Energy Conversion and Management 88 (2014) 1078–1085

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Reduction of FFA in jatropha curcas oil via sequential direct-ultrasonic irradiation and dosage of methanol/sulfuric acid catalyst mixture on esterification process

Cesar Augusto Andrade-Tacca [a],*, Chia-Chi Chang [a], Yi-Hung Chen [b], Dar-Ren Ji [a], Yi-Yu Wang [a], Yue-Quen Yen [a], Ching-Yuan Chang [a,c]

[a] Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan
[b] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan
[c] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

ARTICLE INFO

Article history:
Available online 27 September 2014

Keywords:
Jatropha oil
Esterification
Ultrasonic irradiation
Methyl ester
Acid value

ABSTRACT

Production of jatropha-ester (JO-ester) from jatropha oil (JO) under sequential direct-ultrasonic irradiation (UI) with auto-induced temperature rise followed by adding a mixture of methanol/sulfuric-acid catalyst (M/C) dose between high temperature intervals was studied. Comparisons with various doses of 5, 10, 16.6 and 25 mL at different temperature intervals of 108.9–120 °C, 100–120 °C, 85–120 °C and 75–120 °C respectively were performed. System parameters examined include: esterification times (t_E) for UI, settling time (t_S) after esterification and temperature (T). Properties of acid value (AV), iodine value (IV), kinematic viscosity (kV), density (ρ_{LO}) and water content (m_w) of JO and JO-ester product were measured. The esterification conversion efficiencies (η) were determined and assessed. An η of 99.35% was obtained at temperature interval of 108.9–120 °C with 5 mL per dose for 20 doses and t_E of 167.39 min (denoted as Process $U_{120\text{-}5}$), which is slightly higher than η of 98.87% at temperature interval of 75–120 °C with 25 mL per dose for 4 doses and t_E of 108.79 min (noted as Process $U_{120\text{-}25}$). The JO-ester obtained via sequential UI with adding doses of 5 mL possess AV of 0.24 mg KOH/g, IV of 124.77 g I_2/100 g, kV of 9.89 mm^2/s, ρ_{LO} of 901.73 kg/m^3 and m_w of 0.3 wt.% showing that sequential UI and dose at higher temperature interval can give higher reduction of AV compared with 36.56 mg KOH/g of original oil. The effects of t_S and t_E on AV are of minor and moderate importance, respectively. The combined effects of auto-induced temperature-rise of UI and temperature higher than boiling point of methanol used improve the mixing and esterification extent.

1. Introduction

World population has continued to increase every year meaning that world energy demand also increases in same way. Most energy resources are non-renewables e.g. fossil fuels [1]. Nowadays, oil price, shortage of fossil fuel, and environmental concerns are global issues that have been widely treated. Biodiesel, as renewable energy source, is one of the attractive options to solve this crisis for many countries to improve energy security supply and reduce the impact of oil dependency. Biodiesel is made from biomass sources such as vegetable oils or animal fats [2–4]. It is chemically known as simple mono-alkyl ester (such as methyl ester) [5] and attracted much attention in many countries because of its availability, renewability, non-toxic, biodegradability and less gas emissions reducing the emission of carbon dioxide [6,7]. Biodiesel can be prepared by transesterification processes combining vegetable oil with alcohol in the presence of catalyst to form fatty acid alkyl esters (FAAEs) (i.e., biodiesel) and glycerol [8].

Inedible woody plant oils, such as jatropha curcas linaeus oil (jatropha oil, denoted as JO or J) and tung oil are promising biomaterials around the world [9]. Jatropha curcas is an inedible oil bearing plant that 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 [10,11].

The conventional method for biodiesel production from jatropha oil involves an esterification treatment before the transesterification in order to reduce the high FFA content in jatropha oil, the esterification is a reversible reaction where free fatty acid (FFA) is

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* Corresponding author. Tel./fax: +886 223638994.
E-mail address: candrate@gmail.com (C.A. Andrade-Tacca).

http://dx.doi.org/10.1016/j.enconman.2014.09.020
0196-8904/

converted to alkyl esters via acid catalysis. The reactants including FFA and alcohol are catalyzed by acid to form alkyl ester and water. The simplified form of this chemical reaction is presented by the well-known equation as [12]:

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

The transesterification is sensitive to FFA content in raw JO. The increase in FFA content will reduce the formation rate and yield of fatty acids methyl esters (FAMEs) [13,14]. Further, the high content of FFA of 18.25 wt.% in raw JO may induce the saponification during transesterification. Usually, the AV of raw JO is firstly reduced in esterification process. Baroutian et al. [15], Berrios et al. [16], Corro et al. [17], Deng et al. [18] and Jain et al. [19] have recommended the use of esterification pretreatment before transesterification process when the percentage of FFAs of an oil or fat is high, in order to avoid the saponification and reduction of the yield of FAMEs. Somnuk et al. [12], Gole et al. [20], Lu et al. [21] and Veljkovic et al. [22] recommend that the oils going to alkaline transesterification should contain no more than 1% of FFA. The saponification is giving way to formation of long chain soaps, whose tensile properties do not permit an effective separation of glycerin at the end of process. The saponification may also hinder the separation of ester from glycerin.

