



Novel utilization of waste marine sponge (*Demospongiae*) as a catalyst in ultrasound-assisted transesterification of waste cooking oil



Noor Hindryawati^{a,c}, Gaanty Pragas Maniam^{a,b,*}

^a Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

^b Central Laboratory, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

^c Faculty of Mathematics and Natural Sciences, Mulawarman University, Gunung Kelua, 75113 Samarinda, East Borneo, Indonesia

ARTICLE INFO

Article history:

Received 27 January 2014

Received in revised form 21 April 2014

Accepted 21 April 2014

Available online 5 May 2014

Keywords:

Transesterification

Heterogeneous catalyst

Ultrasound

Waste cooking oil

Biodiesel

ABSTRACT

This study demonstrates the potential of Na-silica waste sponge as a source of low cost catalyst in the transesterification of waste cooking oil aided by ultrasound. In this work an environmentally friendly and efficient transesterification process using Na-loaded SiO₂ from waste sponge skeletons as a solid catalyst is presented. The results showed that the methyl esters content of 98.4 ± 0.4 wt.% was obtainable in less than an hour (h) of reaction time at 55 °C. Optimization of reaction parameters revealed that MeO:H:oil, 9:1; catalyst, 3 wt.% and reaction duration of 30 min as optimum reaction conditions. The catalyst is able to tolerant free fatty acid and moisture content up to 6% and 8%, respectively. In addition, the catalyst can be reused for seven cycles while maintaining the methyl esters content at 86.3%. Ultrasound undoubtedly assisted in achieving this remarkable result in less than 1 h reaction time. For the kinetics study at 50–60 °C, a pseudo first order model was proposed, and the activation energy of the reaction is determined as 33.45 kJ/mol using Arrhenius equation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Concerns about the depleting of the fossil fuel and the demand for fossil fuel have attracted attentions for new and renewable energy such as biodiesel. Producing biodiesel from low cost feedstock and a catalyst from waste source is one of the ways to reduce the production cost. Annually, the EU recorded 0.7–1.0 MT of waste oil, Turkey 0.35 MT and Canada 0.12 MT, in addition to those uncollected oils, which goes as waste trough into soil and water [1]. Waste cooking oil (WCO) is one of the low cost feedstock [2], readily available, and the utilization offers benefits on environmental conservation. Unfortunately, waste oil contains high free fatty acid (FFA) and moisture. Therefore, a two-step transesterification process (acid esterification followed by base transesterification, e.g. ferric sulphate–potassium hydroxide) was developed to remove the high FFA content and to improve the biodiesel yield. The disadvantages of this process are that it is more costly, because of the use of an extra catalyst, high energy-intensive nature of the process, longer reaction time and lower catalyst recovery [3,4].

* Corresponding author at: Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia. Tel.: +60 16 4110236; fax: +60 9 549 2766.

E-mail address: gaanty@hotmail.com (G.P. Maniam).

Recently, the production of biodiesel using heterogeneous base catalyst has become more favorable compared to biocatalyst and ready to be scaled up to an industrial level. Therefore, a process using heterogeneous catalysts has been developed for environmental benefits and reduction on production cost. Many types of heterogeneous catalysts, such as CaO from mud crab shells and cockle shells [5], mix-metal oxide [6], and metal supported in matrix (MSM) [7] have been studied in the literature. MSM, as a catalyst, is an interesting area for the researcher owing to its advantages of reproducibility and long lasting catalyst usage. Several studies on the usage of silica as precursor/support in heterogeneous base catalyst for biodiesel production are published [7,8]. Castro et al. [9] loaded Li on four supports (SiO₂, MgO, Al₂O₃, and Mg(Al)O) and they concluded that Li impregnation onto Mg(Al)O as the most active catalyst and generate higher conversion. Kumar et al. [10] successfully converted *Jatropha curcas* oil using Na/SiO₂ and ultrasonication at reduced reaction time comparing to the conventional batch processes with 98.53% biodiesel yield. Guo et al. [11] soybean oil using calcined sodium silicate at 400 °C with 96% yield while the catalyst is reused for five times. The utilization of catalyst from waste sources could also counter the environmental damage, highly effective, and cost effective. Among the catalysts that have been studied so far, impregnation metal onto silica as a support promising for the transesterification reaction.

