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Esterification of jatropha oil via ultrasonic irradiation with auto-induced temperature-rise effect

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ABSTRACT

Auto-induced temperature-rise effects of ultrasonic irradiation (UI) on the esterification performance of jatropha oil (JO) were studied. Comparisons with other methods of mechanical mixing (MM) and hand shaking mixing were made. Major system parameters examined include: esterification time (t_E), settling time (t_S) after esterification and temperature. Properties of acid value (AV), iodine value (IV), kinematic viscosity (KV) and density of JO and ester product were measured. The esterification conversion efficiencies (η) were determined and assessed. Sulfuric acid was used to catalyze the esterification using methyl alcohol. For esterification without temperature control, η at $t_E = 10$ and 30 min for UI of 56.73 and 83.23% are much higher than those for MM of 36.76 and 42.48%, respectively. At $t_E = 10$ min, the jatropha oil esters produced via UI and MM respectively possess AV of 15.82 and 23.12 mg KOH/g, IV of 111.49 and 113.22 g I_2/100 g, KV of 22.41 and 22.51 mm^2/s and density of 913.8 and 913.58 kg/m^3, showing that UI is much better than MM in enhancing the reduction of AV. The t_E exhibits more vigorous effect on AV for UI than MM. The UI offers auto-induced temperature-rise, improving the mixing and esterification extents.

1. Introduction

It is known that the sources of fossil fuels are limited. An extensive use will result in their complete depletion. Therefore, renewable energy sources have become very desirable [1–5]. Biodiesel, which is made from renewable biological sources such as animal fats and vegetable and plant oils [6,7], has been used as an alternative diesel fuel. It is composed of simple mono-alkyl esters (such as methyl ester). It has recently attracted much attention in many countries because of its availability, renewability, non-toxicity, biodegradability and less air pollutants emissions especially the reduction of emission of carbon dioxide into the environment [8,9]. Biodiesel can be manufactured by transesterification process using source oils to react with alcohol in the presence of the catalyst to form fatty acid alkyl esters (FAAEs) (i.e., biodiesel) and glycerol [10].

Inedible woody oil plants, such as *Jatropha curcas* Linaeus (yielding jatropha oil (JO)) and *Vernicia fordii* (bearing tung oil) are promising biomaterials around the world [11]. *J. curcas* is widespread in arid, semi-arid and tropical regions of the world. It is a drought-tolerant and hardy shrub growing quickly and can be used to prevent and or control erosion, to reclaim land and to grow as a live fence [12].

The conventional method for biodiesel production from jatropha oil involves an esterification treatment before the transesterification. The esterification is a reversible reaction where free fatty acid (FFA) is converted to alkyl esters via acid catalysis. The simplified form of this chemical reaction is presented by the well known equation as:

$$R_1\text{-COOH (FFA)} + R_2\text{-OH (Alcohol)} = R_1\text{-COO-}R_2 + H_2O \qquad (1)$$

The transesterification is sensitive to the FFA content in raw jatropha oil. The increase in FFA content will reduce the formation rate [13] and yield [14] of fatty acids methyl esters (FAMEs). Further, the high content of FFA of raw jatropha oil such as 18.29 wt.% (standard deviation $\sigma_{n-1} = 0.28$ wt. %) encountered in this work

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may also induce the saponification possibility during transesterification [12–14]. Usually, the acid value (AV) of FFA is firstly reduced in esterification. Berrios et al. [15], Deng et al. [16], Jain et al. [17] and Corro et al. [18] have recommended the application of esterification pretreatment before transesterification process, when the FFA content of an oil or fat is high, in order to avoid the saponification and the reductions of the yield and formation rate of FAMEs. The saponification may also hinder the separation of the ester from glycerin.

The esterification treatment greatly reduces the AV of raw oil which saves the operation cost and processing time. Kywe and Oo [19] carried out the production of biodiesel in pilot plant using raw jatropha oil with an FFA of 8.8 wt. % and produced biodiesel with an FFA of 0.5 wt. %. Deng et al. [16] studied a two-step process using acid esterification to remove the FFA of jatropha oil followed by base transesterification with the application of ultrasonic irradiation (UI). They reported that FFA was reduced from 5.25% to 0.61% at 60 °C using H_2SO_4 for 60 min reaction time in the first step. Chen et al. [12] examined the acid esterification and base transesterification with mechanical mixing (MM), obtaining a jatropha oil biodiesel with AV of 0.12 mg KOH/g. Corro et al. [18] reported a novel solar esterification treatment by solar radiation employing Zn filings as solid catalyst with followed base transesterification, indicating that the AV was reduced from 18.5 to 0.38 mg KOH/g in the jatropha oil biodiesel.

The UI method uses less amount of catalyst, reduces the esterification time, while offers an excellent mixing with effective emulsification and mass transfer. The rate of ester formation is significantly enhanced, due that the esterification reaction is controlled by mass transfer which is improved by UI. The UI also generates heat with an increase of temperature offering a positive influence on esterification. Therefore, the UI gives esterification conversion efficiency (η) higher than the conventional mechanical mixing promoting the biodiesel yield, in addition to its wide availability, low cost, non-contamination and easy implementation.

In the above-mentioned studies, the reaction temperatures were held constant for mechanical mixing MM as well as UI. One should note that UI may also induce the heating effect. This can increase the temperature and thus in turn enhance the reaction extent. The application of UI should keep the advantage of simultaneous temperature rise. Hence, this study was aimed at examining the auto-induced temperature-rise roles of UI during the esterification of jatropha oil. Effects of major system parameters on the esterification performance emphasized on the reduction of AV were elucidated. These include esterification time (t_E), settling time (t_S) and reaction temperature (T).

2. Materials and methods

2.1. Materials

Jatropha oil was supplied by Ozone Environmental Technology Co., Yi-Lan County, Taiwan, with acid value AV = 36.56 ($\sigma_{n-1} = 0.56$) mg KOH/g, iodine value (IV) = 102.23 ($\sigma_{n-1} = 4.87$) g I_2/100 g, kinematic viscosity (KV) at 40 °C = 31.30 ($\sigma_{n-1} = 2.27$) mm^2/s and density (ρ_{LO}) at 15 °C = 918.45 ($\sigma_{n-1} = 0.24$) kg/m^3. Its molecular weight (MW) is 871.5 g/mol [20]. Methyl alcohol of anhydrous assay with purity of 99.8% and sulfuric acid of 96.7% purity were obtained from Mallinckrodt, Phillipsburg, NJ and Sigma–Aldrich, St. Louis, MO, respectively.

