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Full Length Research Paper

Utilizing ultrasonic energy for reduction of free fatty acids in crude palm oil

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Recently, biodiesel production from abundant bio-sources has drawn the attention of the academic and the industrial community. In this study, crude palm oil (CPO) containing 8.7% free fatty acid content (FFA) was used as raw material. Different common types of acid catalysts (sulfuric acid, methanesulfonic acid and hydrochloric acid) were optimized to investigate the catalytic activity of each acid in the pre-treatment of CPO by the esterification process. Ultrasonic energy was used for the reduction of FFA in CPO. FFA content was measured at different sonication intervals, and the optimum time was determined. Hydrochloric acid showed the highest catalytic activity in the reduction of FFA content in CPO, as well as in converting FFA to fatty acid methyl ester (FAME). From this work, it is reasonable to conclude that there is significant enhancement in the pre-treatment of oils by applying ultrasonic energy using long sonication time.

Key words: Biodiesel, crude palm oil, free fatty acids, ultrasonic energy.

INTRODUCTION

In many countries, biodiesel fuel is receiving an upsurge interest as alternative and renewable energy, due to diminishing petroleum reserves, increasing fuel prices and raising environmental concerns (Ma and Hanna, 1999; Demirbas, 2008; Canakci, 2007). Biodiesel production from abundant bio-sources has drawn the attention of the academic, as well as the industrial community in recent years (Demirbas, 2009; Mahmood and Hussain, 2010; Meher et al., 2006; Hayyan et al., 2010). Biodiesel can be made from renewable biological sources, such as vegetable oils, animal fats (Ghadge and Raheman, 2005; Chew and Bhatia, 2008). The main merits of using biodiesel as engine fuel are reducing the reliance on petroleum fuel and reducing air pollutant emissions from diesel engines (Ma and Hanna, 1999; Canakci and van Gerpen, 2001; Wang et al., 2000; Durán et al., 2005; Demirbas, 2009).

However, in spite of the favorable impact, the economic aspect of biodiesel production is still a barrier for its development, mainly due to the lower price of petroleum fuel (Antolin et al., 2002). The high value of edible vegetable oils as a food product makes production of biodiesel fuel very challenging, as the cost of raw materials accounts for 60 to 70% of the total production cost of biodiesel fuel (Ma and Hanna, 1999; Ghadge and Raheman, 2005). Therefore, exploring new methods to

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Abbreviations: CPO, Crude palm oil; **FFA,** free fatty acid; **FAME,** fatty acid methyl ester; **GC/MS,** gas chromatography–mass spectrometry.

produce biodiesel from low cost of raw materials are the main interest in recent biodiesel research. However in Malaysia, there are large amounts of low grade oils from palm oil industry that can be converted to biodiesel, such as crude palm oil (CPO) (Elsheikh et al., 2011). The use of CPO can lower the cost of biodiesel production significantly (Elsheikh et al., 2011). Recently, ultrasonic energy has been used in biodiesel production in many studies as a new approach (Stavarache et al., 2005; Ji et al., 2006). The hypothesis of using ultrasonic energy in ultrasonic irradiation causes cavitation of bubbles near the phase boundary between the alcohol and oil phases. As a result, micro fine bubbles are formed. The asymmetric collapse of the cavitation bubbles disrupts the phase boundary, and impinging of the liquids creates micro jets, leading to intensive mixing of the system near the phase boundary (Stavarache et al., 2005). In this study, the esterification of CPO was carried out applying ultrasonic energy instead of mechanical stirring to pretreatment of CPO, by applying ultrasonic energy to convert free fatty acid (FFA) to fatty acid methyl ester (FAME) through esterification reaction in the presence of different acid catalysts such as (sulfuric acid, methanesulfonic acid and hydrochloric acid).