The current work focuses on production of biodiesel using ultrasound as an eco-extraction process. Ultrasound-aided transesterification is reported previously in the production of biodiesel using vegetable oil, WCO and spent bleaching clay [12–14] as feedstock. The use of ultrasound promises simpler process with higher product purity and the process can be completed in shorter reaction time as well as reducing the amount of solvent being used as compared to the conventional extraction methods and with lower energy consumption. According to Gude et al. [15], transesterification using a hot plate requires much more energy than ultrasonic process. The reduction of energy consumption is one of the advantages of ultrasound technique in ME production. This study demonstrates the potential of Na-waste marine sponge as a low cost source of catalyst in a transesterification reaction aided by ultrasound. Waste marine sponge skeletons are high in natural silica [16] and can be found at seaside area easily; unfortunately with no or less application. To validate the characteristic of this new catalyst, kinetic study is performed to predict the extent of the reaction at any time under particular conditions. Many of such kinetic study were done with basic homogeneous transesterification in the methanol/oil system using conventional method [17,18]. To the best of our knowledge, there is no published report on kinetics of Na-loaded waste marine sponge as a solid catalyst in transesterification using ultrasound as compared to mechanical stirring as a control. The reaction rates at different temperatures were determined, and the activation energy was established. Several parameters were investigated including catalyst amount, reaction time, tolerant toward FFA, moisture/water content and reusability of the catalyst.

2. Experimental and mathematical modeling

2.1. Materials

The WCO was collected from local hawker in Gambang, Malaysia (acid value was found to be 3.54 ± 0.05 mg KOH/g, equivalent to 1.77% FFA (as oleic acid) and 0.28 ± 0.04 of moisture content). Waste sponge (WS) was collected from Tanjung Lumpur shore in Kuantan, Malaysia, and were cut into small pieces ($0.5\text{--}1.0\text{ cm}^3$), cleaned with water several times and air-dried for 24 h. The WS fragment was then calcined at $500\text{ }^\circ\text{C}$ in air, the calcined WS is labeled as silica waste sponge (SWS). The chemicals purchased from Sigma–Aldrich (Switzerland) include sodium hydroxide (analytical grades), phenolphthalein ($H_L = 8.2$), 2,4-dinitroaniline ($H_L = 15.0$) and 4-nitroaniline ($H_L = 18.4$), and methyl heptadecanoate (as an internal standard) GC grades ($>99.1\%$). Methanol (anhydrous, $\geq 99.8\%$), and hexane (anhydrous, $\geq 99.8\%$) were purchased from Hamburg (Germany).

2.2. Preparation of catalyst (silica waste sponge with sodium)

Silica waste sponge with sodium (SWSS) was prepared using impregnation method. SWS was suspended in water in the first step. An aqueous solution of sodium hydroxide was then slowly added to the suspension. All reactions were performed at $\text{Na}^+:\text{Si}$ molar ratio of 2:1. The mixture obtained was then stirred and heated at $90\text{ }^\circ\text{C}$ for 2 h. Lastly, the mixture was dehydrated at $200\text{ }^\circ\text{C}$ for 30 min, and then calcined at $500\text{ }^\circ\text{C}$ for 3 h.

2.3. Material characterization

The SWS and SWSS were identified by X-ray diffraction (Rigaku) with Cu K α X-ray as a source. FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of catalyst and support at $400\text{--}4000\text{ cm}^{-1}$ range. The catalyst

was examined by thermogravimetric analysis (TGA) using Mettler Toledo TGA instrument, from $25\text{ to }900\text{ }^\circ\text{C}$ with $10\text{ }^\circ\text{C}$ heating rate. Surface analysis of the catalyst was examined by using Micromeritics ASAP 2000. Prior to the analysis, all the samples were degassed at $105\text{ }^\circ\text{C}$ and the adsorption of N_2 was measured at $-196\text{ }^\circ\text{C}$. The size and morphology of the catalyst were observed by FE-SEM (JSM-7800F). The basicity of catalyst (H_L) was determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein ($H_L = 8.2$), 2,4-dinitroaniline ($H_L = 15.0$) and 4-nitroaniline ($H_L = 18.4$). About 5.0 mL of a solution of Hammett indicator diluted with methanol and mixed with 25 mg of catalyst, and left to equilibrate for 2 h. After the equilibration, the color change of the solution was noted.

2.4. Experimental setup

The transesterification reaction was carried out in a 250 ml two neck round-bottom glass flask equipped with a condenser to reduce the losses of methanol due to the evaporation and thermocouple thermometer. The ultrasonic reaction was performed using Branson (USA) ultrasonic bath (42 kHz) with the power dissipation 100 W and the exact power dissipation at 40 W determined calorimetrically [19–21]. The bath was filled with distilled water up to 1/3 of its volume. The temperature was controlled and maintained at desired level ($\pm 0.1\text{ }^\circ\text{C}$) by water circulating from a thermostated bath by means of a pump. A constituent of 50 ml oil [22] with desired amount of catalyst and methanol, was immersed in an ultrasound (US) waterbath. The effect of catalyst amount (0–9 wt.%), reaction duration (0–80 min), addition of water (0–17%) and FFA (0–9%, oleic acid) on the conversion of triglycerides to biodiesel were investigated, with the temperature ranging from $50\text{ to }60\text{ }^\circ\text{C}$. The conversion of WCO to methyl esters (ME) by mechanical stirring (MS) was performed in a 250 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer at 300 rpm. The transesterification reaction between oil and methanol was carried out in liquid phase under atmospheric pressure, at temperature ranging from $50\text{ to }60\text{ }^\circ\text{C}$ with continuous stirring. After the transesterification, the reaction mixture was allowed to cool. Then, to further separate the product (ME and glycerol) and the catalyst centrifugation at 4000 rpm for 5 min was performed. The excess methanol was evaporated before the chromatographic analysis. The reaction was carried out three times in order to reflect the precision and errors of the results.

