

Fuel qualities of alkyl esters have received varying evaluations in terms of the alcohol used. Saraf and Thomas [3] observed that higher or branched alcohols can produce biodiesel with better fuel properties. Tyson [4] however, holds a contrast view to this as he indicated that the products of methyl and ethyl esters are similar in heat content, except that ethyl esters are slightly less in viscosity compared to methyl esters [5].

The process of transesterification is catalyzed by alkalis, acids or enzymes. Alkali catalysts have proven to be more practical and industrially applied because of their short reaction times and non-corrosive nature compared to acid catalysts. They are also less expensive when compared with enzymes. Glycerol, a valuable by-product of alkali catalyzed reactions is also used in soaps and cosmetics industries [6].

Various methods such as conventional, non-catalytic supercritical, microwave and ultrasound-assisted are used in biodiesel production [7–10]. Among the methods, conventional stirring and ultrasonication are much preferred and studied with different feedstocks [11]. While conventional stirring is preferred in most cases because of its easy and simple nature of application, ultrasonication on the other hand can be a preference for the fact that it increases the interaction between the phases due to the collapse of cavitation bubbles and the ultrasonic jet. This causes impingement of one liquid to another which consequently enhances the reaction and also offers potentially shorter reaction times [11].

Both edible and non-edible oils are used for biodiesel production. But the majority currently used are edible [2,12]. Biodiesels from edible oils are presently affected by the issue of cost because of the competition that exists between food and fuel from edible oils; a major factor arousing interest for more non-edible low-cost alternative feedstocks.

In China, biodiesel is currently produced from oils including rape seed, soybean, castor oils, etc. Recent studies however, indicate that there are alternative non-edible oil-yielding crops which can be used as feedstocks [13,14]. A boost to the search for more of the non-edible oils is the emergence of *Silybum marianum* oil [15] which has gained a lot of prominence in medicinal and pharmaceutical studies [16,17] but scanty in terms of biodiesel production.

S. marianum, a wild annual plant of Compositae family is widely cultivated in China and naturally grows at mild climatic regions of different parts of Asia particularly, Iraq [15,18]. In China, some of the notable provinces into its cultivation include: Guangdong, Hubei, Shanxi and Qinghai. The medicinal and pharmaceutical aspects of the plant have been researched over the years [16,17]. The extract from the seeds for instance is used traditionally for treatment of hepatotoxicity and acute and chronic liver diseases [16,17]. Morazzoni and Bombardelli [19] indicated that the pharmacologically active component of the extract (silymarin) is made of isomeric mixture of flavonolignans, silychristin, silydianin, diastereoisomers silybin and isosilybin. Current studies reveal that the seeds of the plant contain a lot of oil [20,21]. While Ghavami and Ramin [20] reported the oil content of the seed to be more than 28%, Li et al. [21] even indicated it to be more than 45%. Also in silymarin industrial oil production, the oil is considered a by-product and not much utilized. For full development and utilization of *S. marianum* oil, this study was undertaken to investigate biodiesel production from crude *S. marianum* seed oil using conventional stirring (600 rpm) and ultrasonication (40 kHz) with methanol and ethanol, to study the kinetics model of transesterification of the oil, and to compare the biodiesel properties to international standards.

2. Experimental

2.1. Materials

The seeds of *S. marianum* oil were obtained from Zhongxing Pharmaceutical Co., Ltd. (Zhenjiang, Jiangsu, China). All chemicals used in the experiments including methanol, ethanol, KOH, petroleum ether (30–60 °C, 60–90 °C), n-hexane and tetradecane (internal standard

for GC) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and were all of analytical reagent (AR) grade.

2.2. Extraction of oil

S. marianum seeds were dried at 60 °C for 12 h in an oven to remove excess moisture prior to the extraction process. The dried seeds were then weighed and ground into particles of 0.5–10 mm. The oil was extracted using soxhlet extractor with petroleum ether (60–90 °C) as the solvent. The duration for each batch of extraction was 10 h. The volume of solvent per gram of seed was 10 mL. After extraction, the oil was obtained through rotary evaporator. The amount of the oil in the seeds was then calculated using Li et al. [21] recommend method. The fatty acid composition was subsequently determined and identified using GC–MS (as in Sections 2.4 and 2.5).

2.3. Transesterification of *S. marianum* biodiesel

30 g of the oil (extracted) with a varied molar ratio (4:1–12:1) of alcohol (methanol or ethanol) to oil and KOH in various amounts (0.25%, 0.5%, 1.0%, 1.5%, 2.0% w/w) with reference to the weight of the oil was refluxed together in a 250 mL three-neck reaction flask equipped with a condenser and magnetic stirrer (600 rpm) or an ultrasound processor (KQ-250B, Q/320583GSFY008-2006, 250W) of 40 kHz at different temperatures (30–80 °C) and time (5–70 min). After the completion of each reaction, alcohol was removed with rotary evaporator. Each mixture was then transferred to a separatory funnel and allowed to stand for phase separation. The upper layers comprised alkyl esters and the lower layer was made of slight glycerol. After the phase separation, the biodiesel were washed with water for three times before drying and analyzing.

2.4. Analyses of biodiesel yields

The analyses of the biodiesel samples were carried out by 7890A gas chromatograph (Agilent Technology Inc. USA), equipped with a flame-ionization detector (FID) and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). Helium was used as the carrier gas. The oven temperature ramp program was held at 160 °C for 1 min, increased to 210 °C at 20 °C/min for 2 min, then increased from 210 °C to 213 °C at 0.3 °C/min for 3 min, and finally increased from 213 °C to 250 °C at 30 °C/min for 1 min. The flow rate of hydrogen was 40 mL/min and that of air was 400 mL/min. The temperature of the injector and detector were 250 °C each with injection pressure of 100 kPa. The injection was performed in split mode with a split ratio of 50:1. Specific analysis of each sample was done by dissolving 1 mL of sample with 5 mL of petroleum ether (30–60 °C) in the presence of tetradecane (an internal standard) and 0.5 μL of the solution injected into GC. The yield of each sample was then determined from the content of esters using the following equation:

$$\text{Biodiesel yield} = \frac{w_{\text{tetradecane}} \times A_B \times f_{\text{tetradecane}}}{A_{\text{tetradecane}} \times w_s} \times 100\% \quad (2)$$

where $w_{\text{tetradecane}}$ is the weight of the internal standard, A_B is the peak area of alkyl esters, $f_{\text{tetradecane}}$ is the response factor, $A_{\text{tetradecane}}$ is the peak area of the internal standard, and w_s is the weight of the sample. All data in this study are presented as mean (values) of triplicate of experimental and GC determinations.

