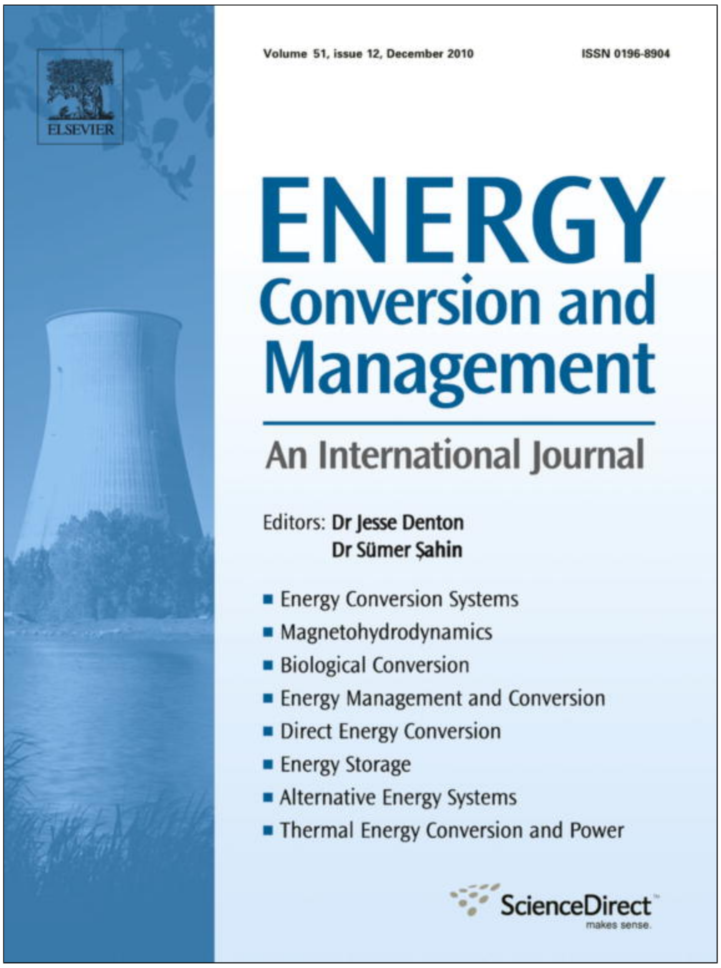

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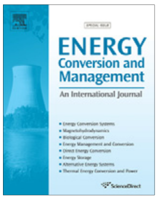

Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process

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ABSTRACT

Transesterification of high free fatty acid content *Jatropha* oil with methanol to biodiesel catalyzed directly by NaOH and high-concentrated H_2SO_4 or by two-step process were studied in an ultrasonic reactor at 60 °C. If NaOH was used as catalyst, biodiesel yield was only 47.2% with saponification problem. With H_2SO_4 as catalyst, biodiesel yield was increased to 92.8%. However, longer reaction time (4 h) was needed and the biodiesel was not stable. A two-step, acid-esterification and base-transesterification process was further used for biodiesel production. It was found that after the first-step pretreatment with H_2SO_4 for 1 h, the acid value of *Jatropha* oil was reduced from 10.45 to 1.2 mg KOH/g, and subsequently, NaOH was used for the second-step transesterification. Stable and clear yellowish biodiesel was obtained with 96.4% yield after reaction for 0.5 h. The total production time was only 1.5 h that is just half of the previous reported. The two-step process with ultrasonic radiation is effective and time-saving for biodiesel production from *Jatropha* oil.

1. Introduction

Biodiesel is a fuel obtained from renewable biomass feedstock that can be used in diesel engines as neat fuel or blended at various proportions with conventional fossil diesel fuel [1–4]. It consists of mono-alkyl esters usually produced by transesterification of vegetable oils, animal fats and cooking oils with low-molecular weight alcohols, most commonly methanol or ethanol. Biodiesel is an excellent substitute for conventional diesel fuel because of being renewable, nontoxic and biodegradable. The energy content, cetane number and viscosity of biodiesel are similar to those of petroleum-based diesel fuel. Moreover, it is essentially sulfur-free and emits significantly fewer particulates, unburnt hydrocarbons and less carbon oxides as compared with conventional fossil fuels [5–13].