2.2. Esterification procedures

The acid catalyzed esterification pretreatment was carried out in a 500 mL batch reactor without and with cooling/heating systems. The cooling and heating were, respectively, operated by a refrigerated and heating bath circulator, model B10/-40, Firsteck Scientific Co., Taipei, Taiwan. A sample of 183.82 g jatropha oil was employed for a batch test. The sample was mixed with methanol with molar ratio of methanol to oil (M/O) = 11 and sulfuric acid as a catalyst with wt. % relative to oil (m_C) = 0.92 wt. %. The total sample volume (V_L) was 300 mL. The mixed sample was immediately subjected to the UI by an ultrasonic probe (Model 300 W, from Hoyu Technology Co., Taipei, Taiwan) operated at 25 kHz with power (P_{WUI}) at 90% (270 W) of its maximum power (300 W). The esterification times t_E for UI (t_{UE}) were conducted at 5, 10, 15 and 30 min. Different settling times t_S of 5, 10, 15, 20, 30, 40 and 1440 min at ambient temperature were kept after UI to allow post esterification reaction. The reaction temperature of sample (inside the reactor) during the esterification reaction was measured by a thermal couple (Firstteck Scientific, model-B403, Taipei, Taiwan).

After esterification, the sample was generally settled for proper t_S of 10 min unless otherwise specified. The reaction was then terminated by washing with saturated sodium chloride solution. After the mixture was settled for 3 h, it was separated into three layers. The lower, middle and upper layers of (1), (2), and (3), respectively, are (1) salt water, (2) mixture of glycerol, residual catalyst, methanol and soap, and (3) jatropha oil crude ester, which can be drawn out easily from the top of the separation funnel. The jatropha oil crude ester was then kept in the refrigerator waiting for analysis and avoiding its decomposition.

For the comparison of UI with sole mechanical mixing MM, the same experimental conditions, except the temperature, were carried out for MM with stirring speed (r_S) of 250 rpm. Cases for mechanical mixing examined include (1) without temperature control with initial temperature at ambient temperature (Case MNAT), and (2) with temperature in sample controlled by employing external heating using water bath of 65 °C (Case MHFT). The esterification times t_E for mechanical mixing (t_{ME}) were tested for 2, 5, 10, 15 and 30 min.

2.3. Analysis

The properties of crude jatropha oil ester such as AV, IV, KV and ρ_{LO} were measured according to the standard methods suggested by Manh et al. [9], Chen et al. [12] and Van Gerpen et al. [21]. These methods along with those of flash point and cetane number are outlined in Table 1 and may be further referred to Biofuel Systems [22] and TBOS (Taiwanese Bureau of Standards, Metrology and Inspection) [23]. Standard deviations σ_{n-1} were presented to reflect the errors of the data.

The acid values AV of initial jatropha oil JO and those after esterification treatment were determined according to ASTM D664 standard method employing an automatic potentiometric titration system using potassium hydroxide solution. The quality control of AV is important since the AV increases when the fuel itself deteriorates. The acid value is a measure of free fatty acids which can lead to corrosion and are symptom of water in the fuel or fuel oxidation.

The iodine value IV was measured following ASTM D1959 standard test method by an automatic potentiometric titration system with iodine. The IV is expressed in grams of iodine for the amount of halogens linked with 100 g test sample. The most important application of the IV is to determine the amount of unsaturation contained in fatty acids. This unsaturation is in the form of double bonds, which react with iodine compounds. A higher IV means that more unsaturated fatty acid bonds are present in a fat.

Kinematic viscosity KV was analyzed employing a Cannon–Fenske style glass capillary viscometer. The resistance to flow of a

Table 1
Some biodiesel fuel standards and test methods.

Property	European biodiesel standards N14214[a,b]	American biodiesel standards ASTM D6751[a,b]	Taiwanese biodiesel standards CNS-15072[a,c]
	Test method	Test method	Test method
Acid value (AV) (mg KOH/g)	EN 14104 (<0.5)	D 664 (0.5 max)	CNS-14669 (<0.5)
Iodine value (IV) (g I_2/100 g)	EN 14111 (120 max)	D 1959[d]	CNS-15060 (120 max)
Kinematic viscosity at 40 °C (mm^2/s)	EN ISO 3104 (3.5–5)	D 445 (1.9–6)	CNS-3390 (3.5–5)
Density at 15 °C (kg/m^3)	EN ISO 3675 EN (860–900)	D5002 (860–900)	CNS-12017 (860–900)
Flash point (°C)	ISO/CD 3679e (>101)	D 93 (130–170)	CNS-3574 (120 min)
Cetane number	EN ISO 5165 (51.0 min)	D 613 (47 min)	CNS-5165 (51 min)

[a] Adopted from Chen et al. [12].
[b] Details can be referred to Biofuel Systems [22].
[c] Details can be referred to TBOS [23].
[d] Not specified.

fluid under gravity is named kinematic viscosity. The time was measured for a fixed volume of liquid to flow under gravity through the capillarity of a calibrated viscometer under a reproducible driving head and at a closely time controlled and known temperature (say, 40 °C).

The measurement of density was conducted at 15 °C. Density Meter model DMA-35 made by Anton Paar GmbH (Graz, Austria) was used.

The esterification conversion efficiency η was determined as below:

$$\eta(\%) = [(AV_1 - AV_2)/AV_1] \times 100 \tag{2}$$

where AV_1 and AV_2 were, respectively, the acid values before and after esterification reaction. According to Zou and Lei [14] and Deng et al. [16], the FFA content of oil can be calculated according to the following equation:

$$\text{wt.\% FFA} = ([AV]/2)\text{wt.\%} \tag{3}$$

where [AV] is the magnitude of AV with AV expressed in unit of mg KOH/g. FFA content is in proportion to AV [14].

The chemical composition analysis of FFA of jatropha oil JO can be performed by gas chromatography with mass spectrum (GC–MS) according to EN 14103. The FFA composition of jatropha oil reported by Jain and Sharma [17] is listed in Table 2 for reference. Their results depicted that the major fatty acids in jatropha oil are oleic (C18:1) and linoleic (C18:2) acids. Thus, it contains large amounts of unsaturated carbon–carbon double bonds [12,17].

Although the composition of FAMEs of biodiesels can be also determined by GC–MS analysis, however, the total amounts of FAMEs of biodiesels were analyzed by ^{1}H nuclear magnetic resonance (NMR) method in this study. The same technique has been also employed by Manh et al. [8,9]. Methyl esters yield (Y_F) is calculated based on the ratio of the peak area of methoxy protons of FAMEs at 3.7 ppm to that of methylene protons adjacent to the esters group of triglyceride at 2.3 ppm in the ^{1}H NMR spectrum.

Table 2
Free fatty acid (FFA) composition of jatropha oil[a].

Fatty acid	Systematic name	Structure	Amount %
Palmitic acid	Hexadecanoic acid	(C16:0)	14.1
Palmitoleic acid	Cis-9-hexadecanoic acid	(C16:1)	0.5
Stearic acid	Octadecanoic acid	(C18:0)	6.8
Oleic acid	Cis-9-octadecanoic acid	(C18:1)	38.6
Linoleic acid	Cis-9-cis-12-octadecadienoic acid	(C18:2)	36
Linolenic acid	Cis-6-cis-9-cis-12-octadecatrienoic acid	(C18:3)	0.2
Arachidice acid	Eicosanoic acid	(C20:0)	0.2
Gadolic acid	Tetracosanoic acid	(C24:0)	3.6

[a] Adapted from Jain and Sharma [17].