2.5. Analysis

The concentration of ME in the sample was determined by following the European regulation procedure EN 14103. In this study, GC–MS (Agilent Technologies, 7890A GC-System) with capillary column DB-wax (length $30 \times$ diameter $0.25\text{ mm} \times$ film thickness $0.25\text{ }\mu\text{m}$) using methyl heptadecanoate as an internal standard. Helium was used as a carrier gas with a linear velocity of 40 cm/s . The oven temperature was programmed at $190\text{ }^\circ\text{C}$, held for 2 min, then ramped at $10\text{ }^\circ\text{C per min}$ until it reached $230\text{ }^\circ\text{C}$, and with a final hold time of 8 min. The sample volume of $0.6\text{ }\mu\text{L}$ was injected into GC. The peaks of ME were identified by comparing them with their respective ME standards and the ME content was quantified using the following formula:

$$\text{ME content (\%)} = \frac{(\sum A) - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{m} \times 100$$

Where

$\sum A$ = total peak area of ME from C12:0 to C18:1

A_{ISTD} = peak area of methyl heptadecanoate

C_{ISTD} = concentration, in mg/mL, of the methyl heptadecanoate solution

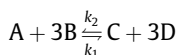
V_{ISTD} = volume, in mL, of the methyl heptadecanoate solution
 m = mass, in mg, of the sample

The concentration of methyl heptadecanoate solution (C_{ISTD}) is at 10 mg/ml (in heptane) whereas the volume (V_{ISTD}) is at 0.5 ml.

In order to examine the potential of catalytic reutilization, a used catalyst was subjected for subsequent reactions. For the purpose, the used solid catalyst that recovered by centrifugation was then regenerated by washing with methanol and then with n-hexane. The dried used catalyst was directly used as a catalyst for the repeated reactions. The final product was tested for viscosity, acid number, free fatty acid (FFA) and density following the EN 14214 method.

2.6. Determination of transesterification kinetics

Generally, ME can be produced from transesterification reaction of triglyceride (TG) (the main component of vegetable oils or animal fats) with short chain alcohol (mainly methanol) and with the presence of catalyst. In general, the overall transesterification reaction stoichiometrically can be written as:



where A is the waste cooking oil; B is the methanol; C is the glycerol and D is the ME.

The rate determination step in transesterification reaction starts with the attacks on the carbonyl carbon atom of TG, diglyceride (DG), and monoglyceride (MG) molecules by methoxide ions (CH_3O^-). The elementary reaction step is methanol (B) adsorbed on the active site of catalyst. The base catalyst can drive the reaction with a shorter reaction time because of the cation that is very reactive to drive methanol to form the active species (CH_3O^-). Then, the nucleophilic attack of CH_3O^- on the carbonyl carbon of triglyceride (A) forms a tetrahedral intermediate structure (one ME and diglyceride). Afterwards, the protons from the cation were transferred to diglyceride anions to generate diglyceride. The rearrangement of the structure (diglyceride further reacted with methanol to generate monoglyceride, then monoglyceride reacted with adsorbed methanol) resulted in the formation of ME (D) and glycerol (C) [23]. It was reported by Nouredini et al. [18], from the rate determination step of the transesterification reaction, it shows that the reaction of TG with alcohol was slower than those of di- and monoglyceride. In their studies the k_1 values were lower than others. The subsequent reactions with di- and monoglyceride are faster, until equilibrium is achieved.

The schematic in the transesterification reaction of the overall transesterification reaction as shown above requires three moles of methanol to react with one mole of oil. Transesterification reaction is reversible, so if alcohol is in excess, it can drive the equilibrium towards the formation of esters. The kinetic equation for the transesterification reaction is:

$$r = -\frac{d[A]}{dt} = k_1[A][B]^3 - k_2[C][D]^3 \quad (1)$$

As methanol is normally used in excess, therefore, the reverse reaction can be ignored and the reaction rate is zero at the start ($t = 0$). The conversion of TG follows the pseudo-first order reaction kinetic and, the mass balance for the oil can be written as follows:

$$r = -\frac{d[A]}{dt} = k[A] \quad (2)$$

$$\frac{d[A]}{[A]} = -kdt \quad (3)$$

k = pseudo-first order reaction constant, where, t is the time (min), $[A_0]$ is the concentration of WCO in the first reaction and x is the total conversion, the reaction equation may be written as:

