007.
d Additional costs.
e For the current study the oil cost is less due to the fact that less oil is used to produce the same amount of fuel with the glycerol decomposition products included.

In order to compare these results with those for a conventional method, we selected the reported costs of Van Gerpen (2007). Similarly, we have not included in the production costs the interest on the borrowed amount for the capital investment (e.g., the interest on the borrowed amount for the capital investment) and Van Gerpen (2007) (e.g., laboratory charges, operating supplies, local taxes and insurance, patents and royalties). However, for the reasons cited earlier, we did not include in COM the costs of R&D, selling, and distribution.

3.2.7.1. Other TE processes

A comparison of the production and processing costs of BD fuels by conventional and SC methods for 5 × 10^6 gal/year (18.925 × 10^6 L/year) capacity as well as the costs for the base-capacity of 0.84 × 10^6 gal/year (3.18 × 10^6 L/year) is provided in Table 9. For the latter capacity, these costs are reported for only the SC method. Oil and methanol costs (August 2007) were updated for each column and freight charges were added to these costs. Various cost items reported in this table were calculated by using Turton et al. (2003). Interest on capital investment was additionally considered at the rate of 6% compounded annually for 10 years. In the cited reference (Van Gerpen, 2007), the depreciation/interest, labor, maintenance, administration and overhead costs seemed to be lower for the total capital investment of $5.26 × 10^6. Also, the labor cost was reported there for only one shift and we updated this cost for 3 shifts per day. Furthermore, maintenance costs reported by Kasteren and Nisworo (2007) and in this study were calculated at 3.8 and 6% of FCI, respectively. However, the complexity and the number of the equipment units for the two methods as shown in Figs. 2 and 3 should render the conventional plant maintenance rather more costly. Laboratory charges, operating supplies, local taxes and insurance, patents and royalties costs (Turton et al., 2003) were additionally considered in the first column of Table 9.

Most of the total COM comes from the raw materials and labor costs (Table 9). Although little can be done to reduce the raw materials cost, the COM per unit volume of product would be significantly reduced for a larger size plant since the number of operators would not change (2 operators per shift were already significantly rounded up from a required number of 1.2). Also some savings in capital cost would be realized with a larger capacity plant. Thus, the COM for a plant capacity of 15,000 gal/day (56,775 L/day) was calculated to a reduced break-even cost of $3.34/gal or $0.88/L (about the same with the current diesel fuel).
for comparison purposes on a common base. Net production cost was calculated by subtracting byproduct revenues from the total production cost and the processing cost was calculated by subtracting raw materials costs from the net production cost. The oil and methanol costs are higher in the first column of Table 9 as compared to those in the columns 2 and 3 since less biodiesel is produced by conventional method (glycerol is separated out as a byproduct) from the same quantity of raw materials.

Furthermore, we can compare our production and processing cost with those reported in the only economic analysis for another SC method available in literature (Kasteren and Nisworo, 2007). At comparable capacity levels (e.g., $2.5 \times 10^8$ gal/year or $9.46 \times 10^6$ L/year), our calculated production cost of $3.50$ (gal) ($0.92$ L) is higher than that reported, $2.30$ (gal) ($0.61$ L). The main reason for this difference has to be considered the lower cost of waste cooking oil. However, our processing cost of $0.43$ (gal) ($0.11$ L) is much lower than that in the above reference of $1.43$ (gal) ($0.38$ L) due to architectural differences of the two technologies and the associated process conditions.

Raw materials cost, depreciation, interest, local taxes and insurance, utilities, administration and overhead and maintenance costs for the process without power generation were found to be higher than those for the process with power generation (column 3 versus column 2 in Table 9). From the results obtained we can conclude that BD production with power generation seems to be more advantageous than that without power generation for the plant capacities for which this economic analysis was performed. Also, processing cost for BD produced by the proposed SC method is approximately half of that reported for the conventional methods.

The costs for SO (CME Group, 2007) and methanol (Methanex, 2007) as well as the diesel fuel cost (Department of Energy, 2007) exhibit timely market fluctuations. However, the processing cost is much more stable such that it can be stated that the BD price is the price of SO and methanol plus the processing cost of $0.26$ (gal) or $0.07$ (L) (for $5 \times 10^8$ gal/year or $18.925 \times 10^6$ L/year plant capacity). It is also important to note that since the diesel fuel has to be used by soybeans cultivation and SO production and that SO cost produced this way is near the cost of diesel fuel, the BD price will be always above the price of diesel fuel. Otherwise, the diesel fuel has to be replaced by BD all along these processes.

### 4. Summary

Selected ranges of the laboratory-scale TE conditions (e.g., 350–400 °C, 100–300 bar, and alcohol to oil ratios at about stoichiometric value of 3:1) providing near complete conversions of oil to BD products have been employed to design an industrial SC TE technology associated with power cogeneration. The proposed technology consists in one-step BD production without complex separation/purification processes and basically all of the glycerol produced will decompose to smaller molecular compounds blended within BD fuel. SC TE products generated under the above conditions consist in one homogeneous liquid phase with viscosity, cloud/pour point and composition superior to those of current commercial BD fuel. By using close to stoichiometric oil–alcohol mixtures, the power required to recycle large excess of alcohol is eliminated with significant technological and economic benefits.

An economic analysis of the proposed SC TE process has been performed. It was found that the BD processing cost through the proposed technology could be half of that of the actual conventional methods. (i.e., $0.26$ (gal) or $0.07$ (L) versus $0.51$ (gal) or $0.13$ (L) (Collins, 2006; Van Gerpen, 2007)). Associated with some other incentives along with higher diesel fuel prices, this new cost-saving technology is likely to make BD production profitable.

### Acknowledgements

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### References


ABSTRACT

A method for producing biofuel by a transesterification reaction of an alcohol and a triglyceride such as an oil or fat is carried out at supercritical conditions in a reactor using a stoichiometric excess of alcohol. The reaction products of biofuel and gaseous mixture of glycerin and alcohol are recycled through a series of heat exchangers which transfer heat to respective pre-heaters to sequentially raise the temperature and pressure of the reaction mixture prior to delivery to the reactor. Any excess alcohol after separating and recovering gaseous glycerin therefrom is recycled and mixed with “fresh” alcohol. Preferably, the process is a non-catalytic continuous process.
BIO DIESEL FUEL AND METHOD OF MANUFACTURE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of co-pending U.S. application Ser. No. 12/074,441, filed Mar. 4, 2008, which claims the benefit of U.S. Provisional Application No. 60/904,946, filed Mar. 5, 2007, for “Biodiesel Fuel and Method of Manufacture,” the entire disclosure of which is hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention
[0003] The present invention pertains to biodiesel fuels. More particularly, this invention relates to the manufacture of biodiesel fuels. Even more particularly, the present invention pertains to a transesterification process for the manufacture of biodiesel fuels and methods of recovery therefor.
[0004] 2. Description of the Prior Art
[0005] As is known to those skilled in the art to which the present invention pertains, growth in the utilization of biodiesel fuels has proliferated. With the demand for reduction in petroleum oil consumption there is a growing recommendation for turning to renewable fuel sources. In this regard, the art has developed means and methods for the manufacture of biofuel and, in particular, biodiesel fuels.
[0006] Generally, such fuels are prepared by the transesterification of a triglyceride(s) either: (a) in the presence of a catalyst; or (b) by using the alcohol in a supercritical condition. In a transesterification reaction, usually, a fat or oil from any suitable source, such as corn oil or the like, is reacted with the alcohol to form a fatty acid ester which can then be successfully deployed as a fuel. This transesterification process is well-known, such as described in U.S. Pat. Nos. 6,570,030, 6,187,939, and 6,090,959; as well as U.S. Publication No. 2006/0025620, the disclosures of which are hereby incorporated by reference.

[0007] However, the efficiency of such processes is not satisfactory. In the catalytic reaction, because of the presence of the catalyst and the potential for soap by-products, the efficiency of such a reaction system is somewhat degraded. Similarly, in the non-catalytic reaction, because excess stoichiometric quantities of alcohol are used, the economics of the process lessen the practicality of using same.

[0008] Thus, there exists a need for improvements in the manufacturing process whereby the excess reactants can be recycled and reused. It is this to which the present invention is directed.

SUMMARY OF THE INVENTION

[0009] In accordance with the present invention, a biofuel is prepared by the transesterification of a triglyceride, i.e. fat or oil with an alcohol, the alcohol being in a supercritical state.
[0010] According to the present invention, and in a preferred embodiment, a stoichiometric excess of an alcohol is reacted with a vegetable oil in a suitable reactor which is maintained at supercritical conditions, i.e. at a temperature above about 180° C. and a pressure greater than about 1450 psi. Prior to delivering the reactants to the reactor, the alcohol is passed through a series of pre-heaters. The pre-heaters use recycled reaction products to pre-heat the alcohol.

[0011] According to the present invention, after leaving the reactor, a portion of the reactor products are passed into a heat exchanger to transfer heat to a proximal pre-heater and then on to a first flash drum which condenses the biodiesel fuel while leaving the excess alcohol and glycerol by-product in a gaseous state. Liquid fuel is collected from the bottom of the drum and sent into another heat exchanger which transfers heat to a first intermediate pre-heater. The liquid fuel is then collected, while the alcohol and glycerol are transferred to an additional heat exchanger which transfers heat to a second intermediate pre-heater, and then into a second flash drum.

[0012] The second flash drum is then set to a temperature and pressure that causes the glycerol to condense, while leaving the alcohol in a gaseous state. The glycerol is collected from the second drum and the gaseous alcohol is then recycled, condensed, and mixed with fresh alcohol which, in turn, is then pumped into the reactor through the pre-heaters.

[0013] Preferably, the reaction is a continuous process, although a batch process could be employed.

[0014] It should be noted that although the catalytic reaction can be used, it is preferred that the supercritical reaction be employed for efficiency and not having to recover the catalyst.

[0015] For a more complete understanding of the present invention, reference is made to the following detailed description and accompanying drawing. In the drawing, like reference characters refer to like parts throughout the several views in which:

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 is a flow chart showing a first embodiment of the present process;
[0017] FIG. 2 is a flow chart showing a second embodiment hereof; and
[0018] FIG. 3 is a perspective view of the present invention assembled on a mobile platform.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0019] As noted above, the present invention contemplates a continuous process wherein an alcohol and a triglyceride, i.e. an oil or a fat, are reacted together in a suitable reactor or furnace, wherein the furnace maintains the alcohol at a supercritical temperature, i.e. above 180° C. and at a pressure greater than about 1450 psi.

[0020] More particularly, and in a first embodiment hereof, the present invention contemplates an alcohol or source which is passed through a series of pre-heaters, mixed together with a triglyceride source, and the resulting admixture is then pumped, under pressure, into a reactor maintained at an elevated temperature and pressure.

[0021] Prior to entering the reactor, the alcohol is fed through a series of pre-heaters. The pre-heaters use the heat of the reactants to pre-heat the alcohol by recycling the reactants. Thus, after the reaction is complete, the reactants then pass through a first proportioning valve. The first proportioning valve directs a first proportion of the reactants into a heat exchanger which transfers heat to a proximal pre-heater and, therefrom, into a first flash drum. The first proportioning valve also directs a second proportion of the reactants directly into the first flash drum. The volumes of the first and second
proportions are determined by adjusting the first proportioning valve settings. The settings of the first proportioning valve can be manually adjusted.

[0022] The biodiesel fuel is condensed in the first drum while gaseous alcohol and glycerol by-product remain in the gaseous state. The biofuel is transferred through a heat exchanger which transfers heat to a second intermediate pre-heater so as to pre-heat the alcohol therein. The biofuel is then drawn off and collected.

[0023] The gaseous components exiting the first flash drum then pass through a second proportioning valve. The second proportioning valve directs a first proportion of the gaseous components into a heat exchanger that transfers heat to a second intermediate pre-heater and, therefrom, into a second flash drum. The second proportioning valve also directs a second proportion of the gaseous components directly into the second flash drum. The volumes of the first and second proportions are determined by the settings of the second proportioning valve, which may be manually adjusted as well.

[0024] In the second flash drum the glycerol is condensed, drawn off, and collected while the alcohol remains in a gaseous state. The gaseous alcohol is then passed through an additional heat exchanger to liquefy the alcohol, and then recycled into an alcohol feed tank and mixed with fresh alcohol.

[0025] In carrying out the reaction, the first component, as noted, is an alcohol or alkanol. Typically, these alcohols correspond to the formula:

$$C_{n}H_{2n+1}(OH)$$

wherein n ranges from about one to about ten and, preferably, from about one to about four.

[0026] Among the useful alcohols are methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol and the like, as well as mixtures thereof.

[0027] Preferred alcohols are methanol, ethanol, n-propanol, isopropanol and the like and mixtures thereof. Most preferred is methanol, alone, or in admixture with any of the other alkanols.

[0028] Where an alcohol admixture is used, the admixture will comprise a methanol to other alkanol volumetric ratio of about 99:1 to about 1:99, and preferably, at least a 50:50 volumetric ratio of methanol to other alkanol.

[0029] The second component in the present process comprises a triglyceride(s), i.e. a fat or oil. Useful and preferred are vegetable oils derived from renewable sources such as corn, soybean, rapeseed or the like. However, other vegetable oils can be used such as sunflower seed oil, peanut oil, and the like. Preferably, because of its abundance, soybean oil is used.

[0030] Useful fats include animal fat.

[0031] In carrying out the reaction, a stoichiometric excess of alcohol is used to ensure maximum transesterification, i.e. about 95%.

[0032] By carrying out the reaction in a supercritical state, usually at a temperature greater than 180°C, and at a pressure greater than about 1400 psi, the need for a catalyst is eliminated.

[0033] Referring now to the drawings and, in particular to FIG. 1, there is shown a flow chart for carrying out a first embodiment of the present process. As shown, initially, there is provided an alcohol source and a triglyceride source, comprising feed tanks, 10 and 12, respectively.

[0034] The alcohol is pumped under pressure, via pump 15, through delivery line 18 and into a distal pre-heater 24. The distal pre-heater 24 elevates the alcohol to a temperature below the supercritical temperature and a pressure below 1450 psi.

[0035] As shown, the pre-heater 24 is in fluid communication with a first intermediate pre-heater 26 via delivery line 25. Delivery line 25 feeds the first intermediate pre-heater 26 via the pump 15. In the first intermediate pre-heater 26, the alcohol is further heated to a temperature, but still below about 180° C., while maintaining an elevated pressure, but below 1450 psi.

[0036] As explained subsequently hereinbelow, each of the pre-heaters uses a countercurrent flow heat exchanger to transfer heat through a recycling of reaction products.

[0037] From the first intermediate pre-heater 26, the reaction mixture is, preferably, transferred to a second intermediate pre-heater 32 via delivery line 27 where the temperature of the reaction mixture is elevated still further but below the flash temperature of the alcohol while still maintaining a pressure below 1450 psi.

[0038] Still referring to FIG. 1, the heated and pressurized alcohol is then transferred or delivered to a proximal pre-heater 34 where the alcohol is further heated while still elevating the pressure. The alcohol exits the proximal pre-heater 34 via a delivery line 37.

[0039] The triglyceride is pumped from the feed tank 12 by a pump 33 through a delivery line 39. The alcohol and triglyceride are directed into a common delivery line 35. The alcohol and triglyceride are mixed together as they enter the common delivery line 38, thus forming an admixture, or reactants, before entering the reactor or furnace 36.

[0040] As noted, the reactor 36 is a continuous reactor maintained at supercritical conditions, i.e. at a pressure greater than about 1450 psi and at a temperature greater than 180° C., and preferably, greater than 300° C. The reactor 36 is equipped with means for stirring, such as a static mixer (not shown), to ensure that the reactants are maintained in turbulent mixing to ensure contact therebetween.

[0041] Depending on the flow rates into the reactor 36, the reaction is usually complete within about 5 to about 10 minutes. The resulting reaction product is a biofuel and glycerol-alcohol gaseous mixture.

[0042] The reaction products then flow, under pressure, to a first proportioning valve 38 via delivery line 38.

[0043] Proportioning valves are well known and commercially available and, generally, comprise a valve capable of distributing input flows into one or more output lines. A proportioning valve can be adjusted to increase or decrease the flow into each of the output lines. The proportioning valves provided herein can divert between 0% and 100% of the total flow to any output line. The proportioning valves are provided in the present invention to regulate the temperature of reaction products entering the flash drums, as is discussed in more detail below.

[0044] The first proportioning valve 38 directs a first proportion of the reaction product into a proximal heat exchanger 41 which provides some of the reaction’s heat to the proximal pre-heater 34. The proximal heat exchanger 41, as well as additional heat exchangers mentioned below, is discussed in further detail hereinbelow. The proximal heat exchanger 41 transfers heat from the reaction product to the alcohol in the proximal pre-heater 34. The first proportion of the reaction...
product is then transferred from the proximal heat exchanger 41 to a first flash drum 40 via delivery line 42.

[0045] The first proportioning valve 20 also directs a second proportion of the reaction product to bypass the proximal heat exchanger 41 and to enter the first flash drum 40 via delivery line 43.

[0046] Flash drums are well known and commercially available and, generally, comprise an elongated tubular member having separation plates contained therewithin to permit liquid condensates to be collected at the bottom of the drum with the gaseous components rising to the top.

[0047] Generally, in the practice of the present invention, the first flash drum 40 is maintained at a temperature less than that of the reactor, i.e. from about 280°C to about 290°C and at a pressure less than that of the reactor pressure but greater than atmospheric. In this manner, the hot liquid alkyl fatty acid ester biofuel condenses and is collected at the bottom of the drum and withdrawn therefrom and recycled into a first intermediate heat exchanger 48 which is paired with the first intermediate pre-heater 26 via delivery line 45, thereby transferring additional heat to the alcohol. The biofuel exits the first intermediate heat exchanger 48 and is then collected.

[0048] The excess alcohol and glycerol in the first flash drum 40 remain in a gaseous state and are transported through a delivery line 44 to a second proportioning valve 51. The second proportioning valve 51 directs a first proportion of the gaseous components into a second intermediate heat exchanger 53 which is paired with the second intermediate pre-heater 32. The second intermediate heat exchanger 53 transfers some of the gaseous components' heat to the alcohol. After the heat transfer, the glycerol-alcohol mixture remains gaseous. The gaseous components are then transferred from the second intermediate heat exchanger 53 to a second flash drum 46 via delivery line 47.

[0049] The second proportioning valve 51 also directs a second proportion of the gaseous components to bypass the second intermediate heat exchanger 53 and to enter the second flash drum 46 via delivery line 47.

[0050] The second flash drum 46 is similar to the first flash drum 40. The second flash drum 46 is maintained at a temperature ranging from about 66°C to about 289°C and at a pressure less than that of the first flash drum 40 but greater than atmospheric. In the second flash drum 46, glycerol is condensed and collected at the bottom 49 while gaseous alcohol is further recycled.

[0051] As shown, the alcohol exits the second flash drum 46 via delivery line 50 which then directs the alcohol into a distal heat exchanger 54 which is paired with the distal pre-heater 24. The distal heat exchanger 54 transfers sufficient heat from the gaseous alcohol to the alcohol in the distal pre-heater 24 such that the gaseous alcohol condenses into a liquid. The recovered liquid alcohol is then recycled via delivery line 52 and admixed with fresh alcohol thereat.

[0052] According to the present method, the recovery of and reuse of the stoichiometric excess of alcohol lowers the amount of "fresh" alcohol necessary to be used in the reaction, while effectively recovering the biofuel.

[0053] Furthermore, the heat transferred to the pre-heaters reduces the amount of heat lost in the reaction by-products, thereby increasing the energy efficiency of the entire process.

[0054] In addition, glycerol, which is recovered as a by-product, can then be used for various other compositions in which glycerol or glycine is a component.

[0055] In a second embodiment hereof, and as shown in FIG. 2, an angled reactor 136 is provided. The reactor 136 is angled with respect to its vertical orientation so as to provide an increased surface area for the reactants contained therein. In all other respects the process is the same as described with respect to the first embodiment.

[0056] It is noted that the reactants flow through the system, preferably, in a turbulent state.

[0057] It is further noted that each of the pre-heaters comprises a counter-current or countercurrent heat exchanger. Such are well known and commercially available and, generally, include concentric tubes formed from a suitable non-reactive material having sufficient thermal conductivity to enable sufficient heat transfer from the reaction product(s) to the reactants. Any such heat exchanger can be used herein so long as it withstands the processing parameters and is non-reactive.

[0058] As shown in FIG. 3, it is appreciated that an apparatus 55 for performing the method described hereinabove may be assembled as a single mobile unit 56 which is portable from one location to another. The mobile unit 56 includes, but is not limited to, a portable platform 58, the apparatus 55, and a structural support 60. The apparatus 55 includes, but is not limited to, components such as the feed tanks, flash drums, pre-heaters, proportioning valves, and reactor.

[0059] The platform 58 is preferably substantially rectangular in shape, and has substantially planar upper and lower surfaces. It may be formed from any suitable material, such as wood, metal, plastic, or the like. The platform 58 must be sufficiently rigid to provide support, to the mobile unit 56. However, it is noted that the platform 58 should be light enough so that it does not impede portability. The platform 58 may be moved by a forklift or the like and, preferably, it has means for receiving forks 59 from a fork lift. The means for receiving forks may be through-slots extending into the platform 58, recesses along the lower surface of the platform 58 to receive the forks between the platform 58 and the ground, or any other suitable means which are well known to one of ordinary skill in the art.

[0060] The mobile unit 56 also comprises a structural support 60 which may be formed from metal, plastic, wood, or the like. The structural support 60 includes a plurality of vertically-oriented pillars 62 and a plurality of horizontally-oriented struts 64. The pillars 62 extend upwardly from the platform 58 and are secured thereto by means which are well known in the art, for instance, by welding, bolts and nuts, fasteners, or the like. The horizontally-oriented struts 64 act as crossbeams which extend generally horizontally between the pillars 62. The pillars 62 and struts 64 are secured or affixed to each other at their respective intersections by suitable means which are well known in the art, such as brackets, nuts, bolts, welding, brackets, and so forth.

[0061] The apparatus 55 includes components such as the feed tanks, flash drums, pre-heaters, proportioning valves, and reactor. The components of the apparatus 55 are secured to the structural support 60 so that they do not shift while the mobile unit 56 is being moved. The components of the apparatus 55 are secured to the structural support 60 and/or the platform 58 by means which are well known in the art, such as metal straps, brackets, bolts, nuts, and the like. Furthermore, the components of the apparatus 55 are secured into the mobile unit 56 such that they are sufficiently braced for transport from one location to another.

[0062] The mobile unit 56 may also comprise suitable hook-up connections 66 required for operation of the com-
ponents of the apparatus 55, such as electricity, gas, compressed air, or the like. Each of the hook-up connections 66 are operably connected to their respective component of the apparatus 55. For instance, the reactor 36 may include either a gas or electrical connection, and venting, possibly, as well. As such, the mobile unit 56 provides suitable hook-up connections 66 to components of the apparatus 55 as is well known to those having skill in the art.

It is also to be appreciated that the mobile unit 56 includes any other necessary elements to enable the apparatus 55 to carry out the method for manufacturing biofuel as described above. For instance, any items, such as pumps or delivery lines, which are described hereinabove, are included in the mobile unit 56 as well.

The mobile unit 56 is intended for use in which it may be easily moved and quickly and readily hooked-up for use. Therefore, the platform 58 is designed so that the mobile unit 56 may be easily and quickly placed onto a vehicle 68 for relocation, such as the flatbed of a truck.

From the preceding, it is apparent that there has been described herein an improved process for the production of biodiesel.

It is contemplated that the present method will enable a 95% conversion rate. It should be noted that typically the alcohol and oil will be used in about a 2:1 feed rate into the reactor to provide the requisite excess alcohol.

As noted above, a batch process, with the same process parameters, can be used with the amounts of reactants adjusted to accommodate the necessary stoichiometric excess of alcohol, while still recovering and recycling same.

Having thus described the invention what is claimed is:

1. A method for manufacturing a biofuel by a transesterification process comprising:
   (a) providing an alcohol source;
   (b) providing a triglyceride source;
   (c) mixing together a triglyceride and an alcohol to form a reaction mixture;
   (d) transferring the reaction mixture to at least a distal pre-heater to heat the mixture to a temperature below about 180° C. and at a pressure of below about 1450 psi;
   (e) transferring the pre-heated reaction mixture to a reactor maintained at a temperature greater than about 180° C. and at a pressure of greater than 1450 psi to form:
      (1) a liquid biofuel and
      (2) a glycerine and excess alcohol gaseous mixture;
   (f) collecting the so-produced biofuel;
   (g) collecting the glycerine, and;
   (h) recycling the excess alcohol to the alcohol source.

2. The method of claim 1 wherein in a stoichiometric excess of alcohol is used.

3. The method of claim 3 which further comprises:
   (a) providing a proximal pre-heater in fluid communication with the distal pre-heater and the reactor, and a first flash drum, transferring the alcohol from the distal pre-heater to the proximal pre-heater, mixing the alcohol with the triglyceride to form the reaction mixture, and then transferring the reaction mixture to the reactor;
   (b) providing a proximal heat exchanger configured to transfer heat to the proximal pre-heater, the proximal heat exchanger in fluid communication with the reactor and the first flash drum; and
   (c) after the reaction is complete, directing a first proportion of the reaction products to the proximal heat exchanger and therefrom to the first flash drum, and directing a second proportion of the reaction products directly to the first flash drum.

4. The method of claim 3 wherein the proximal pre-heater is interposed the distal pre-heater and the reactor, the proximal pre-heater being at a temperature and pressure greater than that of the distal pre-heater but below about 180° C. and about 1450 psi.

5. The method of claim 4 wherein the proximal pre-heater is interposed the distal pre-heater and the reactor, the proximal pre-heater being at a temperature and pressure greater than that of the distal pre-heater but below about 180° C. and 1450 psi.

6. The method of claim 4 which further comprises:
   (a) providing a first intermediate pre-heater and a second intermediate pre-heater, the first intermediate pre-heater in fluid communication with the distal pre-heater, and the second intermediate pre-heater being in fluid communication with the first intermediate pre-heater and the proximal pre-heater;
   (b) providing a first intermediate heat exchanger configured to transfer heat to the first intermediate pre-heater, the first intermediate heat exchanger in fluid communication with the first flash drum;
   (c) providing a second intermediate heat exchanger configured to transfer heat to the second intermediate pre-heater, the second intermediate heat exchanger in fluid communication with the first flash drum;
   (d) transferring the biofuel from the first flash drum to the first intermediate heat exchanger to heat the alcohol in the first intermediate pre-heater to a temperature and pressure above the distal pre-heater but below that of the second intermediate pre-heater;
   (e) collecting the biofuel from the first intermediate heat exchanger;
   (f) transferring a first volume of the alcohol and glycerine gasous mixture from the first flash drum to the second intermediate heat exchanger to pre-heat the alcohol in the second intermediate pre-heater to a temperature and pressure above that of the first intermediate pre-heater but below that of the proximal pre-heater.

7. The method of claim 6 which further comprises:
   (a) providing a second flash drum;
   (b) providing a distal heat exchanger configured to transfer heat to the distal pre-heater, the distal heat exchanger in fluid communication with the second flash drum;
   (c) transferring the first volume of the glycerine and alcohol mixture from the second intermediate heat exchanger to the second flash drum to condense the glycerine;
   (d) transferring a second volume of the glycerine and alcohol mixture from the first drum directly to the second drum to condense the glycerine;
collecting the glycerin from the second flash drum; 
transferring the remaining gaseous alcohol to the distal 
heat exchanger to pre-heat the alcohol in the distal pre-
heater; 
delivering the so-recycled alcohol from the distal heat 
exchanger to the source of alcohol; and 
mixing the recycled alcohol with the alcohol source.

8. The method of claim 6 wherein: 
transerification the reactants are an alcohol and an oil, 
the alcohol corresponding to the formula:
\[ C_{n}H_{2n+1}(OH) \]
wherein n ranges from about 1 to about 10 and the oil is a 
vegetable oil.

9. The method of claim 8 wherein the method is a continu-
ous process.

10. The method of claim 2 wherein the reactor is angled 
with respect to its vertical axis.

11. The method of claim 2 where the alcohol is methanol.

12. (canceled)

13. A mobile unit assembly for manufacturing a biofuel by 
a transesterification reaction of a triglyceride and a stoichio-
metric excess of an alcohol where the reaction is carried out at 
a supercritical state, the assembly comprising:

a platform having substantially planar upper and lower 
surfaces;
a structural support, the structural support comprising a 
plurality of pillars and a plurality of struts, the pillars 
extending upwardly from the platform, and the struts 
extending between the pillars, the pillars and struts being 
secured to each other at their respective intersections;
an apparatus for manufacturing the biofuel, the apparatus 
comprising a source of an alcohol, a source of a triglyc-
eride, at least one flash drum, at least one pre-heater, and 
a reactor;
wherein the apparatus is secured to the structural support 
such that the apparatus is braced for transport from one 
location to another.