2.5. Identification of the ester content

The contents of esters were identified by GC–MS. This was done using Agilent HP-6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) with a HP-5MS 5% phenylmethylsiloxane capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm; Restek, Bellefonte,

PA). Helium was used as the carrier gas at the flow rate of 1.0 mL/min. Each sample (1 μ L) of methyl and ethyl esters was injected into the column at a split ratio of 50:1. The oven temperature ramp program was carried out using the same method as GC (Section 2.4). The identification of fatty acid alkyl esters was performed by comparing the obtained mass spectra with NIST05.LIB and NIST05s.LIB (National Institute of Standards and Technology) library data using AMDIS-Chromatogram (GC–MS system) software.

2.6. Kinetics model of transesterification of *S. marianum* oil

Using the stoichiometric relationship of the reactants and the products (Eq. (1)), the general equation of reaction rate is presented below [22]:

$$-\frac{dC_T}{dt} = kC_T^\alpha C_A^\beta \quad (3)$$

where the consumption of triglycerides (T) per unit time (t) is reaction rate constant (k), concentrations of triglycerides (C_T) and alcohol (A) after time interval (t). The reaction order of triglycerides is α , while that of alcohol is β . The concentration changes of reactants are consequently, described below:

$$C_T = C_{T_0}(1-X) \quad (4)$$

$$C_A = C_{T_0}(\theta_A - 3X) \quad (5)$$

$$\theta_A = \frac{C_{A_0}}{C_{T_0}} \quad (6)$$

where C_{T_0} and C_{A_0} are initial concentrations of triglycerides and alcohol respectively, θ is the ratio of C_{A_0} to C_{T_0} , and X is the conversion of triglycerides to esters. In this study, some assumptions for the determination of the reaction kinetics were made: (i) because of the low acid value of the oil (Table 1), saponification reaction was insignificant and the reactions were carried out at optimal reaction temperature with minimal yield losses, (ii) the reaction was the rate-limiting step (RLS), (iii) transesterification of the oils is assumed as a three-single-step reaction and (iv) the real reaction order did not change with the excess amount of methanol. With these assumptions, Eq. (3) could be simplified as follows:

$$\frac{dX}{dt} = kC_{T_0}^{\alpha+\beta-1}(1-X)^\alpha(\theta_A - 3X)^\beta. \quad (7)$$

Table 1
Physico-chemical properties of crude *Silybum marianum* oil.

Property	Method	Crude <i>Silybum marianum</i> oil
Fatty acid composition ^a (%)	AOAC (2005),	
(i) (C16:0) palmitic acid	963.22, 969.33	15.04
(ii) (C18:0) stearic acid		2.78
(iii) (C18:1) oleic acid		8.79
(iv) (C18:2) LINOLEIC acid		65.68
(v) (C20:0) arachidic acid		5.93
Density (kg/m ³) at 15 °C	ASTMD4052-96	921.4
Saponification no.		191.54
Kinematic viscosity at 40 °C, mm ² /s	ASTMD 445-06	37.5
Average molecular weight (g)		887.9
Water content (%) w/w	AOAC 984.20-90	0.089
Free fatty acid content (%) w/w	AOAC 940.28	0.68

^a Other fatty acids (palmitoleic, 10-nonadecenoic, myristic, nonadecanoic, heneicosanoic, and heptadecanoic acid) were present in amounts of <1%.

Definite integrals of Eq. (7) were calculated from a conversion of X = 0 to a conversion of X = X in the time span of t = 0 to t = t. Using Eq. (7), two cases were however, applied for pseudo-first order (Eq. (8)) and second order (Eq. (9)) for rate constant (k) determination [22,23].

$$\text{case1 : } (\alpha = 1, \beta = 0)$$

$$\ln \left[\frac{1}{1-X} \right] = kt \quad (8)$$

$$\text{case2 : } (\alpha = 2, \beta = 0)$$

$$\frac{X}{1-X} = kC_{T_0}t \quad (9)$$

3. Results and discussion

3.1. Extraction of oil

The *S. marianum* oil extracted was a yellowish liquid. The amount of the oil from the seeds was determined to be 46%. This value was comparable to Li et al. [21] findings. The physico-chemical and fatty acid composition of the oil is presented in Table 1. Given that the free fatty acid and water content of the oil were 0.68(%) w/w and 0.089 (%) w/w respectively (figures below 1.0%), alkaline transesterification (KOH) was chosen for the study. This is because high free fatty acid and water content in oils are known to produce large amounts of soap lowering the yields of esters and making the separation of ester and glycerol difficult [24]. The FFA and water content in this study correlated with Nakpong and Wootthikanokkhan [25] for crude roselle oil (FFA 0.67% w/w, water 0.087% w/w) which indicate saponification reaction to be less in the process [24]. The fatty acid composition of the oil is also an important key factor for biodiesel in diesel engines [26]. Saturated fatty acid esters are known to have higher cetane numbers and oxidation stability but poor cold flow properties [27]. The crude *S. marianum* oil contains high proportion of unsaturated fatty acids primarily, linoleic acid (65.68%) and a lower amount of saturated ones, typically palmitic (15.04%) and arachidic acid (5.93%) (Table 1).