$$\frac{d[A_0](1-x)}{[A_0](1-x)} = -kdt \quad (4)$$

$$\int_0^x \frac{d[A_0](1-x)}{[A_0](1-x)} = \int_0^t -kdt \quad (5)$$

$$\ln [A_0](1-x)|_0^x = -kt|_0^t \quad (6)$$

$$\ln [A_0](1-x) - \ln [A_0] = -kt + 0 \quad (7)$$

$$\ln \frac{[A_0](1-x)}{[A_0]} = -kt \quad (8)$$

$$\ln (1-x) = -kt$$

$$k = -\frac{\ln (1-x)}{t} \quad (9)$$

The rate constant (k) can be determined based on the decreased amount of one reactant e.g. WCO or it could be based on the increased amount of the ME that occurs at reaction time interval [24]. From the Eq. (9), x is the ME content, t is the reaction duration, and the rate constant can be readily obtained from the slope of $-\ln(1-x)$ vs. t .

3. Results and discussion

3.1. Characterization of catalyst

The FTIR spectra of silica waste sponge without sodium (SWS) and silica waste sponge with sodium (SWSS) are shown in Fig. 1. The typical one, with the broadband at about $3410\text{--}3470\text{ cm}^{-1}$ is due to the stretching vibration of the O–H bond from the silanol groups (Si–OH) and is due to the adsorbed water molecules on the silica surface, the band at 1654 cm^{-1} is due to bending H–OH bond of adsorbed water molecules. The sharp peaks (Fig. 1a and b) $1020\text{--}1100\text{ cm}^{-1}$ are Si–O–Si bending. The bands (Fig. 1a) at 786 and 973 cm^{-1} are attributed to symmetric O–Si–O stretching and Si–O bending, respectively. Fig. 1b shows, the characteristic absorption peaks at $503\text{--}687\text{ cm}^{-1}$ are attributed to the vibration of the $\text{Na}^+\text{--O}$ bond structure, and the characteristic absorption band from deformation of Na^+OH become Si–O– Na^+ are shown at 865 and bands at 1440 cm^{-1} is attributed to Si–O–Si stretching. Summarizing the FTIR results, it can be concluded that the sodium on silica waste sponge was successfully bound.

The powder XRD pattern of SWS and SWSS are shown in Fig. 2. The diffractograms of SWS (Fig. 2a) showed a hump at 2θ ranging from 16° to 40° , and the presence of large reflection at 22.45° , indicates the presence of amorphous silica particles. The results are similar with reported work by Kalapathy et al. [25] indicating the disordered structure mainly due to amorphous SiO_2 . In Fig. 2b, the intense diffraction peaks found at $25.26\text{--}65.93^\circ$ correspond to the Miller indexes (100), (101), (110), (200), (111), (002), (112), (300) and (302) were confirmed as Na_2SiO_3 (SWSS).

A thermogravimetric analysis (TGA) is an analytical technique used to determine materials' thermal stability, as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The TGA curve of sodium silicate is shown in Fig. 2c. In the first one, ranging from 50 to 175°C , weight loss (4.25%) was attributed to the release of physically bound water on the surface of Na_2SiO_3 particles. The second region, the weight loss (4.66%) at temperature around $180\text{--}380^\circ\text{C}$ is attributed to the removal of organic compound from the SWS and the decomposition of sodium hydroxide (melting point = 318°C). The third endothermic region, the ranging from 650 to 850°C , has a weight loss of 8.81%. The

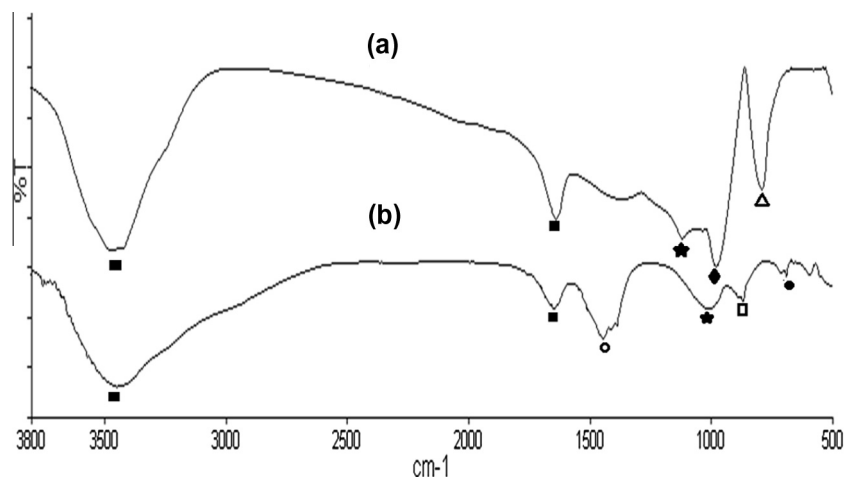


Fig. 1. FTIR spectra of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium; ●: Na–O, △: O–Si–O, □: (Si–O–Si)–(Na⁺–O), ◇: Si–O, ★: Si–O–Si bending, ○: Si–O–Si stretching, ■: –OH.