MATERIALS AND METHODS

CPO was obtained from West Oil Mill, Carey Island, Selangor, Malaysia. It was stored in a cool room. Methyl alcohol anhydrous, sulfuric acid, methanesulfonic acid (MS acid) and hydrochloric acid (HCl) were purchased from Merck Sdn Bhd, Malaysia. The pre-treatment of CPO was carried out by a single-step esterification acid catalyzed process. First the CPO was preheated because it usually exists in a semisolid phase at room temperature (28 ± 2°C). The CPO was molten in an oven at 80°C and the preheated CPO was then transferred into the ultrasonic bath reactor as shown in Figure 1. Design of experiment analysis was conducted on the batch esterification process using single factor optimization in order to find the optimum number of experimental runs needed. High frequency ultrasonic process studied by Mahamuni and Adewuyi (2010) was considered to investigate the effect of process parameters for biodiesel production from soybean oil.

The process conducted by Mahamuni and Adewuyi (2010) used the Taguchi technique to investigate the optimum conditions. Different types of acids were used in this study namely: sulfuric acid, MS acid and hydrochloric acid. The second stage of experiments was the selection of the optimum acid catalyst based on the reduction of FFA content in CPO and the conversion of FFA to FAME. The selected acid catalyst was varied at different dosages (0, 0.5, 1, 2 and 4 wt/wt) in the presence of methanol to reduce FFA of CPO by converting the FFA to FAME. Several batch esterification runs were carried out to study the influence of molar ratio of methanol to CPO in the presence of the acid catalyst (5:1, 10:1, 15:1 and 20:1) and without it. The reaction temperature and the ultrasonic frequency were fixed at 60°C and 47 Hz, respectively. Operating conditions for all experiments were performed at different sonication times (0 to 180 min). The effect of these parameters on the reduction of FFA content and the conversion of FFA to FAME at different sonication times were investigated. The reactions were performed using Branson® ultrasonic bath 3210E-MTH, Frequency: 47 KHz + 6%, power supply: 335 w (220 V), Anschlusswert: 50 to 60 Hz, bath size approximately 12" × 6" × 6".

Analytical process

Fatty acid compositions of CPO were determined using gas chromatography–mass spectrometry (GC/MS) (Agilent Technologies 7890A gas chromatograph equipped with 5975C mass spectrometer). The capillary column was DB-wax 122-7032, with a length of 30 m, film thickness of 0.25 μm and an internal diameter of 0.25 mm. Helium was used as the carrier gas with a flow rate of 1 ml/min, measured at 50°C; the run time was 35 min. One μl of a neat sample was diluted in hexane prior the injection into the GC. The FFA content was determined in this study according to American Oil Chemist's Society (AOCS, 1997) official method Ca 5a-40 for commercial fats and oils. The conversion of FFA to FAME was calculated using Equation 1. It is defined as the number of converted FFA to FAME per number of initial FFA. Catalyst consumption (CC) was calculated. CC is defined as the weight of catalyst consumed per weight of product.

$$\text{Conv.} = \frac{\text{Ni} - \text{Nf}}{\text{Ni}} \quad (1)$$

Where, Conv. = conversion of FFA to FAME, Ni = FFA content at the start of reaction (%), Nf = FFA content at the end of reaction (%).

RESULTS AND DISCUSSION

Characteristics of CPO

The study of chemical properties of oils before the experimental work plays an essential role in understanding the behavior and the structure of materials deeply. This study focused on using the CPO as a renewable and sustainable raw material for biodiesel production. Usually, CPO is traded based on the FFA content, moisture and impurities. Table1 illustrates fatty acid composition of CPO. The results showed that the prevalent fatty acids available were oleic, palmitic, linoleic and stearic acid. Saturated fatty acids in CPO were 44.02 wt% while unsaturated fatty acids were 55.96 wt%. Due to its high percentage of saturated fatty acids and free fatty acids, CPO exists in semisolid phase at room temperature (28 ± 2°C). Hence, CPO has higher pour and cloud points as compared to normal palm oil. Higher saturated fatty acids in oils give a higher cetane number, and the oil is less prone to oxidation (Canakci and Van Gerpen, 2001).