The classical method for production of biodiesel from high FFA via base-catalyzed transesterification need long reaction time with high temperature that will increase the cost and consume of energy however with esterification pretreatment the processing time and energy will be greatly reduced. Kywe and Oo [23] carried out production of biodiesel in pilot plant using raw JO with a FFA of 8.8 wt.% and produced biodiesel with a FFA of 0.5 wt.%. Deng et al. [18] studied the acid catalyzed esterification and base transesterification of jatropha oil by UI reported FFA reduction from 5.25 to 0.61 wt.% at 60 °C using H_2SO_4 as catalyst with reaction time of 60 min in the first step. Chen et al. [10] studied the effect of acid-esterification followed by base-transesterification under classical mechanical-mixing obtaining biodiesel with AV of 0.12 mg KOH/g. Corro et al. [17] reported a novel esterification treatment under solar radiation with Zn filings as solid catalyst followed by base-transesterification indicating AV was reduced from 18.5 to 0.38 mg KOH/g. Worapun et al. [24] reported the two step catalyzed transesterification process coupled with UI at room temperature and reported 98% of conversion to biodiesel. Boffito et al. [3] reported a biodiesel yield higher than 90% by ultrasound-assisted batch transesterification with pulsed UI performed in rosett cell reactor with a reaction time 15 times faster than classic mechanical stirred process.

The UI role on liquid phase and theirs physical and chemical effects of cavitation are referred from studies of Boffito et al. [3], Peters [25], Gonzales-Garcia et al. [26], Shah et al. [27], Kuppa and Moholkar [28], Choudhury et al. [29–30] and Parkar et al. [31]. Recently developments in sonotechnique [22] attracted great attention with the use of the use of UI as new, efficient mixing tool, based on emulsification of immiscible liquids (reactants) by microturbulence, which is generated by radial motion of cavitation bubbles. Although ultrasonic cavitation is a unique way to input energy into reactor through the physical effect of cavitation [27], such as nucleation, growth and transient collapse of tiny bubbles, which are driving by the ultrasound waves. Both of these effects could contribute with the kinetics enhancement and also with the reaction yield, however, in many situations, the influence of one of these effects is more dominant than the other. Therefore, determination of the physical effects of ultrasound cavitation is an important step of investigation in sonotechnique [28]. A combination of high speed liquid jets, high pressure (>1000 atm), high temperatures (>4727 °C) [32], and enormous heating and cooling rates ($>10^9$ Ks^{-1}) occurs and is locally concentrated during the implosive compression of cavitation bubbles [33–35], the principal physical effect of ultrasonic cavitation is formation of fine emulsion between immiscible phases (JO and mixture M/C) eliminating the mass transfer resistance [3], while the principal chemical effect is production of radicals through transient collapse of cavitation bubbles [28]. Choudhury et al. [29,30] have studied the physical aspects of UI assisted heterogeneous catalyzed transesterification and reported that the reaction mixture of sonication of does not change the chemistry of the process and the beneficial effect is only of physical nature, which is further limited by the intrinsic kinetics and mass transfer. Parkar et al. [31] reported that the major physical effect of sonication is fine emulsification that generates enormous interfacial area for reaction that overwhelms the effect of specific rate constant.

Although UI can induce temperature-rise effect, the increase of temperature certainly enhances the reaction rate and yield of products. However, its enhancing effect would be partly offset by the endothermic reaction and the dose of reactants. In this study, sequential applying UI and dosing of active reactants were employed to overcome the temperature decrease. Thus, the temperature decreased due to dosing may be regained by stopping the dose while applying UI. Effects of major system parameters such as esterification time (t_E), settling time (t_S) and reaction temperature (T) on the esterification performance especially on the reduction of AV were elucidated.

2. Materials and methods

2.1. Materials

Jatropha curcas oil was supplied by Ozone Environmental Technology Co., Yi-Lan county, Taiwan, with acid value AV = 36.5 mg-KOH/g, iodine value (IV) = 105.68 g I_2/100 g, kinematic viscosity (kV) at 40 °C = 33.92 mm^2/s and density (ρ_{LO}) at 15 °C = 918.1 kg/m^3. Its molecular weight (MW) is 871.5 g/mol [36]. Methanol (M) of anhydrous assay 99.8% and sulfuric acid (as catalyst denoted as C) of 96.7% purity were obtained from Mallinckrodt, Phillipsburg, NJ and Sigma–Aldrich, St. Louis, MO, respectively.

2.2. Esterification procedures

Direct sonication by inserting a probe directly into a sample vessel is the most common way to process a sample. Energy is transmitted from the probe directly into the sample with high intensity. The acid catalyzed esterification pre-treatment was carried out in a 500 mL batch reactor without cooling/heating systems, the experimental set-up for sequential UI esterification is illustrated in Fig. 1. The total reaction volume is 300 mL (oil + metahol + catalyst). A sample of 183.82 g (Wo) or 200 mL

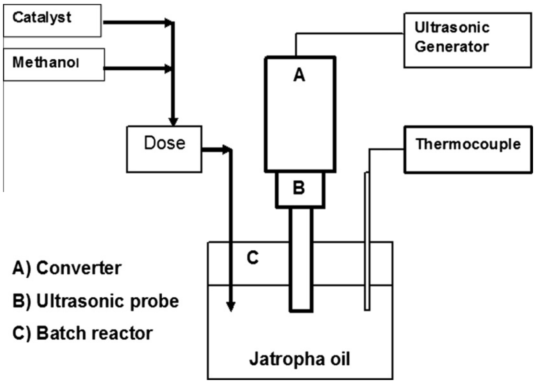

Fig. 1. Schematic diagram for sequential ultrasonic esterification.

(Vo) of JO was employed for a batch test. The total mixture volume of M/C for esterification is 100 mL, which is prepared with methanol to oil molar ratio (M/O) = 11 and sulfuric acid as a catalyst C with wt.% relative to oil (m_C) = 0.92 wt.%. The sample of jatropha oil was mixed with an initial fixed dose of M/C. The mixed sample of jatropha oil and M/C (J/M/C) was immediately subjected to the UI until the temperature has been raised to the pre-set upper temperature (120 °C). A fixed dose of mixture M/C was then added to the sample which caused a decrease of temperature down to the pre-set lower temperature. It was then sequentially followed by UI and dosing until the final fixed dose of mixture of M/C was added and accumulated to 100 mL. The time for adding each dose of M/C is fixed when the temperature rose the 120 °C, and the time interval between each dose are in average as 7.5, 13.47, 19.32 and 24.74 min for dosing of 5, 10, 16.6 and 25 mL of M/C dose respectively.

