Ethanesulfonic acid-based esterification of industrial acidic crude palm oil for biodiesel production


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A B S T R A C T
An industrial grade acidic crude palm oil (ACPO) pre-treatment process was carried out using ethanesulfonic acid (ESA) as a catalyst in the esterification reaction. ESA was used in different dosages to reduce free fatty acid (FFA) to a minimum level for the second stage of biodiesel production via alkaline transesterification reaction. Different process operating conditions were optimized such as ESA dosage (0.25–3.5% wt/wt), methanol to ACPO molar ratio (1:1–20:1), reaction temperature (40–70 °C), and reaction time (3–150 min). This study revealed the potential use of abundant quantities of ACPO from oil palm mills for biodiesel production. The lab scale results showed the effectiveness of the pre-treatment process using ESA catalyst. Three consecutive catalyst recycling runs were achieved without significant degradation in its performance. Second and third reuse runs needed more reaction time to achieve the target level of FFA content. Esterification and transesterification using ESA and KOH respectively is proposed for biodiesel industrial scale production. The produced biodiesel meets the international standards specifications for biodiesel fuel (EN 14214 and ASTM D6751).

1. Introduction
Biodiesel is a promising biofuel made from natural bioresources such as vegetable oils and animal fats (Demirbas, 2009; Hayyan et al., 2010a). Malaysia being one of the largest world palm oil producers and exporters, has the potential of leading the palm oil biodiesel production sector (Kalam and Masjuki, 2002; Chew and Bhatia, 2008; Hayyan et al., 2011). Crude palm oil (CPO) was used as an industrial raw material for biodiesel production because of its availability as a product of industrial mills. CPO after the milling process is non-edible due to its high FFA and impurities content. Hence, CPO is usually sent to the refinery for further processing and purification. CPO is conventionally used as a raw material for biodiesel production (ElSheikh et al., 2011; Crabbe et al., 2001). According to annual statistical reports of MPOB (Malaysian palm oil board, 2010) the estimated production of CPO reached 17.5 million metric tons in 2010. This report highlighted the fact that international prices of CPO were fluctuating according to CPO global market demand. CPO is the raw material for refined palm oil processing industries. Moreover, the composition of CPO involves important constituents with high concentrations such as carotenoids, tocopherols, tocotrienols, sterols, phospholipids, triterpene alcohols, squalene, aliphatic alcohols and aliphatic hydrocarbons (Goh et al., 1985; Gunstone, 2002). CPO value as an edible ingredient for refined palm oil increases its economical importance. Due to limited annual production of CPO and the increasing global market demand, the priority for palm oil mills is to sell CPO to palm oil refineries as a raw material for food processing. In view of the above mentioned facts, many obstacles exist for the commercialization of biodiesel produced from CPO. Hence, finding and highlighting new bio-industrial resources for biodiesel production is one of the urgent priorities of the industrial and academic community in order to make biodiesel production economical and commercially feasible. Acidic crude palm oil (ACPO) is an unfavorable type of CPO produced from palm oil mills due to different operational and processing factors. Possible reasons for producing ACPO involve technical milling problems, long time oil storage, delay of fruit harvesting, unexpected climate changes, in addition to the variation of storage environment and temperature. Usually, CPO with FFA lower than 5% is considered as an acceptable CPO grade which can be sent directly to the palm oil refinery. ACPO has an FFA content higher than 5% and consequently it needs to undergo a pre-treatment stage to remove the high FFA before proceeding to other palm oil refinery processing stages. FFA content is the controlling key factor for pricing different verities of oils and fats.
ACPO as an agricultural raw material with a much lower price compared to CPO due to the unfavorable higher FFA content of ACPO in addition to existence of other undesirable impurities. From an economical point of view, ACPO is a significant raw material for biodiesel production which can reduce the total cost of biodiesel processing. Based on the abovementioned discussion, this study proposes ACPO as a cheap alternative raw material for the biodiesel industry. The cost of feedstock accounts for 60–75% of the total production cost of biodiesel fuel (Krawczyk, 1996; Ma and Hanna, 1999). The remaining cost is related to processing expenses. Exploring ways to enhance process economy in terms of reactor development and reaction engineering are the foci of current biodiesel research studies. Catalyst technology has significant effect on the biodiesel production industry. Many attempts have been made to produce biodiesel using different types of homogeneous catalysts such as methanesulfonic acid and sulfuric acid (Aranda et al., 2008), as well as heterogeneous catalysts such as tri-potassium phosphate (Guan et al., 2009). Lipase enzyme was used as a biocatalyst in the esterification of high FFA content of oils and fats for biodiesel production (Vieira et al., 2006). However, it is noticed that there are very few studies on using sulfonic based acids such as ethanesulfonic acid (ESA) for biodiesel synthesis. The use of p-toluenesulfonic acid (PTSA) in the reduction of high FFA content in acidic oils has been reported in the literature (Di serio et al. 2008; Hayyan et al., 2010b).