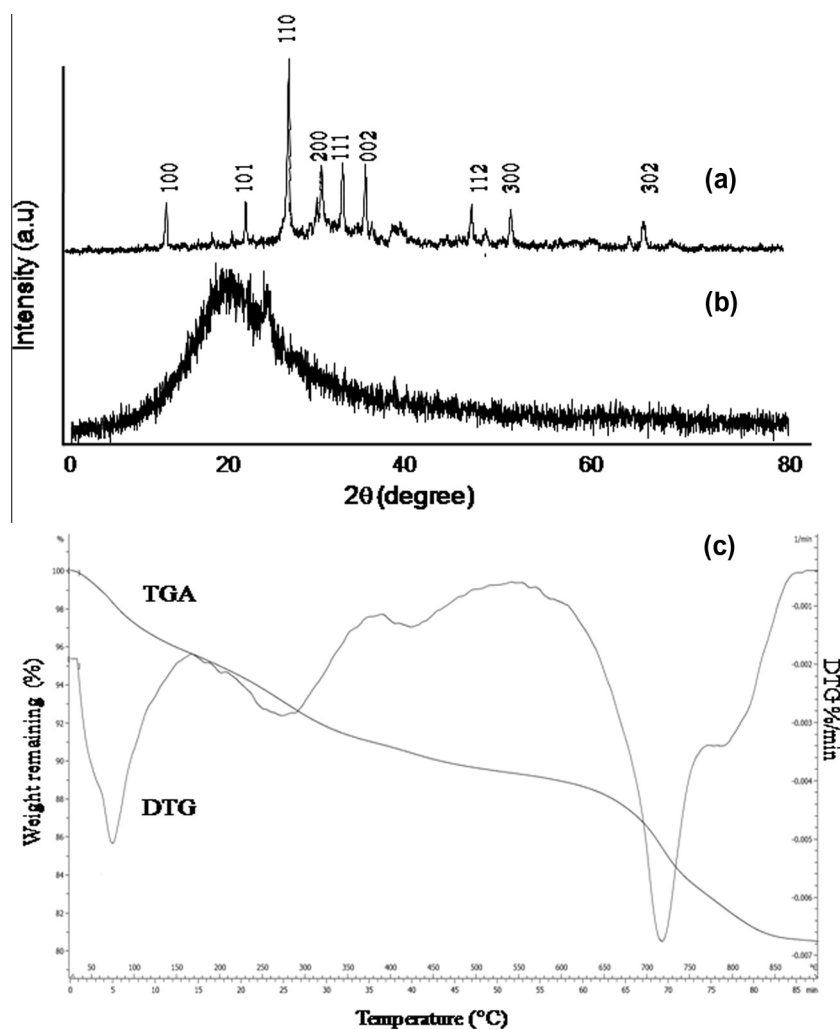


Fig. 2. XRD pattern of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium; (c). DTG/TGA of silica waste sponge with sodium.

weight loss was attributed to water loss from the condensation of adjacent silanol group to form siloxane and sodium silicate bond.

The values of specific surface area and pore volume of considerably decrease after modification of SWS with sodium. The loading

of the sodium with SWS resulted in decrease in both the BET surface area from 11.77 to 5.08 m²/g and the pore volume from 0.15 to 0.08 cm³/g of the SWS and SWSS, respectively. The morphology of SWSS shows the homogenous surface (Fig. 3b), having a smooth

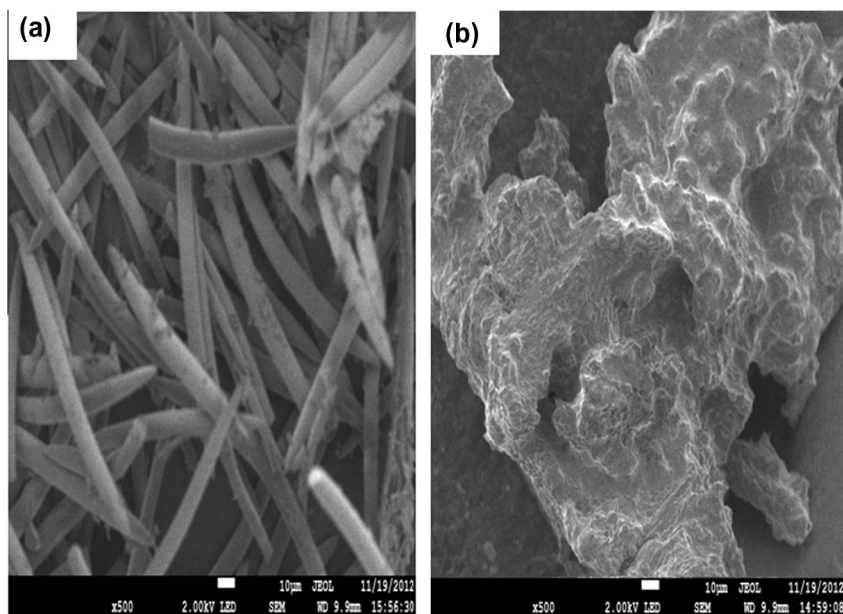


Fig. 3. SEM micrograph of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium.