3.2. Comparison and trend of transesterification reaction conditions on yields of conventional stirring (600 rpm) and ultrasonication (40 kHz)

3.2.1. Effect of alcohol to oil molar ratio

Transesterification reaction consists of a sequence of three consecutive reversible reactions where triglyceride is successively converted to diglyceride, monoglyceride, and to fatty acid alkyl esters (FAAE) and glycerin. The molar ratio of alcohol to *S. marianum* oil can be one of the important factors that can affect the conversion to esters. Stoichiometrically, 3 mol of alcohol is required for each mole of triglyceride, but practically, higher molar ratio is employed to drive the reaction towards completion for higher yields. The yields of alkyl esters of conventional stirring and ultrasonication with varying alcohol to oil molar ratio (temperature 60 °C, time 50 min-conventional stirring, 15 min-ultrasonication, catalyst amount 1%) are indicated in Fig. 1a. As shown in Fig. (1a), the biodiesel yields for the two methods with the two alcohols increased as the alcohol to oil molar ratio increased. The yields increased from 71.26% to 82.35% and 73.85% to 82.46% for conventional stirring and ultrasonication with methanol respectively, with the increase in molar ratio from 4:1 to 8:1. The maximum yield of methyl esters (82.35%-conventional and 82.46%-ultrasonication) were obtained at the molar ratio of 8:1. Similar trend was observed for ethanolysis of the two methods but with low yields. Specifically,

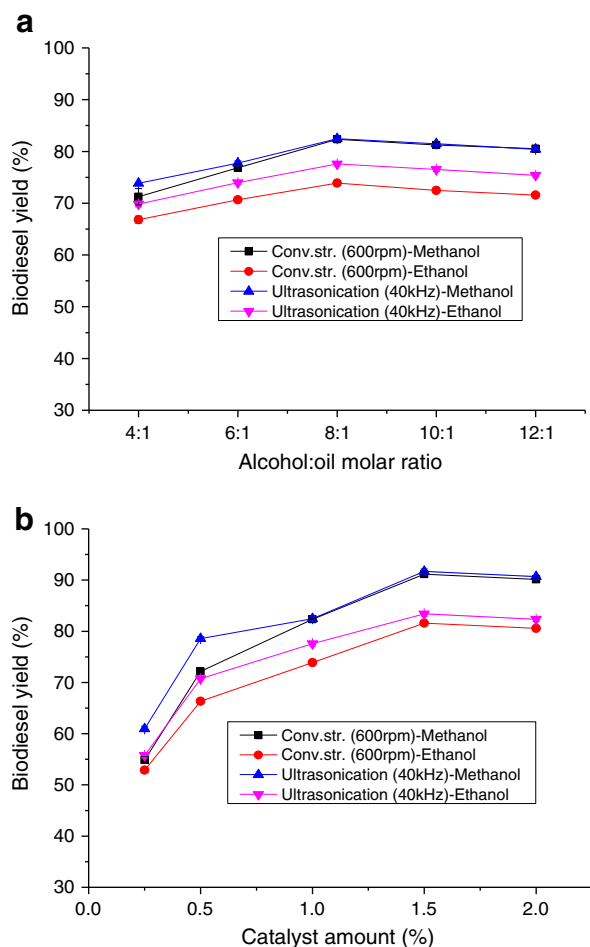


Fig. 1. a. Effect of alcohol to oil molar ratio on FFAE yields of conventional stirring (600 rpm) and ultrasonication (40 kHz). Conventional stirring (600 rpm): reaction temperature 60 °C, reaction time 50 min, catalyst amount 1%. Ultrasonication (40 kHz): reaction temperature 60 °C, reaction time 15 min, catalyst amount 1%. The standard error range is ± 0.02 –1.57. The figure shows the change in biodiesel yields with increase in alcohol to oil molar ratio. b. Effect of catalyst amount on FFAE yields of conventional stirring (600 rpm) and ultrasonication (40 kHz). Conventional stirring (600 rpm): reaction temperature 60 °C, reaction time 50 min, alcohol to oil molar ratio 8:1. Ultrasonication (40 kHz): reaction temperature 60 °C, reaction time 15 min, alcohol to oil molar ratio 8:1. The standard error range is ± 0.05 –0.65. This figure shows the trend of biodiesel yield with increase in catalyst amount from 0.25 to 2.0% w/w.

the yields of ethyl esters increased from 66.82% to 73.89% and 69.84% to 77.59% for conventional and ultrasonication respectively, when the molar ratio of ethanol to oil was increased from 4:1 to 8:1. In general, higher yields were obtained at 8:1 molar ratio. Beyond this, the excessively added alcohol had no positive effect on the production yields. Practically, reaction occurred at ratio of 4:1, but higher ratio was required to obtain higher yields. Though, ratios of 10:1 and 12:1 also provided relatively higher yields (close to 8:1), these molar ratios should be avoided for cost minimization purposes. Observations in this study agree with Meher et al. [28]. It could be deduced from the study that to increase the yield of *S. marianum* biodiesel, the excess amount of alcohol (above stoichiometrical requirement of 3:1) needed was 5:1 to increase the ester yields to maximum and beyond this limit (maximum yield), the excess alcohol slightly decreased the yields and this could be due to the dilution of the oil with the alcohol. Molar ratio of 8:1 was selected as the optimum.

3.2.2. Effect of catalyst amount

Fig. 1b indicates the influence of catalyst amount. Generally, when catalyst amount is less, maximum yield cannot be reached. However,

excessive catalyst amount can also result in saponification reaction. The influence of the catalyst amounts was studied at 50 min for conventional stirring, 15 min for ultrasonication, 8:1 alcohol to oil molar ratio and 60 °C of temperature. The catalyst amount was varied in the range of 0.25%–2.0%. These percentages were weight fractions of the oil used for the study. When the catalyst amount was increased from 0.25% to 1.5%, the yields also increased (for the two methods) with the two alcohols accordingly. However, further increase in the catalyst amount (beyond 1.5%) slightly lowered the yields. According to Meher et al. [28] and Encinar et al. [29], high concentrations of alkaline catalyst form soaps in the presence of high free fatty acids which results in emulsion formation between soaps and water molecules that leads to low yields. In this study, this phenomenon slightly occurred at 2.0% catalyst amount; probably due to the fact that the *S. marianum* seed oil used was crude with little FFA amount (0.68%). Ataya et al. [23] also observed an increase in triglyceride conversion with increase in NaOH concentration between 1.0 and 3.0% w/w, but beyond 3.0%, the yield decreased (using canola oil). The maximum yields in this study (i.e. 91.15%–conventional and 91.71%–ultrasonication) are slightly higher than those reported by Freedman et al. [31] for sunflower seed oil (i.e. 90%) after 60 min of reaction time using molar ratio of 6:1 and 0.5% of sodium methoxide as catalyst and yields (80%) of Ahmad et al. [15] using similar oil within 75 min at 60 °C of 5:1 methanol to oil ratio but lower than yields (99.4%) of Nakpong and Wootthikanokkhan [25] for roselle biodiesel after 60 min at 8:1 methanol to oil molar ratio, 1.5% catalyst amount and 60 °C temperature. For the ethanolysis, the maximum yields were 81.59% for conventional stirring and 83.40% for ultrasonication. The study indicated that the yields of esters isolated with ultrasonication were slightly higher than those with conventional stirring, probably due to better mixing using ultrasonication [11]. The catalyst amount of 1.5% was selected as the optimum.