Vigorous mixing has been achieved by ultrasonic irradiation using an ultrasonic probe (Model 300 W, from Hoyu Technology Co., Taipei, Taiwan) operated with power (Pwus) at 90% (270 W) of its maximum power (300 W). The esterification times t_E for UI (t_{UE}) were conducted at 108.79, 128.23, 145.41 and 167.39 min while the mixture of M/C was added with fixed doses of 25, 16.6, 10 and 5 mL, respectively, with Pwus = 270 W at 25 kHz. The settling times t_S of 10 and 1440 min at ambient temperature were conducted after UI to allow post esterification reaction. The reaction temperature T of sample (inside the reactor) during the esterification was measured by a thermal couple (Firstteck Scientific, model-B403, Taipei, Taiwan).

After esterification, the sample was settled for proper t_S of 10 min and then the reaction was neutralized by washing with saturated sodium chloride solution. After the mixture was settled by 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) liquid composed of glycerol, residual catalyst, methanol and soap, and (3) JO-ester, which can be drawn off simply from the top of the separation funnel. The JO-ester was then kept inside the refrigerator for avoiding its decomposition. The JO-ester posteriorly was analyzed in order to determine its properties (AV, kV, density, IV).

2.3. Analysis

The properties of JO-ester were determined by methods used in biodiesel standards of United States (ASTM D6751), European (EN 14214) and Taiwan (Chinese National Standard, CNS-15072). The AV, IV, kV and ρ_{LO} of crude jatropha ester were measured according to the standard methods suggested by Chen et al. [10], Hung et al. [37], Ramos et al. [38] and Van Gerpen et al. [39]. These are outlined in EN 14104, EN 14111, EN ISO3104, EN ISO 3675 [40] and in Bureau of Standards, Metrology and Inspection of Taiwan (TBOS) [41].

Kinematic viscosity kV was measured with a Canon-Fenske capillarity viscometer (Cannon Instrument Co., State College, Pennsylvania, USA) immersed in a constant temperature bath of 40 °C according to the standard method ASTM D445-06. Water content (m_W) of the esters was determined according to standard CNS-4446 by coulometric method using a KF coulometer 851-Titrando (Metrohm AG, Herisau, Switzerland). For reflecting the precision and errors of the results, the relative standard deviations were computed with values less than 5%.

The esterification conversion efficiency (η) was determined as below:

$$\eta(\%) = [(\mathrm{AV}_1 - \mathrm{AV}_2)/\mathrm{AV}_1] \times 100 \qquad (2)$$

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. [18], the FFA content is in proportion to AV. Therefore the percentage the FFA was calculated dividing the AV by two as follow:

$$\mathrm{wt.\%FFA} = \mathrm{AV}/2 \qquad (3)$$

3. Results and discussion

In a conventional batch reactor, jatropha-ester was obtained by acid-catalyzed esterification. The experimental conditions as molar ratio of methanol to oil M:O of 11:1 and catalyst concentration relative to oil of 0.92 wt.% were adapted in the esterification. Reaction temperature T from 75 to 120 °C and reaction time (t) of 108.79 to 167.39 min were tested.

The investigation is based on adding a certain volume of M/C mixture per dose at the beginning and when the temperature raises to the pre-set value of 120 °C. The appropriate reaction conditions involved using a 5 mL dose of M/C mixture with a reaction temperature interval of 108.9–120 °C, and with a reaction time of 167.39 min. At these proper conditions, an esterification conversion efficiency η as high as 99.35% have been achieved.

In the experiments performed between a temperature interval of 100 and 120 °C. As the methanol was supplied from the bottom and going through the JO to the upper part of reactor. So a part of methanol reacts instantaneously with JO at the bottom and through the JO, meanwhile, the remaining methanol that reaches the upper surface of reactor it was vaporized. The experimental conditions were selected in order to:

- Avoid the water content in samples. Using long esterification time at temperatures above of water boiling point.
- Exclude the reversibility of the esterification reaction (Eq. (1)).
- Prevent the hydrolysis of triglycerides to form FFAs (Eqs. (4)–(6)).
- And prevent the saponification on the following trans-esterification process.
- As the M/C mixture reacts instantaneously with JO, and to reduce the M/C consumption and enhance the esterification reaction different doses of M/C are supplied into the reactor.

As the FFA content in raw JO was 18.28%, so the triglycerides content in raw JO is 81.72%. And after esterification, an esterification conversion efficiency η of 97.56% and a yield (Y_F) of FAME of 56.7% was obtained with a dosing of M/C at 10 mL per dose for 10 doses a temperature interval of 100–120 °C. Therefore all FFA (18.28%) in raw JO were converted to ME and 38.32% (56.7–18.32 = 38.32) of triglycerides in raw JO were converted to FAME. So only 43.4% (81.72–38.32 = 43.4%) of the triglycerides will be going to convert in FAME in the following base-catalyzed transesterification stage.

3.1. Esterification

The esterification reaction is described in Eq. (1). Acid catalyst is usually used to enhance the reaction. The presence of free fatty acids FFAs higher than 2% leads to the saponification reaction in presence of an alkali catalyst during the transesterification reaction. The water produced during the esterification reacts with triglycerides to form FFA, mono-, and di-glycerides according to the following equations [18,42]:

$$\mathrm{Triglyceride} + \mathrm{water} = \mathrm{diglyceride} + \mathrm{FFA} \qquad (4)$$

$$\mathrm{Diglyceride} + \mathrm{water} = \mathrm{monoclyceride} + \mathrm{FFA} \qquad (5)$$

$$\mathrm{Monoglyceride} + \mathrm{water} = \mathrm{glycerol} + \mathrm{FFA} \qquad (6)$$

Therefore the acid-catalyzed esterification pre-treatment is necessary before transesterification process for jatropha oil. It is better to reduce the acid value to 2 mg KOH/g so as to give a higher yield in the transesterification reaction. In order to effectively reduce the FFA and moisture content, choice of proper process parameters of esterification reaction are important.