At present, the high cost of biodiesel is the major obstacle for its commercialization. Approximately 70% of biodiesel cost is attributed to raw feedstocks [14–16]. So using cheap and non-edible vegetable oils, animal fats and waste oils as raw feedstocks for biodiesel production is an effective way to reduce the cost particularly in developing countries. *Jatropha curcas* L. oil is a potential cheap feedstock for biodiesel production as compared with refined and edible-grade oils such as rapeseed oil, soybean oil and sunflower oil that are common feedstocks in USA and Europe. The fatty acid composition of *Jatropha* oil is similar to edible oils but the presence of some anti-nutritional factors such as curcin render this oil unsuitable for cooking purposes [17–19]. The oil content of *Jatropha* seed ranges from 25% to 40% and the kernel from 45% to 60% by weight. It was suggested that *Jatropha*–palm oils as biodiesel raw materials is an optimum mix for Asia [19]. But, palm tree is not grown well in China. Nowadays, only *Jatropha* as an alternative biodiesel tree is widely cultivated in Southwest of China such as Yunnan, Sichuan, and Guangxi provinces. In the near future, it can supply part of raw material for biodiesel production in China.

The conventional industrial production of biodiesel is via transesterification of crude oil with a homogeneous strong base catalyst (e.g., NaOH, KOH or $NaOCH_3$) or acid catalyst (e.g., H_2SO_4) [5,18]. Other methods such as transesterification with solid catalysts, biocatalysts and non-catalytic supercritical methanol were studied extensively [1–5,16,17,20–25]. *Jatropha* oil with high free fatty acids (FFAs) as crude feedstock with KNO_3/Al_2O_3 solid catalyst, 84% biodiesel yield was obtained at 70 °C for 6 h [16]. The maximum biodiesel yield of 94% with immobilized lipase catalyst at 55 °C for 48 h was achieved [23]. Transesterification of *Jatropha* oil using supercritical methanol without catalyst, 100% biodiesel yield could be obtained at 320 °C and 8.4 MPa [22]. The above methods need either long reaction times (up to 48 h) or high temperatures and pressures (e.g., 320 °C and 8.4 MPa) that will increase cost and consume a lot of energy. The objective of this work is to study the production of biodiesel from *Jatropha* oil by conventional methods catalyzed with homogeneous NaOH and H_2SO_4. Since *Jatropha* oil contains high FFAs (up to 15%) [28], when a base

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homogeneous catalyst is used, FFAs react with the catalyst to produce emulsified soap that will inhibit biodiesel production. If an acid catalyst is applied, despite the saponification phenomenon is avoided but the acid has a less catalytic effect on the transesterification thus causes slower reaction rate [26]. Therefore, a two-step process, acid esterification to remove FFAs followed by base transesterification, was used for the study of *Jatropha* oil transesterification. The two-step process was studied extensively before [27,28]. In the previous work [27], FFA was reduced from 14% to less than 1% at 60 °C with H_2SO_4 for 88 min reaction time at the first step. Subsequently, more than 99% biodiesel yield was obtained at 60 °C with KOH for 24 min. In the later work [28], only 1 h was needed to reduce FFA from 15% to less than 1% at 50 °C at the first pretreatment step. Two hours were needed to produce only 90% biodiesel at 65 °C at the second step. Their results are very different. At the pretreatment step, Tiwari et al. used more acid catalyst (2.92 vs. 1 wt.% H_2SO_4) and higher temperature (60 °C vs. 50 °C) but longer reaction time (88 min vs. 1 h) was needed to reduce FFA to less than 1%. Surprisingly, at transesterification step, Tiwari et al. obtained higher biodiesel yield (99% vs. 90%) with a shorter reaction time (24 min vs. 2 h) and less base catalyst (11/35 mol ratio of KOH/NaOH) at the similar reaction temperature. According to their own predicted model [27], using 24 min reaction time, only 71% biodiesel was achieved. Probably, 24 min was a wrong datum, and longer reaction time was needed at the second step to reach 90–99% yield. In order to verify the very different results, further experiments are needed for the two-step process. Since ultrasonic radiation can effectively promote transesterification reaction of crude oil and enormously reduce the reaction times [3], all experiments were conducted in an ultrasonic reactor.