3.2.3. Effect of reaction temperature

The influence of temperature on yields of the two methods with the two alcohols was studied at varying temperatures (30 to 80 °C) at 50 min for conventional stirring, 15 min for ultrasonication, 8:1 alcohol to oil molar ratio and 1.5% catalyst amount. As shown in Fig. 2a, the increase in temperature from 30 °C to 60 °C resulted in increase in yields of methyl esters to the optimum at 60 °C (91.15%–conventional stirring and 91.71%–ultrasonication). For ethyl esters, the optimum yields (84.53% and 85.64% for conventional and ultrasonication, respectively) were obtained at 80 °C, indicating relatively high temperature requirement for alcoholyses [3,4]. Ideally, a more rapid reaction could be obtained at high temperatures [30]. However, in this study, at the higher temperature/s (beyond 60 °C–methanolysis), methanol vaporized and formed bubbles, which might inhibit the reaction on the interface. These findings agree with the results of other studies [28,29,31]. It was noted that reaction occurred at room temperature (30 °C); but could not be completed even after 50 min. This phenomenon could be attributed to the high viscosity of the oil at low temperature, resulting in poor mixing between the oil and potassium hydroxide–alcohol phases [32]. The findings of this study however, differ from those of Stavarache et al. [33] who reported that conversion of vegetable oil to methyl esters was highest (i.e. 95% after 10 min at room temperature using ultrasonication (28 kHz) and 91% after 10 min using mechanical stirring (1800 rpm) for 1.0% (w/w) KOH. But in line with the study (for ethanolysis) is the one by Lifka and Ondruschka [34] who reported the effect of ultrasonication versus mechanical stirring on alkaline transesterification of rapeseed oil at a temperature of 45 °C. A conversion of 80–85% was obtained for both ultrasonication and mechanical stirring after 30 min. The results of methanolysis agree with Siatis et al. [35]. The optimum reaction temperature of 60 °C for methanolysis and 80 °C for ethanolysis was selected in combination with other conditions to determine the optimum time.

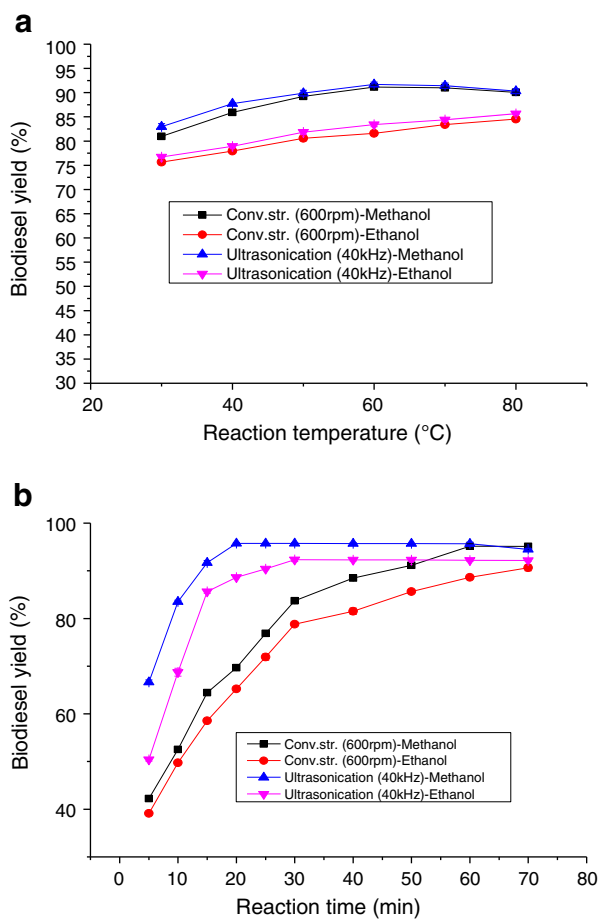


Fig. 2. a. Effect of reaction temperature on FFAE yields of conventional stirring (600 rpm) and ultrasonication (40 kHz). Conventional stirring (600 rpm): catalyst amount 1.5%, reaction time 50 min, alcohol to oil molar ratio 8:1. Ultrasonication (40 kHz): catalyst amount 1.5%, reaction time 15 min, alcohol to oil molar ratio 8:1. The standard error range is ± 0.04 –0.60. The figure indicates that reaction temperature has significant influence on biodiesel yield using both conventional stirring and ultrasonication. b. Effect of reaction time on FFAE yields of conventional stirring (600 rpm) and ultrasonication (40 kHz). Conventional stirring (600 rpm): catalyst amount 1.5%, reaction temperature 60 °C, alcohol to oil molar ratio 8:1. Ultrasonication (40 kHz): catalyst amount 1.5%, reaction temperature 80 °C, alcohol to oil molar ratio 8:1. The standard error range is ± 0.03 –0.81. The figure indicates the reaction time as a function of biodiesel yield using both conventional stirring and ultrasonication with methanol and ethanol for each.

3.2.4. Effect of reaction time

The dependence of biodiesel yield on the reaction time of the two methods with the alcohols was investigated. The reaction time was varied in the range of 5–70 min. Fig. 2b reveals that the transesterification reaction was much dependent on the reaction time. At the beginning (<10 min), the reaction was slow for methanolysis of conventional stirring due to mixing and the dispersion of methanol onto the oil. For ultrasonication, within 20–30 min, the maximum yields (95.75%-methanol and 92.32%-ethanol) were achieved. The excess reaction time (after optimum) resulted in little reduction in the product yields due to backward reaction, resulting in slight loss of esters [36]. The optimum reaction time was 60 and 70 min for conventional stirring with methanol and ethanol respectively, and 20 and 30 min for ultrasonication with methanol and ethanol respectively.