This study proposes ACPO as a renewable raw material for biodiesel production. Pre-treatment of ACPO was conducted via an esterification utilizing ESA as a catalyst. The main objectives of this study are (a) to investigate the usage of ACPO as a low-cost agro-industrial raw material for the biodiesel production; (b) to study the effect of ESA catalyst dosage on reaction yield; (c) to study the effect of other operating parameters such as molar ratio, reaction temperature and reaction time on the pre-treatment of ACPO; (d) to evaluate the recyclability of ESA and characterize the quality of produced biodiesel after transesterification reaction.

2. Methods

2.1. Raw material and chemicals

ACPO was collected from a local mill, Selangor Darul Ehsan, Malaysia. Methanol 99.8% and potassium hydroxide (KOH) pellets 85% were purchased from R&M Chemicals. Ethanesulfonic acid (C2H6O3S) 98% laboratory grades was purchased from Merck Sdn Bhd, Malaysia.

2.2. Synthesis of biodiesel from ACPO

Acidic crude palm oil exists as a semisolid phase at room temperature which leads to difficulties in the transferring, handling and to slow down the reaction. Consequently, ACPO was heated at 70 °C in the oven. Methanol was added to the pre-heated ACPO and mixed for 5–10 min. In order to increase the homogeneity among reactants, ESA catalyst was added to the reactor after a period of 30 min from reaction startup time. The FFA content of the treated ACPO was measured and reported for all experiments. Biodiesel was produced from ACPO via two catalyzed reactions (esterification and transesterification). In the pre-treatment stage, the ACPO sample weight for each experiment was 500 gm. While in the second reaction potassium hydroxide (KOH) was used as a catalyst in order to convert the triacylglycerols (TAG) to fatty acid methyl ester (FAME). The product of the esterification reaction is considered as a raw material for the transesterification reaction. Following transesterification reaction, gravity separation and evaporation of excess methanol were performed. The product was treated by water washing to remove the impurities, free glycerol, soap and residuals of alkaline catalyst.

Validation experiments were conducted several times in order to investigate the optimum conditions of ACPO pre-treatment process. In the second stage, 1% wt KOH was dissolved in methanol (10:1 M ratio) and then the mixture was added to the pre-treated ACPO in the transesterification reactor after a period of 30 min from reaction startup. Recyclability of ESA was examined via separating the spent catalyst and reusing it to treat ACPO for further consecutive runs. The last stage of this study was the characterization of the produced biodiesel using the EN 14214 and ASTM D6751 international biodiesel standards. All experimental runs were performed in a lab scale batch multiunit reactor system with methanol reflux. The reaction temperature and mixing intensity were monitored and controlled using specially designed feedback controllers.

2.3. Chemical analytical analysis

The ACPO FFA content after each experiment was determined according to the American Oil Chemist’s Society (AOCS) official method Ca 5a-40 commercial fats and oils (AOCS, 1997). Characteristics of ACPO were determined according to MPOB test methods (Kuntom et al., 2005). The fatty acid composition of ACPO was determined using GC/MS (Agilent Technologies 7890A gas chromatograph equipped with 5975C mass spectrometer), with a capillary column DB-wax 122-7032. Ester content, mono-, di- and triacylglycerols (TAG), free and total glycerol content were determined using GC/FID (Perkin Elmer Clarus 500).