2. Experimental

2.1. Materials

Ultrasonic cleaner (AS10200BDT, Tianjin Boda ultrasonic cleaner Co., Ltd., Tianjin, China) was used as the reactor for biodiesel production. Methyl esters of palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid and linolenic acid (chromatographically pure) were bought from Sigma–Aldrich. Sodium hydroxide (solid, analytical reagent) and sulfuric acid (98% concentration, analytical reagent) were from Shanghai fine chemical Co. Ltd. *Jatropha* oil with high FFA content (after stored for 1 year) was obtained from our institute that was planted in Xishuangbanna, South of Yunnan province. Its fatty acids were mainly consisted of palmitic acid (15.18%), palmitoleic acid (0.99%), stearic acid (6.25%), oleic acid (41.17%), linoleic acid (31.25%) and linolenic acid (0.08%) (see Tables 1 and 2), analyzed by Gas Chromatography (GC Shimadzu GC-2014). According to the Chinese National Standard GB9104.2-88 and GB164-64, the acid value (AV) and saponification value (SV) of *Jatropha* oil were measured as 10.45 mg KOH/g and 191.02 mg KOH/g, respectively.

Table 2
The properties of Jatropha oil and biodiesel produced.

Properties	Jatropha oil	Biodiesel	Biodiesel standard ASTM
Specific gravity (g/mL)	0.912 (15 °C)	0.882 (15 °C)	0.870–0.900
Viscosity (mm^2/s)	8.72 (40 °C)	3.96 (40 °C)	1.90–6.00
Acid value (mg KOH/g)	10.47	0.32	0.8 max.
Cetane number	57	57	47 min.
Pour point (°C)	−2	6	−15∼10
Water content (wt.%)	0.135	0.047	0.05 max.
Flash point (°C)	125	133	100 min.

So the molecular weigh was calculated as 932 g/mol by the formula: $M = (56.1 \times 1000 \times 3)/(SV - AV)$ [29].

All the following experiments were conducted in the ultrasonic reactor at power of 210 W. A 500-mL three-neck flask filled with sample mixtures (crude oil, methanol and catalyst) stirred at 600 rpm was submerged in water bath at 40 °C in the reactor, and subsequent the water bath was heated to 60 °C for reactions (see Fig. 1).

2.2. Preparation of biodiesel using sodium hydroxide as catalyst

The transesterification reactions with sodium hydroxide catalyst alone were performed at the optimized condition [30], i.e., methanol/oil ratio of 24 vol.% (molar ratio 6:1), catalyst concentration of 1 wt.% (sodium hydroxide solid/*Jatropha*-oil) and reaction time of 1 h. The mixture of 24-mL methanol, 1-wt.% sodium hydroxide catalyst and 100-mL *Jatropha* oil in the flask in the ultrasonic reactor were undergoing the following reactions:

$$\text{triglyceride} + \text{methanol} \rightleftharpoons \text{diglyceride} + \text{methyl ester} \tag{1}$$

$$\text{diglyceride} + \text{methanol} \rightleftharpoons \text{monoglyceride} + \text{methyl ester} \tag{2}$$

$$\text{monoglyceride} + \text{methanol} \rightleftharpoons \text{glycerol} + \text{methyl ester} \tag{3}$$

Transesterification process was a sequence of three equivalents, consecutive and reversible reactions, in which diglyceride and monoglyceride were formed as intermediates that were converted further to final products methyl esters as biodiesel and glycerol [18]. After reaction, glycerol was separated spontaneously by gravity. Biodiesel was purified by distilling the unreacted methanol at 80 °C and by absorbing water with anhydrous Na_2SO_4.

Since *Jatropha* oil contained high FFAs, they would react with catalyst sodium hydroxide to form sodium soap according to the following reaction (4):

$$\text{free fatty acid} + \text{sodium hydroxide} \rightarrow \text{sodium soap} + \text{water} \tag{4}$$

In order to avoid the emulsion by saponification reaction, after the transesterification reactions, 0.1% aqueous citric acid was used as a washing solution to remove catalyst for the biodiesel purifica-

Table 1
GC analysis of crude *Jatropha* oil and biodiesel*.

