A Review of FFA Esterification for Biodiesel Production

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Abstract
Because of the limited reserve of fossil sources such as petroleum, natural gas and coal, biodiesel that is produced from biomass is an attractive energy resource. Biodiesel is a clean energy that has the closest quality to diesel fuel. However, the conventional biodiesel production cost is higher than petroleum-based diesel since its being produced mostly from expensive high-quality virgin oil. Many researchers interest in using low-cost high free fatty acid (FFA) oils as the feedstock for biodiesel production by esterification process. This paper reviews the effect of operating parameters on the FFA conversion to biodiesel with esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount and type. The esterification technologies and economic aspects of biodiesel as also addressed.

Keywords: Esterification; Biodiesel; Free Fatty Acid

1. Introduction
Since 1970, the world wide oil crises and a growing ecological awareness have led to the rediscovery of plant oils as possible alternatives to hydrocarbon-based fuels. The urge to fight agricultural overproduction served as additional incentive to this development. Using fuel from the plants is definitely a way to preserve the environment by helping to decrease the green house effect such as carbon dioxide (CO2) and sulfur dioxide (SO2).

Biodiesel made from vegetable oils or animal fats is renewable source. This bio-fuel is as efficient as petroleum diesel in powering unmodified diesel engines [1]. Today, almost in every country worldwide there are activities in biodiesel production and utilization. Biodiesel is either used in pure form or as blends with fossil diesel fuel that are stable in any concentration [2]. However, the main obstacle of economical biodiesel production is its high raw feedstock cost that is approximately 70-95% of total production costs [3].

An effective way of reducing biodiesel cost is the use of feedstocks having high free fatty acid (FFA) or non-edible oils which tend to be considerably cheaper than edible vegetable oils [4]. The low-cost feedstocks containing high content of FFA have been employed to produce biodiesel. Nevertheless, the FFA causes serve problems for the transesterification catalyzed by base catalyst. FFA can react with the base catalyst (Neutralization) which leads to a loss of catalyst and a production of soap that deactivates the catalyst [5]. Therefore, FFA contained feedstock has to be removed or converted to alkyl ester with acid-catalyzed esterification.

The major objective in this article is to review the high acidic raw materials, operating parameters and their effects on the efficiency of biodiesel production by the esterification process.

2. FFA Esterification
Biodiesel is conventionally produced from an expensive high-quality oil by transesterification that hardly occur if the FFA content in the oil is more than 3% [6]. Consequently, much research work has been reported for the use of high acidity raw materials with a first reaction step in which the acid esterification is carried out, followed by an alkali-transesterification step in which the triglyceride portion is transformed into biodiesel [7-13].

Table 1 The content of FFA in the acidic raw materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>FFA content (%w)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycled oil</td>
<td>0.4–3.3</td>
<td>[14]</td>
</tr>
<tr>
<td>Crude palm oil</td>
<td>3.0–10.0</td>
<td>[15-16]</td>
</tr>
<tr>
<td>Waste frying oil</td>
<td>&gt;10.0</td>
<td>[17]</td>
</tr>
<tr>
<td>Coconut oil</td>
<td>12.0</td>
<td>[18-19]</td>
</tr>
<tr>
<td>Residues from several</td>
<td></td>
<td></td>
</tr>
<tr>
<td>industries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jatropha seed oil</td>
<td>11.5–22.4</td>
<td>[20]</td>
</tr>
<tr>
<td>Mahua oil</td>
<td>15.0</td>
<td>[21]</td>
</tr>
<tr>
<td>Mahua oil</td>
<td>19.0</td>
<td>[22]</td>
</tr>
<tr>
<td>Animal fats</td>
<td>7.0–50.0</td>
<td>[23-25]</td>
</tr>
<tr>
<td>Cotton seed oil</td>
<td>85.3</td>
<td>[26]</td>
</tr>
<tr>
<td>Palm fatty acid distillate (PFAD)</td>
<td>93</td>
<td>[27]</td>
</tr>
</tbody>
</table>

Examples of acidic raw materials are shown in Table 1. These materials can be converted to biodiesel with high yield using acid-catalyzed esterification as a first step. The FFA esterification (Figure 1.) is conventionally carried out with excess of a short chain alcohol as methanol or ethanol, and in the presence of an acid catalyst such as sulfuric acid, phosphoric acid or hydrochloric acid.
In the esterification, FFA that has molecular weight of 256 – 284 will react to give out water that has a molecular weight of 18, in a proportion of 1:1 mole. The water will weigh around 6.3 – 7% of the FFA. In order to obtain a high yield, the water from the reaction should be removed continuously. Kreutzer and Henkel developed a technology based on the principle of the esterification reaction with a simultaneous absorption of superheated methanol vapor and desorption of the reaction water in a countercurrent reaction column [28].