14. The mobile unit assembly of claim 13 wherein the 
source of alcohol and the source of triglyceride each comprise 
a feed tank, each of the feed tanks being secured to the 
structural support.

15. The mobile unit assembly of claim 13 wherein the 
apparatus comprises at least one proportioning valve.

16. The mobile unit assembly of claim 13 wherein the 
reactor is angled with respect to its vertical axis.

* * * * *
ABSTRACT
A biodiesel reactor system includes a reactor recirculation line running from the reactor bottom to a headspace in the top of the reactor. A reactor recirculation pump is in the reactor recirculation line, and a reactor nozzle is positioned in at a reactor recirculation line discharge in the headspace. The reactor nozzle provides back pressure on the reactor recirculation pump to cause a controlled cavitation. The controlled cavitation provides mixing for the various reactants to produce biodiesel fuel.
Biodiesel Production Unit

This application claims priority to U.S. Provisional Patent Application No. 61/107,396, filed Oct. 22, 2008, which is hereby incorporated in its entirety by reference.

BACKGROUND OF THE INVENTION

[0002] a. Field of the Invention
[0003] This invention relates to reactors and process equipment used to produce biodiesel.

[0004] b. Description of the Related Art
[0005] Biodiesel is a fuel which can be produced from commonly available organic oils, such as vegetable oil, cottonseed oil, peanut oil or other organic oils. Once biodiesel is produced it can generally be used in existing diesel engines without any modifications to the engine. The biodiesel can be pumped directly into the fuel tank and used just like regular diesel fuel derived from petroleum. It is also possible to mix biodiesel with standard diesel produced from petroleum in any ratio. So a fuel tank can be filled with 50% biodiesel and 50% petroleum diesel, or it can be 100% biodiesel or 100% petroleum diesel or anywhere in between. This means a person using biodiesel can fill up their tank with petroleum diesel, commonly available at most filling stations, without any concerns. This person can then use biodiesel whenever it is available and convenient.

[0006] Biodiesel fuel does have a few varying characteristics as compared to diesel produced from petroleum products. Biodiesel tends to have a higher lubricity. There are also differences which can be found in the viscosity, the flash point, the color and other aspects of the fuel. However, these variations in physical characteristics are not significant enough to require engine modifications for the use of Biodiesel.

[0007] Biodiesel is generally made by reacting methanol or some other alcohol with an organic oil in the presence of an alkaline catalyst. The catalyst used is generally some sort of alkaline material, such as sodium hydroxide, potassium hydroxide or other basic substance. The reaction produces biodiesel as well as a glycerol by-product. The biodiesel reaction is called a transesterification reaction. Most organic oils include triglycerides in a significant quantity. This triglyceride is broken down to form fatty acids which react with methanol to produce biodiesel and the by-product glycerol, as seen in the following diagram, where "R" represents an aliphatic compound, and the substrates on "R" indicate the aliphatic compound can vary.

\[
\begin{align*}
\text{Triglyceride} & + 3 (\text{H}_2\text{C} \text{O} \text{H}) \\
\text{Methanol} & \rightarrow \text{Biodiesel} + \text{Glycerol}
\end{align*}
\]

[0008] The general process for producing biodiesel may involve cleaning the organic oil to remove solids and other waste material before starting the reaction. Often the organic oil used is waste oil left over from cooking processes, but many other oil sources can also be used. This can include the oil from restaurant’s deep fat fryers and other oil collected from restaurants or large scale kitchens. This oil can be cleaned and charged into a reactor where it is heated. A separate alcohol-catalyst solution can be prepared where the catalyst is dissolves in the alcohol. This can involve dissolving solid sodium hydroxide in methanol, although other alcohols can be used such as ethanol or propanol. Other basic catalysts can be used as well. The alcohol/catalyst solution is then charged to the reactor and the reactor is agitated or mixed.

[0009] The triglyceride breaks down to fatty acids and then combines with the alcohol to form the biodiesel. The glycerol by-product is formed as the triglyceride breaks down. This reaction continues for a period of time called the reaction time; then all mixing and agitation is stopped and the reaction mass is allowed to split. The glycerol layer will settle and form underneath the biodiesel layer such that there are two layers of material in the reactor. The glycerol layer typically appears physically different than the biodiesel layer, so the split can be located by visual inspection.

[0010] The glycerol layer is separated from the biodiesel, and the glycerol can be stored, disposed of, sold or used as a by-product, or used in some other manner. At this point, the biodiesel fuel is typically purified in one manner or another. For example, the biodiesel can be washed with water, or it can be treated with an ion exchange resin. This washing or treating removes excess glycerol as well as any remaining caustic and free fatty acids from the biodiesel. After the purification process the biodiesel can be used, but it is also possible to flash off any remaining alcohol to further purify the biodiesel fuel. Any alcohol recovered can be saved and used as a raw material in a subsequent batch, and the biodiesel can then be stored and used as a regular fuel for diesel engines.

BRIEF SUMMARY OF THE INVENTION

[0011] A biodiesel reactor system includes a reactor recirculation line running from the reactor bottom to a headspace in the top of the reactor. A reactor recirculation pump is in the reactor recirculation line, and a reactor nozzle is positioned in at a reactor recirculation line discharge in the headspace. The reactor nozzle provides back pressure on the reactor recirculation pump to cause a controlled cavitation. The controlled cavitation provides mixing for the various reactants, which produces biodiesel.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 depicts a side view schematic of the reactor with certain internal parts shown.

[0013] FIG. 2 is a process flow diagram of one embodiment of equipment used for producing biodiesel fuel.

[0014] FIG. 3 is a top perspective view of the reaction nozzle.
[0015] FIG. 4 is a bottom perspective view of the reaction nozzle.
[0016] FIG. 5 is a process flow diagram of one embodiment of the equipment used for storing and purifying the biodiesel product.
[0017] FIG. 6 depicts a side view schematic of the pretreatment tank with certain internal parts shown.

DETAILED DESCRIPTION

Biodiesel Reaction

[0018] Several basic raw materials are used for producing biodiesel fuel. One is an organic oil. This organic oil can be vegetable oil, but it can also be a variety of other types of oil including cottonseed oil, peanut oil and other oils obtained from a plant. However, oils obtained from animals, such as animal fats, can also be used as the oil feedstock in the biodiesel production process. In this description, the organic oil before any pretreatment is referred to as a raw oil feedstock, the organic oil after a pretreatment step is referred to as a treated oil feedstock, and both the raw and treated oil feedstock is generically referred to as an oil feedstock.

[0019] The next raw material is an alcohol. The alcohol reacts with the fatty acids produced during the transesterification reaction. The biodiesel fuel is formed when the alcohol combines with the free fatty acid. Methanol is often the alcohol used, but other alcohols can also be used, such as ethanol, propanol, butanol, or others. Using alcohols with longer carbon chains than methanol, such as ethanol or propanol, may result in lower yields. There also may be cost differences to purchase the different alcohol raw materials. When methanol is used, the alcohol charge can be approximately one fifth of the oil feedstock charge.

[0020] A catalyst is also used in the reaction process. The catalyst is a basic material. In one embodiment, solid sodium hydroxide is used as the catalyst. In another embodiment, solid potassium hydroxide is used as the catalyst. Other basic materials can also be used as the catalyst, or different basic materials can be mixed together and used as the catalyst. The amount of catalyst which is charged is determined by titrating the oil feedstock. This titration process to determination the catalyst charge is known in the art. Water is generally considered disadvantageous for the reaction, so aqueous solutions of catalyst are typically avoided. Solid catalysts, such as sodium hydroxide, can be hydrophilic and absorb water from the air. The biodiesel reaction can tolerate small amounts of water, but it is also possible to use desiccants to minimize the amount of water introduced to the reaction system.

[0021] Frequently, the oil feedstocks used include impurities because the oils are typically waste material from cooking or other establishments. Recovery of waste oil can be one advantage of the biodiesel production system, because this reduces overall waste and can result in less expensive raw materials. It is also possible to produce biodiesel from fresh, unused oils, if desired. A variety of methods can be used for pre-treating the raw oil feedstock before beginning the reaction. One method is a glycerol wash where glycerol and the raw oil feedstock are mixed together and then allowed to separate into different layers. The glycerol layer is split from the bottom, and the treated oil feedstock on top is used in the reaction. Another pre-treatment method involves a filtration where the raw oil feedstock is run through a filter before the reaction. Other pre-treatment methods may be used as well, such as a water wash or just splitting off excess water charged with the oil feedstock. The pre-treatment methods can be used alone or in combination, and the order is not critical. It is also possible to proceed with the raw oil feedstock without any pre-cleaning. A more detailed description of one pretreatment embodiment is included below.

[0022] A reactor 10, such as the one shown in FIG. 1 and depicted in the process flow diagram of FIG. 2, can be used to produce biodiesel. It has been found that including a conical section 12 on the bottom of the reactor 10 improves the efficiency of the split and also the overall yield of the biodiesel reaction. This conical section 12 has a cone angle 14 which should be approximately 60°. The reactor 10 also includes a straight section 16 positioned on top of the conical section 12.

[0023] The reactor 10 should be constructed such that the cone section 12 covers approximately 35% of the volume of material in the reactor 10. The straight section 16 should contain approximately 65% of the volume of the reactants in the reactor 10 as well as including approximately 20% excess headspace 15 for gas expansion, agitation, and a safety factor. The use of larger headspace volumes in the straight section 16 is acceptable. Therefore, with a 60 degree cone angle 14, a cone height 18 can be approximately 98% of the straight section height 20. The ratio of the reactant volume in the cone section 12 to the reactant volume in the straight section 16 does effect the split and product yield when producing the biodiesel, but variations in the angles and ratios listed above are possible. In one embodiment, the reactor 10 is sized for a particular volume of reaction mass. The reactor size can be set for a consistent volume of oil feedstock, with a corresponding consistent volume of alcohol. In this description, the alcohol referenced is methanol, but it is to be understood that other alcohols could also be used. With methanol, the alcohol charge can be 20% of the oil feedstock charge. Therefore, if the oil feedstock charge is set at 55 gallons, the methanol charge can be 11 gallons, and the reactor 10 can have a volume of approximately 80 gallons. Other oil feedstock charge volumes and reactor volumes are also possible.

[0024] The oil feedstock is heated in the reactor 10 by a reactor heater 22. The reactor heater 22 includes a reactor cold section 24 and a reactor heater heating portion 28. The reactor cold section 24 is a part of the heater 22 which is not heated, and the heating portion 28 is a part of the reactor 10 which is heated. The reactor cold section 24 is positioned near the reactor discharge 26 such that material exiting the reactor 10 is not exposed to the heating portion 28 as it exits the reactor 10. The reactor cold section 24 can be approximately 2 inches long, but other lengths are also possible. The reactor discharge 26 is positioned near the reactor discharge 26 such that material exiting the reactor 10 is not heated.

The oil feedstock can be preheated to a temperature of 140° F. (Fahrenheit) by the reactor heater 22 before the alcohol and catalyst are charged to the reactor 10. For more even heating of the oil feedstock, the reactor 10 should be mixed while the oil feedstock is heated. In one embodiment, the reactor 10 is mixed with a reactor recirculation line 34, a reactor recirculation pump 36, and a reactor nozzle 35. The reactor recirculation line 34 extends from the reactor discharge 26 to a reactor top inlet 39, so fluid is removed from the bottom of the reactor 10 and returned to the top of the reactor 10. Other mixing embodiments are also possible, such as an impeller powered by a motor, air jets, or other techniques known in industry. The biodiesel reaction is exothermic, so the reactor heater 22 is turned off before the alcohol-catalyst solution is charged to the reactor 10. The reactor 10 can include a reactor temperature indicator 37 and/or a reactor level switch 38,
which can be used with safety interlocks and/or for monitoring process conditions in the reactor 10.

[0025] Alcohol and catalyst are charged to a charge vessel 30 where the catalyst is dissolved in the alcohol. The alcohol and catalyst can be agitated to dissolve any solid catalyst used in the alcohol, or to thoroughly mix any liquid catalyst used in the alcohol. The alcohol and catalyst can be charged to the charge vessel 30 before, during, or after the oil feedstock is charged to the reactor 10 and heated, because the alcohol and catalyst do not have to be used as soon as they are prepared. A charge vessel agitator 32 can be used to help dissolve the catalyst in the alcohol.

[0026] The alcohol—catalyst solution can be charged from the charge vessel 30 to the reactor recirculation line 34 on the suction side of the reactor recirculation pump 36. The alcohol—catalyst solution can also be charged directly into the reactor 10. If the alcohol—catalyst solution is charged to the reactor recirculation line 34, it can be done while the contents of the reactor 10 are being recirculated through the reactor recirculation line 34. If portions of the reaction mass in the reactor contain over 25% by volume of the alcohol—catalyst solution, soap can be made. When soaps are made, the reaction yield is decreased, and the soaps may have negative impacts on the split. Therefore, since the alcohol—catalyst solution can be charged into the recirculation line 34, the alcohol—catalyst charge rate should be no more than 25% of the reactor recirculation rate. Controlling the alcohol—catalyst charge rate can help minimize the production of soaps, and therefore improve yield.

Reactor Mixing

[0027] Mixing in the reactor 10 impacts the yield and the split formed between the biodiesel and the glycerol. In one embodiment, recirculation is the primary method of mixing the reactor 10. If the reactor 10 has too much mixing, it can decrease yields in the biodiesel formation. Insufficient mixing in the reactor 10 can unnecessarily lengthen reaction times and can also result in lower overall yields. Different types of mixing, such as high shear mixing, homogenization, etc. can also impact the reaction yield and the split. Poorer yields tend to result in poorer splits when the glycerol is separated from the biodiesel. The reason different types of mixing affect reaction yields and the split are not known, but extensive experimentation has produced a mixing system with acceptable yields and splits.

[0028] The components used to recirculate in the reactor 10 can be designed and balanced to achieve the proper level of reactor mixing. The components used to recirculate the reactor 10 include the reactor recirculation pump 36, the reactor recirculation line 34, and the reactor nozzle 35. In one embodiment, the reactor recirculation pump 36 can be a peripheral vane pump with an approximately 12.5 gallon per minute pump rating at 15 feet or water head back pressure, but other pumps can be used as well. A peripheral vane pump includes a multi-blade rotating element, called the impeller, centrally located in a housing dimensioned to contain the impeller. Liquid is fed into the housing, and centrifugal force pushes the liquid out through a pump outlet. The impeller can have blades on both sides. In one embodiment, the reactor nozzle 35 is especially designed to control the back pressure on the reactor recirculation pump 36 at approximately 46 feet of water head. This can produce a flow rate of approximately 4.5 gallons per minute in the reactor recirculation line 34 when the reactor 10 is recirculating. The back pressure on the reactor recirculation pump 36 results in a controlled cavitation in the reactor recirculation pump 10, which is a component of the reactor mixing.

[0029] The use of a reactor nozzle 35 with a reactor recirculation pump 36 to obtain a controlled cavitation has several advantages. A properly sized reactor nozzle 35 used in tandem with a reactor recirculation pump 36 can provide a simple, inexpensive, relatively low pressure method for using controlled cavitation to mix the oil feedstock with the alcohol and catalyst. The system can be operated at pressures less than 50 PSI (Pounds per Square Inch). Lower operating pressures can result in fewer maintenance issues, and/or allow for components rated for lower pressures in other portions of the system, which can reduce costs. The relatively low pressures and the use of a reactor nozzle 35 for back pressure can provide controlled cavitation with a relatively common, inexpensive reactor recirculation pump 36. Additional, the reactor recirculation pump 36 can operate with relatively low energy usage, and with a relatively small drive. There can be a portion of the reactor recirculation line 34 between the reactor recirculation pump 36 and the reactor nozzle 35 to facilitate the spraying function and location of the reactor nozzle 35 and the location of the reactor recirculation pump 36.

[0030] Controlled cavitation can provide good mixing, and back pressure on a pump is one method for obtaining controlled cavitation. The back pressure results in some liquid remaining in the reactor recirculation pump 36 as the pump impeller circulates. The liquid can be forced through the gap between the pump impeller and the pump housing, which can produce a high liquid flow rate and a high shear in this gap. The high liquid flow rate reduces the pressure in the liquid, which causes the relatively volatile alcohol to form bubbles, which are then collapsed by the higher pressure in the reactor recirculation pump 36 and the discharge of the reactor recirculation pump 36. The forming and collapsing of bubble is cavitation. The size and type of the reactor recirculation pump 36, the type of alcohol used, and the back pressure produced by the reactor nozzle 35 should be balanced for the proper amount of cavitation. Too much cavitation can produce soaps, which lowers yields, and not enough cavitation can increase cycle times and/or decrease yields by not achieving sufficient mixing.

[0031] One embodiment of the reactor nozzle 35 is shown in greater detail in FIGS. 3 and 4, with continuing reference to FIGS. 1 and 2. This one embodiment of the reactor nozzle 35 is discussed in more detail, but it is to be understood that alternative designs and dimensions are also possible. The reactor nozzle 35 is made of 1/4” pipe bushing, and this pipe bushing can be made of carbon steel. The pipe bushing can also be made from other materials, such as stainless steel, copper, or anything capable of withstanding the conditions at the reactor nozzle 35. The reactor nozzle 35 includes a primary orifice 40 which is approximately 1/8” in diameter. The reactor nozzle 35 also includes a nozzle surface 42 and a bottom surface 44. The primary orifice 40 is counter board from the bottom surface 44 such that the reactor nozzle 35 includes an injection cone 46. The injection cone 46 is counter board from approximately 1/4” at the bottom surface 44 to approximately 1/8’ at an injection cone angle 48 of approximately 60°. The reactor nozzle 35 also includes a fan slot 50 in the nozzle surface 42. The fan slot 50 has a fan slot depth 52 of approximately 1/4” and a fan slot width 54 of approximately 3/8’.

[0032] The reactor nozzle 35 is mounted at a reactor recirculation line discharge 56 positioned inside the reactor 10, as seen in FIGS. 1 and 2. The reactor recirculation line discharge 56 is any locations where fluids are intended to exit the reactor recirculation line 34. In one embodiment discussed below, the
reactor recirculation line discharge 56 is positioned at a reactor recirculation line spray angle 58 of approximately 45°. The reactor recirculation line discharge 56 and reactor recirculation line spray angle 58 are set such that the liquid contents of the reactor recirculation line 34 are sprayed into the reactor 10 such that the spray contacts the surface of the liquid within the reactor 10. The reactor nozzle 35 is positioned in the reactor headspace 15, where the “reactor headspace 15” is defined as the area above the liquid surface in the reactor 10. The reactor nozzle 35 also has a reactor sidewall 59, and the reactor nozzle 35 is directed away from the reactor sidewall 59 so that the reactor nozzle discharge contacts the surface of the liquid in the reactor 10, as opposed to contacting the reactor sidewall 59.

[0033] There are different components of the mixing in the reactor 10. The contact of the reactor recirculation line contents with the reaction mass provides one aspect of the agitation and mixing of the reactor 10. The reactor recirculation pump 36 has a controlled cavitation which results from the back pressure maintained by the reactor nozzle 35, and the controlled cavitation is another aspect of the reactor agitation and mixing. The recirculation action, the controlled cavitation in the reactor recirculation pump 36, and the spraying effect from the reactor nozzle 35 all combine to provide an appropriate degree of mixing in the reactor 10. Experimentation has been conducted to determine the recirculation line spray angle 58, the various dimensions of the reactor nozzle 35, and the back pressure needed to maintain the proper controlled cavitation in the reactor recirculation pump 36. The combination of all these elements provides an acceptable degree of agitation, and changing any one factor can impact biodiesel yields and the biodiesel/glycerol split. The balance described here is one embodiment of the current invention, but it is understood that different dimensions and angles can also be combined to achieve an alternate balance with acceptable mixing and reaction results.

[0034] If the reactor recirculation rate is approximately 4.5 gallons per minute, the alcohol—catalyst charge rate should not exceed approximately 1.5 gallons per minute in order to control the alcohol—catalyst solution concentration in the oil feedstock at no more than 25% of the total volume. A charge vessel pump 260 can be used for charging the alcohol—catalyst solution into the recirculation line 34. The charge vessel pump 260 can be a diaphragm pump, but other charge techniques can also be used, including centrifugal pumps, peristaltic pumps, or gravity feed. The charge vessel pump 260 can also be pneumatically operated, but other power sources can be used as well, such as electricity or gravity.

[0035] A reactor recirculation line charge section 62 can facilitate the proper charge rate of the alcohol—catalyst solution. The reactor recirculation line charge section 62 can be an enlarged area in the recirculation line 34 which can provide a lower pressure for the charge vessel pump 260 to overcome when charging the alcohol—catalyst solution. Providing a lower pressure to overcome can improve the control of the charge rate from the charge vessel pump 260. The pressure can also be reduced by positioning the recirculation line charge section 62 on the reactor recirculation pump inlet line instead of on the reactor recirculation pump discharge line. The inlet side of a pump can be referred to as the low pressure side of the pump, and the outlet side of the pump can be referred to as the high pressure side of the pump, because of the relative pressures on opposite sides of a pump. After all of the alcohol—catalyst solution has been charged to the reactor 10, the reactor recirculation pump 36 can continue to recirculate the reactor 10 until the biodiesel reaction is complete. This can be approximately 30 minutes after the completion of the alcohol—catalyst charge, but other times are also possible.

Separation and Purification

[0036] After the biodiesel reaction is complete, the glycerol is split from the biodiesel. The split is performed by stopping the agitation and mixing in the reactor 10. This can be done by verifying the reactor heater 22 is not turned on and turning off the reactor recirculation pump 36. This allows the reaction mass in the reactor 10 to sit still. The biodiesel has a lower specific gravity than the glycerol, and the glycerol will settle to the bottom with the biodiesel rising to the top. A reactor level site glass 64 can be provided for observing the split and also for verifying the level in the reactor 10. The split is usually complete within approximately 30 minutes to three hours after reactor mixing and agitation is stopped. The cone angle 14 of approximately 60° can impact the time necessary for the split to be completed, and it can also affect the quality of the split. When the split is complete, which can be visually observed in the reactor level site glass 64, the glycerol from the bottom of the reactor 10 can be pumped off and stored in a separate storage container. Alternatively, the glycerol layer can be pumped off using a pump connected to the reactor discharge 26, where the pump used for transferring the glycerol layer can be the reactor recirculation pump 36 or another pump, as the design configuration allows.

[0037] The biodiesel remaining in the reactor 10 still has some impurities, including some alcohol. Biodiesel can be used with alcohol present, but recovery of the alcohol provides a purer biodiesel product and can provide additional alcohol for later use, which can save on product costs. There are several ways to further purify the biodiesel, and these techniques can be used alone or in combination. In one embodiment, the ethanol is recovered from the biodiesel after the glycerol layer is separated. The reactor 10 includes a catch basin 80 positioned in the reactor headspace 15 near the top of the reactor 10. The catch basin 80 has an upside down conical shape, where the point of the conical shape is the lowest point of the catch basin 80. Any liquid falling into the catch basin 80 is drawn by gravity to the point of the conical shape, which can be at or near the center of the catch basin 80. There is a catch basin drain 82 at the lowest portion of the catch basin 80, and collected liquid can flow out of the catch basin 80 through the catch basin drain 82.

[0038] Additional components are connected to the catch basin 80 to facilitate the collection and transfer of liquid. An alcohol drain line 84 is connected to the catch basin 82 such that liquid flows through the catch basin drain 82 into the alcohol drain line 84. The alcohol drain line 84 penetrates the reactor 10, so at least a portion of the alcohol drain line 84 is positioned external to the reactor 10. The alcohol drain line 84 can include a coiled section 86, where liquids can collect in the coils to form a trap or barrier to gas flow. The coiled section 86 could have other shapes, such as one or more goose neck shapes, a “W” shape, or even a simple straight section of line. A heat exchanger 88 can be connected to the alcohol drain line 84 as well. The discharge of the heat exchanger 88 can be directed to a vessel to store alcohol, which can be the charge vessel 30 or some other vessel. There can also be a vacuum pump 90 connected in the alcohol drain line 84 either
upstream or downstream from the heat exchanger. Several different designs could also be used to collect alcohol from the reactor.

One embodiment for recovering alcohol from the biodiesel is discussed below, but other embodiments are also possible. The biodiesel is recirculated in the reactor recirculation line after the glycerol split to collect excess alcohol. The biodiesel can also be heated to help the alcohol vaporize from the biodiesel, and a temperature of approximately 185 degrees Fahrenheit can be used. A slight vacuum can also be pulled in the reactor to help vaporize alcohol, and this vacuum can be drawn by the vacuum pump. The vacuum can be about four (4) inches of water, and this vacuum can be controlled by including a vacuum regulator on the reactor set at the desired amount of vacuum. The above conditions are beneficial for recovering methanol, but other conditions may be more beneficial if different alcohols are used. The increased temperature and decreased pressure in the reactor increases the amount of alcohol vaporizing, and the spraying of the recirculating liquid onto the surface of the reaction mass also helps to vaporize the alcohol.

The catch basin can be positioned beneath an uninsulated portion of the reactor. This uninsulated portion can be a manway for easy access to the catch basin, but the uninsulated portion does not have to be at a manway. The entire reactor can be uninsulated, and in one embodiment the uninsulated area over the catch basin can be a thinner material than most of the reactor, to facilitate cooling. The cooler surface of the reactor over the catch basin condenses the alcohol, which eventually forms drops and falls into the catch basin. The catch basin catches the condensed drops of alcohol, and directs the liquid flow through the catch basin drain to the alcohol drain line and eventually to a storage vessel, such as the cargo vessel. Pulling vacuum through the alcohol drain line can induce a flow into the alcohol drain line, which may further facilitate the collection of alcohol from the reactor. Liquid condensed alcohol can be pulled into the vacuum pump and pumped by the vacuum pump to the charge vessel.

The shape of the uninsulated portion of the reactor can include structures to facilitate drop formation and dripping into the catch basin, but shapes which do not facilitate drop formation and dripping into the catch basin can also be effective. The collected alcohol can then be used in the production of a subsequent batch of biodiesel.

After the glycerol layer and alcohol have been removed from the biodiesel, there are still some remaining impurities in the biodiesel which can be removed. A water wash can be used for this removal, but it is also possible to use an ion exchange resin for purifying the biodiesel. The ion exchange resin can be stored in a resin column, as seen in FIGS. 6 and 2. The ion exchange resin can be a resin such as that sold under the trademark of AMBERLITE® BD10DRI®Y®, but other types of resin can also be used. The ion exchange resin can be held in the resin column using a mesh in the bottom of the resin column. The amount of ion exchange resin can be based on the planned oil feedstock batch size, and manufacturer recommendations can be used to determine the quantity of ion exchange resin used. The mesh can be supported on a grate and secured in place with a bracket such that the mesh is sandwiched between the grate and the bracket. The biodiesel should not be charged through the resin column at too fast a rate, or the ion exchange resin may not complete the purification process. Ion exchange resins often include specific recommendations for the rate at which material can be passed through the resin, and following these recommendations can improve results.

The biodiesel production unit can be designed to control the charge rate through the resin column. One embodiment for controlling the charge rate is to provide a bypass line with a bypass spring loaded check valve on the discharge side of the reactor recirculation pump. The bypass line can be directed from the high pressure side of a pump to the low pressure side of a pump, or it can be directed from the high pressure side of a pump back to a storage vessel. Other flow control measures can also be used, including a needle valve, an orifice in the line, or control valves.

The biodiesel product can be passed through the ion exchange resin at several places in the process. The biodiesel can be transferred from the reactor to a biodiesel storage tank to make room in the reactor for the next batch of biodiesel. The biodiesel can be passed through the resin column between the reactor and the biodiesel storage tank. Alternatively, the biodiesel can be passed through the resin column after being transferred from the reactor to the biodiesel storage tank. This can be done by recirculating the biodiesel through the resin column and back to the biodiesel storage tank, or it can be done by passing the biodiesel through the resin column when the biodiesel storage tank contents are transferred to another container for shipment or use.

An optical sensor can be positioned next to the reactor level sight glass to detect when the reactor is empty. This allows a computer or other controlling device to automatically turn off the reactor recirculation pump when the reactor is empty, and thereby reduce hazards caused by running a pump with no fluids present. Other devices can be used to detect when the reactor is empty as well, such as level indicators or weight cells.