surface and similar to each other. In contrast, the SWS showed a bulky substance. The skeleton consisted of needle shaped spicules that are bundled together (Fig. 3a). SWSS could change the color from colorless to pink (phenolphthalein) and from yellow to mauve (2,4-dinitroaniline) but failed to change the color of 4-nitroaniline. The basic strength SWSS is in the range of $15 < H_- < 18.4$. On the other hand, SWS has failed to change the color of all Hammett indicators. Therefore, SWS does not have basic properties and suitable to be used as a support material.

3.2. Effect of reaction duration

The effect of the reaction duration as shown in Fig. 4 is one of the critical parameters for biodiesel production. The reaction duration was varied from 0 to 80 min. As can be observed, at the optimum reaction conditions of 3 wt.% catalyst and methanol to oil molar ratio of 9:1 at 55 °C, ME content under US increased within the first 10 min. At 30 min, the ME content increased to above 90% and remained almost constant as a result of near equilibrium at $98.2 \pm 0.4\%$. Any further time increase has no appreciable changes in the content probably due to equilibrium. On the other hand, it is noted that by using MS, the ME content, reached the peak ($87.7 \pm 0.6\%$) at 80 min. The transesterification reaction using US is the most efficient reaction.

The difference of ME content between MS and US is about 38% as noted at 30 min. According to the results, the optimal method for ME formation is the transesterification using ultrasound. The ultrasound could affect the content ME in shorter reaction time, due to the acoustic cavitations mixing the oil and methanol molecules to form the microscale fine emulsions that enhance the interfacial area for the reaction [26], causing the oil and methanol molecules easily suspend into each other. The increasing of the interfacial area of medium will accelerate the reaction and provide necessary activation energy for the reaction compare to the conventional process.

3.3. Effect of catalyst amount

The amount of catalyst was varied in the range of 0–9 wt.%. As shown in the Fig. 5, a plot of catalyst amount vs. ME content for the

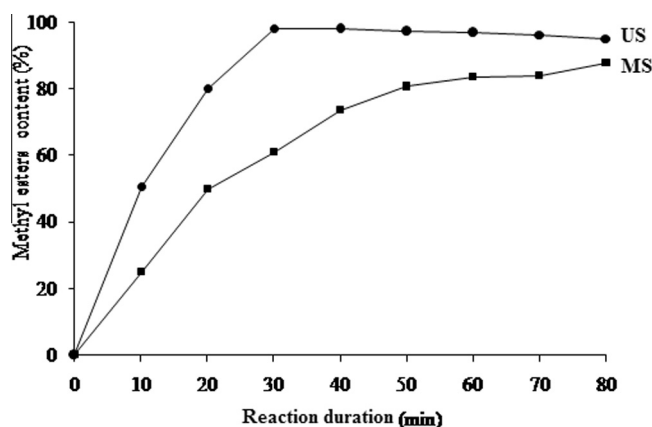


Fig. 4. Effect of reaction duration (0–80 min) on methyl esters content (reaction conditions: catalyst amount, 3 wt.%; MeOH:oil molar ratio, 9:1; reaction temperature 55 °C; US: ultrasound, MS: mechanical stirring).

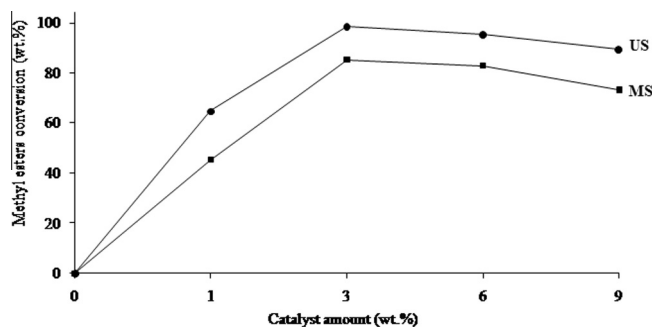


Fig. 5. Effect of catalyst amount (0–9 wt.%) on methyl esters content (reaction conditions: MeOH:oil molar ratio, 9:1; reaction duration 80 min; reaction temperature 55 °C; US: ultrasound, MS: mechanical stirring).

