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

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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 (tE), settling time (ts) 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 tE = 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 tE = 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 886 223638994.


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]. Bio-diesel, 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 Linnaeus (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:

R₁-COOH (FFA) + R₂-OH (Alcohol) = R₁-COO-R₂ + H₂O (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 σn-1 = 0.28 wt. %) encountered in this work
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 H2SO4 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 to 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 (tE), settling time (tS) 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 (σn−1 = 0.56) mg KOH/g, iodine value (IV) = 102.23 (σn−1 = 4.87) g I2/100 g, kinematic viscosity (KV) at 40 °C = 31.30 (σn−1 = 2.27) mm2/s and density (ρD) at 15 °C = 918.45 (σn−1 = 0.24) kg/m3. Its molecular weight (MW) is 871.5 g/mol [20]. Methyl alcohol of anhydrous assay with purity of 95.8% 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, Firststeck 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 (mC) = 0.92 wt. %. The total sample volume (Vt) 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(W)) at 90% (270 W) of its maximum power (300 W). The esterification times tE for UI (tEUI) were conducted at 5, 10, 15 and 30 min. Different settling times tS 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 (Firststeck Scientific, model-B403, Taipei, Taiwan).

After esterification, the sample was generally settled for proper tS 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 (tS) 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 tE for mechanical mixing (tEMM) 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 ρD 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 σn−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 a 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
The FFA content of oil can be calculated according to the following equation:

\[
\text{FFA} = \frac{\text{wt.\% FFA}}{\text{wt.\% [AV]}} \times 100
\]

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 spectrometry (GC–MS) according to EN 14103. The FFA composition of jatropha oil esters group of triglyceride at 2.3 ppm in the \(^1\)H NMR spectrum.

### 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 K\(\text{OH}\)/g, K\(\text{V}\) 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 K\(\text{V}\) 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 \(t_{\text{UE}}\), \(t_{\text{ME}}\) and \(t_{\text{HE}}\) 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-E1050 and UNVT-E1050, MNAT-E1050 and MNAT-E1050, and HNAT-E1050 and HNAT-E1050 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, \(\eta\), in terms of the percentage of AV reduction from the highest are in the order of UI (62.45 (E1050) and 56.73% (E1050)), mechanical mixing (28.25 (E1050) and 36.76% (E1050)) and hand shaking mixing (17.34 (E150) and 28.45% (E150)). 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
mechanical mixing. Although a prolong the convenience of practical operation, the adoption of

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

3.3. Effect of settling time $t_5$ on AV

The influence of $t_5$ 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 $t_5 = 0$ to 10 and 1440 min, the esterification conversion efficiency $\eta$ increases from 28.25 to 36.76 and 51.83%, respectively, showing a maximum difference of increase of $\eta$ of 23.58% (=51.83−28.25%). However, the corresponding acid values for UI at $t_5 = 0$, 10, 20, 30, 40 and 1440 min were 13.73, 13.82, 11.21, 10.27 and 7.45 mg KOH/g, much lowering than those of mechanical mixing. The $\eta$ values for UI were 62.45 to 79.62% and 79.62% at $t_5 = 0$ to 10 and 1440 min, respectively, with a maximum difference of improvement of $\eta$ of 22.89% (=79.62−56.73%). Therefore, the effect of $t_5$ on AV employing UI is as significant as that using mechanical mixing. Although a prolong $t_5$ of 1440 min can offer a maximum difference of increase of $\eta$ of 22.89% (=79.62−56.73%). However, for the convenience of practical operation, the adoption of $t_5$ 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 $5^\circ$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 $47.6^\circ$C using external heating with water bath of 65°C; symbol ◯ in Fig. 3.
(4) Case UCVT-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 $t_5$ of 10 min. The temperature variations during esterification are illustrated in Fig. 4.

The results indicate a decrease of AV (or increase of $\eta$) 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 $\eta = 42.48\%$.

However, Case UCVT-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.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Ultrasonic esterification time ($t_{UI}$)</th>
<th>Mechanical esterification time ($t_{ME}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 min</td>
<td>10 min</td>
</tr>
<tr>
<td>AV</td>
<td>mg KOH/g</td>
<td>29.99 (1.05)²</td>
<td>28.97 (0.20)²</td>
</tr>
<tr>
<td>IV</td>
<td>g l⁻¹/100 g</td>
<td>114.50</td>
<td>113.20</td>
</tr>
<tr>
<td>KV at 40 °C</td>
<td>mm²/s</td>
<td>23.53</td>
<td>23.68</td>
</tr>
<tr>
<td>Density at 15 °C</td>
<td>kg/m³</td>
<td>913.88 (0.30)³</td>
<td>914.25 (0.19)³</td>
</tr>
<tr>
<td>$\eta$</td>
<td>%</td>
<td>17.97</td>
<td>20.76</td>
</tr>
</tbody>
</table>

² UI with varied temperature in sample without temperature control, while externally cooled by water bath of 5°C. Cases at $t_{UI} = 5$, 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 $t_5 = 10$ min are symbolized as UCVT-E5S10, UCVT-E15S10 and UCVT-E30S10.
³ 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 $t_5 = 10$ min are expressed as MHFT-E5S10, MHFT-E10S10 and MHFT-E30S10.