**Pretreatment**

The oil feedstock can be pretreated before conversion to biodiesel. Including a pretreatment system with the reactor can simplify the pretreatment process. In one embodiment, a pretreatment tank is included with the biodiesel reactor system, as shown in FIGS. 6 and 1, with continuing reference to FIG. 2. A line connects the pretreatment tank to the reactor, where the line can contain liquids for a fluid transfer. A pump can be connected in the line for the transfer as well. In general, the pretreatment tank can use the same design, materials, shape, and dimensions as the reactor. This can simplify construction, because fewer vessel designs are needed. Also, the pretreatment process can begin converting some oil feedstock to biodiesel, and the reactor design facilitates this conversion. The pretreatment process also can clean undesirable impurities from the oil feedstock.

The pretreatment tank can have many features the same as in the reactor. For example, the conical section, the cone angle, the straight section, the cone height, and the straight section height can all be the same in the pretreatment tank as in the reactor. A pretreatment heater can have the same design as the reactor heater, with a pretreatment cold section and a pretreatment heater heating portion. The recirculation
system can also have the same design, where a pretreatment discharge 206, a pretreatment recirculation line 208, a pretreatment recirculation pump 210, a pretreatment nozzle 212, a pretreatment top inlet 213, a pretreatment headspace 215, and a pretreatment recirculation line discharge 214 are all the same as the reactor discharge 26, the reactor recirculation line 34, the reactor recirculation pump 36, the reactor nozzle 35, the reactor top inlet 39, the reactor headspace 15, and the reactor recirculation line discharge 62 respectively. The design elements, positioning, and location of the pretreatment nozzle 212 can be the same as that described for the reactor nozzle 35 above. Additionally, a pretreatment temperature indicator 216, a pretreatment level switch 218, and a pretreatment level sight glass 220 can be the same as the reactor temperature indicator 37, the reactor level switch 38, and the reactor level sight glass 64 as described above, respectively. It is also possible for the pretreatment tank 200 to have a different design than the reactor 10.

[0047] The pretreatment tank 200 can differ from the reactor 10 in the alcohol recovery system. In some embodiments, no alcohol is recovered from the pretreatment tank 200, so the pretreatment tank may not have comparable components to the catch basin 80, the catch basin drain 82, the alcohol drain line 84, the coiled section 86, the heat exchanger 88, and the vacuum pump 90 used with the reactor 10.

[0048] In the pretreatment step, raw oil feedstock is treated and converted to treated oil feedstock. Raw oil feedstock is charged to the pretreatment tank 200, and the glycerol split from the bottom of the reactor 10 is also charged to the pretreatment tank 200. The glycerol contains alcohol and catalyst impurities, so these impurities are available to react with the raw oil feedstock, similar to the biodiesel reaction in the reactor 10. The temperature of the raw oil feedstock and glycerol can be elevated somewhat, such as above 100 degrees Fahrenheit, but a wide variety of starting temperatures are possible. The glycerol and raw oil feedstock can be charged in any order, but in one embodiment the glycerol is charged into the pretreatment recirculation line 208 while the raw oil feedstock is being recirculated within the pretreatment tank 200.

[0049] The raw oil feedstock and the glycerol are recirculated in the pretreatment tank 200 the same as described for the reactor 10. The glycerol contains some alcohol and catalyst, but not enough to completely convert the raw oil feedstock to biodiesel, but some of the raw oil feedstock may be converted to biodiesel. This recovers the alcohol and catalyst that otherwise remains as an impurity in the glycerol, which can improve overall costs. Also, some of the “globs” and thicker portions of the raw oil feedstock seem to become less viscous and go into solution during this pretreatment step. This can improve the overall oil feedstock conversion ratio, because untreated “globs” can be filtered out before conversion to biodiesel. The “globs” may thin and go into solution in the pretreatment process because of partial reaction, or because of changes in the solvent properties of the oil feedstock, or perhaps for other reasons. The pretreatment process may also shorten cycle times for the biodiesel reaction step, and the pretreatment can be performed during the biodiesel reaction, so there may be no delay to the overall process.

[0050] The pretreatment process can include one or more of a reaction process, a split process, and a filtration process in essentially any combination. The reaction process is performed by combining the glycerol from the reactor 10 split with the raw oil feedstock, and recirculating in the pretreatment recirculation line 208. The split process can follow the reaction process, where the pretreatment tank 200 is not heated or recirculated, and the glycerol and oil feedstock are allowed to split. The lower glycerol layer can then be split off and stored, sold, disposed of, or used in any way desired. Many impurities in the raw oil feedstock may remain in the glycerol, because the glycerol is a more polar compound and is heavier than the oil feedstock. This includes compounds such as water, which tend to remain in the glycerol layer. The filtration process can be completed before or during the transfer from the pretreatment tank 200 to the reactor 10, and can be performed with a filter. The filtration process can also be performed when the raw oil feedstock is charged to the pretreatment tank 200. The filtration process can remove solid contaminants from the oil feedstock.

[0051] Different pretreatment processes can also be used. For example, a water wash can be used, or multiple filtrations can be performed. These steps may be added to the steps described above if desired, or even used in place of the steps described above. After the pretreatment process, the raw oil feedstock has been changed to treated oil feedstock, which can be charged to the reactor 10. It is also possible to charge raw oil feedstock directly to the reactor 10, and completely skip the pretreatment process. However, the pretreatment process can improve yields and also generally improve operations.

Equipment

[0052] Several items in FIGS. 2 and 5 can be utilized to facilitate the biodiesel production process, with continuing reference to FIGS. 1 and 6. Several symbols are used repeatedly, and reference will be made here to those symbols such that they can be understood by the reader. The process flow diagram includes manual valves 118, three way valves 120, check valves 122 which prevent backflow and only allow fluid to flow in one direction, and bag filters 126. There is also a vacuum regulator 128 which can be set at approximately 1/2 pounds per square inch and a pressure regulator 130 which can also be set at approximately 1/2 pounds per square inch, although other settings are also possible.

[0053] The vacuum and pressure regulators 128, 130 can be used to control the pressure in the headspace above liquids in the reactor 10 and in the pretreatment tank 200, as well as any other vessels as desired. An open vent 132 can also be utilized, such as is shown on the charge vessel 30. Couplings can be used at the end of lines when frequent connections are needed, and plugs can be used at the end of lines when frequent connections are not needed. Plugs can include such things as caps, blind flanges, or even welds. A pressure indicator 140 can be utilized to measure pressure at almost any location in the process.

[0054] It should be noted that many different configurations are possible which would achieve similar results. Processes can be highly automated or they can be more manual, as desired. Different size lines can be used and different devices can accomplish similar results. For example, the level of a tank can be determined by a see through line which has a connection near the top and near the bottom of the tank. It is also possible to measure the level of the tank with level indicators which electronically measure the tank. The level of a tank can also be determined with weigh cells, where the weight of the material in the tank is generally know, and a wide variety of other methods can also be used. This is true throughout this disclosure. In the chemical processing indus-
try it should be understood that a wide variety of different configurations can be utilized which will accomplish similar results to those shown. However, certain components, as has been mentioned, have been specifically designed and optimized for biodiesel production, and it has generally been found that these components, elements, dimensions, angles, etc., have an impact on the cycle time, yield and quality of the biodiesel fuel produced.

[0055] The combination of the reactor with the conical section and the recirculation process for mixing are the result of experimentation. Use of this equipment can provide good biodiesel yields, relatively clean biodiesel/glycerol splits, and relatively short cycle times in the biodiesel production process.

[0056] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed here. Accordingly, the scope of the invention should be limited only by the attached claims.

1 claim:
1. A biodiesel reactor system comprising:
   a reactor having a reactor bottom discharge and a reactor top inlet;
   a reactor recirculation line extending from the reactor bottom discharge to the reactor top inlet, where the reactor recirculation line includes a reactor recirculation line discharge;
   a reactor recirculation pump connected to the reactor recirculation line; and
   a reactor nozzle connected to the reactor recirculation line discharge, where the reactor nozzle provides backpressure to the reactor recirculation pump such that cavitation occurs in the reactor recirculation pump.

6. The biodiesel reactor system of claim 1 where the reactor further comprises a reactor headspace, and the reactor nozzle is positioned in the reactor headspace.

7. The biodiesel reactor system of claim 6 where the reactor includes a reactor sidewall, and the reactor nozzle is directed away from the reactor sidewall.

8. A biodiesel reactor system comprising:
   a reactor;
   a pretreatment tank including a pretreatment bottom outlet and a pretreatment top inlet;
   a line connecting the reactor to the pretreatment tank;
   a pretreatment recirculation line extending from the pretreatment bottom outlet to the pretreatment top inlet, where the pretreatment recirculation line includes a pretreatment recirculation line discharge;
   a pretreatment recirculation pump connected to the pretreatment recirculation line; and
   a pretreatment nozzle connected to the pretreatment recirculation line discharge, where the pretreatment nozzle provides backpressure to the pretreatment recirculation pump such that cavitation occurs in the pretreatment recirculation pump.

9. The biodiesel reactor system of claim 8 where the pretreatment recirculation pump is a peripheral vane pump.

10. The biodiesel reactor system of claim 9 where the pretreatment recirculation pump has a discharge pressure of less than 50 pounds per square inch.

11. The biodiesel reactor system of claim 10 where the pretreatment tank further comprises a pretreatment tank sidewall, and the nozzle is directed away from the pretreatment tank sidewall.

12. A biodiesel reactor system comprising:
   a reactor having a headspace;
   a catch basin positioned in the headspace, where the catch basin includes a catch basin drain;
   an alcohol drain line connected to the catch basin drain, where the alcohol drain line is at least partially positioned external to the reactor vessel; and
   a heat exchanger connected to the alcohol drain line.

13. The biodiesel reactor system of claim 12 where:
   the reactor includes a reactor bottom outlet, a reactor top inlet, a reactor headspace, and a reactor sidewall, the biodiesel reactor system further comprising:
   a reactor recirculation line extending from the reactor bottom outlet through the reactor top inlet, where the reactor recirculation line includes a reactor recirculation line discharge;
   a reactor recirculation pump positioned in the reactor recirculation line a reactor nozzle connected to the reactor recirculation line discharge, where the reactor nozzle provides backpressure to the reactor recirculation pump such that cavitation occurs in the reactor recirculation pump, and where the reactor nozzle is positioned in the reactor headspace and directed away from the reactor sidewall.

14. The biodiesel reactor of claim 13 further comprising:
   a pretreatment tank including a pretreatment bottom outlet, a pretreatment top inlet, a pretreatment headspace, and a pretreatment sidewall;
a line connecting the reactor to the pretreatment tank;
a pretreatment recirculation line extending from the pre-
treatment bottom outlet to the pretreatment top inlet, where
the pretreatment recirculation line includes a pretreatment recirculation line discharge;
a pretreatment recirculation pump in the pretreatment recirculation line; and
a pretreatment nozzle connected to the pretreatment recirculation line discharge, where the pretreatment nozzle
provides backpressure to the pretreatment recirculation pump such that cavitation occurs in the pretreatment recirculation
pump, and where the pretreatment nozzle is positioned in the pretreatment headspace and directed away from the pretreatment sidewall.

**15.** A method of producing biodiesel comprising:
(a) charging an oil feedstock to a reactor;
(b) recirculating the oil feedstock in the reactor using a
reactor recirculation line and a reactor recirculation pump such that the reactor recirculation pump cavitates while recirculating;
(c) charging a catalyst and an alcohol to the reactor;
(d) allowing the oil feedstock to split after step (c); and
(e) splitting a glycerol layer from a biodiesel layer formed during step (c).

**16.** The method of claim 15 where the reactor recirculation line includes a low pressure side and a high pressure side on opposite sides of the reactor recirculation pump, and the catalyst and alcohol are charged on the low pressure side of the reactor recirculation line.

**17.** The method of claim 15 further comprising:
(f) spraying the oil feedstock onto a reactor liquid surface through a nozzle during step (b).

**18.** The method of claim 15 further comprising:
(g) recirculating the biodiesel layer after step (e);
(h) heating the biodiesel layer while recirculating; and
(i) catching alcohol in a catch basin positioned in a reactor
headspace within the reactor.

**19.** The method of claim 15 further comprising:
(j) charging an oil feedstock to a pretreatment tank;
(k) charging the glycerol from step (e) to the pretreatment tank;
(l) recycling the oil feedstock and glycerol in the pretreatment tank through a pretreatment recirculation line and a pretreatment recirculation pump such that the recirculation pump cavitates;
(m) allowing the oil feedstock to split from the glycerol after step (l); and
(n) splitting the oil feedstock from the glycerol after step (m).

**20.** The method of claim 19 further comprising charging the oil feedstock from step (n) into the reactor in step (a).

* * * * *
PROCESS FOR THE CONVERSION OF RENEWABLE OILS TO LIQUID TRANSPORTATION FUELS

Inventors: Joshua R. Strege, Grand Forks, ND (US); Benjamin G. Oster, Thompson, ND (US); Paul D. Pansegrau, Grand Forks, ND (US); Chad A. Woeken, Grand Forks, ND (US); Ted R. Aulich, Grand Forks, ND (US)

Correspondence Address:
CONLEY ROSE, P.C.
David A. Rose
P. O. BOX 3267
HOUSTON, TX 77253-3267 (US)

Assignee: Energy & Environment Research Center, Grand Forks, ND (US)

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ABSTRACT
A method of producing a hydrocarbon product by hydrotreating a feedstock comprising triacylglyceride (TAG) in the presence of a nonsulfided hydrotreating catalyst to produce a first product comprising hydrocarbons. A method of producing a transportation fuel by selecting an undoped feedstock comprising virgin TAG, used TAG, or a combination thereof; hydrotreating the undoped feedstock in the presence of an unsulfided hydrotreating catalyst to produce a first product; and subjecting the first product to at least one process selected from aromatization, cyclization, and isomerization; to produce a second hydrocarbon product selected from gasoline, kerosene, jet fuel, and diesel fuels.
PROCESS FOR THE CONVERSION OF RENEWABLE OILS TO LIQUID TRANSPORTATION FUELS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] This invention was made with U.S. government support under Contract No. W911NF-07-C-0046 awarded by the Defense Advanced Research Projects Agency (DARPA). The government has certain rights in this invention.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] Not Applicable.

BACKGROUND

[0003] 1. Field of the Invention
[0004] The invention relates to a method for the conversion of renewable oils (triacylglycerides or TAGs) to hydrocarbons. The oils may be derived from plants, animals, or algae or mixtures thereof. The method is applicable to the manufacture of liquid transportation fuels, especially gasoline, kerosene, and jet and diesel fuels.
[0005] 2. Background of the Invention
[0006] Increasing costs for petroleum-derived fuels are driving interest in alternative feedstocks. Additionally, concern over increasing atmospheric carbon dioxide levels has spawned interest in “carbon-neutral” fuels. One possible solution to both of these issues is the utilization of TAG feedstocks for the production of hydrocarbon-based transportation fuels.
[0007] Certain TAGs are already utilized as feedstocks for the production of “bio-diesel.” In this process, the TAG is transesterified with methanol to provide a fatty acid methyl ester (FAME) and glycerine. The FAME is separated, purified, and sold as an additive, supplementing petroleum-derived diesel fuel. FAME diesel additives provide certain specific benefits to their use (i.e., lubricity), but suffer serious physical limitations when used as the sole fuel and not as a blendstock (i.e., cold-flow properties).
[0008] FAME diesel fuel represents a first-generation bioderived fuel. The shortcomings of this generation of fuel are directly related to the fuel possessing oxygen functionality. A second-generation fuel possesses no oxygen functionality, providing a more petroleum-like product with respect to elemental composition, and is oftentimes termed “renewable diesel.”
[0009] Both Natural Resources Canada and Fortum Oil (now known as Neste Oil) have described processes and methods for the conversion of renewable feedstocks to diesel fuel. Although these second-generation fuel processes remove oxygen functionality of the fuel, these hydrodeoxygenation processes do not control the amount of even- and odd-numbered hydrocarbon chains.
[0010] Canadian Patent 2,149,685 (Natural Resources Canada) describes the conversion of depitched tall oil to a diesel fuel additive. The patent describes a hydrodeoxygenation process utilizing a hydrotreating catalyst. The catalyst is activated by presulfiding. The sulfided nature of the catalyst may be maintained by adding sulfur to the tall oil feedstock at a level of 1000 ppm. The doping agent is carbon disulfide. The hydrodeoxygenation conversion is then performed at 410° C. and 1200 psi.

[0011] United States patent application 2007/0010682 (Neste Oil) describes the preparation of a diesel fuel from a vegetable TAG oil. The TAG oil is doped with 50 to 20,000 ppm sulfur. The hydrodeoxygenation step is performed between 580 psi and 725 psi and 305° C. and 360° C.

[0012] Accordingly, there is a need for a method of producing paraffinic hydrocarbons from a feedstock comprising TAGs without the need for presulfiding the hydrotreating catalyst or doping the feedstock with sulfur. In addition, there is a need for a hydrotreating process where the resulting hydrocarbon chain lengths are distributed similarly as in conventional petroleum-derived fuels.

SUMMARY

[0013] Herein disclosed is a method of producing a hydrocarbon product by hydrotreating a feedstock comprising TAG in the presence of a nonsulfided hydrotreating catalyst to produce a first product comprising hydrocarbons. The feedstock comprising TAG may be selected from the group consisting of yellow grease, brown grease, virgin TAG, and combinations thereof. The method may further comprise selecting a feedstock comprising a ratio of virgin TAG to used TAG such that the first product has a desired composition of hydrocarbons. Hydrotreating may provide a hydrocarbon product possessing both even- and odd-numbered carbon chains. Hydrotreating may comprise decarboxylation and decarboxylation reactions.

[0014] In applications, the nonsulfided hydrotreating catalyst comprises at least one metal selected from Groups VIII and VIIB of the Periodic Table. In embodiments, the hydrotreating catalyst comprises at least one metal selected from the group consisting of palladium (Pd), platinum (Pt), nickel (Ni), and combinations thereof. The hydrotreating catalyst may comprise nickel and molybdenum (Mo) or cobalt (Co) and molybdenum. The hydrotreating catalyst further comprises a support selected from alumina, silica, and combinations thereof. In embodiments, the feedstock is not doped with sulfur prior to hydrotreating.

[0015] Hydrotreating may be performed at a temperature in the range of from about 340° C. to about 400° C. and a pressure in the range of from about 100 psig to about 200 psig. The first product may comprise at least 50% normal alkanes. In applications, the first product comprises at least 70% normal alkanes. The first product may further comprise at least 10% normal alkanes.

[0016] The method may further comprise subjecting the first product to at least one process selected from isomerization, cyclization, and aromatization to produce a fuel selected from the group consisting of gasoline, kerosene, jet, and diesel fuels.

[0017] In some embodiments, hydrotreating is performed at a temperature in the range of from about 470° C. to about 530° C. and a pressure in the range of from about 750 psig to about 1000 psig. The first product may comprise primarily saturated and aromatic hydrocarbons. The first product may be suitable as a liquid transportation fuel with minimal or no secondary petroleum refining and processing operations. In embodiments, the first product further comprises olefinic hydrocarbons, and the ratio of the saturated hydrocarbons to the aromatic hydrocarbons to the olefinic hydrocarbons in the first product may be varied so as to produce feedstocks ideally suited for the production of at least one fuel selected from gasoline, kerosene, jet, and diesel fuels.
Also disclosed is a method of producing a transportation fuel, the method comprising: selecting an undoped feedstock comprising virgin TAG, used TAG, or a combination thereof; hydrotreating the undoped feedstock in the presence of an unsulfided hydrotreating catalyst to produce a first product; and subjecting the first product to at least one process selected from aromatization, cyclization, and isomerization, to produce a second hydrocarbon product selected from gasoline, kerosene, jet, and diesel fuels. The first product may comprise aromatic, saturated and olefinic hydrocarbons, and the composition of the feedstock may be selected such that the ratio of saturated to aromatic to olefinic hydrocarbons in the first product is suitable for the production of the second hydrocarbon product. Hydrotreating may be performed in the absence of sulfur injection into the process or the feedstock.

Notation and Nomenclature

The term “brown grease” comprises trap grease, sewage grease (e.g., from a sewage plant), and black grease. Brown grease from traps and sewage plants are typically unsuitable for use as animal feed. The term “brown grease” also encompasses other grease having a free fatty acid (FFA) content greater than 20% and being unsuitable for animal feed.

The term “yellow grease” comprises used frying oils from deep fryers and restaurant grease traps. It also encompasses lower-quality grades of tallow from rendering plants.

Fatty acids can be bound or attached to other molecules, such as in triglycerides or phospholipids. When they are not attached to other molecules, they are known as “free” fatty acids. The uncombined fatty acids or free fatty acids may come from the breakdown of a triglyceride into its components (fatty acids and glycerol). For example, a free fatty acid may break off through hydrolysis, for example, from steam cooking foods, salts, chemicals, heat, etc., work together to break chains off triglycerides. In the presence of a catalyst (e.g., acid), a free fatty acid may combine with a methanol to produce a molecule of biodiesel. The FAA in crude vegetable oils ranges from about 1% to about 4% (olive oil may comprise up to about 20%). The amount of FAA in yellow grease (e.g., recycled cooking oil) generally ranges from about 4% to about 15%. Brown grease (e.g., trap grease) may comprise a FFA composition of from about 50% to 100% of raw material.

Here the term “hydrotreatment” is used to refer to a catalytic process in which oxygen is removed from organic compounds as water (hydrodeoxygenation); sulfur from organic sulfur compounds as dihydrogen sulfide (hydrodesulfurization); nitrogen from organic nitrogen compounds as ammonia (hydrodenitrogenation); and halogens, for example, chlorine from organic chloride compounds as hydrochloric acid (hydrodechlorination).

The term “normal alkanes” is used to refer to n-paraffins or linear alkanes that do not contain side chains.

DETAILED DESCRIPTION

I. Overview

It is the purpose of this invention to describe a method and process by which renewable feedstocks can be converted to gasoline, kerosene, jet fuels, and diesel fractions. According to this disclosure, TAG feedstocks are converted to a product comprising paraffinic hydrocarbons without the need for presulfiding of a hydrotreating catalyst or the requirement of the feedstock being doped with sulfur. In embodiments, TAG feedstocks are converted to a product comprising paraffinic hydrocarbons whereby the hydrocarbon chain length distribution is controlled to provide a distribution that is similar to petroleum-derived fuels. Control of the process may be achieved by allowing for simultaneous decarbonylation and decarboxylation reactions. Key control parameters are the temperature, pressure, and the use of a nonsulfided hydrotreating catalyst. The nonsulfided hydrotreating catalyst allows for both the decarbonylation and decarboxylation reactions to run simultaneously over a range of conditions. The results show (vide infra) that TAG feedstock can be converted to a paraffinic product at lower temperatures and pressures than those described previously. The paraffinic product may further undergo isomerization, cyclization, and/or aromatization steps to provide distinct blendstocks. When skillfully blended, these distinct blendstocks can become drop-in compatible and fit-for-purpose gasoline, kerosene, jet fuels, or diesel fuels. These fuels have similar chemical composition as the hydrocarbons and are fully fungible with petroleum-derived fuels. That is, the fuels produced may be identical in virtually all respects to commercially available petroleum-derived fuels.

According to this disclosure, a feedstock comprising TAG is hydrotreated (hydrodeoxygenated). The TAG may be obtained from terrestrial or marine sources. The feedstock may comprise triacylglycerides derived from plants, triglycerides derived from animals, triglycerides derived from algae, or combinations thereof. The TAG feedstock may further comprise diacylglycerides, monoaoylglycerides, FFAs, and combinations thereof as contaminants. The TAG feedstock may comprise yellow grease, brown grease, or a combination thereof. The TAG feedstock may comprise a blend of fresh TAG and used TAG (i.e., yellow grease and/or brown grease). According to this disclosure, the feedstock is not doped with sulfur. The ratio of the virgin and used TAG and/or the composition of the TAG feedstock may be selected such that hydrotreating produces a desired hydrocarbon product slate.

The TAG feedstock is hydrotreated using a hydrotreating catalyst that is not presulfided. In the hydrotreating, TAG, fatty acids, and fatty acid derivatives in the TAG feedstock are deoxygenated, denitrogenated, and desulfurized. The hydrotreating catalyst may be any nonsulfided hydrotreating catalyst. In embodiments, the hydrotreating catalyst is a nonsulfided hydrogenation catalyst. The hydrotreating catalyst may contain one or more metals from Group VIII and VIIB of the Periodic Table of the Elements. The one or more metals may be selected from palladium (Pd), platinum (Pt), nickel (Ni), and combinations thereof. In embodiments, the catalyst is a NiMo catalyst comprising nickel and molybdenum. In embodiments, the catalyst is a CoMo catalyst comprising cobalt and molybdenum. The hydrotreating catalyst may comprise supported or unsupported metals. In embodiments, the catalyst comprises a support. In applications, the support comprises alumina, silica, or a combination thereof. The catalyst may be a supported NiMo or CoMo catalyst. In embodiments, NiMo/Al2O3, SiO2 or CoMo/Al2O3 catalyst is utilized.

II. Product Comprising Predominantly Normal Alkanes

In applications, a product comprising predominantly normal alkanes is produced. In such applications, the
Hydrotreating of the TAG feedstock is operated at modest temperatures and pressures (relative to referenced methods). In these embodiments, the temperature is in the range of from about 340° C. to 410° C. In embodiments, the temperature is in the range of from about 390° C. to 410° C. In embodiments, the temperature is about 400° C. Preferred pressures in such applications are in the range of from about 100 psig to 200 psig. In some embodiments, the pressure is in the range of from about 150 psig to about 200 psig. In embodiments, the temperature is about 400° C., and the pressure is about 200 psig. Suitable pressure is below that typically employed in processes utilizing sulfided hydrotreating catalysts.

0028 The paraffinic hydrocarbon product produced in this manner may comprise predominantly normal alkanes. The product may comprise more than about 50% normal alkanes, more than 60% normal alkanes, more than 70% normal alkanes, or about 75% normal alkanes. The product may further comprise normal alkenes. The product may comprise more than about 10% normal alkenes, more than 15% normal alkenes, more than about 20% normal alkenes, or about 10% normal alkenes. The paraffinic product may further comprise a trace of fatty acids. The product may comprise less than about 20% fatty acids, less than about 15% fatty acids, less than about 5% fatty acids, or less than or about 3% fatty acids. This desired outcome is achievable through the use of a non-sulfided hydrotreating catalyst, thus providing excellent conversion of TAG feedstock to paraffinic product. The paraffinic product is convertible to liquid transportation fuels by standard petroleum refining and processing methods. For example, the paraffinic product may further undergo isomerization, cyclization, and/or aromatization steps to provide distinct blendstocks from which desired transportation fuels may be obtained.

0029 This application offers advantages over prior art in that the very nature of the catalyst is different, thus potentially allowing the ability to operate at lower temperatures and/or pressures while achieving the same or superior outcome as prior art. This may offer economic advantages in large-scale production settings.

III. Product Comprising Saturated and Aromatic Hydrocarbons

0030 In another embodiment, higher pressures may be utilized in order to produce a product comprising aromatic hydrocarbons along with saturated hydrocarbons. The operating temperature for such embodiments may be in the range of from about 470° C. to 530° C. In embodiments, the temperature is in the range of from about 480° C. to 500° C. In embodiments, the temperature is about 480° C. The operating pressure may be in the range of from about 650 psig to about 1000 psig. In embodiments, the hydrotreating pressure may be in the range of from about 700 psig to 800 psig. In some applications, the pressure is about 750 psig. In some applications, the temperature is about 480° C., and the pressure is about 750 psig.

0031 In embodiments, the TAG feedstock is converted to a product comprising predominantly saturated hydrocarbons and aromatic hydrocarbons. The saturated/aromatic hydrocarbon product produced in this manner may comprise predominantly saturated hydrocarbons. The product may comprise more than about 60% saturated hydrocarbons, more than about 70% saturated hydrocarbons, or about 75% saturated hydrocarbons or about 77% saturated hydrocarbons. The saturated/aromatic hydrocarbon product may comprise more than about 10% aromatic hydrocarbons, more than about 20% aromatic hydrocarbons, more than about 30% aromatic hydrocarbons, or about 17% aromatic hydrocarbons. In embodiments, the saturated/aromatic product further comprises alkene hydrocarbons. The product may comprise less than about 20% normal alkenes, less than about 10% normal alkenes, or less than about 5% normal alkenes.