3. Results and discussion

3.1. Characteristics of ACPO

Investigating feedstock characteristics during the early stage of research is a crucial requirement for any industrial application. In this work ESA was used as sulfonic acid based catalyst in the esterification reaction. The pre-treatment of high content oils and fats by esterification reaction was proposed in different studies (Liu, 1994; Canakci and Van Gerpen, 2001; Naik et al., 2008; Hayyan et al., 2010b). Pre-treatment of acidic oils or fats before biodiesel production is considered as an essential stage especially if the raw materials are of high FFA content (Ma and Hanna, 1999; Canakci and Van Gerpen, 2001; Demirbas, 2009). Thus, an acid catalyzed pre-treatment step by esterification reaction to convert the FFA to FAME followed by transesterification reaction using alkalii-catalyzed offers an effective and efficient method to convert high FFA feedstock to biodiesel fuel (Canakci and Van Gerpen, 2003). The physicochemical properties of various oils as products or by-products of industrial palm oil mills vary in accordance with many factors such as the milling process conditions, the location from which oil was produced (within the mill), water content, storage time, technical problems during milling etc.

Sludge palm oil (SPO) was previously studied as a possible raw material for biodiesel production (Hayyan et al., 2010b, 2011). The physicochemical properties of SPO are very close to that of ACPO because both oils share the same origin from industrial mills with different FFA content. ACPO and SPO have lower quality compared to crude palm oil in terms of FFA, moisture and other contaminants contents. Table 1 shows the similarities and differences between SPO and ACPO. Generally, industrial mill byproducts such as SPO and ACPO are traded based on FFA, moisture and impurities contents (Lin, 1989). Due to its lower specifications, ACPO has less cost per ton than that of CPO. Table 1 shows that the peroxide value of ACPO is higher than that of SPO. While the FFA content in ACPO lies

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between that of SPO and CPO which indicates that ACPO ranks after CPO and before SPO in terms of quality. ACPO and SPO are of lower quality compared to CPO in terms of FFA, moisture and other contaminants contents. The FFA content of ACPO in this study was 8.6% while the corresponding CPO value was below 5% (Tan et al., 2009). An oil with FFA content higher than 15% is considered as SPO (Lin, 1989). The water content in SPO and ACPO was higher than that of CPO. Based on the saponification value of ACPO, the calculated average molecular weight was 827 which was used in the molar ratio calculation. ACPO has low grade characterization parameters such as FFA, peroxide value and moisture content due to long storage conditions. Products and byproducts of industrial palm oil mills such as CPO and SPO are generally traded based on FFA, moisture and impurities contents (Lin, 1989). Table 1 shows a comparison of properties between SPO and ACPO. It is clear that ACPO has the highest FFA content and poor quality indicators which highlight the importance of a reliable pre-treatment stage in its processing. Accordingly, an acid-based esterification is needed prior to the main transesterification stage.

### 3.2. Fatty acid composition of ACPO

The fatty acid composition of ACPO plays an essential role in qualifying the structure of oils and fats. Table 2 shows the fatty acid composition of ACPO. The principal ACPO fatty acids are: oleic, palmitic, linoleic and stearic acid. Saturated fatty acids in ACPO were 50.23 wt.% while unsaturated fatty acids were 49.70 wt.%. The composition of saturated and unsaturated fatty acids obtained in this work were slightly different compared to those reported by Elsheikh et al., 2011. According to the results obtained by Hayyan et al., 2010b, saturated fatty acids in SPO were 47.17 wt.% while the unsaturated fatty acids were 50.83 wt.%. The chemical compositions of fatty acids from various products and by-products of industrial mills are very similar in many aspects.

FFA content of ACPO increased proportionally with storage time. It was observed that FFA content of ACPO increased at room temperature by an amount of 1% after 6 months storage time.