	Crude *Jatropha* oil (%)		Biodiesel (esters, %) (by two-step)		Biodiesel (esters, %) (with acid catalysis)	
	New-extracted	Stored for 1 year	New-produced	Stored for 1 year	New-produced	Stored for 1 year
Palmitic acid (C16:0)	16.09	15.18	13.79	13.72	14.43	14.32
Palmitoleic acid (C16:1)	1.09	0.99	0.95	1.09	0.93	0.96
Stearic acid (C18:0)	6.44	6.25	6.33	6.44	6.23	6.65
Oleic acid (C18:1)	42.10	41.17	42.61	42.81	40.41	43.90
Linoleic acid (C18:2)	28.72	31.25	26.34	26.40	31.14	28.10
Linolenic acid (C18:3)	0.81	0.08	0.06	0.20	0.34	0.16
Others	4.75	5.08	9.92	9.34	6.52	5.91
Acid value (mg KOH/g)	4.60	10.45	0.32	0.36	1.21	1.84

* Biodiesel was produced from the *Jatropha* oil stored for 1 year.

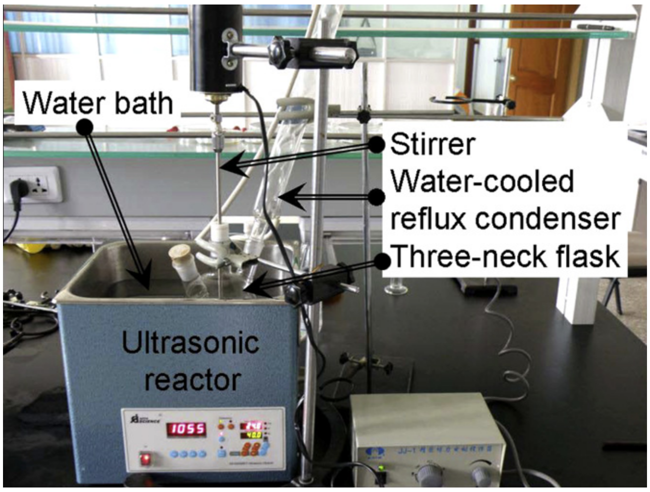

Fig. 1. Experimental set-up for ultrasonic production of biodiesel.

tion. In the following biodiesel production, sulfuric acid was only used as catalyst to avoid saponification reaction by sodium hydroxide.

2.3. Preparation of biodiesel using concentrated sulfuric acid as catalyst

Similar to the above experiments, 4-mL high-concentrated sulfuric acid was added to the flask with a reflux condenser filled with 100-mL *Jatropha* oil and 40-mL anhydrous methanol, and subsequently the mixture was undergoing reactions. Biodiesel was formed in the flask according to the above Eqs. (1)–(3) catalyzed by sulfuric acid. In this case, FFAs in the *Jatropha* oil formed methyl ester as biodiesel rather than soap according to reaction (5):

$$\text{free fatty acid} + \text{methanol} \rightarrow \text{methyl ester} + \text{water} \tag{5}$$

After the reaction, biodiesel was refined as described above for acid value examination and biodiesel analysis. Even though saponification phenomenon was eliminated, however acid was not active as base catalyst. Long reaction times were needed (e.g., 16–24 h) and acid was corrosive to the practical reactors [26]. Therefore, a two-step process was proposed in the next section.

2.4. Two-step process preparation of biodiesel

First, only sulfuric acid was used as catalyst for acid-esterification pretreatment in the ultrasonic reactor to remove the FFAs (Eq. (5)). In this step, different catalyst concentrations (1%, 2%, 3%, 4%, 5% and 6%; sulfuric acid/*Jatropha*-oil, vol.%) and methanol/oil ratios (16%, 24%, 32%, 48%, 48%; vol.%) were used to study their influence on reduction of the acid value of *Jatropha* oil. The three-neck flask with a water-cooled condenser was filled with 200-mL *Jatropha* oil and appropriate volume of anhydrous methanol and sulfuric acid. The mixture was vigorously stirred and refluxed for the required reaction times. After the reaction, the mixture was filtered and the unreacted methanol was separated from the liquid phase via rotary evaporation. After pretreatment, the acid value of *Jatropha* oil could be reduced to as low as 1.2 mg KOH/g.

