Treatment of industrial low grade palm oil via esterification reaction using sonoreactor

Adeeb Hayyan a,b,*, Mohd Ali Hashim a,b, Mohamed E.S. Mirghani c, Maan Hayyan b,d, Inas M. AlNashef e

a Department of Chemical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
b University of Malaya Centre for Ionic Liquids (UMCiL), University of Malaya, Kuala Lumpur 50603, Malaysia
c Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, Kuala Lumpur 50728, Malaysia
d Department of Civil Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
e Chemical Engineering Department, King Saud University, Riyadh 11421, Saudi Arabia

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A B S T R A C T
In this study, the reduction of free fatty acid (FFA) in low grade palm oil (LGPO) was conducted at various sonication times, ranging from 30 to 300 min. Screening of various acids was reported and selected acid was considered for further study. The results found that strong acids such as sulfuric acid to be superior to other acids. The FFA content of LGPO decreased from 20% to less than 3%, using sulfuric acid at optimum conditions. Treated LGPO can be used as a new type of fuel for various applications such as biodiesel production.

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1. Introduction

In developing countries, biodiesel fuel has received renewed interest as a sustainable energy source because of increasing fuel prices and rising environmental concerns [1]. Biodiesel production from abundant bioresources has drawn the attention of academics as well as the industrial community in recent years [2]. The advantages of using biodiesel as engine fuel include reducing dependence on petroleum fuel and reducing hazardous air emissions from diesel engines [3–6].

The main obstacle to biodiesel production is its high cost compared to production of petroleum diesel fuel [7]. Therefore, much contemporary research is directed at finding new techniques to produce biodiesel from cheap raw materials. In Malaysia, large amounts of acidic oils, such as low grade palm oil (LGPO) and sludge palm oil (SPO), are produced as by products in palm oil mills. These oils can be converted to biodiesel and glycerol. According to Hayyan et al. [8,9], annual production of SPO and LGPO reaches 41 million tons. This huge amount of LGPO and SPO could be used to produce biodiesel, which would lower the total cost of biodiesel production significantly. Hayyan et al. [8,9] used sulfuric acid and toluene-4-sulfonic monohydrate acid to treat the high acidity in SPO using a chemical reactor with a mechanical stirrer. Acidic crude palm oil (ACPO) has also been used as an agro-industrial feedstock to produce biodiesel using acid catalyst such as ethanesulfonic acid [10].

Palm fatty acid distillate (PFAD) is low cost industrial acidic oil generated from palm oil refineries [11]. Deshmale et al. [12] used ultrasound technique to prepare biodiesel from PFAD. The main problem with palm acidic oils such as SPO, ACPO, PFAD and LGPO is their high free fatty acid (FFA) content. An esterification reaction needs to be performed to convert FFA to fatty acid methyl ester (FAME) [13]. Cavitation reaction engineering is very important field for cleaner and environmental production of products. Definition of cavitation is “the formation and activity of bubbles or cavities in a liquids and it can be a result of the enlargement of cavities that are already present in the bulk liquid” [14]. Ultrasound energy or ultrasound irradiation has been used in a wide range of applications and fields such as preparation of nanomaterials, food processing, polymer chemistry, electrochemistry, green chemistry and biodiesel production [15]. Ultrasound used widely for kinetics enhancement of many chemical reactions such esterification of FFA [16].

Ultrasound energy can also be used to reduce FFA to an acceptable level before transesterification to produce biodiesel [17,18]. Sonoreactor has been found to be an effective tool for...
estimation of fatty acids [19]. Parkar et al. [19] studied the physical mechanism and kinetic aspects of ultrasound energy on methylation of soybean using sulfuric acid as catalyst. While Kalva et al. [20] discriminating between physical and chemical effects of ultrasound for biodiesel preparation. A comprehensive review on biodiesel production using sonoreactor was reported by Gole and Gogate [21].