3. Results and discussion

3.1. Properties of raw oils and the resulting esters

The properties of jatropha oil are described in Section 2.1. Compared with regulation standards of biodiesel [22], the IV of 102.23 g I_2/100 g is satisfactorily below the 120 g I_2/100 g max, however, the AV of 36.56 mg KOH/g, KV of 31.30 mm^2/s and density of 918.45 kg/m^3 are higher than 0.5 mg KOH/g max, 3.5–5.0 mm^2/s and 860–900 kg/m^3, respectively. Therefore the esterification pretreatment is needed. After applying the esterification, the properties of the crude ester obtained are shown in Tables 3 and 4. The significant reductions are found in AV and KV with AV showing greatest decrease. The changes of other properties of IV and density are slight between the original jatropha oil and resulted crude ester. Thus the esterification is mainly to low down the AV, consuming the carboxylic content of jatropha oil in consistence with the function of esterification reaction illustrated in Eq. (1).

3.2. AV of crude esters applying different esterification methods

The acid values AV of esters from jatropha oil obtained using different esterification methods were compared. These include (1) UI without temperature control, while with varied temperature in sample and with initial temperature at ambient temperature (UNVT), (2) mechanical mixing MM without temperature control with initial temperature at ambient temperature (MNAT) and (3) hand shaking mixing (HM) without temperature control with initial temperature at ambient temperature (HNAT). The tests were, respectively, carried out for ultrasonic irradiation, mechanical mixing and hand shaking mixing with esterification times t_{UE}, t_{ME} and t_{HE} of 10 (E10), 10 (E10) and 1 (E1) min. Two settling times t_S of 10 (S10) and 0 (S0) min were examined. The AV of Cases UNVT-E10S0 and UNVT-E10S10, MNAT-E10S0 and MNAT-E10S10, and HNAT-E1S0 and HNAT-E1S10 are 13.73 and 15.82, 26.23 and 23.12, and 30.22 and 26.16 mg KOH/g, respectively. The magnitudes of esterification conversion efficiencies, η, in terms of the percentage of AV reduction from the highest are in the order of UI (62.45 (E10S0) and 56.73% (E10S10)), mechanical mixing (28.25 (E10S0) and 36.76% (E10S10)) and hand shaking mixing (17.34 (E1S0) and 28.45% (E1S10)). The results for these esterification methods are presented in Table 5 and Fig. 1. The superiority of ultrasonic irradiation is due to its combined enhancing effects of mixing and heating. By applying the UI with the conditions of Case UNVT, the water content of jatropha oil ester shown in Table 3 is as low as 0.33

Table 3
Properties of crude jatropha oil ester obtained by esterification without external cooling or heating.

Property	Unit	Ultrasonic[a] esterification time (t_{UE})			Mechanical[b] esterification time (t_{ME})		
		UNVT-E5S10	UNVT-E10S10	UNVT-E30S10	MNAT-E5S10	MNAT-E10S10	MNAT-E30S10
		5 min	10 min	30 min	5 min	10 min	30 min
AV	mg KOH/g	24.75 (1.73)[c]	15.82 (3.76)[c]	6.13 (1.08)[c]	26.65 (1.25)[c]	23.12 (1.18)[c]	21.03 (0.62)[c]
IV	g I_2/100 g	111.92	111.49	111.22	109.41	113.22	112.58
KV at 40 °C	mm^2/s	22.10	22.41	20.49	26.05	22.51 (0.06)[c]	21.78
Density at 15 °C	kg/m^3	912.75 (0.06)[c]	913.8 (0.08)[c]	916.1 (0.15)[c]	915.4 (0.25)[c]	913.58 (0.44)[c]	913.4 (0.06)[c]
Water content	wt.%	0.37 (0.02)[c]	0.48 (0.02)[c]	0.33 (0.01)[c]	–	–	–
η[d]	%	32.3	56.73	83.23	27.11	36.76	42.48

[a] UI without temperature control, while with varied temperature in sample and with initial temperature at ambient temperature (UNVT). Cases at esterification (*E*) time t_{UE} = 5, 10 and 30 min (instant temperature = 49.6, 63.4 and 65.4 °C; average temperature = 33.2 (1.7)[c], 43.3 (3.6)[c] and 56.7 (2.2)[c] °C) with settling (*S*) time t_S = 10 min are denoted as UNVT-E5S10, UNVT-E10S10 and UNVT-E30S10.

[b] Mechanical mixing without temperature control with initial temperature at ambient temperature (MNAT). Cases at esterification time t_{ME} = 5, 10 and 30 min (instant temperature = 24.6, 24.0 and 21.7 °C; average temperature = 24.8, 24.5 and 23.3 °C) with t_S = 10 min are noted as MNAT-E5S10, MNAT-E10S10 and MNAT-E30S10.

[c] Standard deviation (σ_{n-1}).

[d] Esterification conversion efficiency (η).

to 0.48 wt.%, ensuring the good quality of ester with negligible water content.

3.3. Effect of settling time t_S on AV

The influence of t_S for longer time after esterification of jatropha oil on the reduction of AV is further illustrated in Fig. 2. For settling times of 0, 10, 20, 30, 40 and 1440 min, the acid values for mechanical mixing were 26.23, 23.12, 23.65, 21.89, 22.39 and 17.61 mg KOH/g with decreasing trend in general. At t_S = 0–10 and 1440 min, the esterification conversion efficiency η increases from 28.25 to 36.76 and 51.83%, respectively, showing a maximum difference of increase of η of 23.58% (=51.83–28.25%). However, the corresponding acid values for UI at t_S = 0, 10, 20, 30, 40 and 1440 min were 13.73, 15.82, 11.8, 11,21, 10.27 and 7.45 mg KOH/g, much lowering than those of mechanical mixing. The η values for UI were 62.45 to 56.73 and 79.62% at t_S = 0–10 and 1440 min, respectively, with a maximum difference of improvement of η of 22.89% (=79.62–56.73%). Therefore, the effect of t_S on AV employing UI is as significant as that using mechanical mixing. Although a prolong t_S of 1440 min can offer a maximum difference of increase of η of 22.89–23.58%, however, for the convenience of practical operation, the adoption of t_S should not be too long but rationally kept at appropriate level, say 10–30 min, to give satisfactory esterification conversion efficiency. The results of Fig. 2, as expected, also show that the effectiveness of UI with combined enhancement of mixing and heating is more vigorous than that of mechanical mixing without heating. The beneficial contribution of UI is strongly associated with its auto- or self-induced heating effect.