Pretreatment using different types of acid catalysts

In this study, CPO with 8.7% FFA content and different types of acids were used in order to investigate the effect of each acid in the pretreatment of CPO and to evaluate the catalytic activity of each acid for the conversion of FFA content to FAME. Common acids such as sulfuric acid, MS acid and HCl were used in the pre-treatment of CPO. This study was started by investigating the effect of methanol alone in order to elucidate the role of methanol

Figure 1. Sono-reactor for pre-treatment of CPO.

Table 1. Fatty acid compositions of crude palm oil (CPO).

Fatty acid	Structure	Fatty acids (wt%)
Caprylic acid	C8:0	0.02
Lauric acid	C12:0	0.23
Myristic acid	C14:0	1.497
Pentadecanoic acid	C15:0	0.062
Palmitic acid	C16:0	34.638
Palmitoleic	C16:1	0.314
Stearic acid	C18:0	6.908
Oleic acid	C18:1	41.662
Linoleic acid	C18:2	13.39
Alpha-Linolenic acid	C18:3	0.387
Arachidic acid	C20:0	0.575
Eicosenoic acid	C20:1	0.209
Behenic acid	C22:0	0.0942

during the sonication reaction, and to calculate the actual catalytic activity of each acid in the pre-treatment of CPO. The effect of all types of acids in the reduction of FFA content in CPO was monitored and reported in Figure 2. The comparison of all types of acid catalysts was fixed to be 1% dosage of catalyst to CPO, with a molar ratio of 10:1. Using methanol alone, the findings showed that without the acid catalyst, there was no significant conversion of FFA to FAME, and significant decreases in the FFA content was observed. It can be inferred from Figures 1 and 2 that HCl was the most effective catalyst in the pre-treatment of CPO, compared to MS acid and sulfuric acid. Pre-treatment of CPO using HCl decreased the FFA content from 8.7% to less than 1% (which is the limits of FFA content for transesterification reaction). In order to complete the esterification reaction, sufficient contact time must be provided. Hence, using HCl at 150