0032 The composition of the TAG feedstock may be selected such that the ratios of saturated hydrocarbons to aromatic hydrocarbons to olefinic hydrocarbons are ideally suited to the production of a desired fuel selected from gasoline, kerosene, jet fuels, and diesel fuels. For example, such a saturated/aromatic product may be useful in the production of jet fuel, with minimal secondary processing being required. Secondary processing may comprise standard petroleum refining and processing methods. The amount of aromatic hydrocarbon in the saturated/aromatic product may also be modulated by adjusting the temperature. It should be noted that these conditions offer a direct and economical path for the production of liquid transportation fuels, especially jet fuel, which require minimal secondary processing.

IV. Examples

Examples 1-9

Coconut Oil

0033 The apparatus for all experiments was a continuous-flow reactor comprising a pump system, a gas flow system, a high-pressure reactor vessel, a reactor heater and temperature regulation device, a product collection receptacle, and a pressure regulation device. Appropriate instrumentation and electronics were attached to the whole device to enable control and recording of experimental conditions. Samples of product were removed through the sample receptacle and analyzed with appropriate analytical instrumentation (i.e., gas chromatography mass spectrometry [GC-MS]). Hydrogen was supplied to the reactor system from purchased cylinders. TAG material was supplied to the reactor system via a high-pressure pumping system. In the first series of examples, 1.12 kg of a nonsulfided hydrotreating catalyst was charged to the reactor chamber. The chamber possessed a length-to-diameter ratio of 6. The catalyst was activated by warming to greater than 300° C. while a flow of hydrogen gas was passed over the catalyst. The moisture content of the exiting gas was measured. The activation was judged complete when the water content of the exiting gas decreased.

Example 1

0034 Coconut oil was supplied to the reactor at a rate of 1 pound/hour. Hydrogen was supplied at a rate of 20 standard cubic feet per hour (scfh). The reactor was maintained at 340° C. The hydrogen pressure was regulated to 80 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 2

0035 Coconut oil was supplied to the reactor at a rate of 1 pound/hour. Hydrogen was supplied at a rate of 20 scfh. The reactor was maintained at 350° C. The hydrogen pressure was regulated to 100 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.
Example 3

[0036] Coconut oil was supplied to the reactor at a rate of 2 pounds/hour.

[0037] Hydrogen was supplied at a rate of 40 scfh. The reactor was maintained at 350° C. The hydrogen pressure was regulated to 100 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 4

[0038] Coconut oil was supplied to the reactor at a rate of 1 pound/hour. Hydrogen was supplied at a rate of 20 scfh. The reactor was maintained at 350° C. The hydrogen pressure was regulated to 200 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 5

[0039] Coconut oil was supplied to the reactor at a rate of 2 pounds/hour.

[0040] Hydrogen was supplied at a rate of 40 scfh. The reactor was maintained at 350° C. The hydrogen pressure was regulated to 200 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 6

[0041] Coconut oil was supplied to the reactor at a rate of 1 pound/hour. Hydrogen was supplied at a rate of 20 scfh. The reactor was maintained at 400° C. The hydrogen pressure was regulated to 100 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 7

[0042] Coconut oil was supplied to the reactor at a rate of 2 pounds/hour. Hydrogen was supplied at a rate of 40 scfh. The reactor was maintained at 400° C. The hydrogen pressure was regulated to 100 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 8

[0043] Coconut oil was supplied to the reactor at a rate of 1 pound/hour.

[0044] Hydrogen was supplied at a rate of 20 scfh. The reactor was maintained at 400° C. The hydrogen pressure was regulated to 200 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

Example 9

[0045] Canola oil was supplied to the reactor at a rate of 1 pound/hour. Hydrogen was supplied at a rate of 50 scfh. The reactor was maintained at 400° C. The hydrogen pressure was regulated to 200 psi. The temperature and flow conditions were maintained for 3 hours once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 1.

TABLE 1

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<th>Example</th>
<th>Oil Flow, lb/hr</th>
<th>Temp., °C</th>
<th>Pressure, psig</th>
<th>H₂ Flow, scfh</th>
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<th>Olefinic Hydrocarbons, %</th>
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Examples 10-17

Yellow Grease

[0046] For the second series of experiments, a smaller reactor system was utilized. The reactor tube possessed a length-to-diameter ratio of about 40. The tube was loaded with a total of about 70 grams of catalyst for the experiments listed below. The feedstock for this series of examples was waste TAG (yellow grease) obtained from a French fry factory. The yellow grease possessed a significant (2.6%) FFA content.

Example 10

[0047] Yellow grease was supplied to the reactor at a rate of 1 milliliter/minute (mL/min). Hydrogen was supplied at a rate of 1064 standard cubic centimeters/minute (scm). The reactor was maintained at 474° C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

[0048] A mixture of hydrodeoxygenation, decarboxylation, and decarbonylation reactions occur simultaneously during the conversion of TAG to hydrocarbon product. The
The simultaneous production of both even and odd carbon chains of varying lengths serves to facilitate the ultimate production of a petroleum-like final fuel product (i.e. gasoline, kerosene, jet fuel, or diesel).

Example 11

Yellow grease was supplied to the reactor at a rate of 1 mL/min. Hydrogen was supplied at a rate of 1050 sccm. The reactor was maintained at 480°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

Example 12

Yellow grease was supplied to the reactor at a rate of 1 mL/min. Hydrogen was supplied at a rate of 1050 sccm. The reactor was maintained at 490°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

Example 13

Yellow grease was supplied to the reactor at a rate of 1 mL/min. Hydrogen was supplied at a rate of 1050 sccm. The reactor was maintained at 502°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

Example 14

Yellow grease was supplied to the reactor at a rate of 1 mL/min. Hydrogen was supplied at a rate of 1050 sccm. The reactor was maintained at 530°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

Example 15

Yellow grease was supplied to the reactor at a rate of 1.5 mL/min. Hydrogen was supplied at a rate of 1050 sccm. The reactor was maintained at 498°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

Example 16

Yellow grease was supplied to the reactor at a rate of 4.5 mL/min. Hydrogen was supplied at a rate of 1066 sccm. The reactor was maintained at 482°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

Example 17

Yellow grease was supplied to the reactor at a rate of 4.5 mL/min. Hydrogen was supplied at a rate of 1088 sccm. The reactor was maintained at 487°C. The hydrogen pressure was regulated to 750 psi. The temperature and flow conditions were maintained for 30 minutes once steady-state conditions were achieved. The product was collected and analyzed. Results are shown in Table 2.

<table>
<thead>
<tr>
<th>Example</th>
<th>Oil Flow, mL/min</th>
<th>Temp., °C</th>
<th>Pressure, psig</th>
<th>H₂ Flow, sccm</th>
<th>Saturated Hydrocarbon</th>
<th>Aromatic Hydrocarbon</th>
<th>Olefinic Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>474</td>
<td>750</td>
<td>1064</td>
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<td>0%</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>480</td>
<td>750</td>
<td>1050</td>
<td>64%</td>
<td>32%</td>
<td>1%</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>490</td>
<td>750</td>
<td>1050</td>
<td>56%</td>
<td>32%</td>
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<td>750</td>
<td>1050</td>
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<td>2%</td>
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<td>14</td>
<td>1</td>
<td>510</td>
<td>750</td>
<td>1050</td>
<td>57%</td>
<td>60%</td>
<td>1%</td>
</tr>
<tr>
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<td>498</td>
<td>750</td>
<td>1050</td>
<td>91%</td>
<td>7%</td>
<td>2%</td>
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<tr>
<td>16</td>
<td>4.5</td>
<td>482</td>
<td>750</td>
<td>1066</td>
<td>63%</td>
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<td>750</td>
<td>1088</td>
<td>62%</td>
<td>13%</td>
<td>23%</td>
</tr>
</tbody>
</table>

Example 18

Product Fuels

Hydrocarbon product obtained from process conditions such as those described in Tables 1 and 2 was subjected to petroleum-refining operations, including isomerization, aromatization, hydrogenation, and distillation under conditions known to those skilled in the art, such that a fuel was...
produced that complied with the military specification for JP-8 (MIL-DTL-83133E). The fuel possessed a flash point of 49°C, a freeze point of ±52°C, and an energy density of 42.9 MJ/kg. Furthermore, the fuel complied with all aspects of MIL-DTL-83133E, including physical density, distillation (D-86), etc.

[0058] The processing of TAG, either virgin or waste, according to the examples above, provides a fuel possessing properties consistent with drop-in compatibility and fit-for-purpose usage, according to either MIL-DTL-83133E or MIL-DTL-83133F.

[0059] While preferred embodiments of the invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the disclosure. The embodiments described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from 1 to about 10 includes 2, 3, 4, etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term “optionally” with respect to any element of a claim is intended to mean that the subject element is required or, alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc., should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0060] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the preferred embodiments of the present invention. The discussion of a reference is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent they provide exemplary, procedural, or other details supplementary to those set forth herein.

REFERENCES


What is claimed is:

1. A method of producing a hydrocarbon product, the method comprising:
   - hydrotreating a feedstock comprising TAG in the presence of a nonsulfided hydrotreating catalyst to produce a first product comprising hydrocarbons.
   - The method of claim 1 wherein the feedstock comprising TAG is selected from the group consisting of yellow grease, brown grease, virgin TAG, and combinations thereof.
   - The method of claim 2 further comprising selecting a feedstock comprising a ratio of virgin TAG to used TAG such that the first product has a desired composition of hydrocarbons.
   - The method of claim 1 wherein hydrotreating provides a hydrocarbon product possessing both even- and odd-numbered carbon chains.
   - The method of claim 4 wherein hydrotreating comprises decarboxylation and decarboxylation reactions.
   - The method of claim 1 wherein the nonsulfided hydrotreating catalyst comprises at least one metal selected from Groups VIII and VIIB of the Periodic Table.
   - The method of claim 6 wherein the hydrotreating catalyst comprises at least one metal selected from the group consisting of palladium (Pd), platinum (Pt), nickel (Ni), and combinations thereof.
   - The method of claim 7 wherein the hydrotreating catalyst comprises nickel and molybdenum or cobalt and molybdenum.
   - The method of claim 6 wherein the hydrotreating catalyst further comprises a support selected from alumina, silica, and combinations thereof.
   - The method of claim 1 wherein the feedstock is not doped with sulfur prior to hydrotreating.
   - The method of claim 1 wherein hydrotreating is performed at a temperature in the range of from about 340°C to about 400°C and a pressure in the range of from about 100 psig to about 200 psig.
   - The method of claim 11 wherein the first product comprises at least 50% normal alkanes.
   - The method of claim 12 wherein the first product comprises at least 70% normal alkanes.
   - The method of claim 12 wherein the first product further comprises at least 10% normal alkenes.
   - The method of claim 11 further comprising subjecting the first product to at least one process selected from isomerization, cyclization, and aromatization to produce a fuel selected from the group consisting of gasoline, kerosene, jet fuels, and diesel fuels.
   - The method of claim 1 wherein hydrotreating is performed at a temperature in the range of from about 470°C to about 530°C and a pressure in the range of from about 750 psig to about 1000 psig.
17. The method of claim 16 wherein the first product comprises primarily saturated and aromatic hydrocarbons.

18. The method of claim 17 wherein the first product is suitable as a liquid transportation fuel with minimal or no secondary petroleum refining and processing operations.

19. The method of claim 17 wherein the first product further comprises olefinic hydrocarbons, and wherein the ratio of the saturated hydrocarbons to the aromatic hydrocarbons to the olefinic hydrocarbons in the first product may be varied so as to produce feedstocks ideally suited for the production of at least one fuel selected from gasoline, kerosene, jet fuel, and diesel fuels.

20. A method of producing a transportation fuel, the method comprising:
   selecting an undoped feedstock comprising virgin TAG, used TAG, or a combination thereof; hydrotreating the undoped feedstock in the presence of an unsulfided hydrotreating catalyst to produce a first product; and
   subjecting the first product to at least one process selected from aromatization, cyclization, and isomerization, to produce a second hydrocarbon product selected from gasoline, kerosene, jet fuel, and diesel fuels.

21. The method of claim 20 wherein the first product comprises aromatic, saturated and olefinic hydrocarbons and wherein the composition of the feedstock is selected such that the ratio of saturated to aromatic to olefinic hydrocarbons in the first product is suitable for the production of the second hydrocarbon product.

22. The method of claim 20 wherein the hydrotreating is performed in the absence of sulfur injection into the process or the feedstock.
Annexure 14

(12) United States Patent
Parnas et al.

(10) Patent No.: US 7,544,830 B2
(45) Date of Patent: Jun. 9, 2009

(54) METHODS AND SYSTEMS FOR ALKYL ESTER PRODUCTION

(75) Inventors: Richard Parnas, West Hartford, CT (US); Clifford Weed, Killingworth, CT (US); Nicholas Leadbeater, Southington, CT (US); Matthew Boucher, Cromwell, CT (US)

(73) Assignee: The University of Connecticut, Farmington, CT (US)

(* ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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C07C 67/02 (2006.01)
C07C 67/03 (2006.01)

(52) U.S. Cl. ............................... 560/217, 560/234

(58) Field of Classification Search ....................... None
See application file for complete search history.

(56) References Cited
U.S. PATENT DOCUMENTS
5,354,878 A 10/1994 Connemann et al.

FOREIGN PATENT DOCUMENTS
AT 405938 B 12/1999
DE 20113126 U1 1/2002
DE 10135297 A1 2/2003
DE 1013422 A1 2/2003

OTHER PUBLICATIONS

(Continued)

(57) ABSTRACT

In one embodiment, the method comprises: combining liquid biomass with an alcohol to form a combined liquid stream, introducing the combined liquid stream to a first transesterification reactor between a liquid glycerol outlet and a liquid alkyl ester outlet, reacting the liquid biomass and the alcohol to form liquid glycerol and liquid alkyl ester, and removing a liquid alkyl ester stream from an upper portion of the first transesterification reactor. The combined liquid stream flows upward through the reactor at a rate that is less than a settling velocity of the liquid glycerol.

20 Claims, 2 Drawing Sheets
FOREIGN PATENT DOCUMENTS

EP 0131991 A1 1/1985
WO 03015913 A1 2/2003
WO 2008052308 A1 5/2005

OTHER PUBLICATIONS

Austrian Patent No. 405938B; Publication Date: Dec. 27, 1999; Abstract Only; 1 page.
German Patent No. 10135297; Publication Date: Feb. 6, 2003; Abstract Only; 2 pages.
German Patent No. 10139422; Publication Date: Feb. 27, 2003; Abstract Only; 1 page.
German Patent No. 10138822; Publication Date: Mar. 6, 2003; Abstract Only; 1 page (Equivalent to German Patent No. 20113126U1).
European Patent No. 0131991; Publication Date: Jan. 23, 1985; Abstract Only; 1 page.
International Patent Application No. 03/015913 A1; Publication Date: Feb. 27, 2003; Abstract Only; 2 pages.


* cited by examiner
Fig. 1
1
METHODS AND SYSTEMS FOR ALKYL ESTER PRODUCTION
CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the filing date of U.S. Provisional Application Ser. No. 60/884,273 filed Jan. 10, 2007; the entire contents of which are hereby incorporated by reference.

TECHNICAL FIELD

This application relates to alkyl ester production, and especially relates to the continuous reaction/separation in the production of alkyl ester.

BACKGROUND

One potential solution to mitigate environmental and macroeconomic displacements is the use of energy derived from locally produced biomass. Two particular such bio-fuels are ethanol and biodiesel. While ethanol has garnered more attention due to a longer track record and the activities in Brazil, biodiesel is actually a higher energy fuel with greater environmental benefits. Typically biodiesel is produced by transesterification of triglycerides with methanol.

Most of the production of biodiesel fuel is carried out in batch reactors, where measured quantities of the triglycerides, methanol, and catalyst are added to a tank, heated, and mixed for a period of time ranging from 1 hour to several hours. After a period of time, the reacted mixture is pumped to another vessel and allowed to sit, quiescent for a second period of time. The mixture then phase separates into a biodiesel layer and a glycerol layer, and the glycerol layer is drained. The resulting biodiesel is then further purified.

In some currently used processes, continuous centrifuge technology is used to separate glycerol, and carry out the water washing steps to remove residual alcohol from the biodiesel product. Also, current patent applications include flash separation of methanol from the biodiesel as an alternative method to the water-washing step. Some current processes apply distillation methods to separate the biodiesel from the glycerol byproduct based on their volatility differences. In one current process, biodiesel separation from glycerol is claimed to occur in a reactor where the feed is introduced at the top and an impure biodiesel stream and an impure glycerol stream are both withdrawn near the bottom.

In prior art process, both desired product biodiesel and byproduct glycerol are withdrawn near the bottom of the reactor as liquid streams. The proximity of the withdrawal points for these two product streams implies there will be significant mixing and cross-contamination. This assertion is born out by the presence of many downstream separators and complicated processing required to further purify the products. In this process, the concentration of both products, biodiesel and glycerol, increases towards the bottom of the reactor, thereby hindering the conversion process.

The processes based on reactive distillation produce high purity glycerol and high purity biodiesel with small amounts of residual methanol. However, these processes are energy intensive due to the necessity of providing large quantities of heat to boil the bottoms product and produce the vapor stream for the distillation column. Distillation processes separate materials having different volatility by successively vaporizing higher and higher purity streams of the more volatile material and successively condensing higher and higher purity streams of the less volatile material. This process depends on the equilibrium between vapors and liquids, and is driven by the heat input necessary to boil the material.

Although these processes successfully produce biodiesel fuel, more efficient, economical processes are continuously sought.

BRIEF DESCRIPTION

This disclosure is directed to methods and systems for processing alkyl esters.

In one embodiment, the method comprises: combining liquid biomass with an alcohol to form a combined liquid stream, introducing the combined liquid stream to a first transesterification reactor between a liquid glycerol outlet and a liquid alkyl ester outlet, reacting the liquid biomass and the alcohol to form liquid glycerol and liquid alkyl ester, and removing a liquid alkyl ester stream from an upper portion of the first transesterification reactor. The combined liquid stream flows upward through the reactor at a rate that is less than a settling velocity of the liquid glycerol.

In another embodiment the method comprises: combining liquid biomass with an alcohol to form a combined liquid stream, introducing the combined liquid stream to a first transesterification reactor at a point in a lower 25% of the reactor, between a liquid glycerol outlet and a liquid alkyl ester outlet, reacting the liquid biomass and the alcohol to form liquid glycerol and liquid alkyl ester, removing the liquid alkyl ester stream from the first transesterification reactor, removing the liquid glycerol from the first transesterification reactor, and purifying the liquid alkyl ester stream. The combined liquid stream has a laminar flow. Greater than or equal to about 75 mass % of the liquid glycerol settles towards a bottom of the first transesterification reactor.

In one embodiment, an alkyl ester production system can comprise: a first transesterification reactor comprising a liquid biomass inlet located between a liquid glycerol outlet and a liquid alkyl ester outlet, a water wash vessel comprising an alkyl ester inlet, a water inlet located near a top of the water wash vessel, and a washed alkyl ester outlet located near the top of the water wash vessel, wherein the alkyl ester inlet is located near a bottom of the water wash vessel, and a drier comprising a washed alkyl ester inlet located near a top of the drier, a gas inlet located near a bottom of the drier, and a dried alkyl ester outlet located near the bottom of the drier. The liquid biomass inlet can be in fluid communication with a liquid biomass source and a liquid alcohol source. The first transesterification reactor can be configured for laminar flow and for liquid reactants and products. The alkyl ester outlet can be in fluid communication with the washed alkyl ester outlet.

The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWING

Referring to the figures, which are merely exemplary, not limiting, and wherein like numbers are numbered alike.

FIG. 1 is a graphical illustration of the upward flow speed of the lower density oil phase versus diameter of equivalent sphere of high density phase.

FIG. 2 is a schematic representation of one embodiment of a biodiesel production system.

DETAILED DESCRIPTION

Disclosed herein is a continuous method of producing biodiesel fuel that simultaneously creates the biodiesel prod-
product and separates it from byproduct glycerol. The method achieves separation of reaction products biodiesel and glycerol by buoyancy driven phase separation; the biodiesel flowing upward and the glycerol settling downward. As the reacting stream flows upward, the biodiesel and glycerol are created, they phase separate due to immiscibility, and the heavier glycerol settles if the upward flow speed is less than the settling velocity of the glycerol. The reaction and separation occur in one single vessel, and the reaction and separation occur continuously so that the separated biodiesel and glycerol products continue to emerge from the vessel as long as reactants are fed into the vessel.

The current method constitutes a lower energy consumption process than the reactive distillation process discussed above. Advantageously, the buoyancy driven separation of the present method can be used for all the separation steps, including the washing and moisture removal steps. The reactor/separater for the current process is designed and operated differently than in the reactive distillation process. First, the current process contains only liquid streams, whereas the reactive distillation system contains both liquid and vapor streams. The current process does not require the high energy inputs necessary to generate vapor streams and the reactor/separater does not need the stages and packings associated with the turbulent multi-phase flows used in reactive distillation processes.

Multiple vessels can be concatenated to form a continuous system to achieve conversion of reactants (e.g., complete conversion (i.e., greater than or equal to 99.5 mass percent (mass %) conversion)), separation of glycerol (e.g., nearly complete separation (i.e., removal of greater than or equal to 98 mass % of the glycerol from the biodiesel product)), biodiesel washing to remove residual alcohol, glycerol, and catalyst, and moisture removal from the biodiesel product stream. The units for achieving reaction, separation, washing, and drying can be arranged in a number of configurations including recycle, parallel processing, and hybrid serial/parallel processing to achieve optimal results for a wide variety of feed stocks. This type of reactor/separater can be applied to any chemical system where the reaction products separate into phases of different densities, and especially in the case of reversible reactions.

In the present process, the reacting mixture flows upwards and the glycerol settles downwards. This is significantly different in design and operation than processes where both the biodiesel and glycerol streams are removed from the bottom of the reactor. In the present process, there is little or no cross contamination of the two product streams, biodiesel and glycerol, and they are collected and withdrawn from the reactor at widely separated locations. Hence, subsequent purification is much easier and economical. Furthermore, removing glycerol as the reaction proceeds enhances conversion in the transesterification process. In the present process there is a glycerol concentration gradient in the reacting stream because the glycerol settles downwards, leaving very little glycerol in the upper portion of the reactor. Consequently, conversion is enhanced in the upper portion of the reactor.

The glycerol settles down through the biodiesel and oil mixture with a velocity that depends upon the droplet size of the glycerol. For example, the settling velocity of 5 mm diameter glycerol droplets in biodiesel can be roughly 3 centimeters per second (cm/s). Smaller droplets settle at lower velocities while larger droplets settle at higher velocities. Moreover, as the reaction proceeds and creates glycerol, the molecules of glycerol created aggregate and form droplets that grow, e.g., by coarsening mechanisms. These coarsening glycerol droplets settle out of the reacting mixture, even as the reacting mixture flows upwards, as long as the upward fluid velocity is less than the settling velocity for easily attained glycerol droplet sizes. This continuous flow and settling mechanism also works better if the flow is smooth and laminar, rather than turbulent and mixed. Laminar flow is defined as flow where fluid follows via smooth pathways, does not eddy, and has a Reynolds’s number, Re, less than or equal to 2,100. Once the glycerol produced in the reaction grows to droplets of a size of more than a few micrometers (μm), they settle downwards if the upward flow speed of the oil phase (biomass) is not too large.

Equation I provides a design basis for the reactor.

\[ v_s = v_r - \frac{(\rho_b - \rho_d)gd^2}{18\mu} \]

where: \( v_s \) = settling speed of the high density glycerol phase (centimeters per second (cm/s)), 
\( v_r \) = upward flow speed of the lower density oil phase (cm/s), 
\( \rho_b \) = density of higher density phase (grams per cubic centimeter (g/cc)), 
\( \rho_d \) = density of lower density phase (g/cc), 
\( g \) = gravitational acceleration (cm/s^2), 
\( d \) = diameter of equivalent sphere of high density phase (cm), and 
\( \mu \) = viscosity of lower density phase (g/cm/s).

If \( v_s \geq 0 \), then \( v_s \) can be plotted against the droplet size d. FIG. 1 illustrates the equation for the particular case of glycerol settling through biodiesel fluid. If the fluid rise velocity, \( v_r \), is set, FIG. 1 indicates the droplet size above which settling will occur. This approach is applicable for strongly separating phases like glycerol and methyl ester biodiesel, where the droplets grow to sizes larger than 0.1 cm within a few seconds. Thus, fluid rise velocities up to a few millimeters per second (mm/s) are permissible. This technique can also be used for weakly phase separated mixtures, such as glycerol in ethyl ester biodiesel. In such cases, experimental techniques such as light scattering can be used to ascertain the droplet sizes attained in a reasonable time, and then the acceptable fluid rise velocity can be determined off the graph.

For the biodiesel production, the reactor/separater(s) can be placed in a series, one after the other. In between each vessel, a mixture and reactant addition port can be placed to allow for a stage wise reaction/separation process that can be optimized to maximize biodiesel production and separation efficiencies at the same time. Thus, high conversion efficiencies can be readily attained without the addition of excess alcohol in the first stage to force the high conversion. As a result, high levels of alcohol contamination of the glycerol byproduct are avoided, and minimal alcohol in the biodiesel product is attained. This enables economical production; minimizing alcohol loss, alcohol reclamation costs, and biodiesel cleanup costs. For example, the reactors can use less than or equal to 10% over the stoichiometric amount of methanol for the conversion to biodiesel (i.e., balanced stoichiometry for the transesterification reaction to produce the biodiesel), with substantially below 10% believed possible (e.g., less than or equal to 5% over the stoichiometric amount).
The continuous separation during flow can also be applied to the wash step(s) (e.g., water wash step(s)) and the drying step(s) (e.g., air-drying step(s)). Since the amount of alcohol introduced to the transesterification reactor(s) is a substantially stoichiometric amount, no additional reaction is intended to occur in the wash and air-drying steps (i.e., any reactions are residual reactions from the remaining reactants and are not induced by the addition of new reactants). It is noted that any reaction that does occur is a result of residual reactants from the transesterification reactions and not from the addition of reactants to the water wash vessel or drier. In other words, no alcohol or reacting stream are introduced to the wash steps and the drying steps. In the water wash case, water can be added at the top of the flow vessel by a distribution medium. The water then settles through the biodiesel product at a settling velocity also determined by droplet size, and is collected at the bottom of the vessel. The collected water contains excess alcohol and catalyst. In the air-drying step, air dispersed into the flowing biodiesel rises to the top of the vessel more quickly than the biodiesel due to buoyancy. The residual water is removed with the air from the biodiesel.

The entire integrated process can be a staged set of flow vessels that produce biodiesel continuously. The process is scalable since a wide range of production rates can be achieved by simply selecting the appropriate flow vessel diameter, noting that the flow increases as the square of the diameter if the flow velocity is held constant.

The present process can be employed to produce lower alkyl esters (e.g., C₁ to C₄) from a biomass source such as triglycerides (e.g., higher fatty acid triglycerides (C₁₂-C₂₄ or so)), natural oils (and/or natural fats) comprising free fatty acids, and combinations comprising at least one of the foregoing biomass. Possible biomass sources include oils (e.g., vegetable oil, sunflower seed oil, soybean oil, corn oil, cottonseed oil, almond oil, groundnut oil, palm oil, coconut oil, linseed oil, castor oil, rapeseed oil, industry tallow, abattoir waste, including used oils (such as used (e.g., waste) cooking oils from restaurants), and the like), and combinations comprising at least one of the foregoing biomass.

The biomass source is combined with alcohol and optionally with a catalyst (e.g., with a catalyzed alcohol), to form the reacting stream. Generally, the alcohol can be a C₁-C₄ alcohol(s), such as methanol, ethanol, isopropanol, butanol, multivalent alcohol(s) (such as trimethylolpropane), as well as combinations comprising at least one of the foregoing alcohols. The alcohol can optionally be combined with a transesterification catalyst, e.g., an alkaline catalyst, acid catalyst, and so forth. Possible transesterification catalysts include: metal alkoxyalates, metal hydrides, metal carbonates, metal acetates, sodium alkoxide, sodium hydroxide, potassium hydroxide.