3.4. Effect of esterification time t_E on AV

Effects of esterification time t_E on AV in esterification treatment are shown in Fig. 3 for four different cases as follow.

(1) Case UCVT-S10: UI with varied temperature in sample, while externally cooled by water bath with temperature at 5 °C; symbol ○ in Fig. 3.
(2) Case MNAT-S10: mechanical mixing without temperature control with initial temperature at ambient temperature; symbol ◆ in Fig. 3.
(3) Case MHFT-S10: mechanical mixing with temperature control at about 47.6 °C using external heating with water bath of 65 °C; symbol ◇ in Fig. 3.
(4) Case UNVT-S10: UI without temperature control, while with varied temperature in sample and with initial temperature at ambient temperature; symbol • in Fig. 3.

The acid values AV were measured at t_E of 5, 10, 15 and 30 min with t_S of 10 min. The temperature variations during esterification are illustrated in Fig. 4.

The results indicate a decrease of AV (or increase of η) with increase of t_E as expected obeying the reaction kinetics. For Cases MNAT-S10 and MHFT-S10 of MM with rather constant temperatures at about 23.3 and 47.6 °C, the AV decreases gradually with t_E. For example, the AV of Case MNAT-S10 reduces from 36.56 to 21.03 mg KOH/g at t_E = 30 min with η = 42.48%.

However, Case UNVT-S10 of UI, without temperature control while with varied temperature, exhibits rapid increase of

Table 4
Properties of crude jatropha oil ester obtained by esterification with external cooling or heating.

Property	Unit	Ultrasonic[a] esterification time (t_{UE})			Mechanical[b] esterification time (t_{ME})		
		UCVT-E5S10	UCVT-E10S10	UCVT-E30S10	MHFT-E5S10	MHFT-E10S10	MHFT-E30S10
		5 min	10 min	30 min	5 min	10 min	30 min
AV	mg KOH/g	29.99 (1.05)[c]	28.97 (0.20)[c]	24.87 (0.66)[c]	19.14 (0.01)[c]	16.86 (0.31)[c]	15.70 (0.63)[c]
IV	g I_2/100 g	114.50	113.20	106.96	110.18	113.22	113.63
KV at 40 °C	mm^2/s	23.53	23.68	22.98	20.06	21.94 (0.06)[c]	22.61
Density at 15 °C	kg/m^3	913.88 (0.30)[c]	914.25 (0.19)[c]	914.1 (0.17)[c]	912.0 (0.13)[c]	913.57 (0.15)[c]	914.2 (0.08)[c]
η[d]	%	17.97	20.76	31.97	47.65	53.88	57.06

[a] UI with varied temperature in sample without temperature control, while externally cooled by water bath of 5 °C. Cases at t_{UE} = 5, 10 and 30 min (instant temperature = 27.0, 32.2 and 35.3 °C; average temperature = 20.8, 25.4 and 31.5 °C) with t_S = 10 min are symbolized as UCVT-E5S10, UCVT-E10S10 and UCVT-E30S10.

[b] Mechanical mixing with temperature in sample controlled by employing external heating using water bath of 65 °C. Cases at t_{ME} = 5, 10 and 30 min (instant temperature = 47.8, 46.4 and 47.1 °C; average temperature = 49.5, 48.4 and 47.6 °C) with t_S = 10 min are expressed as MHFT-E5S10, MHFT-E10S10 and MHFT-E30S10.

[c] Standard deviation σ_{n-1}.

[d] Esterification conversion efficiency η.

Table 5
AV and η of crude jatropha oil esters applying different esterification methods.

Property	Unit	Ultrasonic[a] esterification time (t_{UE})		Mechanical[b] esterification time (t_{ME})		Hand shaking[c] esterification time (t_{HE})	
		UNVT-E10s0	UNVT-E10S10	MNAT-E10S0	MNAT-E10S10	HNAT-E1S0	HNAT-E1S10
		10 min	10 min	10 min	10 min	1 min	1 min
AV	mg KOH/g	13.73 (1.06)[d]	15.82 (3.76)[d]	26.23 (1.85)[d]	23.12 (1.18)[d]	30.22 (2.21)[d]	26.16 (0.62)[d]
η[e]	%	62.45	56.73	28.25	36.76	17.34	28.45

[a] UI without temperature control with initial temperature at ambient temperature (UNVT). Cases at esterification (E) time $t_{UE} = 10$ min, with settling (S) time $t_S = 0$ and 10 min are denoted as UNVT-E10S0 and UNVT-E10S10.

[b] Mechanical mixing without temperature control with initial temperature at ambient temperature (MNAT). Cases at esterification time $t_{ME} = 10$ min, with $t_S = 0$ and 10 min are noted as MNAT-E10S0 and MNAT-E10S10.

[c] Hand shaking mixing (HM) with initial temperature at ambient temperature (MNAT). Cases at esterification time $t_{HE} = 1$ min, with $t_S = 0$ and 10 min are noted as MHAT-E1S0 and HNAT-E1S10.

[d] Standard deviation σ_{n-1}.

[e] Esterification conversion efficiency η.

temperature and thus results in fast decrease of AV. As the UI is externally cooled by water bath with temperature at 5 °C (Case UCVT-S10), its enhancing heating effect is partly offset by the opposite cooling, resulting in temperature lower than those of Case UNVT-S10 without cooling and Case MHFT-S10 with heating. The AV of Case UCVT-S10 is thus higher than those of Cases UNVT-S10 and MHFT-S10.

It is of interest that Case UCVT-S10 of UI gives higher AV than Case MNAT-S10 of MM although the former has higher average temperature than the latter. From Fig. 4, the temperatures of early period of the former are lower than those of the latter, indicating that temperature effect is more crucial in the early than the later stage of esterification.

The lower temperature in the early esterification time of Case UNVT-S10 than Case MHFT-S10 also causes the higher AV of the former than the latter. However, as t_E increases longer than 10 min such that the temperature of Case UNVT-S10 is much higher than that of Case MHFT-S10, the former then has AV lower than the latter. Thus, the UI with the feature of auto-induced fast heating accompanied with mixing operated at sufficient time is more advantageous than MM with external heating. For the examples shown in Fig. 3, values of η for Case UNVT-S10 of 56.73 and 83.23% (Table 3) are higher than those for Case MHFT-S10 of 53.88 and 57.06% (Table 4) at $t_E = 10$ and 30 min, respectively. At $t_E = 5$ min, Case UNVT- S10 gives η of 32.30% (Table 3) lower than Case MHFT-S10 of 47.65% (Table 4), simply because the temperature of Case UNVT-S10 is still below that of Case MHFT-S10 as noted above. Hence, the efficiency of ultrasonic irradiation is strongly related with t_E and its auto-induced temperature rise.