Comparing the results of Figs. 1a–2b, it can be observed that the general yields of ethyl esters were lower than the corresponding yields of methyl esters using the two methods. This could possibly be due to the increase in miscibility between ethanol, esters and glycerine which led to difficulty in separation and purification of the ethyl esters from the mixture [34]. The relatively high yields of methyl esters on

the other hand could possibly be due to the fact that methanol is immiscible in hydrocarbons and easily to be separated in the presence of less amount of water with low temperature [37]. On the basis of this, methanol is seen to be more suitable for this study since it sped up the reaction with substantial increase in yields [37]. The high yields of ultrasonication with reduced time as compared to conventional stirring could be assigned to the fact that ultrasonication increased the interaction between the phases due to the collapse of cavitation bubbles and the ultrasonic jet which consequently enhanced the reaction [11]. (Sample chromatograms of the optimum reaction conditions of the maximum methyl and ethyl ester yields are shown in Fig. 3a and b respectively.)

3.3. Kinetics model of transesterification of *S. marianum* oil

Kinetics model of transesterification of *S. marianum* oil was studied using the theoretical equations developed (Eqs. (8) and (9)). The equations were applied on yields of the effect of reaction time with the optimum combination of the other parameters. Table 2 shows the reaction rate constants (k) at 60 °C for methanolysis and 80 °C for

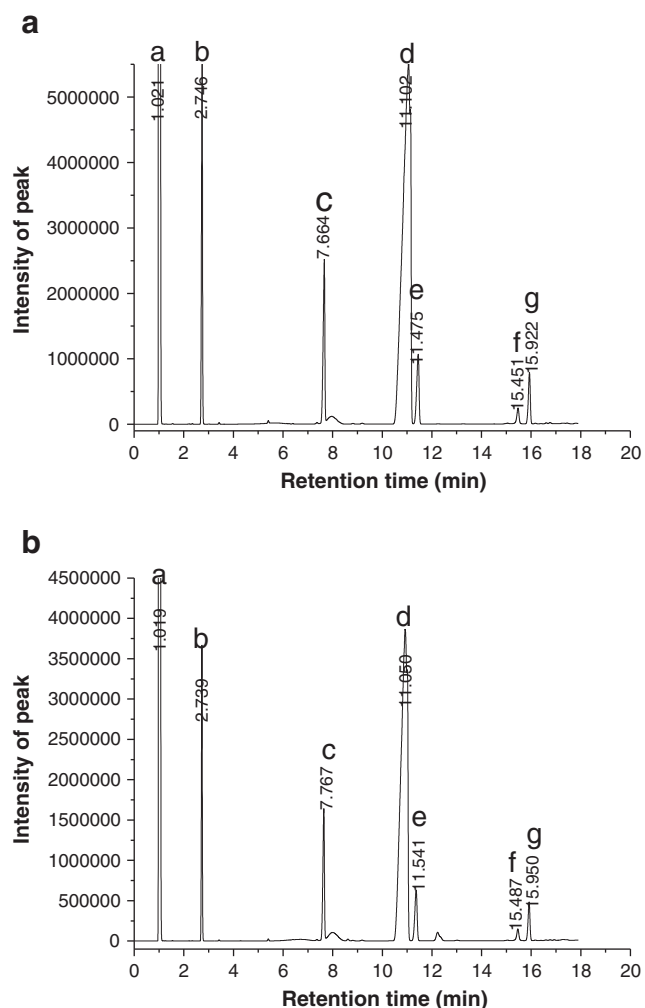


Fig. 3. a. Chromatogram of *Silybum marianum* methyl esters: (a) petroleum ether (solvent); (b) tetradecane (used as internal standard); (c) methyl palmitate; (d) methyl linoleate; (e) methyl oleate; (f) methyl stearate and (g) methyl archidoate. This indicates the fatty acid methyl esters of *Silybum marianum* biodiesel evolved at the optimum reaction conditions. b. Chromatogram of *Silybum marianum* ethyl esters: (a) petroleum ether (solvent); (b) tetradecane (used as internal standard); (c) ethyl palmitate; (d) ethyl linoleate; (e) ethyl oleate; (f) ethyl stearate and (g) ethyl archidoate. The figure shows the fatty acid ethyl esters of *Silybum marianum* biodiesel evolved at the optimum reaction conditions.

Table 2
Reaction rate constants (k) of conventional stirring (600 rpm) and ultrasonication (40 kHz).

Method	Reaction rate constant ($k \text{ s}^{-1}$)	
	Methanol	Ethanol
Mechanical stirring (600 rpm)	5.2×10^{-3}	2.2×10^{-3}
Ultrasonication (40 kHz)	2.3×10^{-2}	7.0×10^{-3}

Conventional stirring (600 rpm): catalyst amount 1.5%, reaction temperature 60 °C, alcohol to oil molar ratio 8:1, reaction time 5–70 min. Ultrasonication (40 kHz): catalyst amount 1.5%, reaction temperature 80 °C, alcohol to oil molar ratio 8:1, reaction time 5–70 min.

ethanolysis. For first order reaction, the plot of $\ln \left[\frac{1}{1-X} \right] = kt$ (Eq. (8)) (where X is the conversion of triglycerides at time t) as a function of time is linear with the slope equal to the reaction rate constant (k) [23]. For the second order reaction, plot of $\frac{X}{1-X} = kC_{T0}t$ (Eq. (9)) as a function of time is a straight line [32]. Imputation of data in Fig. 2b to the above two models indicated a slightly better fit (for a straight line) for first order reaction than for second order reaction. R^2 values for the first order reaction ranged between 0.9829 and 0.9271 (Fig. 4). For the second order reaction, R^2 value was highest (0.9844) in ultrasonication with ethanol and minimum (0.8857) in conventional stirring using methanol (Fig. 5). On the basis of the findings, the reaction in this study can be said to be rather of pseudo-first order than true first order.