At the second step, sodium hydroxide was used as catalyst because it had a higher catalytic activity for the transesterification reactions (Eqs. (1)–(3)). In this process, different catalyst concentrations (0.8%, 1.0%, 1.2%, 1.4%, 1.6%; sodium hydroxide solid/pretreated-oil, wt.%) and methanol/pretreated-oil ratios (16%, 24%, 32%, 40%, 48%; vol.%) were used to investigate their influence on biodiesel yield. The experimental procedure was as follows: first, the catalyst was dispersed and dissolved in methanol under stirring. Then, the above pretreated oil was added into the mixture and reacted in the ultrasonic reactor. After reaction, biodiesel was obtained by separation and purification as described above.

2.5. Jatropha oil and biodiesel analysis

The compositions of *Jatropha* oil and biodiesel were analyzed by Gas Chromatography (GC, Shimadzu, GC-2014) with a flame ionization detector and a capillary column (Rtx-Wax, 30 m × 0.25 mm × 0.25 μm). The analytic conditions for *Jatropha* oil were as follow: oxygen-free nitrogen was used as a carrier gas at a flow rate of 1.4 mL/min, initial oven temperature of 170 °C (2 min), ramp at 5.0 °C/min, final temperature of 220 °C (3 min), injector temperature of 250 °C, detector temperature of 280 °C and the split ratio of 39/1. Analysis was carried out by injecting 1-μL sample solution (0.25-mL *Jatropha* oil or biodiesel dissolved in 9.75-mL dichloromethane) into the GC. The analysis conditions for biodiesel were similar to *Jatropha* oil, but carrier gas at a flow rate of 1.0 mL/min and the split ratio of 20:1. The fatty acids and their esters as well as their compositions of *Jatropha* oil and biodiesel were identified and quantified by comparing their retention times to the standard retention times of fatty acids and their esters.

3. Results and discussion

Jatropha oil was transesterified with methanol catalyzed by sodium hydroxide, sulfuric acid and by a two-step process. Reaction time was 1 h for the experiments with catalyst sodium hydroxide, 4 h with catalyst sulfuric acid, and 1.5 h for the two-step process (1 h for pretreatment, 0.5 h for transesterification).

3.1. Sodium hydroxide as catalyst

When sodium hydroxide was used, at the optimized condition as described above (Section 2.2), biodiesel yield was only 47.2% with many flocs produced as showed in Fig. 2a. After reaction, many white soap foams were formed if the product liquid was dropped in distilled water (Fig. 2b). If the product mixture was not separated in time, it solidified to soap-like material in 2 h (Fig. 2c). Therefore, sodium hydroxide is not suitable as a catalyst for direct biodiesel production from *Jatropha* oil with high acid value. This phenomenon was caused by saponification reaction (Eq. (4)) between sodium hydroxide and FFAs in *Jatropha* oil.

3.2. Concentrated sulfuric acid as catalyst

In order to avoid saponification phenomenon, high-concentrated sulfuric acid as catalyst was used for the biodiesel produc-

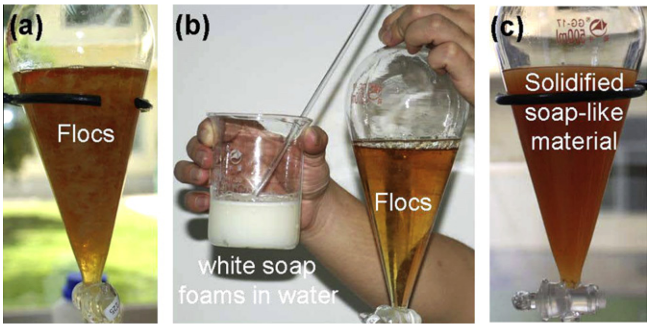

Fig. 2. Images of the saponified product mixture catalyzed by sodium hydroxide: (a) many flocs formed, (b) white soap foams in water, (c) solidified soap-like material after 2 h.