Kekal et al. [22] studied esterification of fatty acids (in range C₁₆−C₁₀₀) for biodiesel production using acoustic and hydrodynamic cavitation. Santos et al. [23] produced biodiesel from Oreochromis niloticus L. oil for biodiesel production. All these studies have used sulfuric acid as a catalyst to convert FFA to FAME. A study on the effect of ultrasonic energy on vegetable oil based biodiesel was carried out by Lee et al. [24]. Recently, biodiesel produced from non-edible oils using a sequential combination of microwave and ultrasound [26]. Likewise, biodiesel was prepared from Nog champu oil with high acid value using sonoreactors [27]. Waste cooking oil was used as a low cost raw material for synthesis of biodiesel [28]. In recent literature, few studies have used chemical reactors to treat acidic oils such as low grade crude palm oil [29,30]. The application of ultrasonic energy for the treatment of high FFA content such as LGPO and for biodiesel production has not been yet studied. Therefore, the main aim of this study is to use LGPO as a cheap raw material, in the presence of an acidic catalyst using ultrasonic energy. Optimization of various parameters was conducted to find the optimum conditions for the pretreatment of LGPO using a sonoreactor. These included the effect of different acids, catalyst dosage, molar ratio, and temperature. Finally, characterization of the biodiesel fuel was carried out using international standards.

2. Materials and methods

2.1. Raw materials and chemicals

LGPO was obtained from a local mill, Selangor, Malaysia. Methanol (99.8%) and potassium hydroxide (KOH) pellets (85%) were obtained from R&M Chemicals. Sulfuric acid (98%) was obtained from Merck Sdn Bhd, Malaysia.

2.2. Methodology

Various types of acid were used for the screening study such as sulfamic acid, formic acid, sulfuric acid, and orthophosphoric acid. The comparison of different types of acids was conducted under fixed conditions such as 1% (dosage of acid to LGPO) with a molar ratio of 10:1 of methanol to LGPO at 60 °C. The selected acid was added into 150 ml of preheated LGPO at various acid dosages (0.5%, 1%, and 2%, w/w) in the presence of methanol to reduce FFA in the LGPO by converting the FFA to FAME. The molar ratio of methanol to LGPO (6:1, 10:1, and 14:1) and reaction temperature (50 °C, 60 °C, and 70 °C, respectively) were reported. The effects of these parameters on the reduction of FFA content at the various sonication times (30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 min) were determined. After each run the sample was transferred to a rotary evaporator to remove the excess methanol. The sample was washed using warm water to remove the residual catalyst and other impurities. After purification of the treated LGPO, the FFA content was measured according to AOCS (Ca 5a-40) [31]. All experiments were performed in an Erlenmeyer-type flask connected to a coil condenser. The pretreatment of LGPO through an esterification reaction was performed using an ultrasonic cleaner (40 KHz), Model: JAC-2010 (P) from KODO Technical Research Co., Ltd (Hwaseong-City, Gyeonggi-Do, Korea). The transesterification reaction of the treated LGPO was performed using 1 wt% KOH dissolved in methanol (10:1 M ratio) for a 60 min reaction time and at 60 °C reaction temperature. After each experiment, the reaction was stopped at a specified time, and the reaction mixture was allowed to settle in a separating funnel for 2 h. The final product was purified and characterized according to EN 14214 and ASTM D6751.

2.3. Analytical analysis

The fatty acid composition of the LGPO was determined using GC/MS (Agilent Technologies 7890A). The capillary column was a DB-wax 122-7032, with a length of 30 m, a film thickness of 0.25 μm, and an internal diameter of 0.25 mm. Helium was used as carrier gas with a flow rate of 36 cm/s, measured at 50 °C. The runtime was 35 min. One micro meter of the neat sample was diluted in hexane before injection into the GC/MS.