However, if the raw material has triglycerides fraction, triglycerides will be changed into FFA by having them to react with hydrolysis before esterification in order to increase %FAME (Fatty acid methyl ester). The hydrolysis (Figure 2.) is normally conducted at 250-260 °C, a pressure of 4.83–5.17 MPa for 2-3 hr. At this high temperature and pressure, hydrolysis gives out FFA and glycerol. This causes the raw material of the esterification to have more FFA and consequentially more FAME (biodiesel) [28].

Examples of biodiesel technologies that were employed by previous research to reduce effectively the FFA content are summarized in Table 2.

### Table 2 Biodiesel technologies for feedstocks with high FFA content

<table>
<thead>
<tr>
<th>High FFA biodiesel Technologies</th>
<th>Feedstocks</th>
<th>Operating Conditions</th>
<th>FFA esterified yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterogeneous acid catalysis</td>
<td>Waste oils</td>
<td>Zn-, Ti- or Sn-silicates and aluminates catalysts, 9:5:1 molar ratio of methanol to oil, 220-250°C and 40-100 bar</td>
<td>&gt;92</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Unrefined oils with high amount of FFA</td>
<td>Zn- and Mn-palmitates and stearates catalysts, 1.5-2.5:1 molar ratio of methanol to oil, 150-250°C and 5-150 bar</td>
<td>&gt;92</td>
<td>[30]</td>
</tr>
<tr>
<td>Homogenous acid catalysis</td>
<td>PFAD</td>
<td>0.5% H₂SO₄ catalyst, 6:1 molar ratio of methanol to oil, 40°C and 120 min.</td>
<td>92.9</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>PFAD</td>
<td>1.34% H₂SO₄ catalyst, 8:1 molar ratio of methanol to oil, 70°C and 60 min.</td>
<td>98.5</td>
<td>[32]</td>
</tr>
<tr>
<td>Enzymatic catalysis</td>
<td>Recycled frying oil (RFO) and tallow</td>
<td>57%w of Pseudomonas cepacia lipase enzyme preparation, 4:1 molar ratio of methanol to triglyceride, 50°C and 24 hr.</td>
<td>92-94</td>
<td>[33]</td>
</tr>
<tr>
<td>Jatropha oil</td>
<td></td>
<td>10%w of Chromobacterium viscorum lipase enzyme preparation, 4:1 molar ratio of ethanol to triglyceride, 40°C and 8 hr.</td>
<td>92</td>
<td>[34]</td>
</tr>
<tr>
<td>Hydrolysis followed by esterification</td>
<td>Soybean soapstock</td>
<td>Lipids in soapstock were hydrolyzed completely by steam prior to esterification with 0.17:1.8:1 molar ratio of sulfuric acid to methanol to FFA, 65°C and 14 hr.</td>
<td>90-95</td>
<td>[35]</td>
</tr>
<tr>
<td>Supercritical methanol</td>
<td>Rapeseed oil</td>
<td>42:1 molar ratio of methanol to oil, 350°C, 20 MPa and 30 min.</td>
<td>87</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>Chicken fat</td>
<td>9:1 molar ratio of methanol to oil, 400°C, 30 MPa and 6 min.</td>
<td>80</td>
<td>[37]</td>
</tr>
<tr>
<td>Reactive extraction</td>
<td>Jatropha curcas</td>
<td>15%w H₂SO₄ catalyst, 43:1 molar ratio of methanol to oil, 60°C and 1,440 min.</td>
<td>99.8</td>
<td>[21]</td>
</tr>
</tbody>
</table>
3. Factors which effect on esterification reaction

3.1 Moisture in material

The presence of water has negative effects on the acid catalyzed reaction [38]. The raw material should consist of the water content below 0.06% [39]. Kusdiana and Saka (2004) studied effects of water on the acid-catalyzed esterification, the conversion was significantly reduced to 6% when only 5% water was added [40].

3.2 Ratio of alcohol to oil

The conversion efficiency and biodiesel production cost depend on significant factors. One of the significant factors is the molar ratio of alcohol to oil. Commonly used short chain alcohols are methanol, ethanol, propanol and butanol. However, the methanol is used commercially because of its low price. But in practice a greater ester product can be obtained when a higher molar ratio is employed to drive the reaction towards completion [41].

Ghadge and Raheman (2005) [22] studied the effect of methanol quantity on the reduction of FFA content of mahua oil. It was found that the optimum molar ratio of methanol to oil was 7.68:1 for reducing the acid level to less than 1% as using sulfuric acid catalyst. After the pretreatment of mahua oil, transesterification reaction was carried out with 6:1, the optimum molar ratio of methanol to oil as using potassium hydroxide catalyst.