tion at the optimized condition [26], i.e., methanol/*Jatropha*-oil volume ratio 0.4:1 (V/V), sulfuric acid catalyst amount 1.0 wt.% (sulfuric acid/*Jatropha*-oil) and reaction time of 4 h. Biodiesel yield was up to 92.8% and its acid value was reduced to 0.95 mg KOH/g. However 4 h reaction time was needed as compared to only 1 h for the above experiment with sodium hydroxide even it was much shorter as compared to 16–24 h without using ultrasonic [26]. The biodiesel was not stable, after stored long time (15 days), some flocs were precipitated (Fig. 3b). As the new-produced biodiesel stored for 1 year (Table 1), its acid value increased from 1.21 to 1.84 mg KOH/g, and ester composition of linoleic acid (C18:2) decreased by 3.04% while that of oleic acid (C18:1) increased by 3.49%. The probable reason was that one of unsaturated carbon in linoleic acid ester was hydrolyzed or oxidized to form oleic acid ester and floc precipitates.

3.3. Two-step process

In order to resolve the above problems of saponification phenomenon, slow reaction rate and biodiesel stability, a two-step process, acid-esterification pretreatment and followed by base-transesterification process, were selected for *Jatropha* oil transesterification.

3.3.1. Acid-esterification pretreatment

Two major factors affecting the rate and conversion efficiency of acid esterification were catalyst concentrations and methanol/*Jatropha*-oil volume ratios [31–34]. So, in the acid pretreatment process, different catalyst concentrations (1–6 vol.%, sulfuric acid/*Jatropha*-oil) and methanol/*Jatropha*-oil ratios (16–48 vol.%) were used to investigate their influence on reduction acid value for 1 h reaction time.

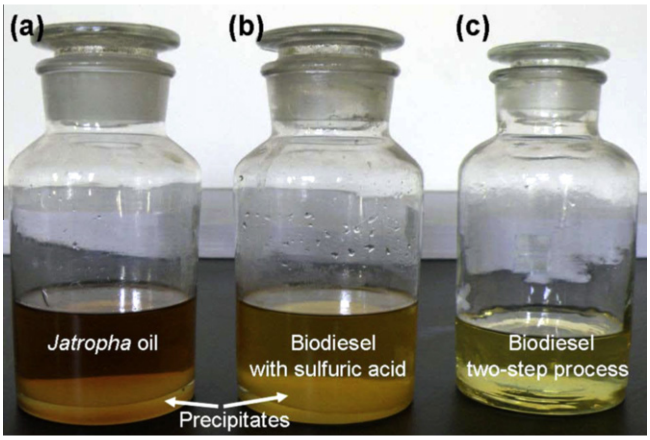

Fig. 3. Images of *Jatropha* oil and biodiesel produced: (a) crude *Jatropha* oil after stored for 1 year, (b) biodiesel produced with sulfuric acid after stored for 15 days (d) biodiesel produced by two-step process after stored for 1 year.

At a fixed methanol/*Jatropha*-oil ratio of 40 vol.%, when sulfuric acid concentration increased from 1 to 4 vol.%, the acid value was found to be decreased from 10.45 to the minimum value of 1.21 mg KOH/g (Fig. 4a). However, as the sulfuric acid concentration increased further, the acid value rose again. The probable reason was that at high acid concentrations, triglyceride was hydrolyzed to form FFAs and low-molecular weight alcohols according to Eq. (6):

$$\text{Triglyceride} + \text{Water} \rightleftharpoons \text{Free fatty acid} + \text{low weight molecular alcohols} \qquad (6)$$

So the optimum condition for acid catalyst concentration was 4 vol.%.