The reaction rate constants (k) for the first order reaction (shown in Table 2) values of ultrasonication with methanol ($2.3 \times 10^{-2} \text{ s}^{-1}$) and ethanol ($7.0 \times 10^{-3} \text{ s}^{-1}$) were $1.95 \times 10^{-2} \text{ s}^{-1}$ and $6.0 \times 10^{-3} \text{ s}^{-1}$ times, respectively higher than those reported in literature by Georgogianni et al. [10] using NaOH at 2% ultrasonication (24 kHz) but lower than the values of Dang et al. [38] conventional transesterification of soybean and palm oils. The differences could possibly be due to the type of oil, catalyst used and the reaction conditions. The slightly low values of k (methanol) in this study compared to other previous studies [32,38] might also be due to the high content of unsaturated fatty acids, linoleic (65.68%) in *S. marianum* oil since soybean and palm oils [32,38] have higher saturated fatty acids. Furthermore, fatty acids with high unsaturated bonds are more prone to thermo-chemical damages than

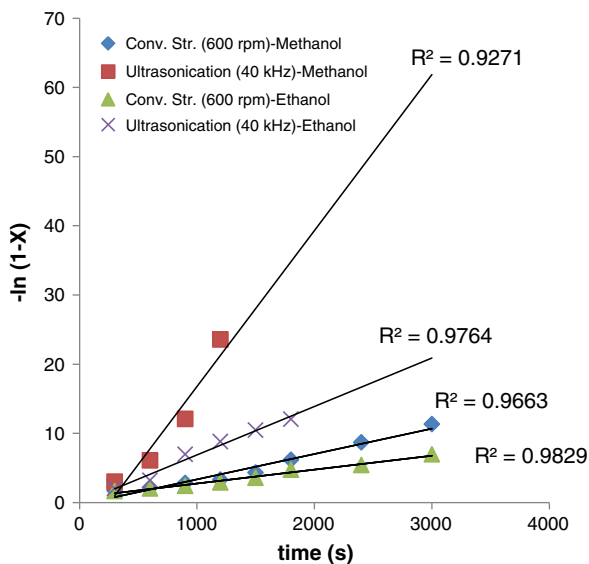


Fig. 4. $-\ln(1-X)$ versus time of conventional stirring (600 rpm) and ultrasonication (40 kHz) using methanol and ethanol (first order). The figure indicates model fit (straight line) for first order reaction for transesterification of *Silybum marianum* oil using ultrasonication (methanol and ethanol) and conventional stirring (methanol and ethanol) with R^2 values in which the reaction rate constants (k) which were the slopes were obtained.

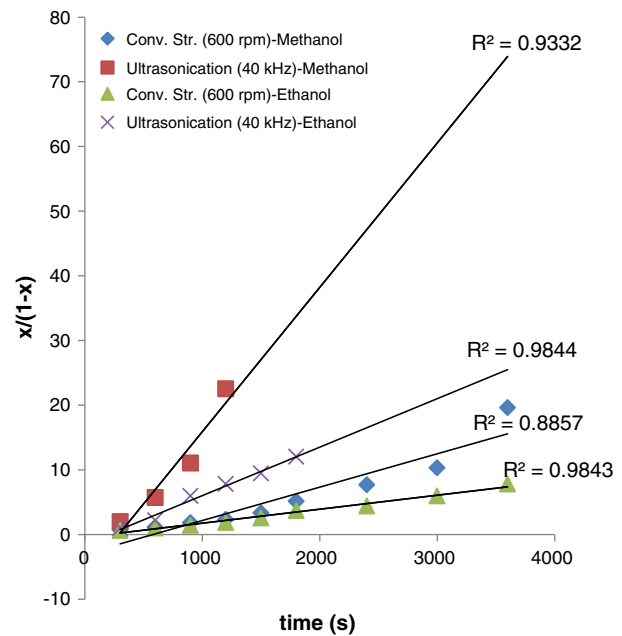


Fig. 5. $X/(1-X)$ versus time of conventional stirring (600 rpm) and ultrasonication (40 kHz) using methanol and ethanol (second order). This figure exhibits the second order reaction, plot of $\frac{X}{1-X} = kC_{T0}t$ as a function of time indicating R^2 values of ultrasonication (methanol and ethanol) and conventional stirring (methanol and ethanol).

saturated fatty acids. That is, because of the high unsaturated fatty acids in *S. marianum* oil, it will be less chemically and thermally stable. Hence, transesterification reaction of *S. marianum* oil would require relatively less rate of reaction to proceed as compared to those of soybean and palm oil. The variations in k in this study with respect to the method and alcohol indicate that the reaction rates (k) were influenced by the method of stirring, the reaction time, temperature and the type of alcohol. The rate constants of conventional stirring in the study were slightly lower than those of the ultrasonication (Table 2).

3.4. Comparison of fuel properties of methanol and ethanol to PRC, ASTM and European Union Standards

For any proposed biodiesel fuel to be acceptable for use in a diesel engine, the essential quality parameters must undergo testing with standard methods for the performance and emission characteristics of diesel engines. By this *S. marianum* biodiesel produce at the optimum reaction conditions using methanol and ethanol were tested for their quality standards and the properties compared with those of PRC-GB/T 20828 (2007), European Union-EN 14214 (2008) and American ASTM D 6751 (07b) standards (Table 3). The properties including cetane numbers, kinematic viscosities, flash points, acid values, copper strip corruptions and water content among others, for the methyl and ethyl esters were comparable to the international standards. Clearly, the alkali-catalyzed transesterification reduced the viscosity of the crude *S. marianum* oil from $37.5 \text{ mm}^2/\text{s}$ to $4.46 \text{ mm}^2/\text{s}$ (methanolysis) and $4.73 \text{ mm}^2/\text{s}$ (ethanolysis), and these values were closer to that of diesel ($3.068 \text{ mm}^2/\text{s}$). The pour point, cloud point and cold filter plugging point of biodiesel reflect its cold weather performance [1]. The test results in Table 3 indicate that the methyl and ethyl esters of *S. marianum* oil can be used as fuels in relatively cold-weather conditions without much problem. The flash points of the biodiesels ($153 \text{ }^\circ\text{C}$ -methanol and $154 \text{ }^\circ\text{C}$ -ethanol) were however, higher than that of diesel ($67.5 \text{ }^\circ\text{C}$). By blending the biodiesels with small amount of fossil diesel, the flash points can be improved (closer to diesel) [2]. The tests also showed that no traces of free glycerol were detected in the biodiesels. However, low contents of total glycerol ($\leq 0.11 \text{ w/w}$ -methanol and $\leq 0.13 \text{ w/w}$ -

Table 3
Comparison of methyl and ethyl esters of *Silybum marianum* oil to international standards.