3. Results and discussions

3.1. Fatty acid profile of LGPO

It was reported that the cavitation phenomena can be affected by the physicochemical properties of the material. The low vapor pressure, low viscosity and higher value of surface tension are important for maximizing the cavitations effects [27]. In the high viscous non-Newtonian liquids, the violent collapse of the cavity is damped severely by the viscoelastic forces [32]. Hence, it has been mentioned that liquids with low viscosity are preferred for use in sonoreactions [15]. In order to reduce the viscosity of LGPO, it was heated at 70 °C for easily handling and use during the experiments.

Table 1 shows the fatty acid composition of the LGPO. As shown, the fatty acids present in LGPO are palmitic acid, stearic acid, oleic acid, and linoleic acid. According to Table 1, it was found that the saturated fatty acid content of LGPO is 50.301 wt%. Hayyan et al. [8] used SPO and Elsheikh et al. [33] used crude palm oil (CPO) for biodiesel production. They reported saturated fatty acid values of 47.17 wt% for SPO and 53.76 wt% for CPO, respectively. The saturated fatty acids in LGPO increase the viscosity and raise the pour point. The high concentration of saturated fatty acids is useful for increasing the cetane number and reducing susceptibility to oxidation [4]. The average molecular weight was calculated based on the saponification value. The average molecular weight of LGPO we found to be 822.5 g/mol. The FFA content of the LGPO used was 20%.

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Type of fatty acid</th>
<th>Structure</th>
<th>wt%a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caproic acid</td>
<td>Saturated</td>
<td>C6:0</td>
<td>0.022 ± 0.001</td>
</tr>
<tr>
<td>Caprylic acid</td>
<td>Saturated</td>
<td>C8:0</td>
<td>0.097 ± 0.05</td>
</tr>
<tr>
<td>Capric acid</td>
<td>Saturated</td>
<td>C10:0</td>
<td>0.082 ± 0.01</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>Saturated</td>
<td>C12:0</td>
<td>1.210 ± 0.95</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>Saturated</td>
<td>C14:0</td>
<td>1.460 ± 0.22</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>Saturated</td>
<td>C16:0</td>
<td>42.94 ± 3.95</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>Unsaturated</td>
<td>C16:1</td>
<td>0.120 ± 0.01</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>Saturated</td>
<td>C18:0</td>
<td>4.110 ± 0.26</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>Unsaturated</td>
<td>C18:1</td>
<td>39.78 ± 1.58</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>Unsaturated</td>
<td>C18:2</td>
<td>09.67 ± 1.40</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>Saturated</td>
<td>C20:0</td>
<td>0.038 ± 0.011</td>
</tr>
<tr>
<td>Alpha-Linolenic acid</td>
<td>Unsaturated</td>
<td>C18:3</td>
<td>0.012 ± 0.022</td>
</tr>
</tbody>
</table>

a Results are the average of three replicates ± standard deviation.
3.2. Screening of different acids

It was stated that transesterification reaction does not occur if the FFA content is more than 5%. However, high FFA content may reduce the yield of biodiesel [34]. Therefore, the limit for FFA content was set to a maximum of 3% for all esterification experiments. The FFA reduction will allow for an efficient transesterification reaction and will increase the yield of biodiesel fuel [29]. Fig. 1 shows the effect of different types of acids for LGPO pretreatment. This study used four types of acids such as sulfamic acid, formic acid, sulfuric acid, and orthophosphoric acid. This study also investigated the effect of methanol without acid. As shown in Fig. 1, methanol in the absence of acid had no catalytic effect. The catalytic activity of the four acids varied depending on whether it was a weak acid (orthophosphoric acid and formic acid) or a strong acid (sulfamic acid and sulfuric acid). As shown in Fig. 1, the weak acids did not cause any reduction of FFA content. Sulfamic acid showed a slight reduction in the FFA content of the LGPO and the reduction was almost constant at approximately 2–4% FFA content at various sonication times. Sulfuric acid, the preferred acid catalyst for the pretreatment of LGPO through an esterification reaction, showed the highest reduction of FFA content in LGPO after 30 min of sonication. Fig. 1 indicates that the sonication time has a significant effect on the reduction of the FFA content. According to the results it was found that 300 min of sonication time is sufficient to achieve the target of 3% of FFA content.