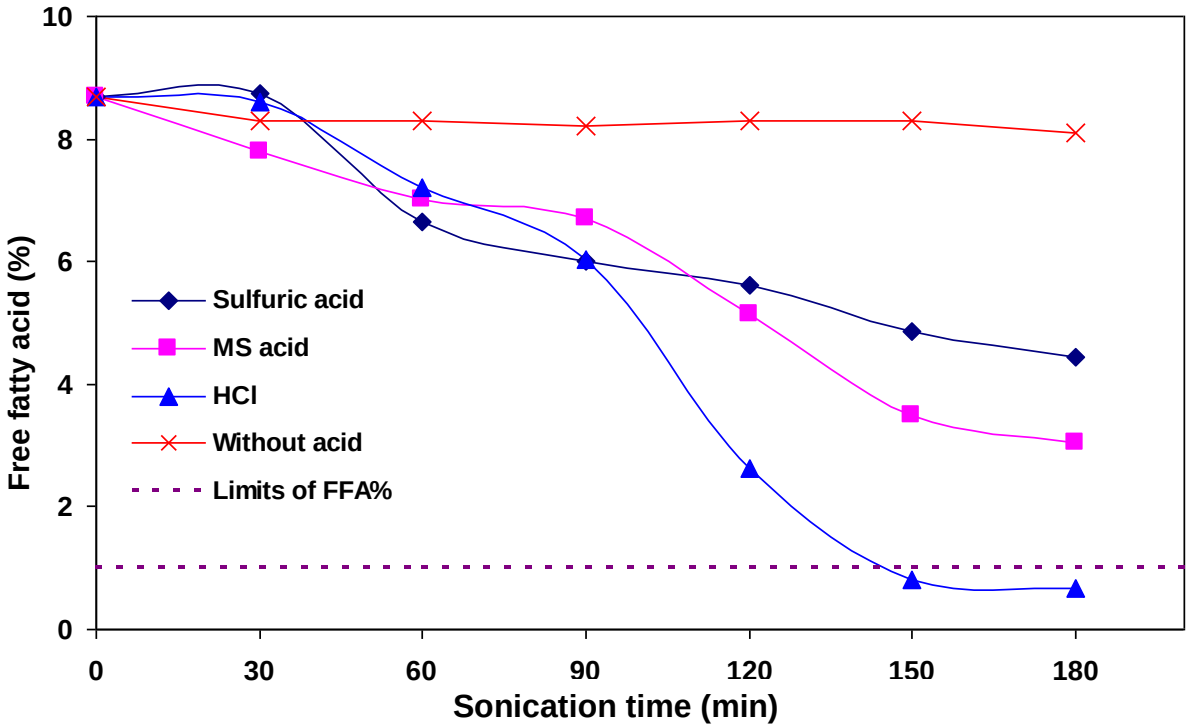

Figure 2. Effect of different acids in the reduction of FFA content of CPO.

min of sonication time was sufficient to complete the reaction. The results illustrated that MS acid was the second acid catalyst in terms of FFA reduction and conversion of FFA to FAME. However, even 180 min of soniction time was not sufficient to decrease the FFA content in CPO using MS and sulfuric acid. It can be concluded that HCl has attained the highest conversion of FAME, and there was no significant change observed at higher sonication time. HCl gave high conversion of FFA content to FAME due to the diffusion in methanol and CPO, compared to MS and sulfuric acid.

Effect of HCl dosage on the pre-treatment of CPO

In this study, the HCl catalyst dosage was varied (0, 0.5, 1, and 2%) in order to investigate the optimum reduction of FFA content in CPO at target level (<1% w/w) with maximum conversion to FAME. Figure 3 shows the effect of different dosages of HCl on the reduction of FFA content in CPO. Figure 4 shows the conversion of FFA to FAME using different dosages of HCl to CPO. The results showed that the dosage of HCl used in the esterification process affected the conversion of FFA to FAME and the reduction of FFA content. Without HCl, no reaction was observed. The FFA content decreased from 8.7% to less than 1% at a sonication time of 90 min, using 2 and 4% of HCl to CPO and there was no significant change at longer reaction time. While using 0.5 and 1 wt% of HCl decreased the FFA content to less than 1% at sonication times of 150 and 180 min, respectively. According to Figure 4, it can be observed that the conversion of FFA to FAME was higher using 2 and 4% of HCl, compared to 0.5 and 1% at 90 min sonication time. However, in order to save the ultrasonic energy and to decrease the catalyst consumption of HCl, the 2% dosage of acid to CPO at 90 min was selected as the optimum conditions to the pre-treatment of CPO, using an ultrasonic reactor. The excessive dosage of HCl did not show any improvement in terms of conversion of FFA to FAME, as the reaction might take place at equilibrium after 90 min. In addition, the low strength of the HCl catalyst might not be sufficient to provide enough catalytic activity to convert FFA to FAME.

Effect of methanol to CPO molar ratio

The esterification process needs more methanol than that needed by the transesterification process. In this study, the molar ratio of methanol to CPO was varied from 5:1 to 20:1 using the optimum dosage of HCl catalyst. Figure 5 shows the effect of the molar ratio on the reduction of the FFA content in CPO. Figure 6 shows the corresponding effect of different molar ratios on the conversion of FFA to FAME. The results showed that the molar ratio of methanol to CPO in the esterification process significantly affected the conversion of FFA to FAME and the reduction of FFA content. There was no reaction observed in the case where methanol was used