In the ultrasonic reactor, at the optimized sulfuric acid concentration of 4 vol.%, the influence of methanol/*Jatropha*-oil volume ratio on reduction of the acid value of *Jatropha* oil was given in Fig. 4b. The acid value was decreased from 6.42 to 1.21 mg KOH/g as methanol/*Jatropha*-oil ratio increased from 16 to 40 vol.%. Moreover, it was observed that at higher molar ratio beyond 40 vol.%, the excessively added methanol had no significant effect on the acid value. So, 4 vol.% concentration sulfuric acid was used to catalytically pretreat *Jatropha* oil with 40 vol.% methanol at 60 °C for 1 h in an ultrasonic reactor to obtain oil with 1.21 mg KOH/g acid value for biodiesel production.

3.3.2. Base transesterification

The pretreated oil produced by the above first step was further transesterified to biodiesel catalyzed by sodium hydroxide. The influence of sodium hydroxide concentration (0.8–1.6 wt.%) at volume ratio of 24 vol.% methanol/pretreated-oil on the yield and acid value of biodiesel was given in Fig. 5. When sodium hydroxide concentration increased from 0.8 to 1.4 wt.%, biodiesel yield rose from 62.8% to the maximum value of 96.4% and its corresponding acid value decreased from 0.99 to the minimum value of 0.32 mg KOH/g. With further increase of sodium hydroxide concentration, biodiesel yield decreased to 87.4% and its acid value increased to 0.44 mg KOH/g, which was possibly due to the hydrolysis reaction (Eq. (6)) that inhibited biodiesel formation. So, 1.4 wt.% sodium hydroxide concentration was selected for biodiesel production.

The volume ratio of methanol/pretreated-oil was one of the important factors that could affect biodiesel yield. Stoichiometrically, three moles of methanol were required for each mole of *Jatropha* oil (Eqs. (1)–(3)). However, in practice, the methanol/oil volume ratio should be higher than that of stoichiometry in order to drive the reaction towards completion and produce more methyl esters. The influence of methanol/pretreated-oil volume ra-

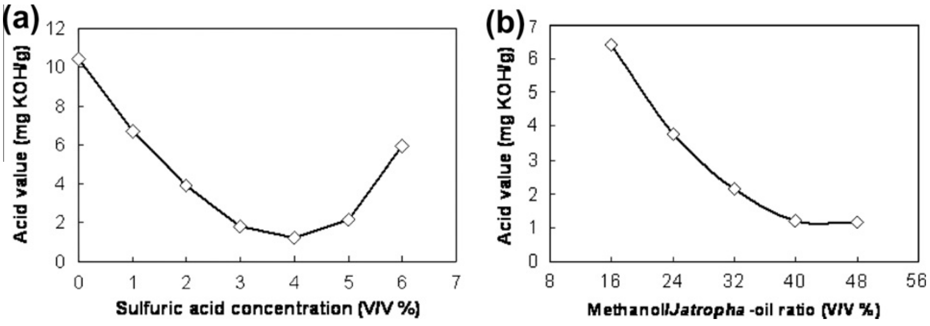

Fig. 4. Acid value of *Jatropha* oil during the first step acid-esterification pretreatment: (a) influence of sulfuric acid concentration (V/V%) and (b) influence of methanol/*Jatropha*-oil volume ratio (V/V%).

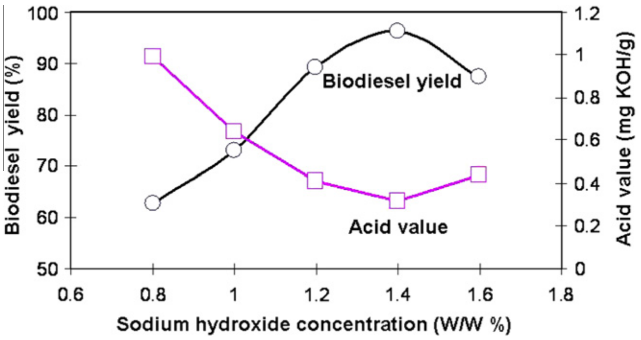

Fig. 5. The influence of sodium hydroxide concentration (W/W%: sodium hydroxide/*Jatropha*-oil) on the biodiesel yield and acid value.