3.2. Loss of weight and volume

The reduction of weight and volume after esterification pre-treatment is shown in Fig. 2, which indicates losses of mass and volume of about 26% and 25%, respectively. This loss is due to the evaporation of bi-product H_2O formed according to reaction 1 and the residual reactant methanol. The release of H_2O promotes the reaction 1. Although different doses of M/C of 5, 10, 16.6 and 25 mL give different t_E, they result in about the same reaction extent regarding the reaction mass and volume. About the same reduction as t_E is greater than 100 min, revealing that the esterification is about completed.

3.3. Dosing effect on acid value

The excess methanol is required to drive the reaction in forward path of reversible esterification reaction 1. To investigate the effect of methanol dose on the reaction, the mixture of M/C was added dose by dose between temperature intervals. The doses tested were of 5 mL, 10 mL, 16.6 mL and 25 mL, which correspond to temperature intervals of 108.9–120 °C, 100–120 °C, 85–120 °C and 75–120 °C, respectively. After applying the UI until the temperature was raised to 120 °C, a fixed dose of M/C was added to the sample. Sequential UI was followed after each dose. In the course of UI, the efficacy depends on the local temperature and pressure effects, and the better emulsification characteristics due to cavitation events generated locally in the reactor. These effects are significant for the intensification of the synthesis of esterification.

The effect of sequential UI and dosing on the change in AV is illustrated in Fig. 3. It has been observed that the initial AV of jatropha oil JO of 36.5 mg KOH/g decreases to 0.413–0.236 mg KOH/g as the amount of dose reduces, i.e. when a lower amount of M/C dose was used. From the reaction stoichiometry 1, it indicates that 1 mol of methanol is required for the reaction of 1 mol FFA. Since this reaction is reversible, the excess amount of methanol is required to drive the reaction in the forward direction. Thus the final AV would be lower where a higher excess of methanol is available in the reaction mixture. A dose of 5 mL per dose for 20 doses between an interval of temperature of 108.9 and 120 °C proceeds with a high temperature and a long esterification time of 167.39 min which is sufficient to reduce the AV to 0.236 mg KOH/g and match with the requirement for carrying out the transesterification reaction. Therefore using the sequential UI at higher temperature interval followed by dosing a mixture of M/C enhances the esterification and decreases the AV.

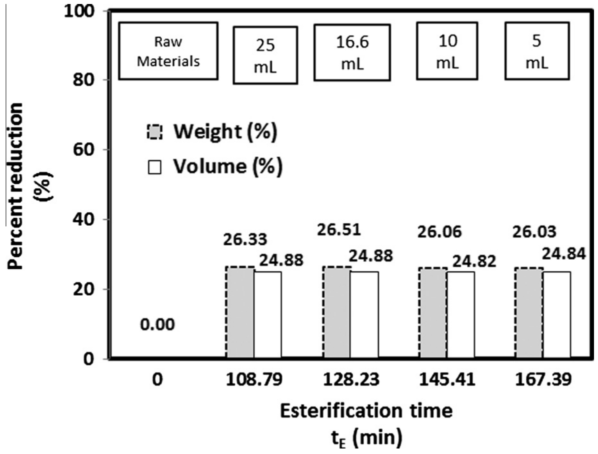

Fig. 2. Comparisons of weight (▨) and volume (☐) reduction (%) of crude jatropha-ester (JO-ester) after esterification by sequential ultrasonic irradiation (UI) with adding a fixed M/C dose (M = methanol, C = Catalyst). Doses of 5 mL (between a temperature intervals of 108.9 and 120 °C), 10 mL (between a temperature intervals of 100 and 120 °C), 16.6 mL (between a temperature intervals of 85 and 120 °C) and 25 mL (between a temperature intervals of 75 and 120 °C).

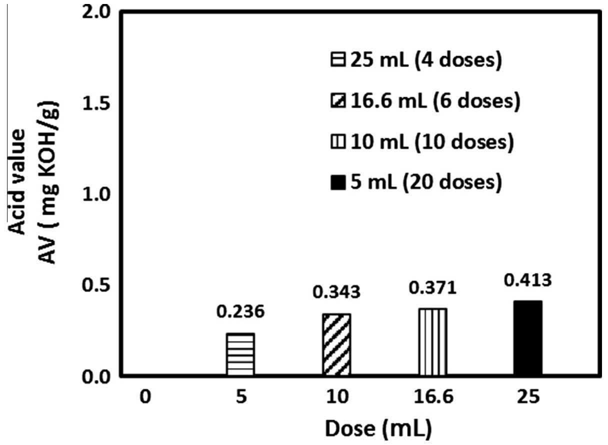

Fig. 3. Dosing effect on acid value (AV) after esterification by sequential UI and adding various fixed M/C doses, for samples with a settling time (t_S) of 10 min with salt-water washing.