reaction conducted under US and MS is illustrated (under the following constant reaction conditions: methanol to oil molar ratio of 9:1 and reaction temperature at 55 °C, for 80 min). The

transesterification depends on the amount of catalyst used, increasing the catalyst from 1% to 3%, increases ME content significantly. This is because the contact opportunity of the catalyst and the reactant, directly affect the reaction speed. In line with the collision theory, lesser energy is needed for chemical transformation when there is a direct contact between catalyst and reactant molecule. More and more molecules will have sufficient energy to react and therefore the reaction rate is increased. Furthermore, the addition of a large amount of catalytic material (above 3%) had not lead to an increase in ME content. This is probably because of the demand of higher power consumption to compensate for an adequate stirring speed, and the solution becoming more viscous. This trend is in agreement with previous reports in which the researcher found that catalyst amounts leads to stirring complication, increasing viscosity and ultimately limits the mass transfer [13,27]. Other researchers also found that the excess solid catalyst reacted with the oil, resulting in emulsion formation between soaps and water molecules, thus leading to low yields of ME and the separation of esters became difficult [28,29]. Therefore, the catalyst concentration is an influencing factor on the amount of methoxide ions formed. By using ultrasound, it enhances the mass transfer between catalyst and reactants as well as maintains the required kinetic energy in the reaction media. The ME content under US ($98.4 \pm 0.4\%$) is higher than that of MS ($87.9 \pm 0.6\%$) at 3 wt.% catalyst. Dispersion due to ultrasonic sound increases the surface area of catalyst available to the reactants [30,31]. Another explanation is due to the wetting of the pores within the catalytic material, hence more surface area is exposed to the reactant. As such, the use of ultrasound promotes the efficiency of acyl conversion in a shorter reaction time.

3.4. Kinetic studies

The experiment was carried out at three different temperatures 50, 55, and 60 °C tested for pseudo-first order kinetic. The experimental data fitted well for pseudo-first order kinetic. As seen in Fig. 6, with increasing reaction temperature and reaction duration, higher ME content is achieved. The average overall reaction rate constant at different temperatures can be calculated according to

Table 1

Reaction rate constant for the transesterification of WCO using ultrasound and mechanical stirring.

Temperature (°C)	Ultrasound		Mechanical stirring	
	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²
50	0.073	0.968	0.020	0.927
55	0.099	0.981	0.031	0.984
60	0.106	0.943	0.039	0.971

the experimental data shown in Table 1. The result of k values which clearly shows that the reaction rate under US method has higher value compared to the MS. For the reaction at 55 °C, kinetic parameter obtained with US (42 kHz) and MS were 0.099 and 0.031 min⁻¹, respectively. It was observed in this study, that US significantly improve the mass transfer of the reaction.

The possibility of a reaction was determined from the thermodynamic parameters. The reaction rate constant is highly depending on the temperature. Arrhenius equation was used to study the influence of temperature on the specific reaction rate as follow:

$$k = Ae^{-(E_a/RT)}$$

where E_a is the activation energy (J/mol), define as the minimum energy required to start a chemical reaction, R is the gas constant (8.314 J.mol⁻¹.K⁻¹), T is the absolute temperature (K), A is the frequency factor (collision factor) and k is the reaction rate constant. The slope and intercept of the graph between $\ln k$ vs. $1/T$ give the values of activation energy and frequency factor, respectively. The activation energy and frequency factor determined from Fig. 6b. Accordingly, the values of E_a and A ultrasound and mechanical stirring were determined as 33.45 kJ/mol; 1.95×10^4 min⁻¹ and 59.81 kJ/mol; 9.70×10^7 min⁻¹, respectively. The result under heterogeneous catalyst is comparable to E_a of homogeneous catalysts under mechanical stirring, ranging from 33 to 84 kJ/mol [17]. The activation energy of 33.45 kJ/mol was suggesting a lower energy barrier is required for the proposed reaction, and indicating that the reaction can be carried out under mild temperature and pressure conditions.