3.3 Temperature

Esterification could occur at different temperatures, depending on the oil used. Biodiesel production from high FFA rubber seed oil obtained the maximum ester yield at the temperature of 45±5°C. When the reaction temperature went above 50°C, the yield decreased. In the case of rubber seed oil, temperatures greater than 60°C should be avoided because they tend to accelerate saponification of the glycerides before completion of the alcoholysis [41].

3.4 Time

The rate of reaction was influenced by time. The ester yield increased with the increase in reaction time. Biodiesel production from high FFA rubber seed oil was obtained after 30 minutes of a sufficient reaction time for the completion of the esterification [41].

The high FFA level of mahua oil was reduced to less than 1% by a two-step pretreatment process. With each step it was found that the reaction progressed rapidly during the first 1 hr with 0.30-0.35 %v methanol to oil and 1 %v sulfuric acid catalyst at 60°C. The reduction in acid value was over 50% at low-methanol and over 80% for high-methanol ratios. There was no significant reduction in the acid value after 1 hr. This might be because the effect of water produced during the esterification of FFA, which prevented further reaction [22].

3.5 Catalysts

A commercial biodiesel production used conventionally an alkali-catalyzed process for the transesterification. Other approaches had been proposed including acid catalysis [38] and enzymatic catalysis [42]. The acid catalysts were useful for pretreating high FFA feedstocks but the rate of reaction for converting triglycerides to FAME were very slow. Enzymes had shown good tolerance for the FFA level of the feedstock, but the enzymes were expensive and unable to provide the degree of reaction completion required to meet the ASTM fuel specification [43].

3.5.1 Homogeneous catalyst

Homogeneous catalysts were taxing on equipment and at a raised temperature severely affected any metallic components. Although, acid-catalyzed reactions were slower than basic ones, they had potential if they could be immobilized. Problems with saponification were not present when esterification occurred and acid catalysts were not affected by FFA’s [44]. Catalytic activities were related to the Lewis acid strength of the metal, which must have an optimum intermediate value, and to the molecular structure of the anion. The best catalyst was lead acetate, Pb(AC)₂, for experiments which were made with the addition of water and FFA to soybean oil (7.4%wt/wt of FFA to oil). It obtained 96% FAME yields and less than 1% final FFA concentration, at 210-220°C in 200 min reaction time by using 0.0004:1 of a weight ratio of catalyst to oil [45].

However, the best commercial acid catalyst for promoting both esterification and transesterification processes was sulfuric acid. It had the advantages of using a lower molar methanol to oil ratio and did not necessitate a heavy neutralization process of the acid catalyst [3].

3.5.2 Heterogeneous catalyst

Heterogeneous catalysts were important to the developments of biodiesel production, combined with their applications in a continuous process and easy separation. They could decrease the production costs. Problems with water had not been fully addressed [44]. Tungstated zirconia-alumina (WZA) was a promising solid acid catalyst for the biodiesel production from soybean oil. Catalysts should be active enough for the esterification of FFA, a source of soap. The acid strength of WZA was suitable for both esterification and transesterification. It obtained over 90% conversions of the esterification of soybean oil with methanol at 175-200°C in 20 h [46].
3.5.3 Enzyme

Enzymes that can catalyze both the hydrolytic cleavage and the synthesis of ester bonds in glycerol esters are lipases. They enable conversion under mild conditions (Mild temperature, pressure and pH). Using an enzyme instead of a basic catalyst makes easier product phase separation [47]. Besides, both the esterification of FFA and the transesterification of glycerides occur in one process step. As a result, high FFA materials can be employed without pretreatment [48].

However, enzymes are easily inactivated by compounds containing in the oil or fat, namely phospholipids that inhibit lipase-catalyzed methanolsis efficiently [49]. Oils must be degummed for enzymatic catalysis. Moreover, the lipases require the presence of water that is an obstacle for the esterification reaction in concentrations ranging from 4-30 %w [50-51] to up to 80 %w [52] to sustain their catalytic activity. And the main drawback to the application of lipases in industrial biodiesel production is their high price [51].

4. Conclusion

This review shows the potential of biodiesel production from low-cost high FFA feedstock. The FAME content changed considerably with molar ratio of alcohol to oil, temperature, time, type and amount of catalyst. A good FAME conversion was obtained from the optimum conditions that depend on the four factors including the amounts of moisture and FFA content in the feedstock.

From Table 2, it implies that homogenous acid catalysis still has been an economical technology more than others. Because the low-cost materials, both oil and catalyst, can be used for operating with mild conditions to produce a high yield of FAME.

Although the use of feedstock having high FFA is an effective way of reducing biodiesel cost, continuous development and improvement of the biodiesel is important to produce cleaner fuel and lower cost compared to fossil fuels.

Eventually government supports can spur the industry and sustain biodiesel as a renewable energy.

References


[19] Benjapornkulapong, S., Ngacharussrivichai, C.