3.4. Time variations of temperature at various doses

Fig. 4 demonstrates the time variations of temperature applying different doses. A shorter esterification time t_E of 108.79 min was done at a lower temperature interval of 75–120 °C with a larger

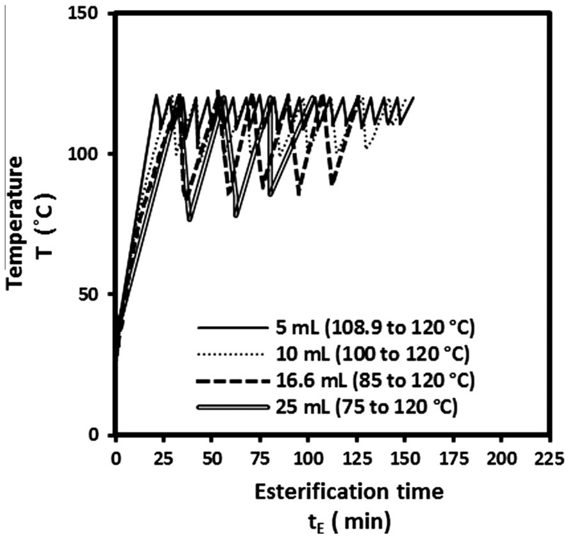

Fig. 4. Variations of temperature with esterification time t_E after esterification by sequential UI and adding various fixed M/C doses. — 5 mL (between a temperature intervals of 108.9 and 120 °C), ··· 10 mL (between a temperature intervals of 100 and 120 °C), ---- 16.6 mL (between a temperature intervals of 85 and 120 °C) and = 25 mL (between a temperature intervals of 75 and 120 °C).

Table 1
Properties JO-ester obtained by sequential ultrasonic irradiation (UI) and dosing of M/C of 5, 10, 16.6 and 25 mL per dose between a temperature intervals of 108.9 and 120 °C, 100 and 120, 85–120 °C and 75–120 °C.

Property	5 mL (20 doses) T = 108.9–120 °C t_E = 167.39[c]		10 mL (10 doses) T = 100–120 °C t_E = 145.41[c]		16.6 mL (6 doses) T = 85–120 °C t_E = 128.23[c]		25 mL (4 doses) T = 75–120 °C t_E = 108.79[c]	
	t_S = 10[d,e] (with washing)	t_S = 1440 (without washing)	t_S = 10[d,f] (with washing)	t_S = 1440 (without washing)	t_S = 10[d,g] (with washing)	t_S = 1440 (without washing)	t_S = 10[d,h] (with washing)	t_S = 1440 (without washing)
Water content, wt.%	0.300 (0.049)	0.023 (0.01)	0.291 (0.019)	0.045 (0.04)	0.308 (0.03)	0.0249 (0.0249)	0.299 (0.02)	0.015 (0.01)
Average *T*, °C	109.25 (0.15)	109.25 (0.15)	104.44 (0.61)	104.44 (0.61)	97.52	97.52	93.30 (0.565)	93.30 (0.565)
Volume V_L, mL	226[b]	226[b]	225.54[b]	225.54[b]	225.35[b]	225.35[b]	225.36[b]	225.36[b]
AV, mg KOH/g	0.236 (0.042)	0.596	0.343 (0.051)	0.892	0.371 (0.239)	0.747 (0.603)	0.413 (0.007)	0.598 (0.096)
IV, g I_2/100 g	124.77 (2.56)	123.81	122.44 (1.27)	129.11	123.76 (0.43)	124.83	122.84	123.68
kV at 40 °C, mm^2/s	9.89 (0.121)	9.84 (0.035)	10.27 (0.178)	10.76 (0.067)	10.91 (0.446)	11.19 (0.012)	11.61 (0.017)	12.160 (0.282)
Density (ρ_{LO}) at 15 °C, kg/m^3	901.73 (0.29)	901.95 (0.06)	902.50 (0.10)	903.08 (0.19)	902.56 (0.87)	903.93 (0.17)	903.87 (0.21)	904.9 (0.07)

[a] Numbers in parentheses are standard deviations (σ_{n-1}).
[b] Mixture of jatropha-oil/methanol/catalyst (J/M/C).
[c] t_E: Esterification time (min).
[d] t_S: Settling time (min).
[e] Temperature at t_S = 10 min is 71.1 °C.
[f] Temperature at t_S = 10 min is 70.3 °C.
[g] Temperature at t_S = 10 min is 70.2 °C.
[h] Temperature at t_S = 10 min is 71.4 °C.

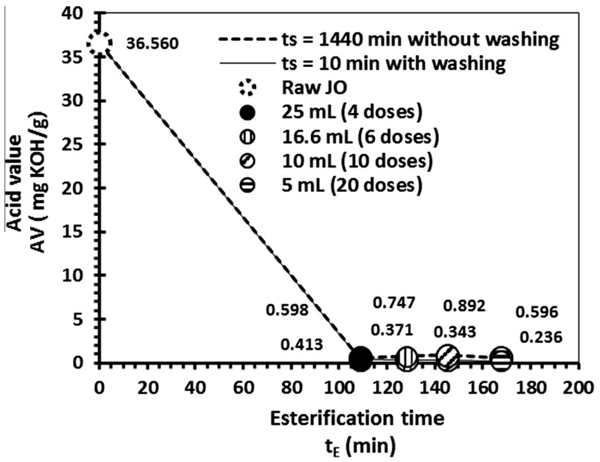

Fig. 5. Effects of t_E on AV after esterification by sequential UI and adding various fixed M/C doses between a fixed temperature interval. ○: Raw JO. Volumes of M/C per dose: ⊖ 5 mL (between a temperature intervals of 108.9 and 120 °C), ⊘ 10 mL (between a temperature intervals of 100 and 120 °C), ⦶ 16.6 mL (between a temperature intervals of 85 and 120 °C) and ● 25 mL (between a temperature intervals of 75 and 120 °C). Solid and dotted lines denote samples with a t_S of 10 min with salt-water washing and samples with a t_S of 1440 min without salt-water washing, respectively.