Fuel property	Method	<i>Silybum marianum</i> biodiesel		China 20828-07	ASTM D6751	EN 14214
		Methanol	Ethanol			
Cetane number	ASTM D6890	51	52	≥49	≥47	≥51
Kinematic viscosity (mm ² /s; 40 °C)	ASTM D445	4.46	4.73	–	1.9–6.0	3.5–5.0
Oxidative stability 110 °C (h)	EN 14112	2.1	2.1	–	≥3	≥6
Cloud point (°C)	GB/T510	–1	–2	–	–	–
Pour point (°C)	GB/T3535	–1	–3	–	–	–
Cold filter plugging point (°C)	GB/T 2540	–2	–3	–	–	–
Flash point (°C)	ASTM D93	153	154	≥130	≥93	≥120
Sulfur content (% w/w)	ASTM D4294	0.003	0.003	≤0.05	≤0.05	–
Ash content (% w/w)	GB/T508	0.007	0.009	≤0.05	≤0.02	≤0.02
Acid value (KOH mg/g)	ASTM D664-01	0.44	0.45	≤0.8	≤0.5	≤0.5
Water content (mg/kg)	ASTM D6304	451	454	≤500	–	≤500
Density (20 °C)	SH/T0248	863	868	820–900	–	860–900
Free glycerol (% w/w)	EN 14105	0	0	–	–	≤0.020
Total glycerol (% w/w)	EN 14105	≤0.11	≤0.13	≤0.024	–	≤0.25
Iodine value g/100	EN 14111	132	133	–	≤120	≤120
Group II metals (Ca + Mg) ppm	ASTM D5185-02	None	None	≤5	–	–
Group I metals (Na + K) ppm	ASTM D5185-02	2.0	2.1	≤5	–	–
Alcohol content % w/w	EN 14110	0.01	0.02	–	–	≤0.2
FAAE content % w/w	–	95.75	92.32	–	–	≥96.5
Triglyceride content % w/w	EN 14105	0	0	–	–	≤0.2
Diglyceride content % w/w	EN 14105	0.017	0.019	–	–	≤0.2
Monoglyceride content % w/w	EN 14105	0.554	0.672	–	–	≤0.8
Sulfated ash content % w/w	ASTM D 874-00	0.006	0.006	–	≤0.020	–
Copper strip corrosion (50 °C; 3 h)	ASTMD 130-94	1a	1a	–	≤No. 3a	≤No. 1a

ethanol) were detected in the biodiesels. The properties of *S. marianum* biodiesel, along with the relatively high content of the esters especially, methyl esters and 0% free glycerols and triglycerides, indicated the completeness of the alkali-catalyzed transesterification of the crude oil at the optimum conditions. With the exception of the oxidative stabilities and iodine values which were out of range but can be improved by using antioxidants and other commercial additives, the properties of methyl and ethyl esters were comparable to international standards.

4. Conclusion

In this study, conventional stirring and ultrasonication transesterification using *S. marianum* oil with methanol and ethanol in the presence of KOH was investigated. Ultrasonication in most instances resulted in similar ester yields as conventional stirring. But slightly higher yields with reduced time were recorded for ultrasonication. Given similar conditions, ultrasonication proved to be substantially more efficient in the triglycerides' conversion than conventional stirring. The optimum conditions for transesterification with ultrasonication (methanol) was methanol to oil molar ratio of 8:1, catalyst amount of 1.5% w/w, reaction temperature of 60 °C, and 20 min of reaction time. For ethanol, the same conditions apply, except increase in time and temperature to 30 min and 80 °C respectively. The maximum yields with these conditions were 95.75% for methanol and 92.32% for ethanol. The reaction rate constants of ultrasonication were also slightly higher than conventional stirring. Ultrasonication with methanol in this study proved more suitable for producing biodiesel from *S. marianum* oil. With the exception of the oxidative stability (2.1 h) and iodine values (132-methyl and 133-ethyl esters), which can easily be improved using commercial additives, the remaining properties including cetane number, flash point and the three key cold flow properties of methyl and ethyl esters were similar and also comparable to the Chinese, ASTM and European Union standards. Considering the encouraging yields and the fuel properties as comparable to international standards, complement with the abundance of *S. marianum* oil at cultivation and silymarin industrial production as by-product, the oil could be recommended as a new non-edible feedstock for biodiesel in China and other Asian countries in which it is grown particularly, Iraq.

Conflict of interest

The authors declare that there are no conflicts of interest.

Acknowledgment

This work was supported financially by the Graduate Innovative Projects in Jiangsu Province (CXLX12_0668).

References

- [1] I.M. Atadashi, M.K. Aroua, A.A. Aziz, Biodiesel separation and purification: a review, *Renewable Energy* 36 (2011) 437–443.
- [2] A.S. Ramadhas, C. Muraleedharan, S. Jayaraj, Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil, *Renewable Energy* 30 (2005) 1789–1800.
- [3] S. Saraf, B. Thomas, Influence of feedstock and process chemistry on biodiesel quality, *Process Safety and Environment Protection* 85 (2007) 360–364.
- [4] K.S. Tyson, Biodiesel Handling and Use Guidelines, National Renewable Energy Laboratory, NREL/TP-580-30004, Golden, September 2001.
- [5] G. Vicente, M. Martinez, J. Aracil, Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield, *Bioresource Technology* 98 (2007) 1724–1733.
- [6] E.-E. Oprescu, E. Stepan, R.E. Dragomir, A. Radu, P. Rosca, Synthesis and testing of glycerol ketals as components for diesel fuel, *Fuel Processing Technology* 110 (2013) 214–217.
- [7] L.S.G. Teixeira, J.C.R. Assis, D.R. Mendonça, I.T.V. Santos, P.R.B. Guimarães, L.A.M. Pontes, J.S.R. Teixeira, Comparison between conventional and ultrasonic preparation of beef tallow biodiesel, *Fuel Processing Technology* 90 (2009) 1164–1166.
- [8] S. Hawash, N. Kamal, F. Zaher, O. Kenawi, G.E. Diwani, Biodiesel fuel from jatropha oil via non-catalytic supercritical methanol transesterification, *Fuel* 88 (2009) 579–582.
- [9] N. Azcan, A. Danisman, Microwave assisted transesterification of rapeseed oil, *Fuel* 87 (2008) 1781–1788.
- [10] K.G. Georgogianni, M.G. Kontominas, P.J. Pomonis, D. Avlonitis, V. Gergis, Conventional and in situ transesterification of sunflower seed oil for the production of biodiesel, *Fuel Processing Technology* 89 (2008) 503–509.
- [11] J.M. Marchetti, V.U. Miguel, A.F. Errazu, Techno-economic study of different alternatives for biodiesel production, *Fuel Processing Technology* 89 (2008) 740–748.
- [12] L.C. Meher, D. Vidya Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, *Renewable and Sustainable Energy Reviews* 10 (2006) 248–268.
- [13] C.-Y. Yang, Z. Fang, B. Li, Y.-F. Long, Review and prospects of jatropha biodiesel industry in China, *Renewable and Sustainable Energy Reviews* 16 (2012) 2178–2190.
- [14] Z.-Y. Yao, J.-H. Qi, L.-M. Yin, Biodiesel production from *Xanthoceras sorbifolia* in China: opportunities and challenges, *Renewable and Sustainable Energy Reviews* 24 (2013) 57–65.