Referring to FIG. 2, an exemplary embodiment of a biodiesel system is illustrated. In this system, the alcohol stream (that is optionally catalyzed) can be combined with the biomass stream using, for example, a static mixer to form a combined stream (e.g., the reacting stream). Although the process can proceed at room temperature, optionally, the biomass stream 4 and/or the combined stream 6 can be heated, e.g., to a temperature of less than or equal to about 65°C. The combined stream 6 can then be introduced to the transesterification reactor 8. The combined stream is introduced to the transesterification reactor 8 between the outlet for the initial biodiesel stream (e.g., the liquid alkyl ester stream) 10 and the outlet for the glycerol stream 12. For example, the combined stream 6 can be introduced to a bottom portion of the transesterification reactor 8, above where a glycerol stream 12 will be removed from the reactor 8. For example, the combined stream can be introduced within the bottom 75% of the reactor so as to flow upwards. In order to attain sufficient residence time and hence biodiesel production, introduction is generally at or below the mid-point of the reactor, or, more specifically, within the lower 25% of the reactor, and above the glycerol removal point. In order to attain the desired separation of the biodiesel, glycerol, and reactants (catalyst, alcohol, and biomass), the flow through reactor 8 is preferably laminar and at a controlled velocity that enables the glycerol to fall to the bottom of the reactor as remaining reactants and biodiesel flow to the top of the reactor.

Once the system is at steady state, as the combined stream 6 flows into transesterification reactor 8, an initial biodiesel stream 10 can be removed from at or near the top of the reactor (e.g., within 10% distance from the top of the reactor), while glycerol stream 12 can be removed from the reactor at a point below where the combined stream 6 enters the transesterification reactor 8 (e.g., at the bottom of the reactor). Since the glycerol stream 12 is removed from the reactor at a point below the introduction point of the combined stream, as the reaction proceeds the reaction equilibrium shifts, driving the reaction to additional conversion to biodiesel and glycerol.

To further enhance the conversion efficiency, the initial biodiesel stream 10 can optionally be combined with an additional catalyzed alcohol stream 14, e.g., via a static mixer, such that a combined stream 16 can be introduced into another transesterification reactor(s) 18, e.g., in the same fashion as introduced to the first transesterification reactor 8 (at a point above where glycerol will be removed from the reactor 18). With the combination of the two transesterification reactors, a virtually 100% conversion efficiency can be attained. As with the transesterification reactor 8, the flow through the transesterification reactor 18 is controlled to allow the settling of the glycerol and the removal of biodiesel and remaining reactants from at or near the top of the reactor 18. Optionally, a portion of the biodiesel stream exiting the transesterification reactor 18 can be recycled in recycle stream 22 to transesterification reactor 8 and/or transesterification reactor 18, while glycerol can be removed from transesterification reactor 18 in glycerol stream 24. The remainder of the biodiesel product stream 20 can optionally be further processed, e.g., passed through additional transesterification reactor(s), washed, and/or dried.

The washing step can be performed in a water wash vessel 28 where the biodiesel product stream 20 enters the bottom of water wash vessel 28, while water is introduced near the top. As the water is dispersed through the biodiesel, it removes excess alcohol and catalyst therefrom to produce a water wash that exits the bottom of the vessel 28 as water wash stream 30. Within this vessel, catalyst and alcohol migrate to the water droplets out of the biodiesel stream. The washed biodiesel stream 32 exiting vessel 28 can then be introduced to the top of a drier 34. Air 36 introduced to the bottom of the drier 34 passes through the washed biodiesel in a countercurrent fashion to remove residual water therefrom. The air stream 38 can then be removed from the top of the drier 34, while the dried biodiesel 40 can be removed from the bottom. It is understood that the various streams can be processed and recycled in various fashions to enhance efficiency and viability of the process. For example, water can be condensed from the air stream 38 to form a dry air stream and a water stream that can be used in the drier 34 and water wash vessel 28, respectively. Furthermore, the alcohol can be recovered (e.g., using a flash reactor) and recycled.
For example, a system comprising 1 reactor, 1 wash, and 1 drier, when operated properly (i.e., in accordance with the present disclosure) will produce ASTM quality biodiesel. ASTM quality biodiesel requires greater than 99 mass % conversion and greater than 99.8 mass % glycerol removal. Although some other systems may claim ASTM quality processing, the National Biodiesel Board estimates that, in 2006, more than half of all biodiesel produced in the USA was not ASTM grade.

The following examples are merely exemplary and are intended to further explain and not to limit the process and system disclosed herein.

EXAMPLES

The basic process configuration with a single reactor/separator was realized for Examples 1 and 2 in a separate funnel, where the valve outlet at the bottom of the funnel was used to draw off the glycerol as it settled out of the reacting mixture. The prototype reactor, a separator funnel, was fitted with a 2-hole stopper at the top to support the tubes for reactant introduction and biodiesel product stream removal. The tube introducing the stream of premixed reactants was inserted such that the reactant stream entered the reactor towards the bottom of the reactor. The tube providing an exit for the biodiesel product stream was inserted such that the biodiesel product stream was withdrawn from the top of the reactor.

Although the reactor could be run using vegetable oil combined with any of several alcohols and catalysts, in these experiments (Examples 1-3) the oil used was soy oil. It was mixed with a stream of methanol already containing dissolved potassium hydroxide.

Example 1

1:6 volumetric ratio of methoxide (1.5% (w/w) potassium hydroxide to oil) in methanol to oil was continuously fed to the reactor for 45 minutes at a flow of 1.1 milliliters per second (ml/s). During this time 400 milliliters (ml) of glycerol was collected from the bottom of the reactor and 1,600 ml of biodiesel product was collected from the top of the reactor. These products were analyzed by gas chromatography and nuclear magnetic resonance. The results showed that during the 15 minute residence time in the reactor/separator, 89 mass percent (mass %) of the vegetable oil was converted to biodiesel (all that was possible due to a limiting amount of methoxide).

Example 2

In the second experiment, a 1:2 volumetric ratio of methoxide to oil was continuously fed to the reactor for 40 minutes at a flow of 2.5 ml/s. During the 6.7 minute residence time, 95.5 mass % of the vegetable oil was converted to biodiesel.

Example 3

A larger prototype reactor was constructed to validate the design concept at a scale similar to commercial production. The reactor that was 4 feet (1.2 meters (m)) long and 6 inches (0.15 m) in diameter was run for a period of 16 hours. During this time period, 230 gallons (871 liters (l)) of waste vegetable oil was converted to 230 gallons (871 l) of ASTM quality biodiesel fuel. The process comprised heating the oil to 120°C (248°F) and mixing it with room temperature methoxide prior to injection into the reactor at a 1:3 to 1:4 volumetric ratio of methoxide to oil at a flow rate of 18.9 liters per hour (l/h) (5 gallons per hour (gph/l)) of 775.7 l/h (20 gal/h).

The chemical conversion of the vegetable oil was checked several times during the 16 hour period by both gas chromatography and nuclear magnetic resonance, and conversion in excess of 99 mass % was maintained over this time period. The resultant stream had a purity of about 97 mass % without further processing. After a single water wash and a single air-drier, the purity of the stream was greater than 99.5 mass %.

The simultaneous separation of glycerol was checked by centrifuging samples leaving the top of the reactor. Well over 95 mass % of the liquid glycerol produced in the reaction settled to the bottom of the reactor for removal as a separate byproduct stream. In other words, less than 5 mass % of the liquid glycerol was removed with the biodiesel. This degree of glycerol removal from the biodiesel stream renders a glycerol separator unnecessary, as the small amount of residual glycerol in the biodiesel stream is further reduced by normal downstream operations. In other words, where other biodiesel forming processes require a special separator as well as a wash and dry step to remove the glycerol, the present process can attain substantially complete glycerol removal with only the wash and drying stages; i.e., with no special (separate) glycerol separation.

Based upon the above examples, it is clear that, using the present counter-current flow process where the reactants flow upward through the reactor and the glycerol settles downward, in a single commercial scale reactor, at least 99 mass % conversion of vegetable oil to biodiesel can be attained and at least 95 mass % of the glycerol can be removed as a separate byproduct stream in the single reactor.

The present process offers numerous advantages including: (i) improved economics (smaller size and simpler operation compared to batch processes, and lower energy consumption in the process compared to continuous processes; e.g., lower temperatures; (ii) facile scalability; (iii) continuous operation (e.g., of a laminar flow, unmixed reactor); (iv) continuous separation of byproduct stream by settling from a flowing stream of reactants; (v) continuous separation of excess reactant and catalyst by washing the flowing product stream; and/or (vi) continuous removal of residual water by countercurrent air bubbling. The reactants and products are and remain in the liquid form throughout the transesterification reactors. The laminar flow within these reactor(s) and flow rate allow the liquid glycerol to settle down through the reactor without the need for a distillation process.

In prior art continuous processes, the reactors require much higher energy input to generate productivity similar to that attained herein and often require additional units to separate glycerol. In some cases, these continuous processes heat a bottom stream to well over 250°F (121.1°C) to separate volatile biodiesel and methanol from glycerol (the reactive distillation processes). These processes must also remove heat at the top of the column to condense the biodiesel stream, and this refrigeration process also consumes lots of energy. In other cases, these continuous processes use various high energy separation devices such as continuous centrifuge to facilitate glycerol and biodiesel separation.

In batch processes, the reactor size is typically much larger to accommodate holding the large batches of fluid for long periods of time necessary to complete the reaction. To achieve similar productivity as attained herein, the batch reactors are at least 100 times the volume of the transesterification reactor disclosed herein.
Ranges disclosed herein are inclusive and combinatorial (e.g., ranges of "up to about 25 wt %", or, more specifically, about 5 wt % to about 20 wt %"); inclusive of the endpoints and all intermediate values of the ranges of "about 5 wt % to about 25 wt %", etc.). "Combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another, and the terms "a" and "an" herein do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. The modifier "about" in connection with a quantity is inclusive of the state value and has the meaning dictated by context, (e.g., includes the degree of error associated with measurement of the particular quantity). The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the reactor(s) includes one or more reactors).

Reference throughout the specification to "one embodiment", "another embodiment", "an embodiment", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and can or cannot be present in other embodiments. In addition, it is to be understood that the described elements can be combined in any suitable manner in the various embodiments. As used herein, the terms sheet, film, plate, and layer, are used interchangeably, and are not intended to denote size.

All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

While the invention has been described with reference to several embodiments thereof, it will be understood by those skilled in the art that various changes can be made and equivalents can be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications can be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention be not limited to the particular embodiments disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

The invention claimed is:

1. A method for the production of alkyl esters, comprising: combining liquid biomass with an alcohol to form a combined liquid stream; introducing the combined liquid stream to a first transesterification reactor between a liquid glycerol outlet and a liquid alkyl ester outlet; reacting the liquid biomass and the alcohol to form liquid glycerol and liquid alkyl ester, wherein the combined liquid stream flows upward through the reactor at a rate that is less than a settling velocity of the liquid glycerol; and removing a liquid alkyl ester stream from an upper portion of the first transesterification reactor.

2. The method of claim 1, further comprising combining the liquid alkyl ester with additional alcohol to form a combined liquid alkyl ester stream; introducing the combined liquid alkyl ester stream to a second transesterification reactor between a second liquid glycerol outlet and a second alkyl ester outlet, wherein the combined liquid alkyl ester stream flows upward through the second transesterification reactor; reacting the liquid alkyl ester and the additional alcohol to form additional liquid glycerol and a second alkyl ester stream, wherein the additional liquid glycerol settles towards a bottom of the second transesterification reactor; and removing the second alkyl ester stream from an upper portion of the second transesterification reactor.

3. The method of claim 2, further comprising washing the second alkyl ester stream to form a washed alkyl ester stream, wherein the second alkyl ester stream is washed by introducing the second alkyl ester stream to near a bottom of a water wash vessel and introducing water to near a top of the water wash vessel; and drying the washed alkyl ester stream.

4. The method of claim 1, further comprising washing the liquid alkyl ester stream to form a washed alkyl ester stream, wherein the liquid alkyl ester is washed by introducing the liquid alkyl ester stream to near a bottom of a water wash vessel and introducing water to near a top of the water wash vessel; and drying the washed alkyl ester stream.

5. The method of claim 2, wherein the combined liquid stream further comprises a first transesterification catalyst.

6. The method of claim 5, wherein the combined liquid alkyl ester stream further comprises a second transesterification catalyst.

7. The method of claim 1, wherein the combined liquid stream further comprises a first transesterification catalyst.

8. The method of claim 1, wherein the biomass is selected from the group consisting of fatty acids, triglycerides, natural oil comprising free fatty acids, natural fat comprising free fatty acid, and combinations comprising at least one of the foregoing biomass.

9. The method of claim 8, wherein the biomass is selected from the group consisting of sunflower seed oil, soybean oil, corn oil, cottonseed oil, almond oil, groundnut oil, palm oil, coconut oil, linseed oil, castor oil, rapeseed oil, industry tallow, abattoir waste, and combinations comprising at least one of the foregoing biomass.

10. The method of claim 8, wherein the biomass comprises used cooking oil.

11. The method of claim 1, wherein the alcohol is selected from the group consisting of C1-C4 alcohols, and combinations comprising at least one of the foregoing alcohols.

12. The method of claim 1, wherein the alcohol is selected from the group consisting of methanol, ethanol, isopropanol, butanol, multivalent alcohol, and combinations comprising at least one of the foregoing alcohols.

13. The method of claim 1, wherein the flow of the combined liquid stream has a Reynold's number of less than or equal to 2,100.

14. The method of claim 1, wherein the combined liquid stream flows upward through the reactor in a laminar flow.

15. The method of claim 1, wherein the amount of alcohol is less than or equal to about 10% greater than a stoichiometric amount for the conversion of the biomass to the liquid alkyl ester, wherein the percent conversion of the biomass to the liquid alkyl ester is greater than or equal to about 95 mass %, and wherein less than or equal to 5 mass % of the glycerol is removed from the first transesterification reactor in the liquid alkyl ester stream.
16. A method for the production of alkyl esters, comprising:
combining liquid biomass with an alcohol to form a combined liquid stream;
introducing the combined liquid stream to a first transesterification reactor at a point in a lower 25% of the first transesterification reactor, between a liquid glycerol outlet and a liquid alkyl ester outlet, wherein the combined liquid stream has a laminar flow in the first transesterification reactor;
reacting the liquid biomass and the alcohol to form liquid glycerol and liquid alkyl ester, wherein greater than or equal to about 75 mass % of the liquid glycerol settles towards a bottom of the first transesterification reactor; and
removing a liquid alkyl ester stream from the first transesterification reactor;
removing a liquid glycerol stream from the first transesterification reactor; and
purifying the liquid alkyl ester stream.
17. The method of claim 16, wherein purifying the liquid alkyl ester stream comprises
washing the liquid alkyl ester stream to form a washed alkyl ester stream, wherein the liquid alkyl ester stream is washed by introducing the liquid alkyl ester stream to near a bottom of a water wash vessel and introducing water to near a top of the water wash vessel; and
drying the washed alkyl ester stream.
18. The method of claim 16, wherein the liquid alkyl ester is formed in only one transesterification reactor, wherein the amount of alcohol is less than or equal to about 10% greater than a stoichiometric amount for the conversion of the biomass to the liquid alkyl ester, and wherein the percent conversion of the biomass to the liquid alkyl ester is greater than or equal to about 95 mass %.
19. The method of claim 16, wherein the combined liquid stream flows upward through the first transesterification reactor at a sufficiently slow rate to enable the liquid glycerol to settle to the bottom of the first transesterification reactor.
20. The method of claim 16, wherein the combined liquid stream flows upward through the reactor in a laminar flow.
Esterification and transesterification systems, methods and apparatus

Inventors: Philip L. Lichtenberger, Thousand Oaks, CA (US); Alan McGrevy, Camarillo, CA (US); Eric Gulliver, Gambrills, MD (US)

Assignee: Four Rivers Bioenergy, Inc., Calvert City, KY (US)

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See application file for complete search history.
ESTERIFICATION AND TRANSESTERIFICATION SYSTEMS, METHODS AND APPARATUS

This application claims the benefit of priority to U.S. Provisional Application Ser. No. 60/784,434, filed on Mar. 20, 2006 and entitled “Esterification and Transesterification Systems, Methods and Apparatus”, which is incorporated by reference in the present application in its entirety.

BACKGROUND

1. Field
An apparatus for esterification and transesterification reactions and associated methods of use is disclosed. More particularly, methods, systems and apparatus are disclosed which increase the efficiency of esterification and transesterification reactions.

2. General Background
Various methods for esterification and transesterification reactions are well known. Esterification reactions are chemical reactions in which two chemicals (typically an alcohol and an acid) form an ester as the reaction product. A typical reaction would include reacting a carboxylic acid and an alcohol in the presence of an catalyst to form the ester and water byproduct.

Transesterification is a special type of an esterification reaction wherein the process involves exchanging the alkoxyl group of an ester compound by another alcohol. An ester is reacted with an alcohol to produce a different ester and a different alcohol or glycol.

One known application of such reactions is the transesterification of biomass with methanol to produce methyl esters of the fatty acids. When these esters are produced to replace or augment petroleum derived diesel fuel, the product is known as biodiesel. In the United States, the acceptability of the product for use as a fuel is governed by specifications set by the ASTM. ASTM D6751 specification sets the standards for biodiesel.

Biomass includes a variety of different materials, including vegetable oils, animal fats, fish oils, plant oils, and recycled cooking greases. Any one of these can be processed with methanol to produce biodiesel and other products including glycerine.

Although the processing of biodiesel is quite well known, improvements are continually being sought because of the economic sensitivity of every part of the process. When food related materials are being processed for fuel use, the key issue is the expense associated with the entire process in order to make the fuel use competitive.

Thus, there is a need to increase the efficiency of the process. A system and method could be improved by increasing the reaction rate. Also, use of cheaper and/or less catalysts would make the process less expensive and more viable.

SUMMARY

In one aspect of the present disclosure, a method to efficiently conduct esterification and transesterification reactions is disclosed. The method involves providing an annular gap reactor to provide more efficient mixing, wherein the annular gap reactor is operating in laminar flow conditions in the absence of Taylor vortices. Reactants are introduced into the annular gap reactor, and mixed to produce the desired ester.

In another aspect, the annular gap reactor comprises a rotor rotating within a stator to provide an annular flow passage comprising a flow path containing a high-shear treatment zone in which the passage spacing is smaller than in the remainder of the zone to provide a subsidiary higher-shear treatment zone.

In another aspect, the annular gap reactor may be modified to provide an evaporator attached to the annular gap reactor, the evaporator including an opening in the stator near the end of the reactor and a series of fins placed in the opening.

In a further aspect, a reactor is disclosed that encompasses a closed system continuous reactor that can increase esterification reaction rates over that of traditional batch style reactions. In some examples, reactor esterifications were 5-120 times faster than with batch systems.

In another aspect of the disclosure, equipment and reagents can help drive the reaction past batch equilibrium yields.

In a further aspect, higher shear rates in the reactor lead to higher yields. Additionally, higher catalyst loadings increase the reaction rate.

In an exemplary embodiment, a transesterification reaction of vegetable oil with methanol to produce methyl esters (biodiesel) was performed in the reactor. The use of the reactor greatly increases the speed of the main reaction. The increase in reaction rate due to use of the annular gap reactor is of much greater importance than either temperature or the type of catalyst used.

In a further aspect, the increase in the reaction rates caused by the reactor allow for the use of less catalyst, less efficient catalysts, lower temperatures and reduction in unwanted side reactions at more economically favorable conditions. In particular embodiments, sodium hydroxide can be utilized, instead of the more expensive sodium methoxide, as a catalyst in the annular gap reactor disclosed herein achieving equivalent yields with less residence time.

DRAWINGS

Particular preferred embodiments of the disclosure will now be described, by way of example, with reference to the accompanying diagrammatic drawings, wherein:

FIG. 1 illustrates a part elevational, part longitudinal cross section through a complete annular gap reactor;
FIG. 2 illustrates a transverse cross section of the annular gap reactor of FIG. 1 to show the cylindrical members and their relation to one another;
FIG. 3 illustrates an exemplary esterification and transesterification reactor apparatus utilizing a modified annular gap reactor;
FIG. 4 illustrates a diagram depicting increases in reaction times for the reaction of oleic acid and n-butanol in accordance with the present disclosure compared to a batch reaction;
FIG. 5 illustrates a diagram depicting increases in reaction times for the reaction of oleic acid and 2-ethyl-hexanol in accordance with the present disclosure compared to a batch reaction;
FIG. 6 illustrates a diagram depicting increases in reaction times for the reaction of adipic acid and 2-ethyl-hexanol in accordance with the present disclosure compared to a batch reaction;
FIG. 7 illustrates a diagram depicting increases in reaction times for the reaction of succinic acid and propylene glycol in accordance with the present disclosure compared to a batch reaction.

DETAILED DESCRIPTION

Particular embodiments are described below in considerable detail for the purpose of illustrating various teachings,
principles and methods of operation. However, various modifications may be made and the scope of the disclosure is not limited to exemplary embodiments described herein.

In particular embodiments, various esterification reactions are operable connected to a reactor apparatus having a chamber or an annular processing gap/processing passage through which reagents are passed. U.S. Pat. Nos. 5,279,463, 5,538, 191, 6,471,392 and 6,742,774 disclose various apparatus that can be modified and utilized in accordance with various aspects of the teachings of the present disclosure and are herein referred to as an annular gap reactor. In the apparatus and system disclosed herein, esterification reactions are precisely controlled as reactants pass through the annular gap/processing passage of the reactor apparatus. In another aspect, the apparatus disclosed herein also provides a novel evaporation method.

U.S. Pat. Nos. 5,279,463 (issued Jan. 18, 1994) and 5,538, 191 (issued Jul. 23, 1996) disclose methods and apparatus for high-shear material treatment, one type of the apparatus consisting of a rotor rotating within a stator to provide an annular flow passage comprising a flow path containing a high-shear treatment zone in which the passage spacing is smaller than in the remainder of the zone to provide a secondary higher-shear treatment zone in which free supra-Kolmogoroff eddies are suppressed during passage of the material therethrough.

U.S. Pat. No. 6,741,392 is also directed to methods and apparatus for material mixing, in particular, mixing that is carried out under conditions and configurations that provide reduction of Taylor vortices.

When the annular gap reactor is in the range as described in this disclosure, flow within the gap is laminar, with no Taylor vortices. Thus, the shear force experienced by the flow is uniform. For example, the flow does not pass through the regions of high shear force in the laminar zone, through regions of different shear force in the Taylor currents, to regions of low shear force in the eddies of the Taylor vortices.

In the system illustrated by FIG. 1, a first reactant (Reactant A) is fed from a supply tank 10 via a metering pump 12 to inlet 14, while a second reactant (Reactant B) is fed from a supply tank 16 via a metering pump 18 to the same inlet 14. If required, an optional catalyst or reactant gas is fed from a supply tank 20 to the inlet 14. If separate inlets 14 are used they must be in close tangential proximity to one another. The processing apparatus comprises a baseplate 22 on which is mounted rotor bearing supports 24, stator supports 26 and a variable speed electric drive motor 28. A cylindrical tube 30 comprising the apparatus stator is mounted on supports 24, and in turn supports along the major portion of its length another cylindrical tube 32 constituting the outer casing of a heat exchanger through which gas or liquid can be passed to control the temperature in the processing chamber. As illustrated in FIG. 2, the annular passage 34 between the cylinders 30 and 32 can be filled with a suitable heat exchange medium, the coolant (or heating fluid if appropriate) entering through inlets 36 and discharging through exits 38. A rotor shaft 40 extends between the supports 24 and is supported thereby, one end of the shaft being connected to the motor 28. The shaft carries a cylindrical rotor 42, which in this embodiment is solid and has its axis of rotation coincident with the longitudinal axis of the stator cylinder 30. An annular cross section processing chamber 44 is formed between the inner cylindrical surface 46 of stator 30 and outer cylindrical surface 46 of rotor 42 and face body 51; the ends of the chamber are closed against leakage by end seals 50 that surround the shaft 40. The reacted material is discharged through an outlet 52.

As the material being processed flows in the processing passage 44 a respective boundary layer forms on each of the cylindrical surfaces 46 and 48, the thickness of which is determined by the viscosity and other factors of the material being processed and the relative flow velocity of the material over the surface.

The internal diameter of the stator surface 46 and the external diameter of the rotor surface 48 are such that the radial dimension of the processing passage 44 is approximately equal to the combined thicknesses of the two laminar boundary layers back-to-back, so that there is no room between them for an intervening bulk layer to turn turbulent and would permit Taylor vortices to be formed and disrupt the thorough and uniform mixing that takes place with the material in the two contacting boundary layers.

As known in the art, there are various aspects to fluid flow in an annulus such as the annular gap/processing passage 44 disclosed herein, such as Reynolds Numbers, Taylor Numbers, shear rates and shear stress. The literature lists several versions of both Reynolds number (Re) and Taylor number (Ta). These dimensionless numbers are ultimately ratios of the momentum in a fluid flow and the viscous forces in the fluid. When viscous forces dominate, flows tend to be laminar and Re and Ta are low, but when momentum dominates the flow, the flow tends toward turbulence and Re and Ta are high. The different versions of Re and Ta result from adapting the equations to different flow configurations. Thus, there are Reynolds numbers for pipe flow, flow in a slot, axial annular flow and tangential annular flow. In the case of a stator 30 and rotor 42, Taylor numbers are specific to annular flow with an inner cylinder (e.g. rotor 42) rotating, but the definitions appear to vary especially when it comes to the critical Taylor numbers used to define the transitions between laminar and turbulent flow. FIG. 2 represents a cross section through the stator and rotor assembly of FIG. 1.

If the cooperating surfaces 46 and 48 in FIG. 2 are coated with a catalyst to facilitate a chemical reaction that constitutes the processing step. The coatings applied must still meet the criteria of the invention as to smoothness in order to obtain the superior mixing that results.

FIG. 3 depicts another exemplary reactor apparatus, modified from the embodiment shown in FIG. 1 to include an evaporator portion along the length of the rotor. This evaporator modified annular gap reactor is equipped with a stator that was opened to allow volatile gases and vapors to be released. In exemplary embodiments, the stator opening 100 is placed next to the exit end of the reactor and, in exemplary embodiments, is approximately ½ the length of the rotor. A series of fins 110 is placed in the opening. The bottoms of the fins are curved in the direction of the rotor rotation and were placed just above the rotor. The fins 110 prevent fluid in the reactor from being flung off the rotor once it reaches the opening. The fins 110 also allow gasses and vapors to escape from the rapidly sheared fluid surface. The opening 100 in the stator is constructed so that a tent-like condenser could be placed over the opening to collect the vapors escaping from the reaction. Additionally, vacuum may be pulled to lower operating temperatures as well.

Taylor rings (vortices) have not been observed in a rotor/stator device/process as described herein. In addition, the calculations that follow suggest that the experimentally determined upper bound of the preferred conditions may coincide with the formation of Taylor vortices. The lack of Taylor rings allows us to apply a uniform shear force. If there are Taylor rings, it means there will be both currents and eddies. Each of these will apply a different amount of shear. The laminar flow generating the Taylor vortices will apply a third amount of shear.
The boundaries between laminar and turbulent flow seem to coincide with the upper boundary of the preferred conditions as outlined below. The discussion of the different versions of Reynolds and Taylor numbers is included as a way to reconcile differences and to show that they tend to coincide with the experimentally determined upper bound of the preferred conditions, and to provide a method for determining operation conditions in different mechanical configurations with different cell cultures and media. Bird, Stewart and Lightfoot (“Transport Phenomena”, R. B. Bird, W. E. Stewart and E. N. Lightfoot, John Wiley & Sons, New York, (1960), pp. 96) define the Reynolds number for tangential flow in an annulus (\( \text{Re}_{9u} \)) and the critical Reynolds number for transition from laminar to turbulent flow as:

\[
\text{Re}_{9u} = \frac{\Omega d^2 \rho}{\mu} \left( \frac{41.3}{(1 - \kappa)^2} \right)
\]

Where:
\( \Omega \) = angular velocity of the inner cylinder (radians/s or 1/s),
\( \kappa \) = radius of the inner cylinder divided by radius of the outer cylinder (none),
\( R_o \) = radius of the outer cylinder (m),
\( \rho \) = fluid density (kg/m³) and
\( \mu \) = fluid viscosity (kg/m s)

Defined also is the Reynolds number for axial flow in an annulus (\( \text{Re}_a \)) (on pp. 54) and note that the transition from laminar to turbulent flow occurs at Reynolds numbers of about 2000. For example and in this case, the Reynolds number is:

\[
\text{Re}_a = \frac{2\Omega r \left( 1 - \kappa / R_o \right) \rho}{\mu} \quad (0.2)
\]

Where:
\( R_o \) = radius of the outer cylinder (m),
\( \kappa \) = radius of the inner cylinder divided by radius of the outer cylinder (none),
\( \langle \nu \rangle \) = average fluid velocity in axial direction (m/s),
\( \rho \) = fluid density (kg/m³) and
\( \mu \) = fluid viscosity (kg/m s)


\[
\text{Re}_k = \frac{R_o \Omega d^2}{\nu} = \frac{R_o \Delta d \rho}{\mu}
\]

Where:
\( R_o \) = inner cylinder radius (m),
\( \Omega \) = angular velocity of inner cylinder (1/s),
\( d \) = annulus gap width (m),
\( \nu \) = fluid kinematic viscosity [Note: \( \nu = \mu / \rho \) (m²/s)],
\( \mu \) = fluid viscosity (kg/m s) and
\( \rho \) = fluid density (kg/m³)

At the same time Kataoka defines the Taylor number (\( \text{Ta}_k \)) as:

\[
\text{Ta}_k = \frac{R_o \Omega^2 d^2}{\nu^2} = \frac{R_o \Delta d^2 \rho^2}{\mu^2}
\]

(0.4)

Where,
\( R_o \) = inner cylinder radius (m),
\( \Omega \) = angular velocity of inner cylinder (1/s),
\( d \) = annulus gap width (m),
\( \nu \) = fluid kinematic viscosity [Note: \( \nu = \mu / \rho \) (m²/s)],
\( \mu \) = fluid viscosity (kg/m s) and
\( \rho \) = fluid density (kg/m³)

In this work, Kataoka goes on (p. 243) to define the critical Taylor number (\( \text{Ta}_c \)) as the threshold below which “infinitesimal disturbances are damped owing to the action of viscosity” and above which “some of them are amplified with increasing time”. This is taken to mean that \( \text{Ta}_c \) is the threshold for formation of Taylor rings (i.e., Taylor vortices). It is stated therein, that for very narrow gap widths (i.e., \( d / R_o \ll 1 \)) \( \text{Ta}_c \) approaches 1708 but that it tends to increase with increasing \( d / R_o \).