In order to further understand the proper choice of esterification time t_E in conjunction with settling time t_S, the esterification of jatropha oil by mechanical mixing for Case MNAT without temperature control with initial temperature at ambient

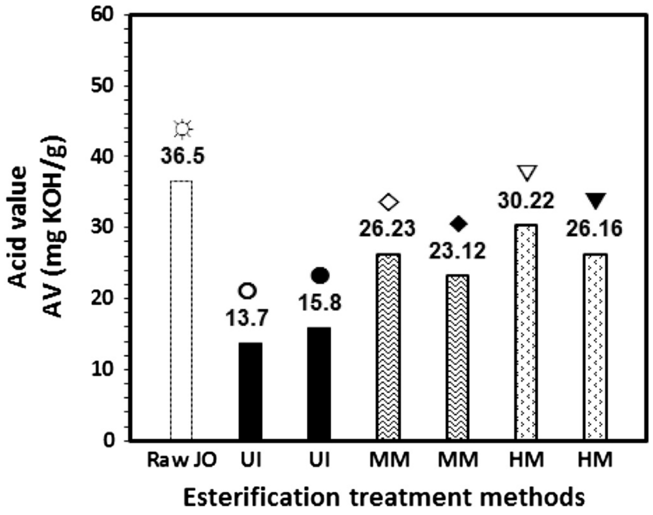

Fig. 1. Acid value (AV) of jatropha oil after different esterification methods of ultrasonic irradiation (UI), mechanical mixing (MM) and hand shaking mixing (HM). Symbols: ☼ (raw jatropha oil); ○ (UNVT-E10S0), ● (UNVT-E10S10), ◇ (MNAT-E10S0), ◆ (MNAT-E10S10), ▽ (HNAT-E1S0), ▼ (HNAT-E1S10). Notations: as specified in Table 5.

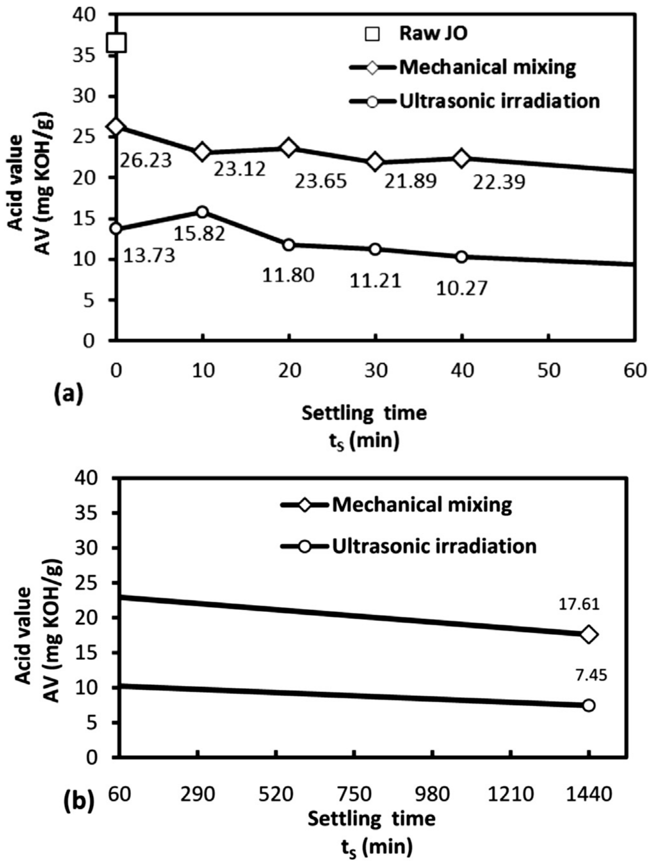

Fig. 2. Effects of settling time t_S on acid value AV of jatropha oil (JO) at esterification time $t_E = 10$ min □: Raw JO. ◇, ○: MNAT-E10, UNVT-E10. MNAT: mechanical mixing without temperature control with initial temperature at ambient temperature; E10: at $t_E = 10$ min. UNVT: UI without temperature control, while with varied temperature in sample and with initial temperature at ambient temperature. (a) t_S: 0–60 min; and (b) t_S: 60–1440 min.

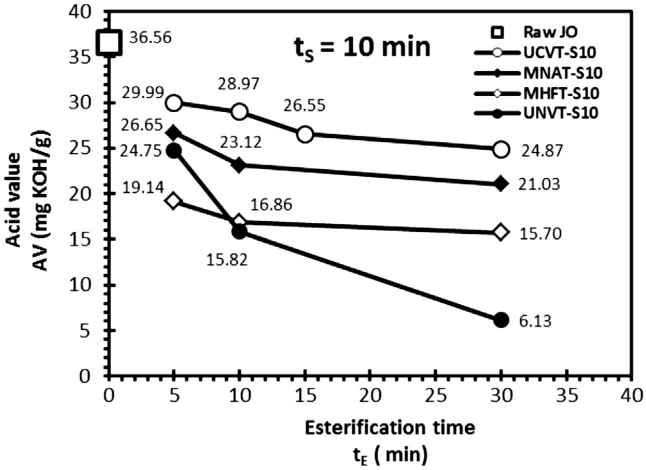

Fig. 3. Effects of t_E on AV. □: Raw JO. ○, ◆, ◇, ●: UCVT-S10 (UI with varied temperature in sample without temperature control, while externally cooled by water bath of 5 °C with average temperature of sample of 31.5 °C at $t_E = 30$ min), MNAT-S10 (MNAT with average temperature of sample of 23.3 °C at $t_E = 30$ min), MHFT-S10 (MM with temperature in sample controlled by employing external heating using water bath of 65 °C with average temperature of sample of 47.6 °C at $t_E = 30$ min), UNVT-S10 (UNVT with average temperature of sample of 56.7 °C at $t_E = 30$ min). MNAT, UNVT: as specified in Fig. 2. S10: at $t_S = 10$ min.

temperature were performed with t_S of 1440 min at various t_E with results of AV illustrated in Fig. 5. For very long t_S, say 1440 min, the effect of t_E is insignificant as t_E is equal or longer than 2 min, giving AV lower than 17.11 mg KOH/g (η higher than 53.20%). Note that the AV at $t_E = 30$ min decreases only to 15.97 mg KOH/g ($\eta = 56.32\%$). It indicates that long t_S may be an alternative choice instead of long t_E for applying the mechanical mixing at ambient temperature. This can reduce the esterification time and thus the mechanical mixing cost, with the compensation of long settling time.