3.3. Effect of sulfuryc acid dosage in the reduction of FFA content

The cavitation effects can be classified as a chemical effect and a physical effect (liquid circulation with intense turbulence). This cavitation will enhance the rate of transport processes [21]. Cavitation occurs at millions of locations in the sonoreactor simultaneously and generates conditions of very high temperatures and pressures [21]. The esterification reaction takes place due to the high catalytic activity of the catalyst and sufficient cavitational effects. Therefore, the role of catalyst is very important to complete the reaction and to convert FFA to FAME effectively. The high catalytic activity of catalyst will enhance the esterification reaction significantly.

Esterification mechanism involves an acid-catalyzed nucleophilic acyl substitution. An alcohol such as methanol is not strong enough nucleophile to attack the carbonyl group of a carboxylic acid [35]. In this study, ultrasonic energy was used to enhance the acid catalyst (sulfamic acid) to protonate the carbonyl group toward nucleophilic attack via waves generated from ultrasonic cleaner. When ultrasound operated for a certain frequency, the waves will start to vibrate the FFA of LGPO with reactants include methanol and the catalyst. This vibration will provide such mixing or contacting between FFA and the reactants. The vibration with temperature will enhance the esterification reaction and speed it up. Hence, ultrasonic cleaner can be considered as reactor (sonoreactor). During esterification reaction micro-emulsion will be formed between FFA with reactants due to the random distribution of ultrasound waves and cavitation bubbles generated in the sonoreactor. There are many factors effecting the esterification reaction in sonoreactor such as temperature, time of sonication and the frequency rate. However, Parkar et al. [19] stated that the macroscopic rate of reaction depends on the interfacial area between oil and reactants.

The results showed that sulfuric acid is a highly effective catalyst in the esterification reaction. Fig. 2 shows the effect of various quantities of sulfuric acid on the FFA content of LGPO. The FFA content decreased from 20% to less than 3% when using 2% (w/w) (sulfuric acid to LGPO) after 300 min of sonication. The 2% (w/w) value of sulfuric acid yielded the lowest FFA content. The 0.5% and 1% (w/w) values of sulfuric acid to LGPO did not reduce the FFA content to below 3%, even after sonication for 300 min. The conversion yields of FFA to FAME using 0.5%, 1%, and 2% sulfuric acid to LGPO in 300 min were 83.6, 85.1%, and 86.6%, respectively. Santos et al. [23] used sulfuric acid as a catalyst and found the optimum quantity of the acid catalyst to be 2%, which is similar to the results obtained in the present study.

3.4. Effect of molar ratio in the reduction of FFA content

The molar ratio is one of the most important factors in the conversion of FFA to FAME, as well as in the overall production cost of biodiesel [8]. In this study, the molar ratio of methanol to LGPO was 6:1; 10:1, and 14:1. Fig. 3 shows the effect of the molar ratio on the reduction of FFA content in LGPO. The reduction of FFA content using a 6:1 ratio was low compared to ratios of 10:1 and 14:1. When the molar ratio increased from 10:1 to 14:1, there was no significant change in the reduction of FFA content. Using a minimum amount of methanol can reduce the cost of the pretreatment process. Thus, molar ratio of 10:1 was the optimum ratio to convert FFA to FAME. This ratio reduced the FFA content of LGPO from 20% to approximately 3%, which is the upper limit of the FFA content for the transesterification reaction. The conversion of FFA to FAME using molar ratios of 6:1; 10:1, and 14:1 methanol to LGPO for 300 min were 81.6%, 85.1%, and 85.8%, respectively. Deng et al. [24] used an ultrasonic reactor in the esterification of Jatropha curcas L. oil in the presence of 4 (v/v%) of sulfuric acid to Jatropha oil and a methanol/oil volume ratio of 40 (v/v%). The LGPO pretreatment involved using little or less amount of methanol, and the FFA content was much higher than in Jatropha curcas L. oil.
3.5. Effect of reaction temperature in the reduction of FFA content

In this study, the reaction temperature was set at 50 °C, 60 °C, and 70 °C with different sonication times. Fig. 4 shows the effect of the reaction temperature on the reduction of FFA content of the LGPO. At 70 °C the rate of reaction increased and the reaction completed in a shorter time (180 min). High reaction temperatures reduce the viscosity of the LGPO. Thus, the reaction is accelerated by easier mixing between the LGPO and other reactants.