### Table 1

**Characteristics of ACPO.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SPO</th>
<th>ACPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free fatty acid, FFA (%)</td>
<td>22.33 ± 0.77</td>
<td>8.6 ± 0.40</td>
</tr>
<tr>
<td>Peroxide value (ml mol/kg)</td>
<td>1.52 ± 0.40</td>
<td>7.45 ± 0.55</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>1.20 ± 0.06</td>
<td>1.105 ± 0.2</td>
</tr>
<tr>
<td>Iodine value, IV</td>
<td>53.4 ± 0.71</td>
<td>56 ± 0.52</td>
</tr>
<tr>
<td>Impurities (%)</td>
<td>0.05 ± 0.007</td>
<td>0.056 ± 0.006</td>
</tr>
<tr>
<td>Saponification value (mg KOH/g oil)</td>
<td>190 ± 1.41</td>
<td>197.0 ± 1.70</td>
</tr>
<tr>
<td>Unsaturation matter (%)</td>
<td>1.47 ± 0.26</td>
<td>6.70 ± 0.26</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>0.015 ± 0.001</td>
<td>0.011 ± 0.001</td>
</tr>
<tr>
<td>Anisidine value (AV)</td>
<td>–</td>
<td>3.3 ± 0.052</td>
</tr>
<tr>
<td>Acid value (mg KOH/mg)</td>
<td>48.88 ± 1.70</td>
<td>17.02 ± 0.5</td>
</tr>
<tr>
<td>DOBI (Index)</td>
<td>0.55 ± 0.03</td>
<td>1.80 ± 0.033</td>
</tr>
</tbody>
</table>

Note: Hayyan et al., 2010b.

There are many other factors that affect the degree of oils decomposition and increase the FFA content such as water content of oil, storage time, environment and temperature of the storage place also the type of container can effect if the container isolated or it was opened to air for long time etc. Storage time has a significant effect on the increase of high FFA content of ACPO. Naturally, ACPO exists in a semisolid or solid form at room temperature (27 ± 2°C) due to the availability of saturated fatty acids and the high content of FFA compared to CPO or refined palm oil. Therefore, ACPO has higher pour and cloud points as compared to low FFA content crude palm oil. Consequently, ACPO should be pre-heated before proceeding to the pre-treatment stage using the esterification reaction. On the other hand, higher saturated fatty acids in oils give a higher cetane number and make the oil less prone to oxidation (Canakci and Van Gerpen, 2001).

### 3.3. Pre-treatment of ACPO using ESA

The FFA content of untreated ACPO used in this study was 8.6%, which is not favorable for biodiesel production. The study conducted by Canakci and Van Gerpen (2001, 2003) indicated that the transesterification reaction will not occur if the FFA content in oil is more than 3%. However, Ramadhas et al., 2005 recommended a level of FFA of less than 2% while most studies recommended the reduction of FFA content to less than 1% for transesterification reaction using homogeneous base catalyst (Liu, 1994; Canakci and Van Gerpen, 2001; Naik et al., 2008; Demirbas, 2009). Thus, in this study, the FFA limit was set to a maximum of 1%. The ESA dosages, molar ratio of methanol to ACPO, reaction temperature and reaction time are the main factors affecting the pre-treatment stage via the esterification reaction.

#### 3.3.1. Effect of ESA dosage

Catalyst dosage plays a very important role during the esterification reaction. Finding the optimum dosage of catalyst has the priority among all reaction parameters due to its effectiveness to the whole process. Fig. 1 shows the effect of ESA dosages on reducing the FFA content in ACPO, conversion of FFA to FAME and yield of treated ACPO. The FFA content was reduced from 8.6% to less than 1% in the range of 0.75–3.5 wt.%. Low ESA dosage less than 0.75 wt.% was insufficient to decrease the FFA content to the target FFA content. As indicated by Fig. 1, a catalyst dosage of 0.25% reduced the FFA content to 2.22% while using a dosage of 0.5%, the FFA content was reduced to 1.3%. The FFA reduction achieved by the 0.5% dosage was very close to the industrial acceptable limit. An FFA content below 2% can be used for biodiesel production via alkaline transesterification. In order to enhance the reaction and to increase the efficiency of the pre-treatment process, an