3.5. *Effect of t_E on temperature during esterification via UI*

The marked variation of temperature with t_E in esterification employing UI is shown in Fig. 4. For Case UNVT-S10 of UI without temperature control, while with varied temperature, the temperature quickly increases from ambient temperature at the beginning to about 63.4 °C in 10 min and reaches to plateau temperature of 65.4 °C at 30 min of irradiation time with average temperature of 56.7 °C for 30 min. The corresponding AV also dramatically decrease in 10 min while moderately reduces during 10–30 min as shown in Fig. 3. The results indicate that the esterification reaction of jatropha oil via UI is reaction control which is significantly affected by the reaction temperature. The temperature effect can be further clarified by comparing the results of Case UNVT-S10 with those of Case UCVT-S10 of UI with external cooling by water bath with temperature at 5 °C. The temperatures of Case UCVT-S10 vary from 12.4 to 32.2 and 35.3 °C during 0–10 and 30 min, respectively, with average temperature of 31.5 °C for 30 min, being much lower than those of Case UNVT-S10. The low temperature then gives high AV or low η. Thus, the effect of heating giving rise of temperature is more significant than that of mixing in enhancing the esterification extent for the UI. However, it should be noted that the heating is auto-induced by the cavity effect and micro-mixing generated through UI.

Fig. 4 also presents the temperature variations with t_E in esterification applying mechanical mixing MM. Case MHFT-S10 is with temperature control adopting external heating water bath of 65 °C. The temperature are nearly constant keeping in 48.0 to 47.10 °C during 0–30 min with average temperature of 47.6 °C for 30 min. Case MNAT-S10 is without temperature control with initial temperature at ambient temperature. The temperatures are kept in 25.1 to 21.70 °C for $t_E = 0$–30 min with average temperature of 23.3 °C for 30 min. The results indicate that the heat of esterification reaction is insignificant on affecting the system temperatures. This finding of constant temperature for the cases of mechanical mixing incorporated to the temperature rise during the esterification via ultrasonic irradiation thus further reveals the unique auto-induced heating effect of the latter.

It is noted that the temperatures at $t_E = 0$ min for the cases without and with external cooling or heating are different as shown in Fig. 4. All samples were prepared at ambient temperature before applying different esterification methods. For Cases UNVT and MNAT without external cooling or heating, the initial temperatures were at ambient temperature. However, for Cases UCVT and MHFT with external cooling and heating, the temperature of sample rapidly decreased and increased due to the heat exchange of sample with external cooling and heating, respectively. Thus, the difference in initial temperatures for the cases with and without external cooling and heating is naturally and simply caused by the

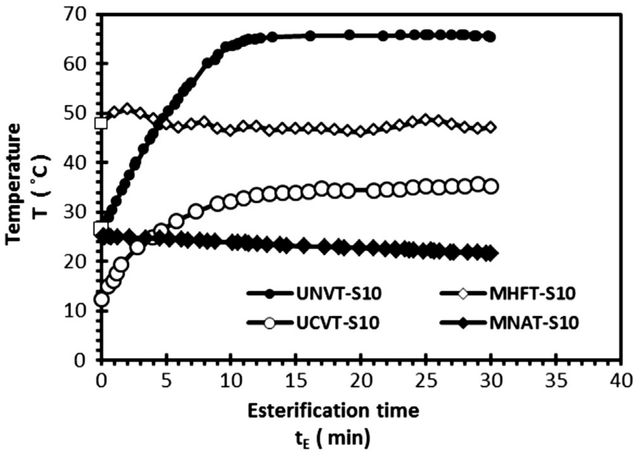

Fig. 4. Temperature (T) variations during esterification. ●, ◇, ○, ◆: UNVT-S10, MHFT-S10, UCVT-S10, MNAT-S10. UNVT and MNAT, MHFT and UCVT: as specified in Figs. 2 and 3.

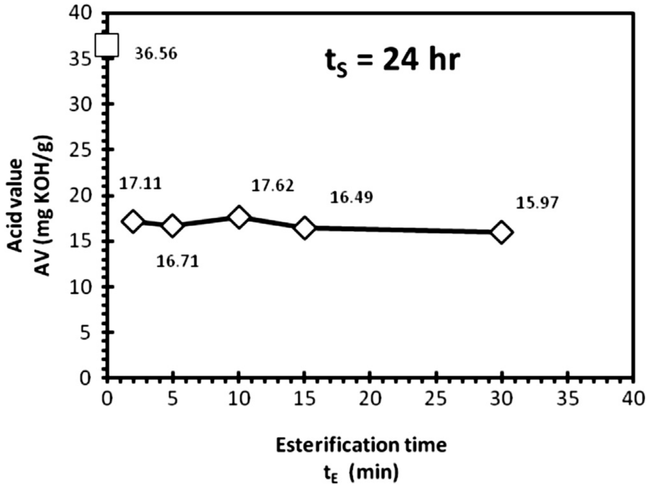

Fig. 5. Effect of t_E on AV applying mechanical mixing with long t_S of 24 h. □: Raw jatropha oil. ◇: MNAT-S1440; S1440: $t_S = 1440$ min. MNAT: as specified in Fig. 2.

application of external heat exchange. As illustrated in Fig. 4, the initial temperatures for the four cases are 48 °C (MHFT), 28 °C (UNVT), 25 °C (MNAT) and 11 °C (UCVT), respectively. A higher temperature would result in lower acid value AV or higher esterification conversion efficiency η. The enhancing effect of high temperature on the reduction of AV thus gives the acid values of 19.14, 24.75, 26.65 and 29.99 mg KOH/g from low at $t_E = 5$ min for Cases MHFT, UNVT, MNAT and UCVT. This is in consistence with the initial temperatures for the corresponding processes of 48 °C, 28 °C, 25 °C and 11 °C from high.

3.6. Combined effects of mixing and heating on AV

The variations of instantaneous reaction temperature during the esterification of jatropha oil by four cases, namely Cases UCVT-S10 (○), UNVT-S10 (●), MNAT-S10 (◆) and MHFT-S10 (◇), are illustrated in Fig. 4 and already discussed in the preceding section. The role of UI in liquid phase can be referred to the studies of Peters [24] and Gonzales-Garcia et al. [25]. They reported that the energy wave of ultrasound collapses the bubble cavities, disrupts the phase boundary and induces emulsification, functioning as a jet that induces the collision of liquids. Therefore, the UI provides not only mixing but also energy. The collapse of bubble cavities thus induces heat and gives rise of temperature. To further examine the effectiveness of combined effects of mixing and auto-induced heating of UI on AV, comparison of AV vs. T_{avg} for the UI and mechanical mixing MM was made. The results of above four cases at $t_E = 5$ and 10 min are compared as presented in Fig. 6. The average temperature T_{avg} at specific t_E is computed from the beginning to t_E.

At $t_E = 5$ min, the auto-induced heating of Case UCVT-S10 is offset by external cooling, resulting in a lower T_{avg} while higher AV of 20.8 °C and 29.99 mg KOH/g than Case MNAT-S10 of 24.8 °C and 26.65 mg KOH/g, respectively, as expected. As the esterification proceeds further to $t_E = 10$ min, the Tavg of Cases UCVT-S10 and MNAT-S10 are close with 25.4 °C and 24.5 °C, respectively. However, the former has an AV of 28.97 mg KOH/g ($\eta = 20.76\%$) higher than the latter of 23.12 mg KOH/g ($\eta = 36.76\%$). This is due to the cause of external cooling which might hinder the unique mixing function of UI.