Standard deviation ($\sigma_{AV}$).
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 \( \eta \) 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 \( \eta \) 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 temperature was conducted at \( t_E = 10 \) min, with \( t_S = 0 \) and 10 min are denoted as MNAT-E10S0 and MNAT-E10S10.

### Table 5

<table>
<thead>
<tr>
<th>Property Unit</th>
<th>Ultrasonic(^a) esterification time (( t_{UE} ))</th>
<th>Mechanical(^b) esterification time (( t_{ME} ))</th>
<th>Hand shaking(^c) esterification time (( t_{HE} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AV ( \text{mg KOH/g} )</td>
<td>13.73 (1.06) (^d)</td>
<td>15.82 (3.76) (^d)</td>
<td>23.12 (1.18) (^d)</td>
</tr>
<tr>
<td>( \eta ) ( % )</td>
<td>62.45</td>
<td>56.73</td>
<td>36.76</td>
</tr>
</tbody>
</table>

\(^a\) 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 \( s_n / \sqrt{n} \).

\(^e\) Esterification conversion efficiency \( \eta \).
temperature were performed with $t_5$ of 1440 min at various $t_E$ with results of $AV$ illustrated in Fig. 5. For very long $t_5$, say 1440 min, the effect of $t_5$ is insignificant as $t_5$ is equal or longer than 2 min, giving $AV$ lower than 17.11 mg KOH/g ($\eta$ higher than 53.20%). Note that the $AV$ at $t_5 = 30$ min decreases only to 15.97 mg KOH/g ($\eta = 56.32$%). It indicates that long $t_5$ 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 $t_E$ is insignificant as $t_E$ is equal or longer than 2 min, giving $AV$ lower than 17.11 mg KOH/g ($\eta$ 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 $t_5$ 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.

Fig. 3. Effects of $t_5$ on AV. $\square$: Raw JO, $\bullet$, $\circ$, $\diamond$: 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 $t_5 = 30$ min), MNAT-S10 (MNAT with average temperature of sample of 23.3 °C at $t_5 = 30$ 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 $t_5 = 30$ min), UNVT-S10 (UNVT with average temperature of sample of 56.7 °C at $t_5 = 30$ min). MNAT, UNVT: as specified in Figs. 2, S10: at $t_5 = 10$ min.

Fig. 4. Temperature ($T$) variations during esterification. $\bullet$, $\circ$, $\diamond$: 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 $t_5$ of 24 h. $\square$: Raw jatropha oil. $\circ$: MNAT-S1440; S1440: $t_5 = 1440$ 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 (η = 20.76%) higher than the latter of 23.12 mg KOH/g (η = 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 (η = 56.73%), however, is lower than that of the latter of 16.86 mg KOH/g (η = 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.

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 x 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.
Acknowledgments

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Nomenclature

**Abbreviation and symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AV</td>
<td>acid value</td>
</tr>
<tr>
<td>E, E1, E5, E10, E30</td>
<td>esterification or esterification time</td>
</tr>
<tr>
<td>FFAEs</td>
<td>fatty acids alkyl esters</td>
</tr>
<tr>
<td>FAMES</td>
<td>fatty acids methyl esters</td>
</tr>
<tr>
<td>FFA</td>
<td>free fatty acid</td>
</tr>
<tr>
<td>HNAT</td>
<td>hand shaking mixing without temperature control with initial temperature at ambient temperature</td>
</tr>
<tr>
<td>KV</td>
<td>kinematic viscosity at 40 °C</td>
</tr>
<tr>
<td>LO</td>
<td>density of liquid sample</td>
</tr>
<tr>
<td>NTU</td>
<td>ultrasonic irradiation</td>
</tr>
<tr>
<td>UI</td>
<td>ultrasonic irradiation</td>
</tr>
<tr>
<td>UNVT</td>
<td>Ultrasound-assisted process</td>
</tr>
<tr>
<td>W</td>
<td>total volume of liquid sample</td>
</tr>
<tr>
<td>σn-1</td>
<td>standard deviation</td>
</tr>
<tr>
<td>η</td>
<td>esterification conversion efficiency</td>
</tr>
<tr>
<td>ρo</td>
<td>density of liquid sample</td>
</tr>
</tbody>
</table>

Greek symbols:

- \( \eta \) esterification conversion efficiency
- \( \rho_o \) density of liquid sample
- \( \sigma_{n-1} \) standard deviation

**References**