The boiling point of methanol is 64.5 °C [6,8,9]. The conversion of FFA to FAME using reaction temperatures of 50 °C, 60 °C, and 70 °C for 300 min was 92%, 85.3%, and 91.6%, respectively. Because of the low conversion rate of FFA to FAME at 60 °C, this temperature value was eliminated as the optimum reaction temperature to achieve the targeted FFA content. To save energy and to lower the cost of the process, a reaction temperature of 50 °C is preferable to those ones of 60 °C and 70 °C. At a reaction temperature of 50 °C, the FFA content of the LGPO decreased from 24.5% to 2.8% after 180 min of sonication, and to 1.9% after 300 min.

3.6. Transesterification of the treated LGPO

Transesterification reactions can be applied after treatment of acidic oils via esterification reaction [4,9]. The FFA content in treated oils should be as low as possible in order to avoid the saponification reaction [27]. Treated LGPO is used as raw material for the transesterification reaction in the presence of an alkaline catalyst such as KOH. The FFA content was reduced from 20% to less than 3% using the optimum conditions for the esterification.

Table 2

| Fatty acid composition of biodiesel from LGPO. |
|---|---|---|---|
| Systematic name of FAME | Carbon chains | Type of fatty acid | wt%<sup>a</sup> |
| Dodecaneic acid methyl ester | C12:0 | Saturated | 0.00 ± 0.01 |
| Tetradecanoic acid methyl ester | C14:0 | Saturated | 0.05 ± 0.03 |
| Hexadecanoic acid methyl ester | C16:0 | Saturated | 0.20 ± 0.03 |
| Hexadecenoic acid methyl ester | C16:1 | Unsaturated | 0.00 ± 0.03 |
| Nonadecanoic acid methyl ester | C18:0 | Saturated | 0.00 ± 0.03 |
| Cis 9-Octadecenoic acid methyl ester | C18:1 | Unsaturated | 0.00 ± 0.03 |
| All cis 9,12-Octadecadienoic acid methyl ester | C18:2 | Unsaturated | 0.00 ± 0.03 |
| All cis 9,12,15-Octadecatrienoic acid methyl ester | C18:3 | Unsaturated | 0.00 ± 0.03 |
| Eicosanoic acid methyl ester | C20:0 | Saturated | 0.00 ± 0.03 |

<sup>a</sup> Results are the average of three replicates ± standard deviation.