For the UI without temperature control while with varied temperature of Case UNVT-S10, its AV of 24.75 mg KOH/g at $t_E = 5$ min is higher than that of 19.14 mg KOH/g for Case MHFT-S10 of mechanical mixing MM with temperature control at about 47.56 °C using external heating water bath of 65 °C. This is because the former gives T_{avg} of 33.2 °C much lower than the latter of 49.5 °C. Further at longer $t_E = 10$ min, the temperature rise of Case UNVT-S10 becomes more pronounced giving T_{avg} of 43.3 °C which though is slightly lower than that of 48.4 °C of Case MHFT-S10. The AV of the former of 15.82 mg KOH/g ($\eta = 56.73\%$), however, is lower than that of the latter of 16.86 mg KOH/g ($\eta = 53.88\%$). All these thus elucidate that the mixing extent of UI is enhanced by the auto-induced heating, offering more contribution to the esterification than the temperature effect compared to MM with temperature control applying external heating water bath.

Chen et al. [12] have conducted mechanical stirring esterification of jatropha oil at 60 °C for 1 h and reported an esterification conversion efficiency η of 95.5%. In the present study, a η of 57.86% was obtained for the mechanical mixing esterification of Case MHFT-E30S10 which was performed at lower average temperature T_{avg} of 47.6 °C for shorter esterification time of 30 min. Further, the initial AV of jatropha oil of 36.5 mg KOH/g of this work was 1.34 times higher than that of 27.2 mg KOH/g of Chen et al. [12]. Moreover, a η as high as 83.23% was achieved for the UI esterification of Case UNVT-E30S10, being close to 88.42% of Deng et al. [16] employing two-step UI esterification and transesterification. In comparison with the work of Deng et al. [16], however, the UNVT-E30S10 process of this study is more beneficial with about half esterification time, half reaction temperature and 4 times lower catalyst, while 3.5 times higher initial AV of jatropha oil.

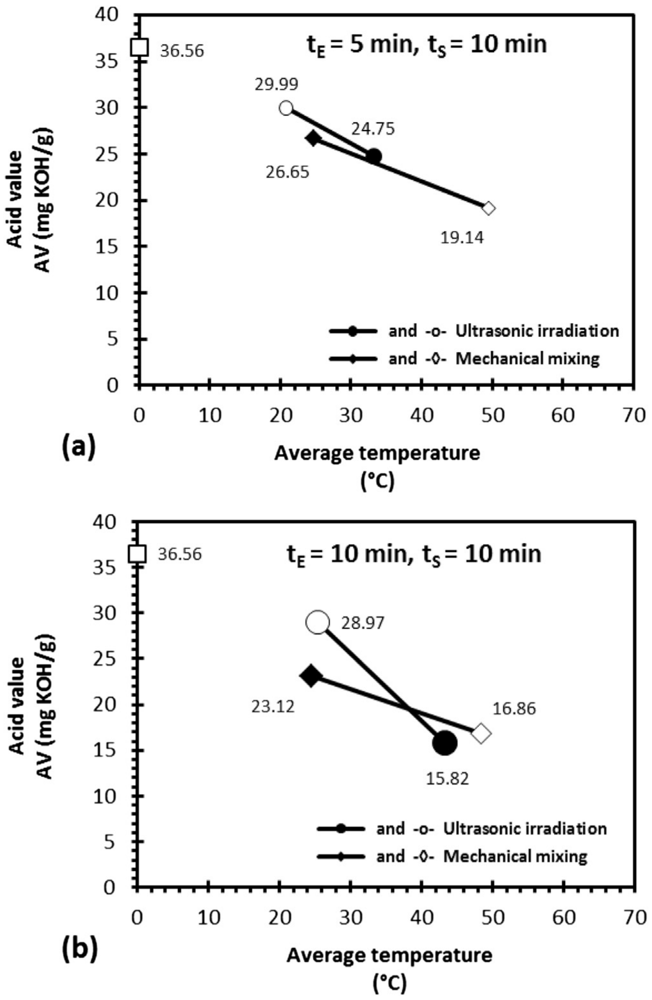

Fig. 6. Effects of temperature T on AV. □: Raw JO. ○, ●, ◆, ◇: UCVT-S10, UNVT-S10, MNAT-S10, MHFT-S10. Temperature shown is the average from beginning to t_E. Notations: As specified in Fig. 4. a and b: with $t_E = 5$, 10 min.

4. Conclusions

Ultrasonic irradiation (UI) with auto-induced temperature-rise effect offers better esterification performance than mechanical mixing (MM) with external heating. The content of free fatty acid (FFA) in the ester produced from jatropha oil (jatropha oil ester) is 7.91 wt. % by employing UI at esterification time (t_E) of 10 min. The corresponding esterification conversion efficiency (η) of the FFA is 56.73%. The effect of settling time on acid value (AV, = 2× wt. % FFA) applying UI is as significant as compared with that applying MM. The effect of t_E on AV is of more importance for UI than MM. The η increases from 56.73% to 83.23% as t_E prolongs from 10 to 30 min for UI esterification. The UI auto-induces temperature rise, resulting in more pronounced temperature effect than MM. The mixing extent of UI is enhanced by the auto-induced heating, giving significant contribution to the esterification.