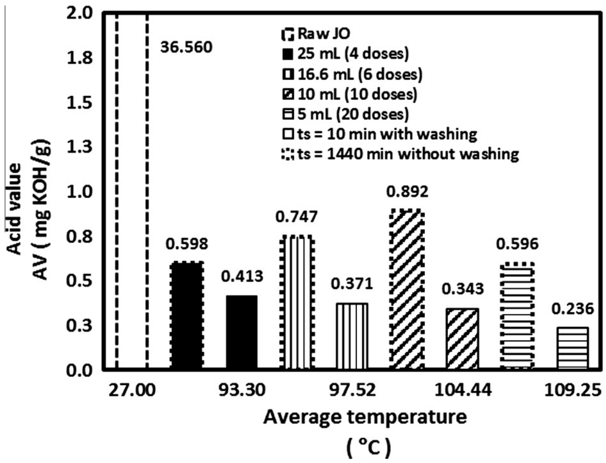

Fig. 6. Effects of average temperature (Tav) on AV after esterification by sequential UI and adding various fixed M/C doses between a fixed temperature interval. ⬚: Raw JO. Volumes of M/C per dose: ▤ 5 mL (between a temperature intervals of 108.9 and 120 °C), ▨10 mL (between a temperature intervals of 100 and 120 °C), ▥16.6 mL (between a temperature intervals of 85 and 120 °C) and ■ 25 mL (between a temperature intervals of 75 and 120 °C). Symbols with solid and dotted boundaires denote samples with a t_S of 10 min with salt-water washing and samples with a t_S of 1440 min without salt-water washing, respectively.

dose of 25 mL per dose for 4 doses. This obtains a slightly lower esterification conversion efficiency η of 98.87% as compared with that of the case with 5 mL per dose for 20 doses. The latter gives t_E of 167.39 min, temperature interval of 108.9–120 °C, and η of 99.35%. Meanwhile a dose of 10 mL per dose for 10 doses offers t_E of 145.41 min, temperature interval of 100–120 °C, and η of 99.06%, while a dose of 16.6 mL per dose for 6 doses results in t_E of 128.23 min, temperature interval of 85–120 °C, and η of 98.98%. Therefore when the amount of mixture M/C dose decreases, the esterification time and the lower level of temperature interval both increase, thus enhancing the esterification. The temperature interval higher than 100 °C further promotes the forward esterification of reversible reaction 1 by H_2O evaporating.

3.5. Properties of JO and JO-ester

The properties of jatropha oil JO are described in Section 2.1. Comparing with regulation standards of biodiesel [40,41], 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 36.5 mg KOH/g, kV of 31.30 mm^2/s, density of 918.5 kg/m^3 and water content m_w of 0.11 wt.% are higher than 0.5 mg KOH/g max, 3.5–5.0 mm^2/s, 860–900 kg/m^3 and 0.05 wt.% max, respectively. Therefore the esterification pretreatment is necessary. The properties such as AV, IV, ρ_{LO}, kV, and m_w of the JO-ester as a final product obtained using sequential UI and dosing of mixture M/C are shown in Table 1. Note that washing with salt water is used to remove the impurities from crude ester; however it causes the absorption of water into ester. Increasing the settling

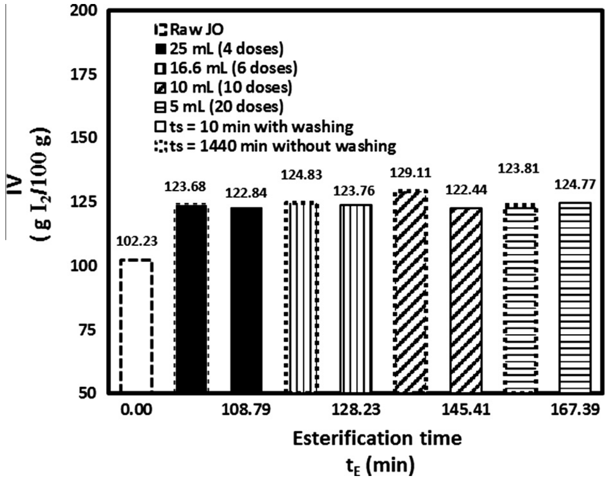

Fig. 7. Effects of t_E on IV after esterification by sequential UI and adding various fixed M/C doses between a fixed temperature interval. ⬚: Raw JO. ▤, ▨, ▥, ■, Symbols with solid and dotted boundaire as specified in Fig. 6.

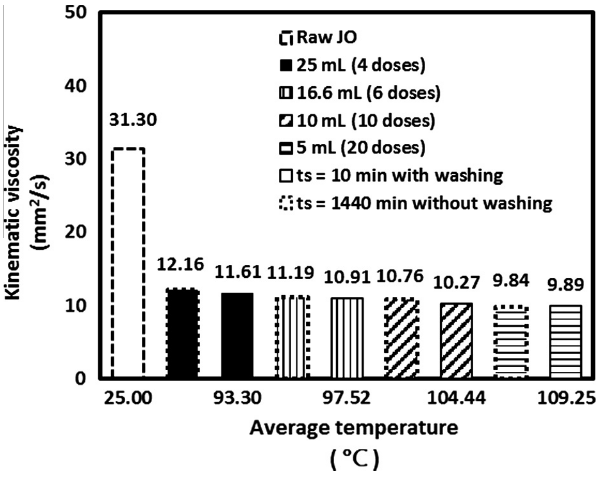

Fig. 8. Effects of Tav on kV after esterification by sequential UI and adding various fixed M/C doses between a fixed temperature interval. ⬚, ▤, ▨, ▥, ■, Symbols with solid and dotted boundaire as specified in Fig. 6.

time without washing not only prevents the absorption of water but also further reduces the water content. It was observed that the properties of JO-ester obtained, only the AV matches with the ASTM D6751 and CNS-15072 standards, however the IV, kV, ρ_{LO} and m_w slightly deviate from such standards, in spite of the FFA of 0.118% (=0.236/2% for dose of 5 mL) satisfying with the requirement for the transesterification process.