![Fig. 1. Effect of ESA dosages on FFA content reduction, conversion of FFA to FAME and yield of treated ACPO at 10:1 M ratio, 60°C reaction temperature, 60 min reaction time and 300 rpm stirrer speed.](image-url)
3.3.2. Effect of molar ratio

Methanol is one of the major components in the pre-treatment process via esterification reaction. Its molar ratio significantly affects the conversion of FFA to FAME during the course of reaction. From an economic perspective, controlling the molar ratio results in reducing the overall production cost of biodiesel. In this study, the molar ratio was studied in the range (1:1–20:1). Fig. 2 shows the effect of molar ratio on the reduction of high FFA content in ACPO, conversion of FFA to FAME and yield of treated ACPO. Low loading of methanol makes the reaction insufficient to decrease FFA content to the target FAME level. The reduction of FFA content using molar ratios of 1:1 and 5:1 was 5.66% and 2.32% respectively. Based on the stoichiometry of the esterification reaction a molar ratio of 1:1 is needed in order to drive the reaction towards completion (Demirbas, 2009; Park et al., 2010). On the other hand, results of this study showed that a 1:1 M ratio was not enough to reduce the FFA content to less than 1%. Practically, the molar ratio of esterification reaction should be much higher than 5:1. Hence, further molar ratios were studied in order to select the optimum value and to investigate the pre-treatment process economy. The FFA content was decreased from 8.6% to less than 1% using the molar ratios range of 10:1–20:1. A 10:1 M ratio was sufficient to decrease the high FFA content in ACPO from 8.6% to 0.56%. Excess molar ratio did not show any improvement in the reduction of FFA content. Therefore, 10:1 was selected as the optimum value for esterification reaction using ESA catalyst. Using this molar ratio, the yield of treated ACPO was 96% while the conversion of FFA to FAME was 93.47%. This corresponds to the same finding reported by Hayyan et al. (2010b, 2011) using SPO for biodiesel production.

3.3.3. Effect of reaction temperature

Biodiesel production reactors involve a highly complex set of chemical reactions and heat transfer characteristics (Mjalli et al., 2009). At high temperatures, methanol tends to evaporate faster and finally the reaction loses one of the important ingredients in esterification reaction. Moreover, energy consumption for industrial scale production will increase with the increase of reaction temperature and the total operating cost of process will be higher. In this study, the reaction temperature was varied from 40 °C to 70 °C. Fig. 3 shows the effect of the reaction temperature on the reduction of high FFA content in ACPO, conversion of FFA to FAME and yield of treated ACPO. A low reaction temperature of 40 °C was not sufficient enough to reduce the FFA content in ACPO. On the other hand, the FFA content using 50 °C reaction temperature was exactly 1%. The recommended FFA content for transesterification was less than 1%. Higher reaction temperature such as 70 °C showed significant reduction of FFA content and slightly lower FFA content compared to that at 60 °C. In order to save the energy of the pre-treatment process to the minimum level, the reaction temperature of 60 °C was excluded. Hence, 60 °C was selected as the optimum reaction temperature. At this reaction temperature the resulting FFA content was 0.5%, with a treated ACPO yield of 98% and an FFA to FAME conversion of 94.14%. The optimum reaction temperature in this study was in agreement with that reported by many previous studies (Sharma et al., 2008).

Fig. 2. Effect of molar ratio on FFA content reduction, conversion of FFA to FAME and yield of treated ACPO at 0.75% dosage of ESA to ACPO, 60 °C reaction temperature, 30 min reaction time and 300 rpm stirrer speed.