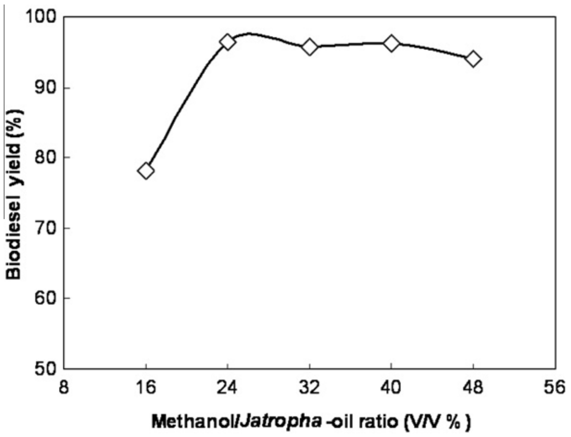

Fig. 6. The influence of methanol/*Jatropha*-oil volume ratio (V/V%) on the biodiesel yield.

tios (16%, 24%, 32%, 40% and 48%) at sodium hydroxide concentration of 1.4 wt.% on biodiesel yield was studied and its results were given in Fig. 6. When the methanol volume ratio was increased from 16% to 24%, biodiesel yield rose from 78.2% to 96.4%. The maximum yield of 96.4% was at the volume ratio of about 24%. The higher volume ratio than the stoichiometric value resulted in a higher rate of ester formation and could ensure complete reaction [35]. It could be assumed that, the reaction was incomplete for a volume ratio less than 24%. When the volume ratio was increased further from 24% to 48%, the excessively added methanol had little effect on the yield, but a longer time was required for the subsequent separation step since separation of the ester layer from the glycerol was difficult [35,36]. This was due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier. Hence, the best results were obtained for a methanol/oil volume ratio of 24% that was identical and used in the above experiments for optimizing sodium hydroxide concentration.

After the two-step process, clear and yellowish biodiesel was produced (Fig. 3c). The main compositions of biodiesel were identified and quantified as: palmitic acid (13.79%), palmitoleic acid (0.95%), stearic acid (6.33%), oleic acid (42.61%), linoleic acid (26.34%) and linolenic acid (0.06%) (see Table 1). The biodiesel was very stable even stored for 1 year without any precipitation (Fig. 3c) and chemical changes that was confirmed by GC analysis in Table 1. The new extracted *Jatropha* oil with low acid value (4.6) hydrolyzed to FFAs (Eq. (6)) after stored for 1 year, and the acid value increased to 10.45 mg KOH/g. Hydrolysis and oxidation reactions resulted in linoleic acid increase and many flocs precipitated (Fig. 3a).

The properties of Jatropha oil and biodiesel produced determined at room temperature were given in Table 2. It could be seen from Table 2, the specific gravity, viscosity and acid value of Jatropha oil were higher than those of standard biodiesel (ASTM), so Jatropha oil was not suitable as an engine fuel directly. It would corrupt engine and deposit carbon. But after transesterification process, the properties of biodiesel were close to those of standard biodiesel (ASTM). Therefore, the two-step process with ultrasonic radiation is effective and time-saving method for biodiesel production from *Jatropha* oil with high FFAs.

4. Conclusion

Mixtures of *Jatropha* oil, methanol and catalyst (NaOH or high-concentrated H_2SO_4) stirred at 600 rpm were reacted for biodiesel production in an ultrasonic reactor at power of 210 W and 60 °C. Either NaOH or H_2SO_4 alone was not suitable as catalyst for biodiesel production. Saponification phenomenon occurred when NaOH catalyst was used that caused low biodiesel yield. On the other hand, H_2SO_4 catalyst needed long reaction time (4 h) and produced unstable biodiesel. Both H_2SO_4 and NaOH were used as catalysts for the two-step, acid esterification and base-transesterification process to produce biodiesel. It was found that at the first step, the acid value of *Jatropha* oil was reduced to 1.2 from 10.45 mg KOH/g in 1 h. At the subsequent second step, 96.4% biodiesel yield with 0.32 mg KOH/g acid value was achieved for 0.5 h transesterification reaction. The two-step process only needed 1.5 h to achieve 96.4% diesel yield that is half time of the previous work of Berchmans and Hirata [28]. It could be concluded that the two-step process coupled with ultrasonic radiation is an efficient method for biodiesel production from crude oil with high FFA value, and might find a practical application.

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