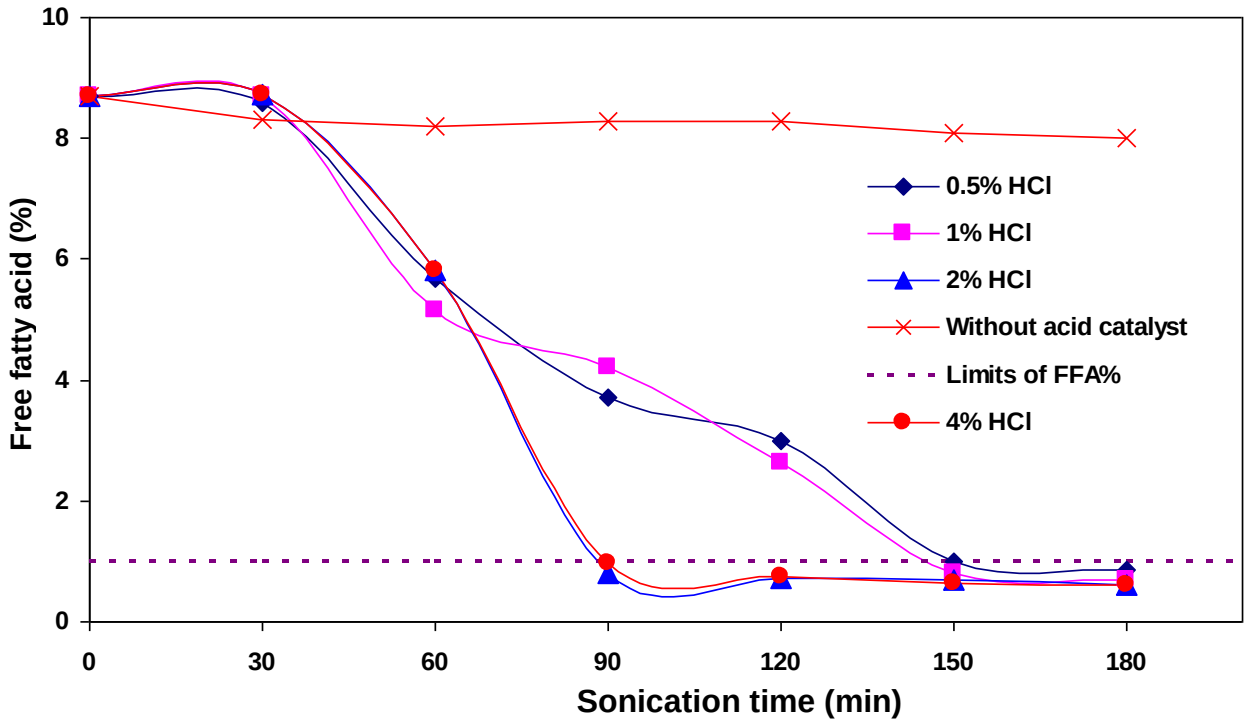

Figure 3. Effect of dosages of HCl on reduction of FFA content of CPO.