Fig. 3. Effect of reaction temperature on FFA content reduction, conversion of FFA to FAME and yield of treated ACPO at 0.75% dosage of ESA to ACPO, 10:1 M ratio, 30 min reaction time and 300 rpm stirrer speed.
needed for ACPO reported in this study. A simple correlation between the FFA content and reaction time can be formulated as: for every 1% FFA content reduction 2.5–3.5 min of reaction time is needed. However, this correlation is approximate and used only to give a rough estimate of the reaction time needed. This is due to the effect of other factors such as the quality of oils and their sources.

3.3.5 Validation of optimal esterification conditions

The optimum conditions for esterification reaction using ESA were found to be 0.75% (wt/wt) dosage of ESA to ACPO, 10:1 M ratio, 60 °C temperature and 30 min reaction time. Using these optimum conditions the FFA was reduced from 8.6% to 0.8%, with 96% yield of treated ACPO and 90.7% conversion of FFA to FAME. Comparing the performance of ESA catalyst with other sulfonic based catalysts such as PTSA indicate the close behavior in terms of activity (Hayyan et al., 2010b). In that study, the optimum reaction conditions based on PTSA catalyst were: 0.75% (wt/wt) dosage of PTSA to SPO, 10:1 M ratio, 60 °C temperature and 60 min reaction time. The yield of treated SPO was 96%, conversion of FFA content to FAME was 90.93% and FFA was reduced from 22.33 to less than 2%. Another study by Di Serio et al. (2008) reported the use of $6.4 \times 10^{-5}$ mol of PTSA and found that this dosage of catalyst can decrease the FFA content in soybean oil from 20.5% to 1.1% and the yield obtained after reaction was 48% with the reaction conditions of 12:1 M ratio, 180 °C reaction temperature, and 60 min reaction time.

3.3.6 Recycling study of ESA catalyst

The viability of using the catalyst in an economical way is determined by the frequency of its recycling. Successful recycling technology can lead to significant reduction in the total cost of the pre-treatment process. In this study, ESA was recycled and its activity was studied using the verified optimum conditions. The catalyst was recycled for three consecutive runs without adding new amount of catalyst. According to the experimental results, fresh ESA has very high catalytic activity to reduce the FFA content to the minimum level and to convert FFA to FAME. Esterification was completed within 15–30 min and the FFA content was decreased from 8.6% to 0.8%. In the second recycling run the FFA content was lowered from 8.6% to 4.0% at the same reaction time. In order to complete the reaction, longer reaction time was necessary. Therefore, 60 min were needed to reduce the FFA content from 8.6% to less than 1% for the transesterification reaction. Due to the ESA catalyst miscibility in methanol and sufficient loading dosage, the first run reported high FFA reduction. First and second reuse runs showed high catalytic activity due to ESA strong acidity and the high sulfonic group activity. The second recycling run was slightly lower in terms of catalytic activity due to the catalyst loses during the pre-treatment process. Fig. 5 shows the conversion of FFA to FAME at different catalyst recycle runs. The catalytic activity of the third run using ESA was less than first and second runs within the first 30 min of reaction time. Therefore longer reaction time (90–120 min) is recommended for the third recycle run in order to obtain higher reduction in FFA content. It is very important to support the second and third reuse runs with high molar ratio compared to the first run in order
3.3.7. Pilot layout for biodiesel production from ACPO

A suggested layout of the proposed process is given in Fig. 6. ACPO is first pre-heated to reduce its viscosity. The pre-heated ACPO is then fed to the esterification reactor to reduce its FFA content. Methanol is added to the pre-heated ACPO in the esterification reactor. Pre-mixing of methanol and pre-heated ACPO is recommended before adding the ESA catalyst in order to increase the homogeneity of reactants before reaction. The products after esterification reaction are then sent to an evaporation unit to remove excess methanol which is recycled back to the esterification reactor. After removing excess methanol, the treated ACPO and the catalyst are fed to the centrifuge to separate the ESA catalyst and reuse it in the esterification reactor. Treated ACPO is fed to the transesterification reactor. KOH and menthol are mixed before feeding into the transesterification reactor to increase the catalytic activity of catalyst via increasing the homogeneity of the catalyst. Excess methanol is recovered after the transesterification reaction. Two main products generated from the transesterification reaction (Crude glycerol and biodiesel). In order to separate the two products, a settling vessel is used. Crude glycerol is settled in the bottom phase due to high density compared to crude biodiesel. After settling, crude biodiesel is washed with water to remove the impurities such as traces of catalyst and soap. Finally, a dryer is used to dehydrate the washed biodiesel.