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Nomenclature

Abbreviation and symbols

AV	acid value
E	esterification or esterification time
*E*1, *E*5, *E*10, *E*30	esterification times of 1, 5, 10, 30 min
FAAEs	fatty acids alkyl esters
FAMEs	fatty acids methyl esters
FFA	free fatty acid
HNAT	hand shaking mixing without temperature control with initial temperature at ambient temperature
HNAT-E1S0	HNAT with esterification time of 1 min and settling time of 0 min
HNAT-E1S10	HNAT with esterification time of 1 min and settling time of 10 min
IV	iodine value
JO	jatropha oil
KV	kinematic viscosity at 40 °C
m_C	catalyst with wt. % relative to oil
MHFT	mechanical mixing at higher temperature by employing external heating using water bath of 65 °C with average temperature of sample = 49.5, 48.4 and 47.6 °C at $t_{ME} = 5$, 10 and 30 min and $t_S = 0$ min
MHFT-E5S10	MHFT with t_{ME} of 5 min and t_S of 10 min
MHFT-E10S10	MHFT with t_{ME} of 10 min and t_S of 10 min
MHFT-E30S10	MHFT with t_{ME} of 30 min and t_S of 10 min
MHFT-S10	MHFT with t_S of 10 min
MM	mechanical mixing
MNAT	mechanical mixing without temperature control with initial temperature at ambient temperature with average temperature of sample = 24.8, 24.5 and 23.3 °C at $t_{ME} = 5$, 10 and 30 min and $t_S = 0$ min
MNAT-E5S10	MNAT with t_{ME} of 5 min and t_S of 10 min
MNAT-E10	MNAT with t_{ME} of 10 min
MNAT-E10S0	MNAT with t_{ME} of 10 min and t_S of 0 min
MNAT-E10S10	MNAT with t_{ME} of 10 min and t_S of 10 min
MNAT-E30S10	MNAT with t_{ME} of 30 min and t_S of 10 min
MNAT-S10	MNAT with t_S of 10 min
MNAT-S1440	MNAT with t_S of 1440 min
M/O	molar ratio of methanol to oil
MW	molecular weight
P_{WUI}	power of UI, W
r_S	stirring speed of 250 rpm
S	settling or settling time
*S*0, *S*10, *S*1440	settling times of 0, 10, 1440 min
t_E	esterification time
t_{HE}	esterification time for hand shaking mixing
t_{ME}	esterification time for mechanical mixing
t_S	settling time
t_{UE}	esterification time for ultrasonic irradiation
T	temperature or reaction temperature
T_{avg}	average temperature
UCVT	UI with temperature-rise effect, while is externally cooled by water bath with temperature at 5 °C with average temperature of sample = 20.8, 25.4 and 31.5 °C at $t_{UE} = 5$, 10 and 30 min and $t_S = 0$ min
UCVT-E5S10	UCVT with t_{UE} of 5 min and t_S of 10 min
UCVT-E10S10	UCVT with t_{UE} of 10 min and t_S of 10 min
UCVT-E30S10	UCVT with t_{UE} of 30 min and t_S of 10 min
UCVT-S10	UCVT with t_S of 10 min
UI	ultrasonic irradiation
UNVT	UI with temperature-rise effect, with initial temperature at ambient temperature with average temperature of sample = 33.2, 43.3 and 56.7 °C at $t_{UE} = 5$, 10 and 30 min and $t_S = 0$ min
UNVT-E10	UNVT with t_{UE} of 10 min
UNVT-E10S0	UNVT with t_{UE} of 10 min and t_S of 0 min
UNVT-E5S10	UNVT with t_{UE} e of 5 min and t_S of 10 min
UNVT-E10S10	UNVT with t_{UE} of 10 min and t_S of 10 min
UNVT-E30S10	UNVT with t_{UE} of 30 min and t_S of 10 min
UNVT-S10	UNVT with t_S of 10 min
V_L	total volume of liquid sample, 300 mL

Greek

η	esterification conversion efficiency
ρ_{LO}	density of liquid sample
σ_{n-1}	standard deviation

References

[1] Manh DV, Chen YH, Chang CC, Chang MC, Chang CY. Biodiesel production from tung oil and blended oil via ultrasonic transesterification process. J Taiwan Inst Chem Eng 2011;42:640–4.

[2] Boro J, Deka D. A review on biodiesel. J Biobased Mater Bio 2012;6:125–41.

[3] Syu FS, Chiueh PT. Process simulation of rice straw torrefaction. Sustain Environ Res 2012;22:177–83.

[4] Lin YC, Lin JF, Hsiao YH, Hsu KH. Soybean oil for biodiesel production assisted by a microwave system and sodium methoxide catalyst. Sustain Environ Res 2012;22:247–54.

[5] Chen JC, Guo JS. Improving the conversion efficiency of waste cotton to bioethanol by microwave hydrolysis technology. Sustain Environ Res 2013;23:333–9.

[6] Knote G, Steidley KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compounds structure and comparison to petrodiesel fuel components. Fuel 2005;84:1059–65.

[7] Drapcho CM, Nhuan NP, Walker TH. Biofuels engineering process technology. New York: McGraw-Hill; 2008.

[8] Manh DV, Chen YH, Chang CC, Chang CY, Minh CV, Hanh HD. Parameter evaluation of biodiesel production from unblended and blended tung oils via ultrasound-assisted process. J Taiwan Inst Chem Eng 2012a;43:368–73.

[9] Manh DV, Chen YH, Chang CC, Chang CY, Hanh HD, Chau NH, et al. Effects of blending composition of tung oil and ultrasonic irradiation intensity on the biodiesel production. Energy 2012b;48:519–24.

[10] Jain S, Sharma MP. Biodiesel production from *Jatropha curcas* oil. Renew Sustain Energy Rev 2010;14:3140–7.

[11] Shang Q, Jiang W, Lu H, Liang B. Properties of tung oil biodiesel and its blends with 0# diesel. Bioresour Technol 2010;101:826–8.

[12] Chen YH, Chen JH, Luo YM, Shang NC, Chang CH, Chang CY, et al. Property modifications of jatropha oil biodiesel by blending with other biodiesels or adding antioxidants. Energy 2011;36:4415–21.

[13] Santos FFP, Malveira JQ, Cruz MGA, Fernandes FAN. Production of biodiesel by ultrasound assisted esterification of *Oreochromis niloticus* oil. Fuel 2010;89:275–9.

[14] Zou H, Lei M. Optimum process and kinetic study of jatropha curcas oil pre-esterification in ultrasonical field. J Taiwan Inst Chem Eng 2012;43:730–5.

[15] Berrios M, Siles J, Martin MA, Martin A. A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil. Fuel 2007;86:2383–8.

[16] Deng X, Fang Z, Liu YH. Ultrasonic transesterification of *Jatropha curcas* L. oil to biodiesel by a two-step process. Energ Convers Manage 2010;51:2802–7.

[17] Jain S, Sharma MP. Kinetics of acid base catalyzed transesterification of *Jatropha curcas* oil. Bioresour Technol 2010;101:7701–6.

[18] Corro G, Tellez N, Banuelos F, Mendoza ME. Biodiesel from *Jatropha curcas* oil using Zn for esterification step and solar radiation as energy source. Fuel 2012;97:72–9.

[19] Kywe TT, Oo MM. Production of biodiesel from jatropha oil (jatropha curcas) in pilot plant. Proc World Acad Sci Eng Technol February 2009;38. ISSN: 2070-3740.

[20] Knothe G, Van Gerpen J, Krahl J. The biodiesel handbook. Champaign IL: AOCS Press; 2005.

[21] Van Gerpen J, Shanks B, Knothe G, Pruszko R. Biodiesel analytical methods. National Renewable Energy Laboratory; 2004. NREL/SR-510-36240.

[22] Biofuel Systems, ASTM D6751-07b, EN14214:2008, EN 590. Biodiesel information [accessed December 2012], http://www.biofuelsystems.com/idex.html; 1999.

[23] TBOS (Bureau of Standards, Metrology and Inspection of Taiwan). CNS 15072. CNS (Chinese National Standards) online service [accessed December 2012], http://www.cnsonline.com.tw/.

[24] Peters D. Ultrasound in materials chemistry. J Mater Chem 1996;6:1605–18.

[25] Gonzalez-Garcia J, Iniesta J, Aldaz A, Montiel V. Effects of ultrasound on the electrodeposition of lead dioxide on glassy carbon electrodes. New J Chem 1998;22:343–9.