In an example, he states that when \( d / R_o = 0.33 \), \( \text{Ta}_c = 2.453 \). Kataoka provides two equations for estimating \( \text{Ta}_c \):

\[
\text{Ta}_c = \frac{R_o \Omega^2 d^2}{\nu^2} = \frac{R_o \Omega^2 d^2}{\nu^2} \quad (0.5)
\]

\[
\text{Ta}_c = 169 \left( 1 + \frac{d}{2R_o} \right) \quad (0.6)
\]

and, for \( d / R_o \ll 1 \):

where,
\( d \) = annulus gap width (m), and \( R_o \) = inner cylinder radius (m).

Kataoka further notes that as the rotor rpm increases, the Taylor rings become unstable such that the vortex boundaries are S-shaped or wavy. There is a second critical Taylor number (\( \text{Ta}_{c2} \)) and a second critical Reynolds number (\( \text{Re}_{9u2} \)) that corresponds to this instability. \( \text{Ta}_{c2} \) and \( \text{Re}_{9u2} \) both depend on the radius ratio of the rotor and stator (\( \eta = R_o / R_{st} \)).

York, (1955) [Reissued in 1987] on pp. 526-529 gives the following equation for the Taylor Number (Ta, d):

\[ Ta = \frac{Ud}{\nu \sqrt{\frac{d}{R_c}}} = \frac{Ud}{\rho \mu \sqrt{\frac{d}{R_c}}} \]  

(0.7)

Where,

- \( U \) = the peripheral or surface velocity of the inner cylinder (m/s),
- \( d \) = the gap width between the two concentrically placed cylinders (m),
- \( \nu \) = fluid kinematic viscosity (m²/s),
- \( R_c \) = radius of the inner cylinder (m),
- \( \rho \) = fluid density (kg/m³) and \( \mu \) = fluid viscosity (kg/m s).

Schlichting gives \( Ta_d \) as 41.3 and states that for \( 41.3 < Ta_d < 400 \) flow is laminar with Taylor vortices while flows with \( Ta_d > 400 \) are turbulent.

Bird, Stewart and Lightfoot's tangential Reynolds number, Kataoka's Taylor number and Schlichting's Taylor produce widely different values for the same flow conditions but if the results are examined in terms of the transition or critical numbers provided with each equation the results are in close agreement. In other words, if Bird, Stewart and Lightfoot's tangential Reynolds number is larger than the critical value for flow instability, Kataoka's and Schlichting's Taylor numbers will be greater than their respective critical values as well.

A guiding principle of fluid mechanics is the no slip rule. This states that fluid in contact with a surface moves at the same velocity as the surface. This produces a velocity in a fluid bounded by two surfaces when one surfaces moves relative to the other. This gradient is called shear rate and is a useful measure of how intensely a material is sheared. Shear Rate (\( \gamma \)) has units of s⁻¹ and is a function of the rotor surface velocity and the rotor-stator gap.

\[ \gamma = \frac{U}{d} \]  

(0.8)

Where,

- \( U \) = the peripheral of surface velocity of the inner cylinder (m/s) and
- \( d \) = the gap width between the two concentrically placed cylinders.

Shear stress (\( \sigma \)) is a measure of the shearing force applied to a material and has units of kg/m s². Since it reflects the force applied to a fluid, it is more likely to reflect the impact a given set of flow conditions will have on cellular organisms. It is possible to subject a fluid to high shear rates but low shear stress. This is because shear stress is a function of shear rate and viscosity.

\[ \sigma = \nu \gamma \]  

(0.9)

Where,

- \( \nu \) = viscosity (kg/m s) and \( \gamma \) = shear rate.

Experiments

To show the improved performance of the method and apparatus providing esterification and transesterification reactions described herein, several examples of esterification reactions were completed in a batch reactor, an annular gap reactor, and a modified annular gap reactor including an evaporator.

Bench-top reactions were carried out in a 500 ml glass reaction kettle. The lid of the kettle had four ports, three around the periphery and the fourth in the center of the lid. An impeller whose shaft entering the reactor through the center port was used to stir the reaction. Reaction temperature was monitored via a thermometer or thermocouple inserted through one of the ports. An inert purge gas was fed through another port. When samples were taken the purge gas feed was removed from the port so that a sampling cup could be inserted into the reactor. A condenser equipped with a gas bubbler was attached to the remaining port when the reaction was run under equilibrium conditions (i.e., when water evolved in the reaction was retained in the reaction). When the reaction was run under non-equilibrium conditions, a distillation head was attached to the condenser, and a collection flask and gas bubbler were placed at the end of the distillation head. An electric heating mantle was used to heat the reaction mixture. The temperature of the heating mantle was controlled with a rheostat. Four reaction systems were examined on the bench-top. The reactants, and reactant stoichiometries for each of the reactions are given in Table 1.

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Acid</th>
<th>Alcohol</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oleic acid</td>
<td>n-Butanol</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>(1.00 moles)</td>
<td>(1.15 moles)</td>
<td>(0.5 wt % &amp; 2.5 wt %)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Oleic acid</td>
<td>2-ethyl-1-hexanol</td>
<td>p-toluenesulfonic acid</td>
</tr>
<tr>
<td>(1.00 moles)</td>
<td>(1.15 moles)</td>
<td>(0.55 wt %)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Adipic acid</td>
<td>2-ethyl-1-hexanol</td>
<td>Fuscat 4102</td>
</tr>
<tr>
<td>(1.00 moles)</td>
<td>(2.15 moles)</td>
<td>(0.2 wt %)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Saproin acid</td>
<td>Propylene glycol</td>
<td>Fuscat 4102</td>
</tr>
<tr>
<td>(1.00 moles)</td>
<td>(1.10 moles)</td>
<td>(0.3 wt %)</td>
<td></td>
</tr>
</tbody>
</table>

Note: Fuscat 4102 is a trademarked product of Atofina. The active ingredient (>98%) is butyltris(2-ethylhexanoate), CAS# 23850-94-4.

All of the reactions shown in Table 1 were performed in an annular gap reactor. Two annular gap reactors were used for the esterification experiments. The size and shape of the annular gap reactors were designed based on the above theories, allowing laminar flow in the reactor, and preventing the formation of Taylor vortices. A annular gap reactor with Size X was used for reaction 1 and an annular gap reactor with Size Y was used for reactions 2-4. Size X reactors control reaction temperature via a heat exchanger wrapped around the stator. In addition to the external heat exchanger, Size Y reactors have a heat exchanger inside the rotor. The crucial reactor dimensions and the shear rates that the reactants were exposed to are summarized in Table 2.

<table>
<thead>
<tr>
<th>Anular Gap Reactor Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction #</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
</tbody>
</table>

TABLE 1

TABLE 2


Two esterification reactions were examined in an evaporator modified annular gap reactor. Table 3 provides the reagents and their stoichiometries. The condenser, or tent, was used for reaction 7 but not for reactions 5 and 6. Table 4 provides the evaporator modified annular gap reactor conditions.

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>Acid</th>
<th>Alcohol</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Stearic acid</td>
<td>n-butanol</td>
<td>p-toluensulfonic acid (0.55 wt %)</td>
</tr>
<tr>
<td>6</td>
<td>Stearic acid</td>
<td>n-butanol</td>
<td>p-toluensulfonic acid (0.55 wt %)</td>
</tr>
<tr>
<td>7</td>
<td>Oleic acid</td>
<td>2-ethyl-1-hexanol</td>
<td>benzenesulfonic acid (0.55 wt %)</td>
</tr>
</tbody>
</table>

Samples from the bench-top and annular gap reactor reactions were analyzed by dissolving the samples in ethanol and titrating with 0.1N sodium hydroxide. Phenolphthalein was used as the indicator and endpoint was taken as the first tinge of pink that lasted 30 seconds or longer. Reaction yield was calculated by comparing the sample titrations with a titration from an unreacted equilibrium mixture of the reagents. This method of assessing yield assumes that no mass is lost from the reaction mixture during the reaction. Reactions run in the evaporator modified annular gap reactor lost both evolved water and at least some of the lower boiling alcohols and could not be analyzed via titration. Therefore, high performance liquid chromatography was used to analyze the results of reactions 5 through 7. The high performance liquid chromatography results were calculated on the basis of acid converted to ester.

The reaction temperatures, and reaction yields at comparable times are summarized for all of the reactions in Table 5. In all of the reaction systems, the water retained batch reaction temperature is lower than the water extracted batch reaction and annular gap reactor reaction temperatures. The heating mantle used for the batch reactions was controlled by a rheostat. Rheostat settings of 50% to 70% were sufficient to heat the water extracted batch reactions up to 195° C, but rheostat settings of 100% produced temperatures 25° C to 50° C lower. This was attributed to the additional energy required to superheat the water generated by the esterification reaction. The temperatures given for the annular gap reactor reactions are the temperatures of the heating oil passed through the reactor heat exchangers. It is likely that the temperature of the reactants was somewhat lower. In addition, the annular gap reactor is a closed system in that there is no way for the evolved water to escape until the reactants leave the reactor. This means that reaction conditions in the annular gap reactor should be similar to the water retained batch reactions.

The evaporator modified annular gap reactor reaction results have been added to Table 5 where they are most comparable. Reactions 5 and 6 were added to the results from reaction 1 because oleic acid and stearic acid are nearly identical compounds and are expected to have nearly identical reactivity with regard to esterification. It should be noted that these reactions were carried out with much larger excesses of n-butanol. In esterification reactions an excess of alcohol is known to drive the reaction further toward completion. The catalyst, p-toluensulfonic acid, used in reactions 5 and 6, is a much weaker acid than the sulfuric acid catalyst used in reaction 1. Esterification reactions proceed much faster when using strong acid catalysts and we would expect this difference to slow the rate of reactions 5 and 6 relative to reaction 1. Reactions 5 and 6 would expect to have a higher overall yield but a slower reaction rate than reaction 1, but the results suggest the opposite.

Reaction 7 was added to the results from reaction 2. In this case acid and alcohol are identical but the catalyst benzenesulfonic acid is slightly weaker than the p-toluensulfonic acid used for reaction 2. The most significant difference is that reaction 7 used 2× more catalyst than reaction 2. The yields from reaction 7 are slightly less than those obtained from reaction 2 but the reaction times are significantly lower. Some of the rate increase may be attributable to the excess alcohol but it seems unlikely all of the rate increase can be explained this way.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Temperature (°C)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch, water retained</td>
<td>70-80</td>
<td>48% @ 60 min.</td>
</tr>
<tr>
<td>Batch, water extracted</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annular Gap Reactor</td>
<td>115</td>
<td>48% @ 0.5 min.</td>
</tr>
<tr>
<td>Evaporator Modified Annular Gap Reactor</td>
<td>115</td>
<td>99% @ 0.6 min.</td>
</tr>
</tbody>
</table>

(Rxn 5 - Stearic acid instead of oleic acid, 4.3X more alcohol, weaker catalyst, 50% to 70% requested, 195° C, 25° C to 50° C lower, additional energy required to superheat water, temperatures in heating oil, reaction conditions similar, high performance liquid chromatography, water retained batch reaction temperature lower than water extracted batch reaction and annular gap reactor reaction temperatures, heating mantle used for batch reactions controlled by a rheostat, settings of 50% to 70% sufficient for water extracted batch reactions, 100% settings produced lower temperatures, additional energy required to superheat water, esterification reactions driven further toward completion with excess alcohol, p-toluensulfonic acid weaker than sulfuric acid, reaction 7 used 2× more catalyst than reaction 2, yields slightly less than reaction 2, reaction times significantly lower, rate increase due to excess alcohol, unlikely all rate increase can be explained this way.)
TABLE 5-continued

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Temperature (°C)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>different analytic method</td>
<td>115</td>
<td>90% @ 0.4 min</td>
</tr>
<tr>
<td>Evaporator Modified Annular Gap Reactor (Rxn 6 - Stearic acid instead of oleic acid, 2.1X more alcohol, weaker catalyst, different analytic method)</td>
<td>115-120</td>
<td>85% @ 130 min</td>
</tr>
<tr>
<td>Batch, water retained</td>
<td>170-175</td>
<td>85% @ 53 min</td>
</tr>
<tr>
<td>Batch, water extracted</td>
<td>170</td>
<td>85% @ 10 min</td>
</tr>
<tr>
<td>Annular Gap Reactor</td>
<td>170</td>
<td>85% @ 3.5 min</td>
</tr>
<tr>
<td>Evaporator Modified Annular Gap Reactor</td>
<td>82% @ 0.9 min</td>
<td></td>
</tr>
<tr>
<td>(Rxn. 7 - 2X more alcohol, weaker catalyst, different analytic method)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Batch, water retained</td>
<td>120-130</td>
<td>&lt;95% @ 375 min</td>
</tr>
<tr>
<td>Batch, water extracted</td>
<td>185-195</td>
<td>62% @ 100 min</td>
</tr>
<tr>
<td>Annular Gap Reactor</td>
<td>180</td>
<td>62% @ 1.5 min</td>
</tr>
<tr>
<td>Batch, water retained</td>
<td>134-145</td>
<td>41% @ 90 min</td>
</tr>
<tr>
<td>Annular Gap Reactor</td>
<td>170</td>
<td>41% @ 10 min</td>
</tr>
</tbody>
</table>

FIG. 4 compares the batch and annular gap reactor yields as a function of time for Reaction 1 (oleic acid and n-butanol). The reactants were fed into the annular gap reactor in two separate room temperature streams. Two catalyst loadings, 0.5 wt % and 2.5 wt % sulfuric acid, were examined in this reaction. Both the batch and annular gap reactor yields increased when the catalyst loading increased. Regardless of the catalyst loading comparable yields are obtained in the annular gap reactor much more quickly that in the batch reactor. The values next to the annular gap reactor data points give the reaction times in minutes. For this reaction, the annular gap reactor yields are obtained up to 120 times faster than equivalent yields from the batch reactors. There is also an unexpected trend in the data from the annular gap reactor reaction using 0.5 wt % catalyst. The reaction yield increases from approximately 20% to almost 50% as the residence time is decreased from 2 minutes to 0.5 minutes. An unexpected result such as is possibly caused by changes in the axial flow regime as the flow rate is increased.

FIG. 5 compares the batch and annular gap reactor yields as a function of time for Reaction 2 (oleic acid and 2-ethyl hexanol). In this case, the reagents were premixed and fed into the annular gap reactor as a single room temperature stream. Both the batch and annular gap reactor yields are higher and reaction rates are faster than Reaction 1. This may be due to the more hydrophobic nature of the alcohol. n-Butanol is soluble in water but 2-ethyl hexanol is not. The n-butanol was not dried before use and it may have contained enough water to slow the reaction. Alternatively, the more hydrophobic 2-ethyl hexanol may have induced phase separation of the water and thus minimized its impact on the reaction. In this system the reaction rate in the annular gap reactor did not accelerate as the flow rate was increased. However, the reaction in the annular gap reactor was still 5 to 13 times faster than the batch reaction.

FIG. 6 compares the batch and annular gap reactor yields as a function of time for Reaction 3 (adipic acid and 2-ethyl hexanol). This reaction was chosen to examine the esterification of a di-acid. Adipic acid was melted and fed into the annular gap reactor hot. The 2-ethyl hexanol was also heated before introduction into the reactor. Suppression of the reaction rate and yield is clearly visible in the batch reaction that retained the evolved water. In the water retained batch reactions we would expect yield to stabilize at the yield dictated by equilibrium between ester formation and ester hydrolysis. However, after 130 minutes the water retained yield increase slows but continues to increase steadily over time. The batch reactor was opened briefly every time a sample was collected. Water vapor escaped the reactor whenever it was opened and this loss of water would be enough to shift the equilibrium yield slightly higher in favor of the ester. This slow upward trend is seen in all of the water retained batch reactions but is most pronounced for Reactions 3 and 4, and it suggests that the equilibrium water retained yields are somewhat lower than those seen here. The two data points from the annular gap reactor show that increasing the shear rate caused the yield to increase from 45% to 62%. At the higher shear rate the annular gap reactor yield is 67 times faster than a comparable yield in the water extracted batch reaction. In addition, the annular gap reactor yield at the higher shear rate is higher than any yield obtained in the water retained batch reaction. This is remarkable because the annular gap reactor is a closed system that does not allow water to be removed during the reaction. It is expected that the maximum yield would be similar but not greater than the yield from the water retained batch reaction. These results suggest that reactions run in the annular gap reactor may be able to achieve yields higher than the water limited equilibrium yield.

FIG. 7 compares the batch and annular gap reactor yields as a function of time for Reaction 4 (sucinic acid and propylene glycol). Since this system contains a diol and a diacid it is capable of polymerization which makes it a good analog for commercial polyester reactions. The melting point of succinic acid was too high for it to be fed into the annular gap reactor as a liquid. Therefore the reactants were premixed and fed into the reactor as a room temperature slurry. The reaction was strongly mass transfer limited because the reaction temperatures were below the melting temperature of the succinic acid. As the concentration of ester increases, succinic acid is more soluble but the initial contact between the reagents could only occur at the solid-liquid interface. This is typical of commercial polyester reactions involving either terephthalic acid or isophthalic acid. For this reaction, the yield from the
The measurement of glycerin is a simple means of determining the completeness of the biodiesel reactions. It has the added advantage that excess formation of sodium salts of fatty acids (soaps) due to either excess catalyst or further reaction in the reaction mixture do not affect the amount of glycerin and thus preservation of the samples is not as critical. Quantitative glycerin analysis can therefore be used to assess the completeness of the reaction and other initial observations on the samples can be used to estimate the formation of soaps which usually create three layers in the final crude product mixture.

All reactions that involve metallic ion catalysis generate some soap. In the analytical determination of the distribution of carboxylic acids (such as in Table 1) that can be produced from any oil, the officially adopted techniques use a very large excess of alcohol to oil (an alcohol weight on the order of 20 times the weight of oil) and an equal weight to the alcohol weight of potassium hydroxide as the catalyst. The very large excess of alcohol reduces that amount of soap formation but does not eliminate it. The methyl esters so produced are used to characterize the oil and determine the weights of the various carboxylic acids in the fraction assuming that the soaps are uniformly distributed. Since every oil sample is different, this analysis has to be performed for every sample of oil used in biodiesel production if the methyl esters themselves are to be used as a measure of the reaction completion. Even in this case one has to make the assumptions that the soaps are negligible.

The requirement for the use of acid catalysis in esterification reactions and base catalysis in transesterification reactions is well known in the literature. In the absence of any catalyst, the normal transesterification to make methyl esters would take months or years at room temperature. Although the annular gap reactor will increase this rate, it will not be as fast as the catalyzed reaction since even a 1 minute reaction in the annular gap reactor could increase the reactor equipment costs by a factor of 60 in a production environment. The surprising result of the rate increase in this reaction can be somewhat understood if we look at the different ways a reaction can be affected kinetically. The formation of the methyl esters from the oil can be thought of as a reaction:

\[
\text{MeOH} + \text{Glyceride} \rightarrow \text{Methyl Esters} + \text{Glycerin (or lower glyceride)}
\]

This reaction is catalyzed by a base which in the two cases above are either \(\text{NaOCH}_3\) or \(\text{NaOH}\). Traditionally, \(\text{NaOCH}_3\) is considered a stronger base and thus in conventional usage a superior catalyst. If we write a simplified expression for the rate of formation of the methyl esters from equation 1 it could be written as:

\[
d[Methyl esters] = -[\text{MeOH}][\text{Glyceride}]
\]

There is an expression like this for every separate triglyceride, then diglyceride and then monoglyceride in the mixture and since the fatty acids are randomly distributed this amounts to some \(9^3 + 9^2 + 9 = 819\) separate equations only for the different glycerides even without taking into account the positional isomers which increases the number further. Only the final reaction of a monoglyceric yields glycerin and there are 27 possible monoglycerides alone when including stereo-isomers.

The point of the current analysis does not change, however, for any one of those equations we would write and, therefore, it is simplified in order to facilitate understanding of the catalytic effects. The differences are not really that large and they can be estimated quite accurately from an engineering point of view by equation 2 written only three times, one for

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Weight (grams/100)</th>
<th>Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12:0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>14:0</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>16:0</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>18:0</td>
<td>3.9</td>
<td>0.6</td>
</tr>
<tr>
<td>20:0</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>16:1</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>18:1</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>18:2</td>
<td>5.8</td>
<td>2.1</td>
</tr>
<tr>
<td>18:3</td>
<td>6.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>
triglycerides, once for diglycerides and finally for the monoglycerides. The exponents on the effects of concentration can be determined experimentally and this has been done for several oils by several.

To understand what a catalyst does, however, we have to look at the rate constant, \( k \), in the equation. The larger the values of \( k \), the faster the methyl esters are produced. For most reactions including transesterifications \( k \) takes on the form:

\[
k = A_0 \exp(-\Delta E/RT)
\]

This expression comes from what is now called transition state theory, and it is not related to Thermodynamics even though some of the terms used are the same. Thermodynamics can only provide information on the “state” of a system and the net changes that occur going from one state to another. Pressure, volume, temperature and composition define a state. Thermodynamics is independent of the path to get from one state to another and can provide no information related to the kinetics other than the likelihood that the transition will occur or not occur. Thermodynamics can define the equilibrium distribution of products from any reaction once (and only when) that reaction has reached equilibrium.

Equation [3] is related to experimental concepts that have been used to understand reaction rates and the specific paths (and mechanisms) going from reactants to products. The expression is usually attributed to Arrhenius but various forms have been used. In this expression \( A \) is called the pre-exponential factor, \( \Delta E \) is the activation energy needed to overcome the transition between the reactants and products, \( R \) is the gas constant (a universal constant) and \( T \) is the temperature in absolute degrees consistent with the units used for \( R \) and \( \Delta E \).

It is common knowledge among chemists that:

1. Catalysts reduce the activation energy thereby increasing \( k \).

2. Increasing the temperature also increases \( k \) since it appears in the denominator of the expression in the exponent.

In addition, if all else is the same, one can show that a change of 10° C. (actually 10° K. absolute which is the same increment) doubles \( k \), a common rule of thumb used by practicing chemical engineers. Even though it is not precisely true for many reactions it provides an order of magnitude assessment that shows us that we do not expect the temperature to provide the benefits we see from the annular gap reactor.

Furthermore, it is also well known that:

1. The pre-exponential factor is related to mixing or the number of collisions per unit time of the molecules.

2. The pre-exponential factor can also contain embedded in it the concentration and exponential dependence of the catalyst.

It should be noted that the difference between the pre-exponential factor in gas phase and liquid phase reactions is considerable and collisions occur much more frequently in liquids. It is therefore tempting to say that the annular gap reactor is simply a better mixing system and therefore \( A \) increases based on increased molecular collisions per unit time. What is surprising, however, is that the effect grows to the point in the transesterification reaction where it actually overcomes the type of catalyst used and even swamps out to a large extent the effects of temperature when this chemistry is performed in the annular gap reactor.

In acid and base catalyzed reactions it is well known that the concentration of the catalyst may enter the rate constant in the form:

\[
k = B_0 \exp(-\Delta E/RT)
\]

Since the catalyst is not strictly a reactant or product and for most reactions it stays relatively constant, the analysis of the catalyst concentration is frequently performed as in Equation [4]. The determination of the exponent in [4] from experimental data has been used to determine the relative quality and concentration dependence of various catalysts in esterification, hydrolysis and transesterification reactions.

A transesterification was carried out in an annular gap reactor using methanol and sodium methoxide (also called sodium methylate) as the catalyst. The reactions were performed using sodium methoxide as the catalyst with reaction times of 1.6 seconds, 0.8 seconds and 0.4 seconds. Temperature ranges were room temperature for two of the samples (1.6 and 0.8 seconds) and 71°C. and 93°C. for all three times the relative layer volumes were measured. This data can be found in Table 7. The layers are listed in volume percentage of product.

### Table 7

<table>
<thead>
<tr>
<th>Reaction Time (seconds)</th>
<th>Temperature</th>
<th>Glycerin Volume (%)</th>
<th>Biodeisel Volume (%)</th>
<th>Soap Layer Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>Room</td>
<td>13</td>
<td>87</td>
<td>0</td>
</tr>
<tr>
<td>71°C</td>
<td>11.3</td>
<td>88.7</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>93°C</td>
<td>5</td>
<td>84</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>Room</td>
<td>11.2</td>
<td>88.8</td>
<td>0</td>
</tr>
<tr>
<td>71°C</td>
<td>11.3</td>
<td>88.7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>93°C</td>
<td>9</td>
<td>91</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>71°C</td>
<td>11</td>
<td>89</td>
<td>0</td>
</tr>
<tr>
<td>93°C</td>
<td>9</td>
<td>91</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

From the table, it is seen that the 1.6 seconds of reaction time at room temperature gave the highest yield. One can also estimate that the highest temperature for the longest time resulted in too much post-reaction to form soaps. Further, one can see that the highest temperature of 93°C. resulted in less glycerin layer than the intermediate temperature of 71°C. This may be due to the fact that the highest temperature is above the boiling point of methanol and this may have interfered with adequate contact in the annular gap reactor. Analysis of the 1.6 second reaction time run at 93°C. shows that there was significant soap formation from sodium methoxide. Table 8 presents the actual chemical analysis of the same samples.

### Table 8

<table>
<thead>
<tr>
<th>Reaction Time (seconds)</th>
<th>Temperature</th>
<th>Reaction Completeness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>Room</td>
<td>100</td>
</tr>
<tr>
<td>71°C</td>
<td>75.8</td>
<td></td>
</tr>
<tr>
<td>93°C</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>Room</td>
<td>94.3</td>
</tr>
<tr>
<td>71°C</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>93°C</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>71°C</td>
<td>98.4</td>
</tr>
<tr>
<td>93°C</td>
<td>82.2</td>
<td></td>
</tr>
</tbody>
</table>
The reaction completeness is calculated on the basis of a theoretical yield of 8.76% of the total sample weight. Table 7 and 8 are in good agreement in terms of the quality of the reaction.

The reaction goes to completion at room temperature somewhere between 0.8 and 1.6 seconds. The reaction proceeds more quickly at 71°C so that the 0.8 seconds is complete at that temperature and even the 0.4 seconds looks good at 71°C. The value of 91°C is simply too high for the system as it is well above the boiling point of methanol and even at 71°C for 1.6 seconds there appear to be artifacts in the data due to losses of the methanol probably during the reaction and possibly incomplete contact in the annular gap reactor due to vapor lock effects. The results at 0.8 seconds and 71°C indicate that this temperature is acceptable at lower reaction times.

It should be noted that losses of methanol from the system will change the completeness of the reaction and that a gas chromatographic analysis of the methyl esters may still look "normal". The only way the methyl ester analysis could be used quantitatively is to perform a "control" experiment on the same oil sample in a manner that guaranteed complete conversion. Since those methods also involve the use of alkali metal hydroxides, the results still raise a question related to the degree of completeness based on the formation of soaps.