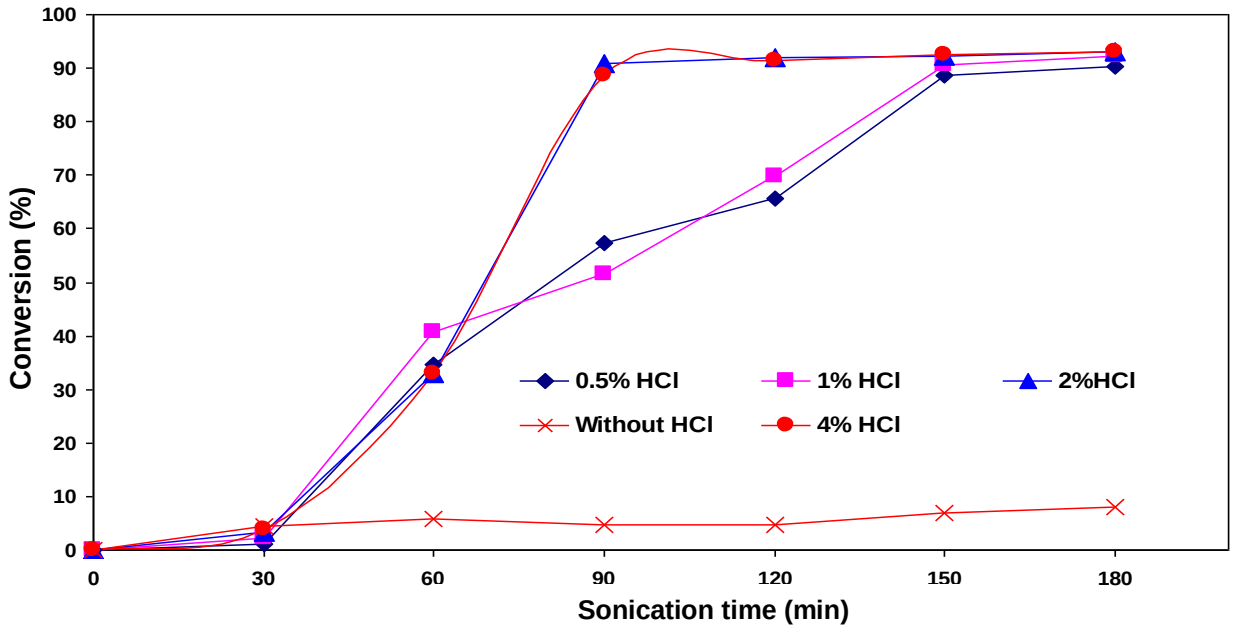

Figure 4. Conversion of FFA to FAME in CPO using different dosages of HCl.

alone without the addition of HCl. The FFA content decreased from 8.7% to less than 1% at a sonication time of 90 min using 15:1 and 20:1 of methanol to CPO, and there was no significant change at longer reaction time. Using 5:1 and 10:1 molar ratios, the FFA content was reduced to its acceptable transesterification reaction value at 150 min. However, the 15:1 molar ratio at 90 min was selected as the optimum conditions for the pre-treatment of CPO using an ultrasonic reactor due to economical reasoning. The effects of various parameters

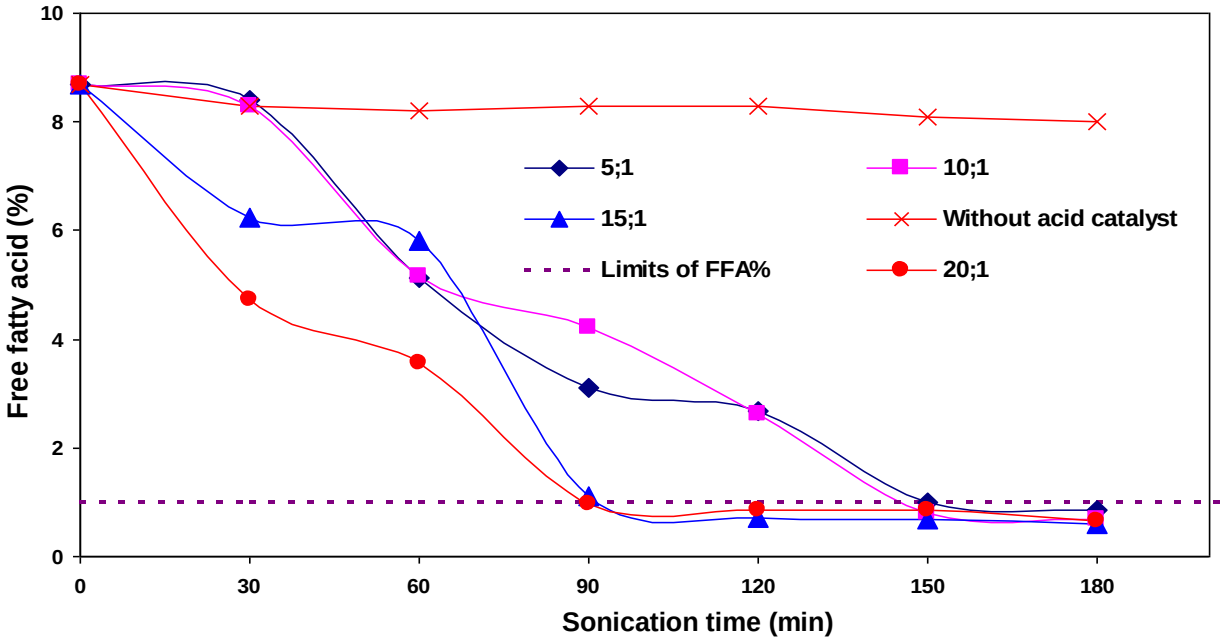

Figure 5. Effect of molar ratio on reduction of FFA content of CPO.