Table 3

Fatty acid composition of biodiesel from ACPO.

<table>
<thead>
<tr>
<th>Systematic name of FAME</th>
<th>Carbon chains</th>
<th>Type of fatty acid</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecanoic acid methyl ester</td>
<td>C12:0</td>
<td>Saturated</td>
<td>0.20</td>
</tr>
<tr>
<td>Tetradecanoic acid methyl ester</td>
<td>C14:0</td>
<td>Saturated</td>
<td>0.93</td>
</tr>
<tr>
<td>Hexadecanoic acid methyl ester</td>
<td>C16:0</td>
<td>Saturated</td>
<td>43.50</td>
</tr>
<tr>
<td>Hexadecenoic acid methyl ester</td>
<td>C16:1</td>
<td>Unsatuated</td>
<td>0.03</td>
</tr>
<tr>
<td>Octadecanoic acid methyl ester</td>
<td>C18:0</td>
<td>Saturated</td>
<td>4.88</td>
</tr>
<tr>
<td>9-Octadecenoic acid methyl ester</td>
<td>C18:1</td>
<td>Unsatuated</td>
<td>40.35</td>
</tr>
<tr>
<td>All cis-9,12-Octadecadienoic acid methyl ester</td>
<td>C18:2</td>
<td>Unsatuated</td>
<td>9.54</td>
</tr>
<tr>
<td>All cis-9,12,15-Octadecatrienoic acid methyl ester</td>
<td>C18:3</td>
<td>Unsatuated</td>
<td>0.25</td>
</tr>
<tr>
<td>Eicosanoic acid methyl ester</td>
<td>C20:0</td>
<td>Saturated</td>
<td>0.30</td>
</tr>
</tbody>
</table>

4. Alkaline catalyzed transesterification

The TAG contained in palm oil are the main ingredients needed to prepare biodiesel. A transesterification catalyzed reaction converts these TAG to biodiesel fuel (Mjalli and Hussain, 2009; Mjalli et al., 2009). The treated ACPO after esterification is considered as the pre-treated material for the transesterification process where TAG are converted to FAME via an alkaline catalyst. Pre-treated ACPO samples with ESA dosages of 0.75% were further transesterified into biodiesel fuel using a KOH catalyst at 10:1 M ratio of methanol to ACPO, 60 °C reaction temperature, 200–400 rpm stirrer speed at 30–60 min and 1% wt/wt KOH (Hayyan et al., 2010a,b). It is clear from the results that all ESA dosages were successful in producing a biodiesel of acceptable yield and conversion. During the esterification reaction, FFA and very small amount of TAG were converted to FAME in the presence of ESA. The remaining TAG were converted to FAME via transesterification reaction. The traces of FFA left (less than 1%) was neutralized by the alkaline catalyst during the transesterification reaction producing soap which is usually removed during washing.

4.1. Characterization of biodiesel from ACPO

Fatty acid composition of biodiesel produced from ACPO is illustrated in Table 3. Gunstone (2002) reported that Malaysian palm oil has a narrow compositional range, as indicated from several surveys carried out between 1977 and 1997. On the other hand, results of this study reported 49.81% of saturated fatty acid composition. While the concentration unsaturated fatty acid was 50.17%. The produced biodiesel from ACPO is more recommended to hot countries due to its high saturated fatty acids and consequently high cloud and pour points. Table 4 shows the properties of ACPO-based biodiesel according to the EN 14214 and ASTM D6751 standards. The produced biodiesel from ACPO was very clean with high quality characteristics. This reflects the efficiency of pre-treatment process using the ESA catalyst. The copper strip corrosion test and the sulfated ash test indicate that no traces of ESA catalyst was present in the produced biodiesel. The high purity of biodiesel fuel shows the effectiveness of the proposed process using esterification and transesterification reactions. The Cetane number was high compared to petroleum diesel which gave significant advantage to use ACPO biodiesel as a blend with petroleum diesel. Other properties of purified biodiesel from ACPO met to the European and American standards (EN 14214 and ASTM D6751 standard) for biodiesel fuel.