Tests were also run on the production of biodiesel with the use of different amounts of sodium hydroxide as the catalyst. The reactions were performed with reaction times of 1.0 seconds and 0.4 seconds. Temperature ranges were 45°C and 93°C. Table 9 provides the qualitative analysis.

### Table 9

<table>
<thead>
<tr>
<th>Reaction Time (seconds)</th>
<th>Temperature</th>
<th>Percentage Sodium Hydroxide (%)</th>
<th>Glycerin Volume (%)</th>
<th>Biodiesel Volume (%)</th>
<th>Soap Layer Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 45°C</td>
<td>0.5</td>
<td>12.5</td>
<td>87.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.75 45°C</td>
<td>1</td>
<td>11.2</td>
<td>74.5</td>
<td>14.3</td>
<td>0</td>
</tr>
<tr>
<td>1 60°C</td>
<td>0.5</td>
<td>13.3</td>
<td>86.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.75 60°C</td>
<td>1</td>
<td>13.3</td>
<td>86.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1 45°C</td>
<td>0.5</td>
<td>13.3</td>
<td>86.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.75 45°C</td>
<td>1</td>
<td>5</td>
<td>73</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>1 60°C</td>
<td>0.5</td>
<td>9.2</td>
<td>89.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.75 60°C</td>
<td>1</td>
<td>14</td>
<td>86</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1 60°C</td>
<td>1</td>
<td>2</td>
<td>80.7</td>
<td>17.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Through analysis of Table 9, a base catalyst is required to greatly speed up the reaction, the side reaction to form the soap dictates that only the least amount needed should be used to avoid the inevitable loss of fatty acid. It is clear that clean products result even at 0.5% NaOH and that a reaction time near 1.0 second gives higher conversion. From this data, it is seen that a reaction time near 1.0 seconds at 0.75% NaOH and 45°C, or 0.5 seconds at 0.75% NaOH and 60°C will lead to reaction completion with clean products.

Table 10 provides the analytical data for the samples of Table 9.

### Table 10

<table>
<thead>
<tr>
<th>Reaction Time (seconds)</th>
<th>Temperature</th>
<th>Percentage Sodium Hydroxide (%)</th>
<th>Glycerin Level (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 45°C</td>
<td>0.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>0.75 60°C</td>
<td>0.5</td>
<td>97.4</td>
<td>100</td>
</tr>
<tr>
<td>1 60°C</td>
<td>0.75</td>
<td>94.4</td>
<td>100</td>
</tr>
<tr>
<td>1,0 45°C</td>
<td>0.5</td>
<td>91.1</td>
<td>100</td>
</tr>
<tr>
<td>0.75 60°C</td>
<td>1</td>
<td>89.3</td>
<td>100</td>
</tr>
<tr>
<td>1 60°C</td>
<td>0.75</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>1 60°C</td>
<td>1</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

These results are reasonably consistent with the qualitative observations. It is to be expected that samples with high levels of soap are more difficult to analyze because of the problem of uniform mixing with the solvent. Despite this problem, reaction completion in as little as 0.5 seconds is observed. High levels of catalyst leading to high levels of soap are again detrimental. The use of low levels of simple NaOH is as good, if not better, than the sodium methoxide.

The increase in the rates due to the reactor allow for the use of less catalyst, poorer catalysts, lower temperature and reduction in unwanted side reactions at more economically favorable conditions. Transesterification reactions show that the type of mixing and intimate contact conferred by the reactor outweighs any of the normal factors associated with increasing the rate constant.

In particular, use of sodium hydroxide in place of sodium methoxide is seen to be at least as efficient, and in some cases more efficient, for the production of biodiesel in an annular gap reactor. Sodium Hydroxide is about 1/30th the cost of sodium methoxide. Consequently, production of actual biodiesel from soy bean oil is lowered by use of the annular gap reactor described herein. The catalyst expense is 1 to 2 cents per gallon of biodiesel produced via the annular gap reactor when sodium hydroxide is used. Expenses are 8 to 9 cents per gallon when sodium methoxide is used as a catalyst.
in other production processes. Accordingly, use of the annular gap reactor greatly reduces the cost of production.

While the above description contains many particulars, these should not be considered limitations on the scope of the invention, but rather a demonstration of implementations thereof. Accordingly, it is not intended that the scope of the disclosure in any way be limited by the above description. The various elements of the claims and claims themselves may be combined in any combination, in accordance with the teachings of the present disclosure, which includes the claims.

What is claimed is:

1. A method to efficiently conduct esterification and transesterification reactions comprising:
   - providing an annular gap reactor to provide more efficient mixing, wherein the annular gap reactor is operating in laminar flow conditions in the absence of Taylor vortices;
   - providing an evaporator attached to the annular gap reactor, the evaporator including an opening in the stator near an end of the reactor and a series of fins placed in the opening to allow gasses and vapors to leave the reactor and prevent fluids from leaving the reactor;
   - providing a condenser placed above the opening to collect the gasses and vapors leaving the reactor;
   - introducing reactants into the annular gap reactor and mixing the reactants to produce the desired ester.

2. A method to efficiently conduct esterification and transesterification reactions comprising:
   - providing an annular gap reactor to provide more efficient mixing, the annular gap reactor comprising a rotor rotating in a direction within a stator to provide an annular flow passage comprising a flow path containing a high-shear treatment zone in which the passage spacing is smaller than in the remainder of the zone to provide a subsidiary higher-shear treatment zone, wherein the annular gap reactor is operating in laminar flow conditions in the absence of Taylor vortices;
   - providing an evaporator attached to the annular gap reactor, the evaporator including an opening in the stator near the end of the reactor and a series of fins placed in the opening, the series of fins each having a bottom curved in the direction of the rotor rotation; introducing reactants into the annular gap reactor; and mixing the reactants to produce the desired ester.

3. The method of claim 2 further comprising providing a condenser placed above the opening to collect gasses and vapors leaving the reactor.

4. The method of claim 1 wherein the reactants include an alcohol and an acid.

5. The method of claim 4 wherein the product includes an ester.

6. The method of claim 1 wherein the reactants include an alcohol and base.

7. The method of claim 1 wherein the system increases efficiency and reduces costs when compared to traditional batch reactors by increasing reaction rates.

8. The method of claim 1 wherein the system increases efficiency and reduces costs when compared to traditional batch reactors by utilizing less expensive catalysts.

9. The method of claim 1 wherein the system increases efficiency and reduces costs when compared to traditional batch reactors by operating at lower temperatures.

10. The method of claim 1 wherein one reactant or combination of reactants is selected from the group including soybean oil, rapeseed oil, canola oil, jatropha oil, castor oil, corn oil, other vegetable oils, animal fats, fish oils, poultry oils and recycled cooking greases, and a second reactant is methanol.

11. The method of claim 10 wherein the products include biodiesel and glycerin.

12. The method of claim 10 further comprising the addition of a catalyst.

13. The method of claim 12 wherein the catalyst includes sodium hydroxide.

14. The method of claim 13 wherein the amount of sodium hydroxide catalyst to achieve the ASTM D6751 specification for biodiesel in less than 1 second reaction time is less than traditional batch reactors.

15. The method of claim 13 wherein the system avoids the formation of a byproduct, the byproduct including soap.
The invention relates to a process of producing biodiesel via transesterification reaction where the feed of vegetable oil and/or animal fat is atomised prior to the reaction. The process is suitable for continuous production of biodiesel.
Figure 1

Alcohol

Condense Alcohol

Catalyst

Combine alcohol and catalyst

Vapourise alcohol and catalyst mix

Possible methanol/catalyst recycle

Excess Alcohol Vapour

Atomised vegetable oil or meat fat reacts with alcohol in presence of catalyst to produce allyl Ester

Atomisation

Heat to melt and/or reduce viscosity

Vegetable Oil or Animal Fat

Recovery of Allyl Ester
METHOD OF BIODIESEL PRODUCTION

FIELD OF THE INVENTION

[0001] The present invention relates to a method of biodiesel production suitable for continuous production at near atmospheric pressure.

BACKGROUND TO THE INVENTION

[0002] Biodiesel fuels have similar properties to those of diesel produced from conventional petrochemical processes. Biodiesel can be used directly to run existing diesel engines. The main advantages of using biodiesels are that they are renewable, biodegradable and require no engine modification. Biodiesels produce better quality exhaust gas emissions as they contain a negligible amount of sulphur, thus reducing the emissions of sulphur dioxide that are responsible for acid rain. If biodiesel could be manufactured at an affordable price, it could play a major role in meeting energy needs.

[0003] There is a large potential for the future application of biodiesel in New Zealand industry for example. Since New Zealand is a major producer of animal fats, the potential for biodiesel production in this country is considerable. Currently in North America and Europe, several biodiesel plants have already been built.

[0004] Biodiesel preparation or alcohol esterification has been around since the 1940s.

[0005] In general, biodiesel production consists of three stages: feedstock refining, product processing (including reaction and possibly post reaction cleaning) and product distribution. Conventionally biodiesel is produced in a batch process using lower alcohols such as methanol and ethanol with animal fats or oils derived from vegetables. However, due to higher production costs, biodiesel has been overlooked as an alternative fuel for the future.

[0006] Biodiesel is produced through a transesterification reaction of triglyceride molecules present in fats and oils with alcohol, such as methanol. Transesterification is a stepwise reaction that breaks down triglyceride to form alcohol ester. The reaction stoichiometry requires a 3:1 molar ratio of alcohol to triglyceride to reach completion as indicated in Equation 1. In practice, a higher ratio is used to drive the equilibrium to the product side to achieve higher yields. Typically a molar ratio of 6:1 is used.

\[
\begin{align*}
\text{CH}_2\text{O} & \quad \text{R}_1 \\
\text{CH}_2\text{O} & \quad \text{R}_2 + 3 \text{CH}_2\text{OH} \\
\text{CH}_2\text{O} & \quad \text{R}_3
\end{align*}
\]

(Mixture of fatty esters)  (Glycerin)

Equation 1: Transesterification Reaction

[0007] Over the years extensive research has been carried out to optimize this process. Previous work in this area has identified the following variables to have the greatest influence on the biodiesel reaction:

[0008] reaction temperature

[0009] ratio of alcohol to oil/fat

[0010] catalyst type and concentration

[0011] mixing

[0012] purity of reactants (% Free Fatty Acid, FFA)

[0013] type of alcohol

[0014] Based on the above variables a standard production method has been created that is followed by many manufacturers today. Typically the transesterification reaction is carried out at 60°C, and at atmospheric pressure. At this temperature, both reactants are in the liquid state. Attempts at using temperatures above 60°C have been few. At these temperatures methanol starts to evaporate, lowering its concentration. This phenomenon occurs in low pressure batch reactors. However, this can be overcome by the use of high pressures. Several processes have used pressures of 9000 kPa and higher. At these pressures a reaction temperature of 200-300°C can be achieved which is desirable but economically unfeasible.

[0015] Usually, biodiesel is manufactured in a batch process using an alkali catalyst. However, in recent years a greater emphasis has been placed on developing continuous processes that are able to use both low and high grade feedstock to reduce the overall production cost.

[0016] In general the reactor design and the catalyst used govern the quality of feedstock which can be used i.e. high or low grade. Both the batch and the continuous processes require high purity feedstock to minimize side reactions such as saponification. This is because the core reaction for both processes is the same (i.e. transesterification), however, the rate at which this reaction is carried out is different.

[0017] The use of high temperatures has been examined as a possible basis for a continuous process. WO 01/88072, describes a process that uses high temperatures as a means for producing biodiesel from vegetable oil in a continuous process. Use of temperatures above the boiling point of the alcohol gives rise to very high yields similar to that of the conventional base reactions in relatively short times. Methanol gas rather than liquid methanol is used under atmospheric pressure.

[0018] In GB 957679 the use of high temperatures to produce alcohol esters from a triglyceride source is also disclosed. Similarly to WO 01/88072, methanol gas at temperatures of 195°C was introduced to a molten source of lauric acid. However, unlike WO 01/88072, this process operates under a vacuum to allow the product methyl ester and excess methanol to vaporise out of the system for collection and
storage. This was achieved by keeping the reaction vessel under vacuum (i.e. 15-50 mm Hg) and at temperatures of 180-200° C.

[0019] In this specification, where reference has been made to external sources of information, including patent specifications and other documents, this is generally for the purpose of providing a context for discussing the features of the present invention. Unless stated otherwise, reference to such sources of information is not to be construed, in any jurisdiction, as an admission that such sources of information are prior art or form part of the common general knowledge in the art.

OBJECT OF THE INVENTION

[0020] It is an object of the present invention to provide an alternative route for biodiesel manufacture, and/or one which may be suitable for a continuous manufacturing process, and/or which at least provides the public with a useful choice.

SUMMARY OF THE INVENTION

[0021] Broadly, in a first aspect of the invention there is provided a process for preparing alkyl ester via transterification from a vegetable oil and/or meat fat containing triglycerides, comprising reacting an atomised feed of vegetable oil and/or meat fat (“the atomised feed”) with gaseous alcohol in a reaction vessel.

[0022] Preferably the process includes reacting the atomised feed with gaseous alcohol in the presence of an effective amount of a transterification catalyst.

[0023] Preferably the process is conducted on a continuous basis.

[0024] Preferably the process includes carrying out the reaction at a temperature above the boiling point of the alcohol. Preferably at least 20-30° C. above the boiling point of the alcohol.

[0025] Preferably the process includes carrying out the reaction at around or slightly above atmospheric pressure.

[0026] Preferably the process includes preparing the atomised feed by passing the vegetable oil and/or meat fat through an atomiser, preferably on entry to the reaction vessel.

[0027] Preferably the process includes heating the vegetable oil and/or meat fat prior to atomisation.

[0028] Preferably the process includes reacting an atomised feed with gaseous alcohol present in a stoichiometric excess above 3:1 to triglyceride of the atomised feed.

[0029] Preferably the process includes mixing the liquid alcohol with the transterification catalyst prior to reaction with the atomised feed, and preferably the mixture is heated to vapourise the alcohol and/or catalyst (and any reaction product formed between the alcohol and the catalyst) prior to reaction with the atomised feed.

[0030] Preferably the process includes recirculating the gaseous alcohol from the reaction vessel, through a condensing step, to an alcohol mixing vessel for mixing with the transterification catalyst.

[0031] In one embodiment the process includes entry of the atomised feed and gaseous alcohol or alcohol-catalyst mixture into the reaction vessel through separate inlets, preferably in a countercurrent direction with respect to each other.

[0032] In an alternative embodiment the process includes entry of the atomised feed and gaseous alcohol or alcohol-catalyst mixture into the reaction vessel through via a coaxial flow inlet.

[0033] Preferably the vegetable oil and/or meat fat is subjected to a pre-atomisation purification step.

[0034] Preferably the vegetable oil and/or meat fat is subject to a pre-atomisation acid catalysed transterification process. Additionally or alternatively the vegetable oil and/or meat fat is subjected to a pre-atomisation alkali refining process.

[0035] Preferably the alcohol is of the formula CₙH₂₄₊₄-OH where n is from 1-5 with the atomised feed, more preferably the alcohol is methanol, preferably high grade.

[0036] Preferably the vegetable oil and/or meat fat is also high grade.

[0037] Preferably the transterification catalyst is selected from H₂SO₄, HCl, NaOH and KOH and corresponding sodium and potassium alkoxides such as but not limited to sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide.

[0038] Preferably the reaction vessel is a tubular reactor.

[0039] Preferably the reaction is carried out in a substantially water-free environment.

[0040] Preferably the process includes purifying one or more of the feed, alcohol and catalyst streams to remove water and/or other impurities detrimental to the reaction.

[0041] According to a second aspect of the invention there is provided a process for preparing alkyl ester via transterification from a vegetable oil and/or meat fat containing triglycerides, comprising reacting in a reaction vessel an atomised feed of vegetable oil and/or meat fat containing triglycerides with an effective amount of vapourised sodium methoxide which has been prepared by the mixing and then vapourisation of methanol with sodium hydroxide in a mixing chamber prior to entry into the reaction vessel, and carrying out the reaction at a temperature greater than 80° C.

[0042] Preferably the process includes reacting an atomised feed of high grade vegetable oil and/or high grade meat fat containing triglycerides, preferably at around or slightly above atmospheric pressure.

[0043] Preferably the process is conducted on a continuous basis.

[0044] According to a further aspect of the invention there is provided a process for preparing alkyl ester via transterification from a vegetable oil and/or meat fat containing triglycerides, comprising within a reaction vessel reacting a feed of vegetable oil and/or meat fat (the feed) with gaseous alcohol in the presence of an effective amount of a transterification catalyst, wherein the surface area of the feed high enough that the reaction has >80% completion within 5 minutes of contact of the reactants.

[0045] Preferably the reaction has >80% completion within 2 minutes of contact of the reactants; more preferably within 30 seconds of contact of the reactants.

[0046] Preferably the process is conducted on a continuous basis.

[0047] Preferably the process includes reacting the feed with gaseous alcohol at least 20-30° C. above the boiling point of the alcohol.

[0048] Preferably the process includes reacting the feed with gaseous alcohol at around or slightly above atmospheric pressure.

[0049] Preferably the process includes reacting an atomised feed with gaseous alcohol present in a stoichiometric excess above 3:1 to triglyceride of the atomised feed.

[0050] Preferably the process includes increasing the surface area of the feed from that of a liquid phase feed by
passing the vegetable oil and/or meat fat through an atomiser prior to reaction with the gaseous alcohol.

[0051] Preferably the vegetable oil and/or meat fat is heated prior to atomisation.

[0052] Preferably the process includes including mixing the liquid alcohol with the transesterification catalyst prior to reaction with the atomised feed and heating the mixture to vaporise the alcohol and/or catalyst (and any reaction product formed between the alcohol and the catalyst) prior to reaction with the atomised feed.

[0053] Preferably the vegetable oil and/or meat fat is subjected to a pre-atomisation purification step.

[0054] Preferably the alcohol is of the formula C\textsubscript{n}H\textsubscript{2n+1}\textsubscript{OH} where n is from 1-5, more preferably the alcohol is methanol.

[0055] Preferably one or both of the methanol and the feed is high grade.

[0056] Preferably the transesterification catalyst is selected from H\textsubscript{2}SO\textsubscript{4}, HCl, NaOH, KOH and corresponding sodium and potassium alkoxides such as but not limited to sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide.

[0057] According to a further aspect of the invention there is provided alkyl ester prepared according to the abovementioned processes.

[0058] According to a further aspect of the invention there is provided a biodiesel suitable for use in a diesel engine wherein the biodiesel has been prepared at least in part according to one of the abovementioned processes.

[0059] Preferably the biodiesel comprises an alkyl ester prepared according to one of the processes of the invention mixed with petroleum diesel, preferably mixed in proportion with 5% to 20% petroleum diesel.

[0060] According to a further aspect of the invention there is provided a method for preparing biodiesel suitable for use in a diesel engine wherein the biodiesel contains alkyl ester at least some of which has been prepared according to a process of the invention.

[0061] Preferably the method includes a step of combining the alkyl ester prepared by the process of the invention with petroleum diesel.

[0062] Other aspects of the invention may become apparent from the following description which is given by way of example only and with reference to the accompanying drawings.

[0063] As used herein the term “and/or” means “and” or “or”, or both.

[0064] As used herein “(s)” following a noun means the plural and/or singular form of the noun.

[0065] The term “comprising” as used in this specification and claims means “consisting at least in part of”, that is to say when interpreting independent paragraphs including that term, the features prefaced by that term in each paragraph will need to be present but other features can also be present.

[0066] The term “vegetable oil” as used in this specification means oil extracted from plant sources. Vegetable oil contains saturated and unsaturated triglyceride molecules. The concentration of these components can vary depending on the type of plant and the type of refining process. Ideally the vegetable oil is pre-refined by the raw material supplier or by the biodiesel manufacturer.

[0067] The terms “meat fat” as used in this specification refers to fat obtained from animal sources including tallow (beef fat); ghee (butter fat); lard (pork fat); chicken fat; blubber and cow liver oil. It is composed predominantly of triglycerides. Ideally but not essentially the meat fat is pre-refined by the raw material supplier or by the biodiesel manufacturer.

[0068] By “high grade” with reference to the vegetable oil or meat fat we mean vegetable oil or meat fat with free fatty acid (FFA) content of <1.0% and low water content. Anything larger than 1 is considered “low grade”.

[0069] The term “biodiesel” as used in this specification means an alkyl ester usually prepared via a transesterification process from vegetable oils or animal fats. Biodiesel is usually comprised of short chain alkyl esters such as methyl ester or ethyl ester or mixtures of these.

[0070] The term “atomisation” as used in this specification means the reduction of a material (such as of a fluid) to a fine spray or mist. This is often achieved by passing the particles through a nozzle. The term includes the process of nebulisation and other variants.

[0071] The term “atomiser” as used in this specification means an atomisation apparatus. Carbureters, airbrushes, misters, and spray bottles are only a few examples of atomisers. An atomiser could be high pressure, rotary, coaxial or others as known in the art.

[0072] The term “continuous process” as used in this specification means a process where the inputs and outputs flow generally continuously throughout the duration of the process. This is in comparison with a “batch process” in which generally a measured quantity of reactant may be added to the reaction vessel, the reaction is carried out, and the products are removed.

[0073] The term “reaction vessel” as used in this specification means any suitable vessel or reactor for conducting the transesterification process. This will be constructed from a material that is inert towards the reactants and catalysts that are being used. It will ideally have high strength to withstand high temperatures and pressures.

[0074] To those skilled in the art to which the invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the scope of the invention as defined in the appended claims. The disclosures and the descriptions herein are purely illustrative and are not intended to be in any sense limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

[0075] The invention will now be described by way of example only and with reference to the drawings in which:

[0076] FIG. 1: is a schematic flow diagram of a process of biodiesel production in accordance with the invention;

[0077] FIG. 2: illustrates one embodiment of plant set up appropriate to the process of the invention;

[0078] FIG. 3: illustrates the reactor component of FIG. 2;

[0079] FIG. 4: illustrates an alternative plant set up for the process of the invention.

[0080] FIG. 5: illustrates an alternative reactor component with coaxial nozzle.

DETAILED DESCRIPTION OF THE INVENTION

[0081] The current invention uses the atomisation of the feed material (vegetable oil or animal fat) in an environment of alcohol which is preferably gaseous and generally in the presence of a catalyst in a reactor to bring about the transe-
terification process. The atomisation gives rise to an increase in contact surface area due to small droplets that are produced.

[0082] This invention is suitable for a continuous production process whereby the feed is continuously atomised and the methanol gas flows through the reactor in the direction against the current, or alternatively in the direction of the current. The process may be modified to suit a batch process as would be known by one skilled in the art, however its real benefit is to the continuous process.

[0083] In addition a higher reaction temperature can be used which increases the solubility of the reactants and reduces the mass transfer resistance. As a result the overall reaction kinetics is improved. Our temperature preference depends upon the alcohol used. We prefer to operate above the boiling point of the alcohol, as discussed below.

[0084] In a preferred form the excess methanol that is used for the reaction is continuously removed from the reactor as methanol vapour. This reduces post reactor cleaning and product separation which is a normal requirement for batch processes.

[0085] FIG. 1 illustrates via a flow diagram the preferred process of the invention.

[0086] FIG. 1 shows that in the preferred process the feed vegetable oil and/or animal fat is heated and then atomised. What is important is that the feed is in an atomised form, available to react inside the reactor. The step of atomisation can occur before or upon entry to the reactor. It can even occur directly after admission to the reactor. In the reactor, it reacts with the combined alcohol/catalyst mixture which ideally enters in the reactor in a pre-formed state, the mixture already having been heated to vapourise the mixture. As would be appreciated by one skilled in the art, it will be possible to use a liquid alcohol/catalyst mixture which is vapourised after entry to the reactor. It is also possible that the catalyst and alcohol are not pre-mixed. This is discussed below. Again with reference to FIG. 1, following the reaction of the feed with the alcohol in the presence of the catalyst, the alkyl ester is recovered on a continuous basis from the reactor whilst the excess alcohol vapour is taken off the reactor and is recycled via condensation and then re-mixing with fresh catalyst. It is also an option that it can be directly recycled back in to the reactor in order to maintain the pressure. A pressure slightly above atmospheric is preferred (as discussed below).

The Reactor

[0087] At the simplest level, the reactor simply must be a contained reaction vessel which is kept free of water, with inlet and outlet connections to allow the reactants and products to flow through the reactor. The connection points will be determined by the required flow rates. A preferred reactor is a tubular reactor which is eventually pipe or tube based. The tubular design of the reactor is purely based on design and safety considerations.

Alcohol

[0088] The preferred alcohol is methanol, predominantly as this is more widely available and cheaper. However, other short chain alcohols (C₅H₁₁OH where n is from 1-5) are suitable. These alcohols must be as water free as possible, thus higher grade alcohols are preferred. However, lower grade or other alcohols which have a water impurity could be employed with a pre-step of drying or distilling. The stoichio-

metic requirement of alcohol to triglyceride for reaction according to a transesterification process is 3:1. However, we prefer to operate in excess of this ratio, up to 20:1. This excess assists in driving the reaction to completion and the methanol is recycled in our process and is not wasted.

Feed Material

[0089] The typical biodiesel feed material is vegetable oil or meat fat. These are categorised into two sections, low and high grade. This is usually specified by the producer. For this process, feed material with free fatty acid (FFA) content of <1.0% is categorised as high grade while anything larger than that is considered low grade. In the preferred or simplest form, higher grade feeds (with FFA levels lower than 1.0%) are used directly into the process. If lower grade feeds are used then these could be handled in one of three ways. They could be used directly in the reaction process but with soap by-products being produced due to the saponification process which will occur under the reactor conditions. Alternatively, lower grade feeds could be pre-treated via a pre-purification process of alkali refining. This requires treatment with an alkali source, such as sodium hydroxide or sodium carbonate. The purified triglyceride output is then fed into the reactor as the feed for the main reaction step. The final option involves carrying out an acid catalysed esterification step to convert the free fatty acid molecules present in the feed source into methyl esters and then feeding the remaining un-reacted triglyceride molecules through the described process for transesterification.

[0090] Our studies have been carried out for Soya bean oil and for beef tallow. It is well known in the art that triglycerides from vegetable oil and meat fat behave similarly. Further sources of mixed vegetable oil and fat can be used such as that obtained from waste cooking oil.

Catalyst

[0091] Transesterification catalysts are known in the art. Preferred catalysts are metal hydroxides, such as NaOH or KOH, and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. However, these are more suitable for high grade feeds. For lower grade feeds an acid catalyst such as HCl or H₂SO₄ is suitable. In our preferred process where high grade feed is used (as discussed above) then NaOH or KOH, more suitably NaOH, will be used. However, if the feed is less pure an acid catalyst is used. In the scenario discussed above of a purification pre-step followed by the main reaction step, then an acid catalyst will be more suitable for the pre-step and the metal hydroxide catalyst for the main reaction.

[0092] It is preferred that the catalyst is mixed with the alcohol prior to entry into the reactor. This is easily achieved by combining the two into a tank, and mixing. They are then heated to a vapour together before entry into the reactor. Methanol and sodium hydroxide are mixed together in the preferred embodiment to produce a sodium methoxide complex. This complex functions as the actual catalyst species. Methanol and sodium methoxide boil at temperatures close to one another (methanol has a boiling point of 64.7°C whilst that of sodium methoxide varies with concentration. At low concentration it is approximately the same as methanol e.g. 64.5°C. Thus they conveniently can be vapourised in the same heating step en route to the reactor. It is possible that the
catalyst is not pre-mixed with the alcohol prior to entry into the reactor and is added separately. However it is likely that this will have a detrimental effect on the speed of the reaction, and though whilst included within the scope of the reaction, is not preferred.

[0093] No stoichiometric requirement of catalyst exists for the transesterification reaction. We prefer to operate at around 3 to 9 g NaOH/L methanol but are not restricted to this. The term “effective amount of transesterification catalyst” is accepted in the art to simply mean sufficient catalyst to ensure the reaction proceeds.

Temperature

[0094] The operation temperature must be above the boiling point of the alcohol. The alcohols of interest and their boiling points are:

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>64.7°C</td>
</tr>
<tr>
<td>ethanol</td>
<td>78.4°C</td>
</tr>
<tr>
<td>propan-1-ol</td>
<td>97.1°C</td>
</tr>
<tr>
<td>propan-2-ol</td>
<td>82.3°C</td>
</tr>
<tr>
<td>butanol</td>
<td>117.73°C</td>
</tr>
<tr>
<td>pentanol</td>
<td>137.98°C</td>
</tr>
</tbody>
</table>

[0095] Our preferred operating temperature is generally of 20-25°C above the boiling point, however, higher operating temperatures can be used to increase the reaction rate.