3.6. Effects of esterification time and temperature on acid value

The influence of t_E on the reduction of AV during esterification of JO is further illustrated in Fig. 5. It indicates more reduction with longer t_E for a small dosing at settling time t_S of 10 min. The AV slightly increases as t_S prolongs from 10 to 1440 min. This may be due to the degradation of oil to form acid or polymer fragments as it is exposed to air causing deterioration rancidity. However, the AVs at t_S = 1440 min are still low enough for the following transesterification stage.

Fig. 6 presents the effect of average temperature (Tav) on acid value. At t_S = 10 min, AV decreases with Tav as expected. Again, AV increases as t_S increases to 1440 min.

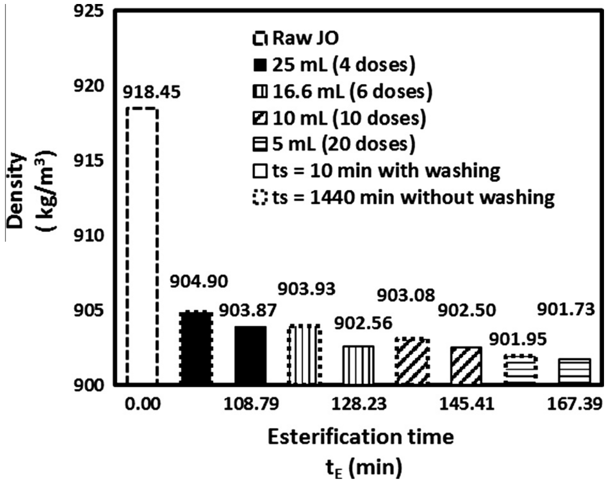

Fig. 9. Effects of t_E on density ρ_{LO} after esterification by sequential UI and adding various fixed M/C doses between a fixed temperature interval. Symbols: As specified in Fig. 6.

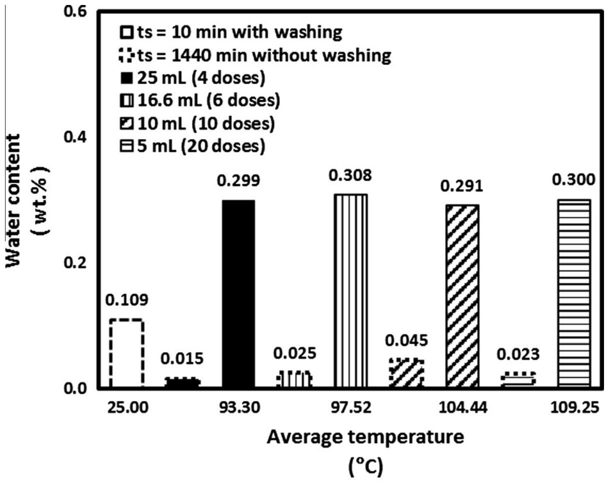

Fig. 10. Effects of Tav on water content m_w after esterification by sequential UI and adding various fixed M/C doses between a fixed temperature interval. Symbols: As specified in Fig. 6.

3.7. Effects of esterification time on iodine value

Fig. 7 demonstrates the effects of t_E on the iodine value IV. For t_E longer than 109 min, the IVs are close being within 122.44–129.11 g I_2/100 g. Although these IVs cannot satisfy the requirement for biodiesel standard of 120 g I_2/100 g as a max, however they are close. Therefore in the next transesterification stage such values could be easily reduced to satisfaction. The increase of IV after esterification may be due to the polymerization of oil by the cause of locally high temperature of cavitation of UI.

3.8. Effects of esterification time on kinematic viscosity

Fig. 8 shows a smaller dose offers a lower AV. This is because that it results in longer t_E and higher Tav. The viscosity of JO-ester decreases as temperature increases. The resulted KVs of 9.84–12.16 mm^2/s are much lower than 31.3 mm^2/s of raw JO.

Table 2
Compeer of properties JO-esters obtained by different treatment methods such as sequential ultrasonic irradiation (UI) and dosing of M/C at 10 mL per dose for 10 doses between a temperature interval of 100 and 120 °C; conventional UI at ambient T without T control; and classical mechanical stirring mixing.

Property	Jatropha oil[a]	Esterification methods		
		Sequential UI with dose effect of 10 mL per dose. T = 100 to 120 °C t_E = 145.41[d] t_S = 10[e]	Conventional UI at ambient T without T control. T = Ambient t_E = 30[d] t_S = 10[e]	Classical mechanical stirring mixing T = 25 °C t_E = 30[d] t_S = 10[e]
Water content, wt.%	0.110 (0.005)	0.291 (0.019)	0.33	–
Average T, °C	–	104.44 (0.61)	56.66 (2.24)	23.3
Volume V_L, mL	300[c]	225.54[c]	226[c]	265[c]
AV, mg KOH/g	36.56 (0.56)	0.343 (0.051)	6.13 (1.079)	21.03 (0.62)
IV, g I_2/100 g	102.23 (4.88)	122.44 (1.27)	111.22	112.58
kV at 40 °C, mm^2/s	31.30 (2.27)	10.27 (0.178)	20.49	21.78
Density (ρ_{LO}) at 15 °C, kg/m^3	918.45 (0.24)	902.50 (0.10)	916.1 (0.15)	913.4 (0.06)

[a] Raw jatropha oil.
[b] Numbers in parentheses are standard deviations (σ_{n-1}).
[c] Mixture of jatropha oil/methanol/catalyst (J/M/C).
[d] t_E: Esterification time (min).
[e] t_S: Settling time (min) with washing.