Table 3

| Specifications of LGPO biodiesel. |
|---|---|---|---|
| Properties | Biodiesel from LGPO | EN 14214 | ASTM D6751 |
| | Test method | Limits | Test method | Limits |
| Ester content | 60.3% (mol mol<sup>−1</sup>) | EN 14103 | 60.5% (mol mol<sup>−1</sup>) min | – |
| Monooctylglycerol content | 0.05% (mol mol<sup>−1</sup>) | EN 14105 | 0.05% (mol mol<sup>−1</sup>) max | – |
| Diactylglycerol content | 0.05% (mol mol<sup>−1</sup>) | EN 14105 | 0.20% (mol mol<sup>−1</sup>) max | – |
| Tetraoctylglycerol content | <0.01% (mol mol<sup>−1</sup>) | EN 14105 | 0.20% (mol mol<sup>−1</sup>) max | – |
| Free glycerol content | <0.01% (mol mol<sup>−1</sup>) | EN 14105 | 0.02% (mol mol<sup>−1</sup>) max | ASTM D 6584 0.02% (w/w) max |
| Total glycerol content | 0.05% (mol mol<sup>−1</sup>) | EN 14105 | 0.25% (mol mol<sup>−1</sup>) max | ASTM D 6584 0.24% (w/w) max |
| Water content | 455 mg kg<sup>−1</sup> | EN ISO 12937 | 500 mg kg<sup>−1</sup> max | ASTM D 2709 0.050% (v/v) max |
| K content | 1 mg kg<sup>−1</sup> max | EN 14108 | 5.0 mg kg<sup>−1</sup> max | UOP 391 5.0 mg kg<sup>−1</sup> max |
| P content | 7.1 mg kg<sup>−1</sup> max | EN 14107 | 10.0 mg kg<sup>−1</sup> max | ASTM D 4951 0.001% (w/w) max |
| Density (15 °C) | 877 kg m<sup>−3</sup> | EN ISO 3675 | 860–900 kg m<sup>−3</sup> | ASTM D 93 130 °C min |
| Flash point | 183.3 °C | EN ISO 3679 | 120 °C min | ASTM D 2500 Not specified |
| Cloud point | 16.07 °C | – | – | ASTM D 874 0.020% (w/w) max |
| Sulalted ash | <0.005% (w/w) | ISO 3987 | 0.02% (mol mol<sup>−1</sup>) max | ASTM D 874 0.020% (w/w) max |
| Total contamination | 0.008 mg kg<sup>−1</sup> | EN 12662 | 24 mg kg<sup>−1</sup> max | – |
| Iodine value | 50.22 ± 12 100 g<sup>−1</sup> | EN 14111 | 120 g I2 100 g<sup>−1</sup> max | – |
| Copper strip corrosion (3 h at 50 °C) | Class 1 | EN ISO 2160 | Class 1 rating | ASTM D130 No. 3 max |
reaction. Treated LGPO is a mixture of triacylglycerols (TAG) and FAME, and contains less than 3% of FFA. It can be used as fuel in boilers and stationary engines. However, this type of fuel is unsuitable for use in diesel engines of vehicles. Further reduction of TAG and FFA content should be performed before direct use in diesel engines. After the transesterification reaction, an 88% yield of biodiesel from treated LGPO was achieved, with satisfactory physic-chemical properties. The fatty acid profile of treated LGPO is shown in Table 2. The fatty acids in the highest concentrations were palmitic acid, oleic acid, and linoleic acid. Biodiesel from LGPO contains 49.67% (w/w) saturated fatty acids. The remaining fatty acids were unsaturated fatty acids. Canakci [36] indicated that saturated fatty acids yield a high cetane number and improved oxidation stability. Table 3 shows the biodiesel properties according to EN 14214 and ASTM D6751. This type of biodiesel, produced from treated LGPO, can reduce the total cost of biodiesel production. Flash point and copper strip corrosion tests yielded promising results regarding safety and corrosiveness compared to petroleum diesel. Further studies are required to investigate the use of ultrasonic energy to treat acidic oils using various acid catalysts to produce products such as biodiesel and glycerol. This study is the first to focus on LGPO with a high FFA content using ultrasonic energy, and further studies on the kinetics of the reaction are necessary.

4. Conclusion

This study described the pretreatment of LGPO using ultrasonic energy. The results showed that sonication time is an important factor in the pretreatment of LGPO. It was found that the pretreatment by esterification using a sonoreactor was a highly effective and useful technique for biodiesel production. The optimum conditions (2% sulfuric acid to LGPO, 10:1 molar ratio, 50 °C temperature at 300 min reaction time) reduced the FFA content in LGPO from 20% to less than 3%. Biodiesel produced from treated LGPO meets the international biodiesel standards such as EN 14214 and ASTM D6751.

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References

[35] L. Chi. The production of methyl esters from vegetable oil/fatty acid mixtures, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Canada, 1999 (Master’s thesis).