- [15] M. Ahmad, M. Zafar, S. Sultana, A. Azam, M.A. Khan, The optimization of biodiesel production from a novel source of wild non-edible oil yielding plant *Silybum marianum*, International Journal of Green Energy 11 (2014) 589–594.
- [16] J.-W. Wu, L.-C. Lin, T.-H. Tsai, Drug–drug interactions of silymarin on the perspective of pharmacokinetics, Journal of Ethnopharmacology 121 (2009) 185–193.
- [17] J. Doehmer, G.P. McGregor, K. Appel, Assessment of a dry extract from milk thistle (*Silybum marianum*) for interference with human liver cytochrome-P450 activities, Toxicology in Vitro (2011) 21–27.
- [18] A.B. Fadhil, K.M. Ahmed, M.M. Dheyab, *Silybum marianum* L. seed oil: a novel feedstock for biodiesel production, Arabian Journal of Chemistry (2012).
- [19] P. Morazzoni, E. Bombardelli, *Silybum marianum* (*Carduus marianus*), Fitoterapia 66 (1995) 3–42.
- [20] N. Ghavami, A. Ramin, Grain yield and active substances of milk thistle as affected by soil salinity, Communications in Soil Science and Plant Analysis 39 (2008) 2608–2618.
- [21] F. Li, L. Yang, T. Zhao, J. Zhao, Y. Zou, X. Wu, Optimization of enzymatic pretreatment for n-hexane extraction of oil from *Silybum marianum* seeds using response surface methodology, Food and Bioproducts Processing 90 (2012) 87–94.
- [22] P. Patil, V.G. Gude, S. Pinappu, S. Deng, Transesterification kinetics of *Camelina sativa* oil on metal oxide catalysts under conventional and microwave heating conditions, Chemical Engineering Journal 168 (2011) 1296–1300.
- [23] F. Ataya, M.A. Dube, M. Ternan, Single-phase and two-phase base-catalyzed transesterification of canola oil to fatty acid methyl esters at ambient conditions, Industrial and Engineering Chemistry Research 45 (2006) 5411–5417.
- [24] A. Demirbaş, Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: a survey, Energy Conversion and Management 44 (2003) 2093–2109.
- [25] P. Nakpong, S. Wootthikanokkhan, Roselle (*Hibiscus sabdariffa* L.) oil as an alternative feedstock for biodiesel production in Thailand, 89 (2010) 1806–1811.
- [26] M.P. Dorado, E. Ballesteros, F.J. López, M. Mittelbach, Optimization of alkali-catalyzed transesterification of *Brassica carinata* oil for biodiesel production, Energy & Fuels 18 (2004) 77–83.
- [27] J.-Y. Park, D.-K. Kim, J.-P. Lee, S.-C. Park, Y.-J. Kim, J.-S. Lee, Blending effects of biodiesels on oxidation stability and low temperature flow properties, Bioresource Technology 99 (2008) 1196–1203.
- [28] L.C. Meher, V.S.S. Dharmagadda, S.N. Naik, Optimization of alkali-catalyzed transesterification of *Pongamia pinnata* oil for production of biodiesel, Bioresource Technology 97 (2006) 1392–1397.
- [29] J.M. Encinar, J.F. González, E. Sabio, M.J. Ramiro, Preparation and properties of biodiesel from *Cynara cardunculus* L. oil, Industrial and Engineering Chemistry Research 38 (1999) 2927–2931.
- [30] Z. Wen, X. Yu, S.-T. Tu, J. Yan, E. Dahlquist, Biodiesel production from waste cooking oil catalyzed by TiO₂–MgO mixed oxides, Bioresource Technology 101 (2010) 9570–9576.
- [31] B. Freedman, E. Pryde, T. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, Journal of American Oil Chemists Society 61 (1984) 1638–1643.
- [32] D. Darnoko, M. Cheryan, Kinetics of palm oil transesterification in a batch reactor, Journal of American Oil Chemists' Society 77 (2000) 1263–1267.
- [33] C. Stavarache, M. Vinatoru, R. Nishimura, Y. Maeda, Fatty acids methyl esters from vegetable oil by means of ultrasonic energy, Ultrasonics Sonochemistry 12 (2005) 367–372.
- [34] J. Lifka, B. Ondruschka, Influence of mass transfer on the production of biodiesel, Chemical Engineering & Technology 27 (2004) 1156–1159.
- [35] N. Siatis, A. Kimbaris, C. Pappas, P. Tarantilis, M. Polissiou, Improvement of biodiesel production based on the application of ultrasound: monitoring of the procedure by FTIR spectroscopy, Journal of American Oil Chemists' Society 83 (2006) 53–57.
- [36] T. Eevera, K. Rajendran, S. Saradha, Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions, Renewable Energy 34 (2009) 762–765.
- [37] A. Demirbas, Biodiesel production via non-catalytic SCF method and biodiesel fuel characteristics, Energy Conversion and Management 47 (2006) 2271–2282.
- [38] T.H. Dang, B.-H. Chen, D.-J. Lee, Application of kaolin-based catalysts in biodiesel production via transesterification of vegetable oils in excess methanol, Bioresource Technology 145 (13) (2012) 175–181.