Table 4

Properties of biodiesel from ACPO.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Biodiesel from ACPO</th>
<th>EN 14214</th>
<th>ASTM D6751</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>96% (mol mol⁻¹)</td>
<td>EN 14103</td>
<td>–</td>
</tr>
<tr>
<td>Monocacylglycerol content</td>
<td>0.1% (mol mol⁻¹)</td>
<td>EN 14105</td>
<td>0.80% (mol mol⁻¹) max</td>
</tr>
<tr>
<td>Diacylglycerols content</td>
<td>0.02% (mol mol⁻¹)</td>
<td>EN 14105</td>
<td>0.20% (mol mol⁻¹) max</td>
</tr>
<tr>
<td>Tricylglycerols content</td>
<td>&lt;0.02% (mol mol⁻¹)</td>
<td>EN 14105</td>
<td>0.20% (mol mol⁻¹) max</td>
</tr>
<tr>
<td>Free glycerol content</td>
<td>&lt;0.01% (mol mol⁻¹)</td>
<td>EN 14105</td>
<td>0.02% (mol mol⁻¹) max</td>
</tr>
<tr>
<td>Total glycerol content</td>
<td>0.05% (mol mol⁻¹)</td>
<td>EN 14105</td>
<td>0.25% (mol mol⁻¹) max</td>
</tr>
<tr>
<td>K content</td>
<td>1 mg kg⁻¹max</td>
<td>EN 14108</td>
<td>5.0 mg kg⁻¹max</td>
</tr>
<tr>
<td>P content</td>
<td>7.4 mg kg⁻¹max</td>
<td>EN 14107</td>
<td>10.0 mg kg⁻¹max</td>
</tr>
<tr>
<td>Sulfated ash</td>
<td>&lt;0.005% (w/w)</td>
<td>ISO 3987</td>
<td>0.02% (mol mol⁻¹) max</td>
</tr>
<tr>
<td>Total contamination</td>
<td>0.002 mg kg⁻¹</td>
<td>EN 12662</td>
<td>24 mg kg⁻¹ max</td>
</tr>
<tr>
<td>Acid value</td>
<td>0.005 mg KOH g⁻¹</td>
<td>EN 14104</td>
<td>0.50 mg KOH g⁻¹ max</td>
</tr>
<tr>
<td>Copper strip corrosion (3 h at 50 °C)</td>
<td>Class 1</td>
<td>EN ISO 2160</td>
<td>Class 1 rating</td>
</tr>
<tr>
<td>Cetane number</td>
<td>76</td>
<td>EN ISO 5165</td>
<td>51 min</td>
</tr>
</tbody>
</table>

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5. Conclusion

Laboratory scale batch experiments were conducted to produce high quality biodiesel from ACPO as agro-industrial feedstock. ACPO is a significant candidate to be utilized as a raw material for biodiesel production with a pre-treatment process by an esterification reaction using ESA as a catalyst. The optimum conditions for esterification reaction were 0.75% wt/wt ESA to ACPO with 10:1 M ratio, 60 °C reaction temperature at 30 min. The FFA content was reduced from 8.6% to less than 0.8% with high yield of treated ACPO and conversion of FAME to FAME. Results of this study showed that ESA attains high catalytic activity and it can be reused for three times without adding any fresh ESA catalyst. The biodiesel produced met the standards specifications for biodiesel fuel (EN 14214 and ASTM D6751). This study recommends ACPO for biodiesel production using ESA and an alkaline catalyst. Further work is underway to investigate the kinetics of the reactions involved in this process.

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References

Lin, S. W., 1989. Quality Index for crude palm oil. PORIM. 89, (00149) d.