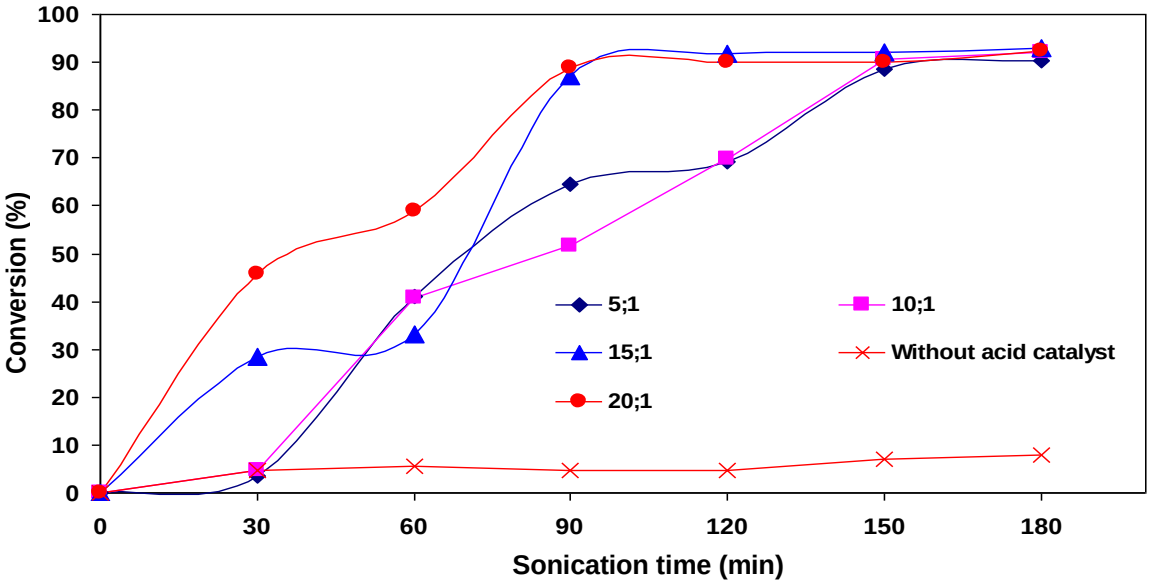

Figure 6. Conversion of FFA to FAME in CPO using different molar ratios.

using high-frequency ultrasound have been investigated. The conversion was more than 90% within 30 min, with relatively low-energy inputs (Mahamuni and Adewuyi, 2010).

Validation and characterization of pretreatment process

Figure 7 shows the effect of 2% HCl dosage catalyst on the yield of treated CPO, as well as the conversion of FFA to FAME and catalyst consumption at different sonication time. It was found that there was significant effect for using 2% HCl on the conversion of FFA to FAME while no noticeable effect was found on the yield of treated CPO and CC. However, based on the optimum conditions, it can be concluded that the yield, CC and conversion of using 2% HCl were 96%, 0.02 mg/gm (mass catalyst per the synthesized mass of product) and 90%, respectively. Fatty acids compositions of raw