[0096] These reaction temperatures are higher than many of the prior art processes. These temperatures result in a higher reaction rate without the need to operate at high pressures. The transesterification process is controlled by both a mass transfer and a kinetic stage. By operating at a higher reaction temperature and using methanol vapour the kinetic barrier can be reduced allowing a shorter reaction time.

Pressure

[0097] One of the benefits of the process of the invention is that the principal reaction can be carried out at atmospheric pressure. This is a distinct advantage simplifying reactor design.

[0098] This process requires less equipment such as mechanical agitators and distillation columns that are required for batch and some continuous processes operating at higher pressures.

[0099] In practice the actual pressure may be slightly above atmospheric due to the influx of gaseous methanol and atomised feed reagent into the reactor.

[0100] Higher pressures can be employed with higher temperatures, as mentioned above, but this will require a suitable reactor able to withstand the harsher conditions.

Atomisation

[0101] This is a key step in the process. The use of atomised feed material gives rise to increased contact surface area thereby assisting the reaction by decreasing the mass transfer resistance. The droplets in our experimental studies were produced using a diesel injection pump and nozzle. Any atomiser as known in the art would be suitable. The atomisation process also reduces or eliminates the need for mechanical mixing.

[0102] As will be understood by those skilled in the art, a certain viscosity of oil or fat will be required in order to make atomisation possible. Thus the oil or fat source will be heated to achieve that viscosity. The viscosity required will depend on the desired droplet size. We typically heat the feed to 100-130°C. Essentially any temperature up to the temperature of degradation of the feed can be used (which is for example, approximately 180°C for vegetable oils). We have used in our studies droplet sizes of 50-150 microns, but any droplet size as would be appreciated by one skilled in the art could be used.

[0103] In the embodiments of the invention discussed herein the atomised feed inlet is separate to and in a counter current direction from the vaporised methanol inlet. However in an alternative embodiment a coaxial flow system could be used within the scope of the invention. This could be by way of a single inlet into the reactor through which both the methanol vapour and feed material enter. The methanol vapour would drive the atomisation of the fat (by breaking up the fat) so that the atomisation pressure required would be reduced. An alternative methanol heating process may be required to what is currently described. For this process methanol at higher pressures may be required than what is used in a counter current embodiment. Hence a small pressure vessel may be required to heat and pressurise the methanol vapour to what is required for atomisation (refer to FIG. 5).

Pre-Steps

[0104] As discussed above, the feed oil or fat can be heated to achieve a desired viscosity prior to the atomisation step.

[0105] Furthermore the methanol and catalyst mix are preferably vapourised in a heating step prior to admission to the reactor.

[0106] As indicated above, in addition to the main reactor step if may be advantageous to include certain other pre-steps in the process. These may be pre-drying steps of the reagents (such as the alcohol), or pre-purification steps of the reagents (the alcohol, or the feed vegetable oil or fat—by esterification using an acid catalyst, or by alkali refining, for example).

[0107] Further, as mentioned above, in the case of a coaxial flow system, there may be a pre-step of pressurising the alcohol or alcohol/catalyst vapour before entry to the reactor.

Other General Comments

[0108] It is important to minimise or ideally eliminate any water from the system. Water impurities will give rise to other chemical processes such as, when NaOH catalyst is used, causing sodium ions to attack the fat of the feed material. This reduces efficiency and causes other unwanted by-products.

[0109] In a preferred form, as illustrated in FIG. 1, there is continuous recirculation of methanol vapour through the reactor and out, to a condenser and then back to the methanol feed line. Since the methanol is in the vapour form it is possible to directly circulate the excess methanol back into the process. However, it may be necessary to continuously introduce a small quantity of methanol/catalyst to maintain a given concentration as the methanol/catalyst mixture is consumed by the reaction.

[0110] A further possibility which assists with energy recovery requires that the hot biodiesel product stream is used to preheat the feed oil/fat using the heat exchangers shown in FIG. 4 for example. However, additional heating may be required as this may not be sufficient to fully heat the stream to the required temperature.
[0111] A further possibility involves multi point feeding: i.e. introduction of the alcohol stream at several points within the reactor. This is to improve the contact rate of the reactants. Vegetable oil or animal fat may be atomised using multiple nozzles, depending the diameter of the reactor.

[0112] The use of a larger number of inlets may be advantageous in a larger set up. We also consider the residence time or time of reaction of our process. We have observed the reaction completes in a matter of seconds of contacting of the reactants.

[0113] There are a number of possible modifications and alterations to the process of the reaction and the plant associated with the process as would be appreciated by one skilled in the art. These modifications and alternations are included within the scope of the invention.

[0114] Preferred forms of the invention are now described with reference to the Figures. FIG. 2 illustrates an initial plant set up for one preferred embodiment of the invention. The feed meat fat or vegetable oil is held in a storage tank 1, which is heated by an external heat supply 2. It is transported via a high pressure pump 3 with further heating 4 to the reactor 5 through an atomisation nozzle (refer to FIG. 3).

[0115] The methanol 6 and the NaOH catalyst 7 are premixed in a separate tank 8 and transported by a pump 9 as a liquid to a heat source such as an evaporator 10. The evaporator 10 heats the methanol to vapourise it. Gaseous methanol/catalyst mixture is then admitted to the reactor 5. In the arrangement of FIG. 2 a counter-current direction from the fat or vegetable oil spray is illustrated. Also illustrated is the recycling of the gaseous methanol which is condensed at a condenser 11 and fed back to the methanol storage tank 8. The product of the transesterification process leaves the bottom of the reactor 5 and transported to a separation unit 12 where the products form layers and can be separated. Where the feed fat or oil is relatively pure the products will be (as illustrated) glycerol and biodiesel (methyl ester). Alternatively when less pure feed the products will be soap, glycerol and biodiesel, as the impurities undergo a saponification reaction to form soap.

[0116] FIG. 3 illustrates the reactor 5 of FIG. 2 in greater detail. The reactor is heated, in this case with a heating jacket 21 fed with a heating fluid inlet 22, the heating fluid leaving at the outlet 23. The temperature is measured throughout the process as indicated by the temperature probes, T1. The feed material (tallow or vegetable oil) enters via the feed inlet 25 and through the feed atomisation nozzle 26 where atomisation takes place. The methanol enters in a counter current fashion at the alcohol inlet 27. A “liquid seal” 28 is in place to stop methanol vapour from escaping through the bottom of the reactor. This liquid seal is achieved by slowing the discharge rate of the reaction products from the reactor to create a back log of liquid and stops the flow of methanol from the bottom of the reactor using a level controller.

[0117] The product leaves the reactor 5 via the product outlet 29. Finally FIG. 3 also illustrates the methanol vapour outlet 30 at the top of the vessel allowing the methanol to be recycled.

[0118] FIG. 4 illustrates an alternative process in accordance with the invention. In this setup the main difference from that of FIG. 2 is that the outlet product stream is used to heat the incoming oil/fat stream. This allows recovery of some of the heat and cooling of the exiting product stream. It should be noted that the heat recovered may not be sufficient to reheat the incoming stream to the desired temperatures. Hence, additional heating (13, refer to FIG. 4) may be required to elevate the feed stream to the desired level. This setup is what would be practiced on a commercial scale where heat recovery is important. The excess methanol/catalyst mixture will be re-circulated back to the reactor together with fresh methanol/catalyst feed from feed tank 8.

[0119] An alternative embodiment employs a coaxial arrangement. In this setup high temperature/pressure methanol may be used to assist with the atomisation of the oil and fat. This will require a multi feed atomisation nozzle. This is illustrated in FIG. 5. Both the vegetable oil/meat fat (at 100°C) (via a first inlet 51) and the methanol/catalyst gas mix (via a second inlet 52) are fed to the coaxial flow injection nozzle 53. Excess methanol is discharged at an outlet 54 at the top of the vessel. The produced is discharged at an outlet 55 at the base of the vessel.

ADVANTAGES OF PREFERRED EMBODIMENTS OF THE INVENTION

[0120] At least preferred embodiments of the process of the invention may have one or more of the following advantages:

[0121] The use of atmospheric pressure simplifying reactor design and reduce its capital and operating cost.

[0122] The use of elevated temperature improving kinetics and reaction rate.

[0123] Since the excess methanol is continuously removed from the reaction the need for post reaction cleaning is reduced. This simplifies the process and makes it more economically feasible.

[0124] There is a possible reduction in catalyst consumption. In batch processes the catalyst is used as a weight percentage of the oil or fat. This can range between 0.5-1 wt % of the feed material. It’s possible to reduce this value even further with this process.

[0125] Use of low-grade tallow or vegetable oil with high free Fatty Acids (FFA). For example it could be possible to process feed material with up to 5% FFA. Larger quantities of FFA may need to be removed or put through a purification process.

[0126] Shorter reaction time.

[0127] The process is suitable for a continuous process.

EXPERIMENTAL

[0128] A gas reactor has been constructed, as illustrated in FIG. 2. Our experiments have examined the effect of feed atomisation, catalyst concentration and reaction temperature (in this case up to 20°C above the alcohol’s boiling point) on the transesterification reaction.

[0129] Our results show that this process can be operated in a continuous fashion with high consistency and a shorter reaction time than standard batch and continuous prior art processes.

[0130] Tables 1 and 2 present the results of a number of runs in the gas-liquid reactor system of the invention. Table 3 provides the details of the conditions and settings of these continuous runs. The input feed used in these runs was high grade Soybean oil and beef tallow. Initially the feed oil or fat was heated to temperatures of 100-130°C or higher. Heating was carried out in a stainless steel vessel with external heating supply. Once at the desired temperature the feed oil/fat was then pumped to the reaction tank where it was atomised. The flow rate of this stream was determined by the speed of the electric motor driving the pump e.g. 10, 15, 20, 25 Hz. Note as illustrated in FIG. 2 the feed stream was reheated after the
pump 3 using a heat exchanger 4 to minimise the heat loss caused by the pump. In a separate stainless steel tank analytical grade methanol and NaOH were mixed together. This was to allow NaOH to dissolve in methanol and to form sodium methoxide which catalyses the reaction. This step was carried out simultaneously as the feed oil was being heated. Once the NaOH was completely dissolved in the feed methanol the mixture was pumped to the reaction tank. For these experiments a catalyst concentration of 3-9 g NaOH/L. Methanol was used. As illustrated in FIG. 2 the methanol/catalyst mixture was passed through a coiled heat exchanger 10. This converted the liquid mixture into a gas phase. The vapour stream was then allowed to enter the reactor where it reacted with the atomised oil/fat droplets. The reactor temperature was kept at 75-90°C using low pressure steam. However, alternative heating sources such as exhaust gases, high pressure steam and electric elements can also be used so that the reaction vessel could be operated at any temperature.

[0131] These experiments were carried out for periods of 15-30 minutes. During the experiment excess methanol from the system was collected by passing the vapours through a condenser. At end of each run the collected methanol was weighed to determine the amount that was consumed by the reaction.

[0132] At the completion of each experimental run the products were collected and allowed to settle into two layers i.e. glycerol and methyl ester. Once the products were separated into two layers of each layer was measured. This was to determine the approximate conversion that had been achieved. Following that the density and the viscosity of the top layer was measured. This was carried out at the temperatures and conditions set down by the New Zealand Biodiesel Standard NZS7500-2005. Tables 1 and 2 present viscosities and densities of the different experimental runs using beef tallow and Soya bean oil. The results obtained illustrated that the viscosities and densities of the products produced by this process meet NZS7500-2005 standard.

[0133] As will be clear from below, our results indicate that the process is similar in performance to a conventional batch reactor (see below discussions and Table 4 batch results) and also fall within the requirements of the New Zealand Biodiesel standards. The products from this process at all the different flow rates had similar properties (density and viscosity) to that of batch process using Soya bean oil and beef tallow. However, unlike conventional batch processes the current process provides a much shorter reaction time. Based on the results the current process is very capable of producing biodiesel continuously at a flow rate of 10 L/hr. The data collected illustrated that the flow rates tested had very little effect on the product quality and conversion. This indicates that the initial experiments were well with the maximum operating limits of the reactor and it is possible for the process to operate at higher flow rates. In addition, as previously mentioned, the process can be operated using beef tallow, vegetable oil or the combination of the two simultaneously (i.e. a mixed feed).

[0134] These tables show that the catalyst concentration within the range we studied did not affect the properties of the methyl ester produced.

### TABLE 1

<table>
<thead>
<tr>
<th>Continuous Production</th>
<th>Soya Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst concentration (grams of NaOH/L MeOH)</td>
<td>3</td>
</tr>
<tr>
<td>Oil pump setting (Hz)</td>
<td>15</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>0.8789</td>
</tr>
<tr>
<td>Kinematic Viscosity</td>
<td>4.21</td>
</tr>
<tr>
<td>Viscosity (Pa.s) (this is an average viscosity)</td>
<td>0.0037</td>
</tr>
</tbody>
</table>

Note, viscosity was measured across a change of rpm from 100-500 @ 40°C.

### TABLE 2

<table>
<thead>
<tr>
<th>Expt #</th>
<th>Avg Operation Time (min)</th>
<th>Catalyst Conc (g NaOH/L MeOH)</th>
<th>Oil type</th>
<th>MeOH flow (Dial Setting)</th>
<th>Oil Flow (Hz)</th>
<th>Total Oil Pumped (L)</th>
<th>Total Product collected (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>6</td>
<td>Tallow</td>
<td>4</td>
<td>25</td>
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<td>Tallow</td>
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<td>2.3</td>
<td>2.35</td>
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<td>2.4</td>
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<td>2.3</td>
<td>2.5</td>
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<tr>
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<td>25</td>
<td>5</td>
<td>Tallow</td>
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<td>25</td>
<td>3.8</td>
<td>4.3</td>
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<tr>
<td>7</td>
<td>25</td>
<td>6</td>
<td>Tallow</td>
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<td>25</td>
<td>3.8</td>
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<td>25</td>
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<td>3.8</td>
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<td>25</td>
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<td>3.6</td>
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<td>11</td>
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<td>3.5</td>
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</tr>
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<td>13</td>
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<td>7</td>
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<td>25</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
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<td>19</td>
<td>8</td>
<td>Tallow</td>
<td>3</td>
<td>25</td>
<td>2.9</td>
<td>3.4</td>
</tr>
<tr>
<td>15</td>
<td>27</td>
<td>9</td>
<td>Tallow</td>
<td>3</td>
<td>25</td>
<td>4.2</td>
<td>4.08</td>
</tr>
<tr>
<td>16</td>
<td>22</td>
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<td>Tallow</td>
<td>4</td>
<td>20</td>
<td>3.4</td>
<td>2.99</td>
</tr>
</tbody>
</table>
### TABLE 2-continued

<table>
<thead>
<tr>
<th>Expt #</th>
<th>Total Bottom layer (L)</th>
<th>Total Top layer (L)</th>
<th>Approx Conv (%)</th>
<th>Density (avg) (g/ml)</th>
<th>Viscosity (avg) (Pa s)</th>
<th>Kinematic Viscosity avg (mm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4</td>
<td>2.5</td>
<td>90.3</td>
<td>0.885</td>
<td>0.00413</td>
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<tr>
<td>2</td>
<td>0.35</td>
<td>2</td>
<td>86.7</td>
<td>0.874</td>
<td>0.00487</td>
<td>5.5705</td>
</tr>
<tr>
<td>3</td>
<td>0.65</td>
<td>2.05</td>
<td>88.8</td>
<td>0.873</td>
<td>0.00551</td>
<td>6.3149</td>
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<tr>
<td>4</td>
<td>0.44</td>
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<td>84.9</td>
<td>0.869</td>
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<td>0.45</td>
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<td>88.6</td>
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<tr>
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<td>0.00404</td>
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</tr>
<tr>
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<td>0.77</td>
<td>3.46</td>
<td>90.0</td>
<td>0.870</td>
<td>0.00400</td>
<td>4.5941</td>
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<tr>
<td>8</td>
<td>0.8</td>
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<td>90.5</td>
<td>0.870</td>
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<td>88.9</td>
<td>0.867</td>
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<td>5.1941</td>
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<td>0.6</td>
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<td>94.1</td>
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</table>

---

1. Operation time excludes initial start-up and shut down time. (i.e. 5 min for start up and 2 min for shut down)
2. Most experiments are repeated a minimum of two times for accuracy and are only shown as averages in this table
3. Viscosity was recorded at 40°C.
4. Density was recorded at 20°C.

---

### TABLE 3

<table>
<thead>
<tr>
<th>Conditions of the Continuous Reactor Runs</th>
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<tbody>
<tr>
<td>Processing time (min)</td>
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<tr>
<td>Initial Reactor Temperature (°C)</td>
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<tr>
<td>Reactor Temperature during experiment (°C)</td>
</tr>
<tr>
<td>Steam Pressure supply to reactor</td>
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<tr>
<td>Methanol Feed Temperature (°C)</td>
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<tr>
<td>Methanol Hot water bath Temperature (°C)</td>
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<tr>
<td>Methanol Flow (ml/min) Dial setting 3</td>
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TABLE 3-continued

<table>
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<th>Conditions of the Continuous Reactor Runs</th>
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<td>Methanol Flow (ml/min) Dial setting 4</td>
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<td>Oil Flow ml/min @ 10 Hz</td>
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<tr>
<td>Oil Flow ml/min @ 15 Hz</td>
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<td>Oil Flow ml/min @ 20 Hz</td>
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<td>Oil Flow ml/min @ 25 Hz</td>
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</table>

[0141] Table 4 is provided for comparative purposes. We conducted a number of runs using a batch process of biodiesel production. These experiments were carried out using high grade Soya bean oil and beef tallow. The experiment methodology was based on the norm practice described by most researchers in this field.

[0142] Initially a given quantity of oil or fat was weighed out and placed in a 500 ml glass reaction vessel equipped with a mechanical stirrer and baffle. The oil/fat was allowed to heat to the required temperature before the methanol/catalyst mixture was introduced. Using a 6:1 molar ratio the required amount of methanol was determined. For these experiments analytical grade methanol and NaOH was used. Similar to the continuous process NaOH was pre-dissolved into the methanol. This mixture was heated to the desired reaction temperature and was introduced into the oil/fat phase. These reactions were carried out for a period of 90 min.

[0143] After each experimental run the products were allowed to separate into layers. Following the separating process the volume of each layer was measured. The top layer was then water washed and neutralised to remove catalyst and excess methanol. In addition the density and viscosity of each layer was also measured. Refer to Table 4 and 5 for results and experimental conditions.

[0144] As will be evident from comparison of the Tables, the physical properties of the products of our continuous process of the invention and that of the batch process, typical of prior art processes, are in the same range.

TABLE 5-continued

<table>
<thead>
<tr>
<th>Conditions of the Batch Reactor Runs</th>
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<td>Reactor Temperature during experiment (° C.)</td>
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<tr>
<td>Heat water bath Temperature (° C.)</td>
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<tr>
<td>Mole ratio (Methanol/Fat or Oil)</td>
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<tr>
<td>Catalyst Concentration Wt% (based on feed oil/fat)</td>
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<tr>
<td>Weight of Fat or Oil (g)</td>
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<tr>
<td>Mixing (rpm)</td>
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</table>

[0145] Finally Table 6 presents the New Zealand Biodiesel Standard NZ57500-2005 for acceptable density and kinematic viscosity. This standard is based on ASTM International standard (the most common standard referenced in the United States) for a number of feeds, again for comparison purposes. For these experiments the physical properties of the top layer was used as measure of quality and reaction conversion. Hence the standard created by ASTM was used as a guideline for our experimental measurements.

TABLE 6

<table>
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<tr>
<th>Property</th>
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<th>Reference Test</th>
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<tr>
<td>Density at 15° C. Kg/m³</td>
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<td>Viscosity at 40° C. mm²/s</td>
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</table>

[0146] The results obtained from both the batch and the continuous process described in this report indicated that the biodiesel produced from them meet the NZ57500-2005 Standards. In addition it also illustrated that the current process produced biodiesel (alkyl ester) to the same quality as that of a batch process. However, this was achieved at a faster rate with less post reactor cleaning common to the batch process.
[0147] Where in the foregoing description reference has been made to elements or integers having known equivalents, then such equivalents are included as if they were individually set forth.

[0148] Although the invention has been described by way of example and with reference to particular embodiments, it is to be understood that modifications and/or improvements may be made without departing from the scope or spirit of the invention.

[0149] In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognise that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

1. A process for preparing alkyl ester via transesterification from a vegetable oil and/or meat fat containing triglycerides, comprising reacting an atomised feed of vegetable oil and/or meat fat ("the atomised feed") with gaseous alcohol in a reaction vessel.

2. A process as claimed in claim 1 including reacting the atomised feed with gaseous alcohol in the presence of an effective amount of a transesterification catalyst.

3. A process as claimed in claim 2 including reacting the atomised feed with gaseous alcohol on a continuous basis.

4. A process as claimed in claim 3 including carrying out the reaction at a temperature above the boiling point of the alcohol.

5. A process as claimed in claim 4 including carrying out the reaction at least 20-30°C above the boiling point of the alcohol.

6. A process as claimed in any one of the preceding claims including carrying out the reaction at around or slightly above atmospheric pressure.

7. A process as claimed in any one of the preceding claims including preparing the atomised feed by passing the vegetable oil and/or meat fat through an atomiser.

8. A process as claimed in claim 7 including passing the vegetable oil and/or meat fat through an atomiser on entry to the reaction vessel.

9. A process as claimed in any one of the preceding claims including heating the vegetable oil and/or meat fat prior to atomisation.

10. A process as claimed in claim 9 including reacting an atomised feed with gaseous alcohol present in a stoichiometric excess above 3:1 to triglyceride of the atomised feed.

11. A process as claimed in claim 9 or 10 including mixing the liquid alcohol with the transesterification catalyst prior to reaction with the atomised feed.

12. A process as claimed in claim 11 including heating of the mixture of liquid alcohol and transesterification catalyst to vapourise the alcohol and/or catalyst (and any reaction product formed between the alcohol and the catalyst) prior to reaction with the atomised feed.

13. A process as claimed in any one of the preceding claims including recirculating the gaseous alcohol from the reaction vessel, through a condensing step, to an alcohol mixing vessel for mixing with the transesterification catalyst.

14. A process as claimed in any one of the preceding claims including entry of the atomised feed and gaseous alcohol or alcohol-catalyst mixture into the reaction vessel through separate inlets.

15. A process as claimed in claim 14 including entry of the atomised feed and gaseous alcohol or alcohol-catalyst mixture into the reaction vessel through separate inlets in a counter current direction with respect to each other.

16. A process as claimed in any one of claims 1 to 13 including entry of the atomised feed and gaseous alcohol or alcohol-catalyst mixture into the reaction vessel through via a coaxial flow inlet.

17. A process as claimed in any one of the preceding claims including subjecting the vegetable oil and/or meat fat to a pre-atomisation purification step.

18. A process as claimed in claim 17 including subjecting the vegetable oil and/or meat fat to a pre-atomisation acid catalysed transesterification process.

19. A process as claimed in claim 17 or 18 including subjecting the vegetable oil and/or meat fat to a pre-atomisation alkali refining process.

20. A process as claimed in any one of the preceding claims including reacting an alcohol of the formula CₙH₂₉₊₁ where n is from 1-5 with the atomised feed.

21. A process as claimed in claim 20 including reacting methanol with the atomised feed.

22. A process as claimed in claim 21 including reacting high grade methanol with the atomised feed.

23. A process as claimed in any one of the preceding claims including preparing the atomised feed from high grade vegetable oil and/or meat fat.

24. A process as claimed in any one of the preceding claims including carrying out the reaction in the presence of an transesterification catalyst selected from H₂SO₄, HCl NaOH and KOH and corresponding sodium and potassium alkoxides such as but not limited to sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide.

25. A process as claimed in any one of the preceding claims wherein the reaction vessel is a tubular reactor.

26. A process as claimed in any one of the preceding claims including carrying out the reaction in a substantially water-free environment.

27. A process as claimed in claim 26 including purifying one or more of the feed, alcohol and catalyst streams to remove water and/or other impurities detrimental to the reaction.

28. A process for preparing alkyl ester via transesterification from a vegetable oil and/or meat fat containing triglycerides, comprising reacting in a reaction vessel an atomised feed of vegetable oil and/or meat fat containing triglycerides with an effective amount of vapourised sodium methoxide which has been prepared by the mixing and then vapourisation of methanol with sodium hydroxide in a mixing chamber prior to entry into the reaction vessel, and carrying out the reaction at a temperature greater than 80°C.

29. A process as claimed in claim 28 including reacting an atomised feed of high grade vegetable oil and/or high grade meat fat containing triglycerides.

30. A process as claimed in claims 28 or 29 including carrying out the reaction at around or slightly above atmospheric pressure.

31. A process as claimed in claim 30 including reacting the atomised feed with an effective amount of vapourised sodium methoxide on a continuous basis.

32. A process for preparing alkyl ester via transesterification from a vegetable oil and/or meat fat containing triglycerides, comprising within a reaction vessel reacting a feed of vegetable oil and/or meat fat (the feed) with gaseous alcohol in the presence of an effective amount of a transesterification
catalyst, wherein the feed has a surface area high enough that the reaction has >80% completion within 5 minutes of contact of the reactants.

33. A process as claimed in claim 32 wherein the reaction has >80% completion within 2 minutes of contact of the reactants.

34. A process as claimed in claim 33 wherein the reaction has >80% completion within 30 seconds of contact of the reactants.

35. A process as claimed in any one of claims 32 to 34 including reacting the feed with gaseous alcohol on a continuous basis.

36. A process as claimed in claim 35 including reacting the feed with gaseous alcohol at least 20-30°C above the boiling point of the alcohol.

37. A process as claimed in claim 36 including reacting the feed with gaseous alcohol at around or slightly above atmospheric pressure.

38. A process as claimed in claim 37 including reacting an atomised feed with gaseous alcohol present in a stoichiometric excess above 3:1 to triglyceride of the atomised feed.

39. A process as claimed in any one of claims 32 to 38 including increasing the surface area of the feed from that of a liquid phase feed by passing the vegetable oil and/or meat fat through an atomiser prior to reaction with the gaseous alcohol.

40. A process as claimed in claim 39 including heating the vegetable oil and/or meat fat prior to atomisation.

41. A process as claimed in any one of claims 32 to 40 including mixing the liquid alcohol with the transesterification catalyst prior to reaction with the atomised feed and heating the mixture to vapourise the alcohol and/or catalyst (and any reaction product formed between the alcohol and the catalyst) prior to reaction with the atomised feed.

42. A process as claimed in claim 41 including subjecting the vegetable oil and/or meat fat to a pre-atomisation purification step.

43. A process as claimed in any one of claims 32 to 42 including reacting an alcohol of the formula CₙH₂₀₊₁OH where n is from 1-5 with the atomised feed.

44. A process as claimed in claim 43 including reacting methanol with the atomised feed.

45. A process as claimed claim 44 where one or both of the methanol and the feed is high grade.

46. A process as claimed in any one of claims 32 to 45 wherein the transesterification catalyst is selected from H₂SO₄, HCl, NaOH, KOH and corresponding sodium and potassium alkoxides such as but not limited to sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide.

47. Alkyl ester prepared according to the process claimed in any one of claims 1 to 46.

48. A biodiesel suitable for use in a diesel engine wherein the biodiesel has been prepared at least in part according to a process claimed in any one of claims 1 to 46.

49. A biodiesel as claimed in claim 52 which includes an alkyl ester as claimed in claim 47 mixed with petroleum diesel.

50. A biodiesel as claimed in claim 49 wherein the alkyl ester is mixed in proportion with 5% to 20% petroleum diesel.

51. A method for preparing biodiesel suitable for use in a diesel engine wherein the biodiesel contains alkyl ester at least some of which has been prepared according to a process claimed in any one of claims 1 to 46.

52. A method as claimed in claim 51 including a step of combining the alkyl ester of claim 47 with petroleum diesel.

53. Apparatus adapted to prepare alkyl ester from vegetable oil and/or meat fat comprising a reaction vessel, an inlet for vegetable oil and/or meat fat, an atomiser associated with the inlet, the apparatus being adapted for a continuous process by including an inlet and outlet of gaseous alcohol or alcohol-catalyst mixture.

54. A method of preparing alkyl ester substantially as herein described and with reference to any one or more the accompanying figures.

55. A method of preparing alkyl ester substantially as herein described and with reference to any one or more the accompanying examples.

* * * * *