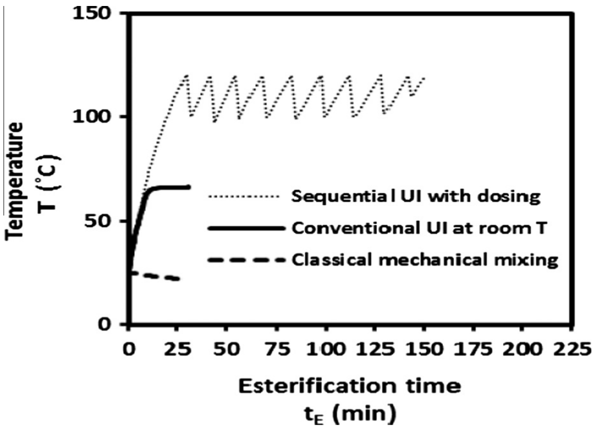

Fig. 11. Variations of temperature with t_E after esterification by sequential UI with addition of a fixed M/C dose of 10 mL per dose for 10 doses (———: T in 100 to 120 °C), conventional UI with addition of M/C of 100 mL in the beginning at ambient T without T control (—: with average T of 56.66 °C) and classical mechanical stirring mixing at ambient T (– – –: with average T of 23.3 °C).

3.9. Effect of esterification time on density

As t_E is longer than 109 min, the densities ρ_{LO} of esterification products are reduced from 918.45 kg/m^3 of raw JO to 901.73–904.90 kg/m^3 as depicted in Fig. 9. The raw JO may be decomposed to light esters via esterification, causing the reduction of its density. For t_E from 109 to 167 min, the values of ρ_{LO} are close.

3.10. Effects of esterification time on water content

Water is formed associated with the esterification as shown in Eq. (1). If it were not removed, it would not only hinder the reaction but also increase the water content m_w of product ester. However, product water can be more easily removed if the reaction temperature increases, enhancing the evaporation of water, as demonstrated in Fig. 10 for the case with salt-water washing. Thus, Tav of 93.3–109.3 °C reduces the m_w from 0.11 wt.% of raw JO to 0.015–0.045 wt.% of products. Note that values of m_w for the case with salt-water washing are about 0.291–0.308 wt.% higher than those of raw JO and case without salt-water washing. The increase of water content in the samples with washing probably is due to the water absorption from sodium chloride solution into the JO-ester.

3.11. Comparison of sequential with conventional UI processes

Comparison of properties of JO-ester obtained by conventional UI esterification process at ambient T without T control with those properties of JO-ester obtained by esterification with sequential UI and dosing of M/C at 10 mL per dose between temperature interval of 100 and 120 °C were illustrated in Table 2. The variations of temperature of these two processes are presented in Fig. 11. Although

Table 3
Results of acid-catalyzed esterification of jatropha oil performed by others authors.

Authors	Method	Initial FFA%	Final FFA%	η%[a]	FAME %	T °C	Time min
This work	Ultrasound[b]	18.28	0.45	97.56	56.7	120	145.41
This work	Ultrasound	18.28	3.07	83.2	20.38	56.6	30
Deng et al. [18]	Ultrasound	5.23	<0.61	88.4	–	60	60
Zou and Lei [14]	Ultrasound	10	0.2	98.0	–	30	90
Worapun et al. [24]	Ultrasound	12.5	<1.5	76.0	–	30	20
Chen et al. [10]	Classical stirring	13.6	<0.61	95.5	–	60	60
Choudhury et al. [30]	Classical stirring	10.78	1.43	86.7	20	65	60
Jain and Sharma [8]	Classical stirring	21.5	<1	98.0	21.2	65	180
Lu H. et al. [21]	Classical stirring	7	<0.5	92.8	–	70	120
Kumar-Tiwari et al. [6]	Classical stirring	14	<1	92.8	–	60	88
Berchmans and Hirata [7]	Classical stirring	15	<1	93.3	–	50	60
This work	Classical stirring	18.28	10.52	42.48	–	23.3	30

[a] Esterification conversion efficiency.
[b] Sequential ultrasonic irradiation with a dose of 10 mL per dose per 10 doses between temperature interval of 110 and 120 °C.

the conventional UI can also induce a temperature rise, it is significantly lower than sequential UI. Thus, the reaction extent of the former (with higher AV) is lower than the later (with lower AV). Moreover, the sequential UI also gives lower kV and density. Therefore, regarding the purpose of esterification, the sequential UI is better than the conventional UI. The comparison of sequential UI with conventional UI and classical mechanical stirring mixing is illustrated in Table 3.

4. Conclusions

The present study clearly demonstrated the new promising way for the esterification pre-treatment of raw jatropha oil (JO) with high acid value AV using sequential effect of ultrasonic irradiation UI with auto-induced temperature rise followed by adding a mixture of methanol/catalyst M/C by dose. The sequential process can be useful to reduce the AV from 36.5 to 0.24 mg KOH/g or free fatty acid FFA% from 18.28% to 0.12% which satisfy with the requirement for transesterification. The AV and water content m_w of ester products obtained match with ASTM and CNS specification for biodiesel. An esterification conversion efficiency η as high as 99.35% was obtained via sequential UI of 200 mL of JO with 5 mL of M/C per dose per 20 doses at temperature interval of 108.9–120 °C. The long esterification time with high temperature induced by UI greatly enhances the esterification obtaining a JO-ester with low water content. It could be concluded that long esterification time at high temperature by UI is more beneficial for esterification than the conventional UI.

Acknowledgments

The authors gratefully acknowledge the National Science Council of Taiwan for supporting this study. Mr. Cesar Augusto Andrade-Tacca also greatly thanks the Ministry of Education of Taiwan (TMOE) and the National Taiwan University (NTU) for the grants supporting his study at the Graduate Institute of Environmental Engineering (GIEE) of NTU.

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