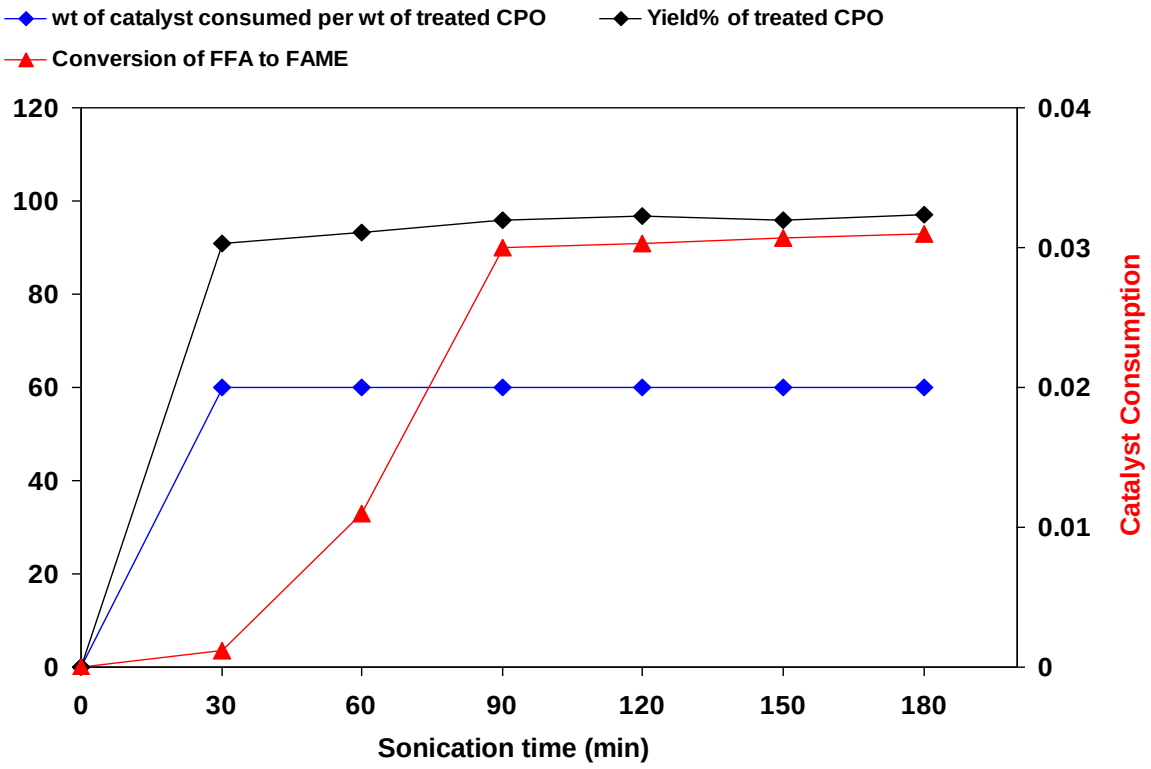

Figure 7. Effect of sonication time on yield of treated CPO, conversion of FFA to FAME and catalyst consumption using 2% dosage of HCl.

Table 2. Fatty acid compositions of treated crude palm oil (CPO).

Fatty acids	Structure	Fatty acids (wt%)
Caprylic acid methyl ester	C8:0	0.017
Lauric acid methyl ester	C12:0	0.18
Myristic acid methyl ester	C14:0	1.38
pentadecanoic acid methyl ester	C15:0	0.059
Palmitic acid methyl ester	C16:0	34.73
Palmitoleic methyl ester	C16:1	0.44
Stearic acid methyl ester	C18:0	6.8
Oleic acid methyl ester	C18:1	41.6
Linoleic acid methyl ester	C18:2	13.48
Alpha-Linolenic acid methyl ester	C18:3	0.397
Arachidic acid methyl ester	C20:0	0.612
Eicosenoic acid methyl ester	C20:1	0.2099
Behenic acid methyl ester	C22:0	0.067

materials determine some of the properties of the produced fuel. It was found that treated CPO contained high concentration of saturated fatty acids. These saturated fatty acids give biodiesel fuel advantages in terms of a higher cetane number and better oxidation stability (Canakci and van Gerpen, 2001). Fatty acids composition of treated CPO is presented in Table 2. The conversion of FFA to FAME was around 11.795 mole/mole.

Conclusion

Laboratory-scale, batch-wise esterification experiments were carried out to treat CPO using ultrasonic energy. The study revealed that HCl has the highest catalytic activity compared to MS and sulfuric acids catalysts. The optimum dosage of HCl to CPO was 2% with 15:1 molar ratio at 90 min sonication time to obtain a high conversion of FAME, and to decrease the FFA content in CPO to

less than 1% (which is the acceptable limit of FFA for the transesterification reaction). Moreover, the ultrasonic energy would be an attractive alternative process for the pre-treatment of oils and biodiesel production. This study showed a positive route for treating high FFA content of oils using ultrasonic energy. This will encourage the industry to utilize the ultrasonic technology in the biodiesel production process.

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