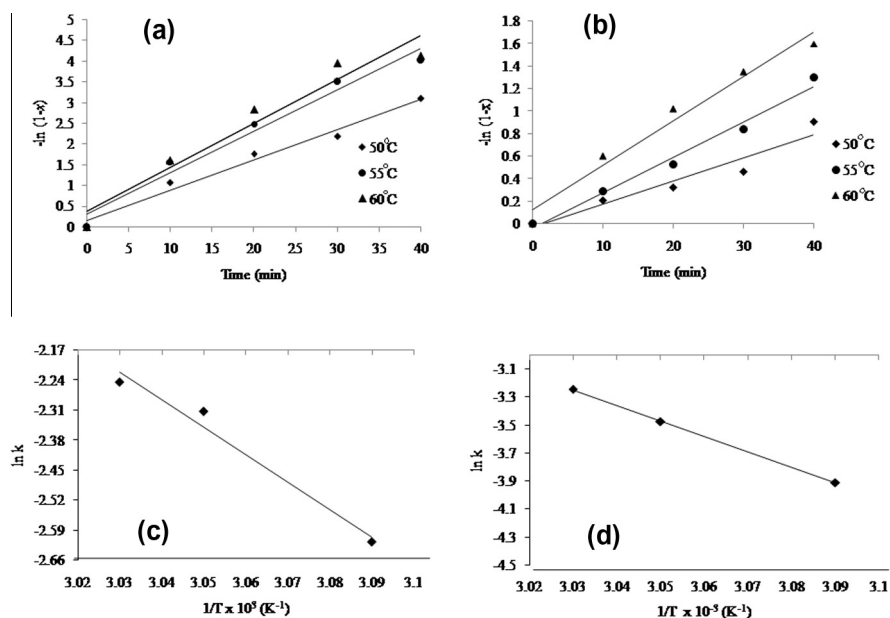


Fig. 6. (a) Plot of $-\ln(1-x)$ vs. time for the ultrasound, (b) Plot of $-\ln(1-x)$ vs. time for the mechanical stirring, (c) Arrhenius plot of $\ln k$ vs. $1/T \times 10^{-3}$ for ultrasound, (d) Arrhenius plot of $\ln k$ vs. $1/T \times 10^{-3}$ for mechanical stirring (reaction conditions: catalyst concentration 3%; MeOH:oil molar ratio (9:1); $T = 50, 55, 60$ °C).

Table 2

Comparative study of reaction rate constant and activation energy between different techniques under the optimum conditions for methyl ester conversion.

Technique	Oil	Catalyst	Optimum condition				k (min ⁻¹)	E_a (kJ/mol)	^a Conv. (wt.%)	Refs.
			Catalyst wt.% of oil	MeOH:oil molar ratio	Reaction time (min)	T (°C)				
Ultrasound	Soybean	Ca(OCH ₃) ₂	1	9:1	90	60	0.0033	71.25	>90	[32]
	Jatropha	NaOH	1	9:1	30	50	0.0910	16.95	>93	[33]
	Sunflower	KOH	0.7	7.5:1	50	40	–	46.20	>90	[34]
	Waste cooking	Na/SiO ₂	3	9:1	30	55	0.0990	33.45	98.4	This study
Mechanical stirring	Palm	KOH	8.5	9:1	480	65	0.0008	79.1	96.2	[35]
	Jatropha	NaOH		21:1	60	105		152	>80	[36]
	Waste frying	CaO	2	6.03:1	480	60		79	99.5	[37]
	Waste cooking	K/CaO	7.5	12:1	70	65	0.0620	54	98	[38]
	Soybean	CaO–La ₂ O ₃	5	20:1	60	58		49.3	94.4	[39]

^a Conv = methyl ester conversion.

Ultrasound increases the frequency of collisions between reactant molecules that accelerate the reaction to occur perfectly. In accordance with Arrhenius equation, greater the collisions, greater the reaction rate constant, thus, US is meaningful since oil and methanol are not readily miscible solutions. ME content and E_a that were reported from previous studies are presented in Table 2 [32–39]. As presented in our study, higher ME content is achieved with lower activation energy and in shorter reaction time as compared to previous studies. Much lower E_a is observed in the previous study using US, however, the work utilized NaOH as a homogeneous catalyst, whereas in our work, we used heterogeneous catalyst. Moreover, much higher E_a is observed under mechanical stirring. Generally reaction rate (k) is dependent on the reaction temperature, methanol/oil ratio, and catalyst amount. Since there are many variables involved in determining the k , it is somehow difficult to perform a direct comparison between reactions. Nevertheless, the transesterification of WCO under ultrasound technique provides a possibility for producing cheap and efficient alternative biofuel, which will reduce the energy consumption and at the same time reduces the environmental pollution.

3.5. Tolerance towards water and free fatty acid of SWSS

The presence of water and FFA in base-catalyzed transesterification inhibits the reaction by promoting saponification. Triglyceride hydrolyzes into FFA and glycerol in the presence of water while

FFA reacts with basic catalyst to form soap. Soap formation complicates ME separation thereby lowering the content. In order to examine the effect of water and FFA on the activity of SWSS, 0–17 wt.% water and 0–9 wt.% of FFA were added and the results were recorded. Fig. 7a indicates that the addition of water slightly decreased the content of ME. As indicated by Fig. 7a where the ME content is still high (92.8 ± 0.5%) even in the presence of 8% water. The result indicates that SWSS has a remarkable tolerance to water in the transesterification of waste cooking oil, indicates that H₂O up to 8% has little effect on the total basicity of the catalyst. Effect of FFA on ME content using SWSS catalyst is shown in Fig. 7b. It was found that with increasing FFA, the ME content is decreasing. For the oil with 6% of FFA, the content of ME was at 78 ± 0.5%, however, at 9% FFA content reduced to about 29 ± 0.6% (This observation indicates that at higher FFA content (9%), saponification takes place). Soap formation complicated the mixing and product separation process, meanwhile water accelerated formation of FFA from the remaining triglycerides [40].

3.6. Reusability of catalyst

Reusability is one of the factors in the economical application of SWSS as the solid base catalyst. The catalyst was reused without any further activation. The results provided in Fig. 8, show that the SWSS can be used up to seven cycles while maintaining the activity at considerable ME content (86.3%). After the transesterification reaction is completed, the SWSS was decanted with simple

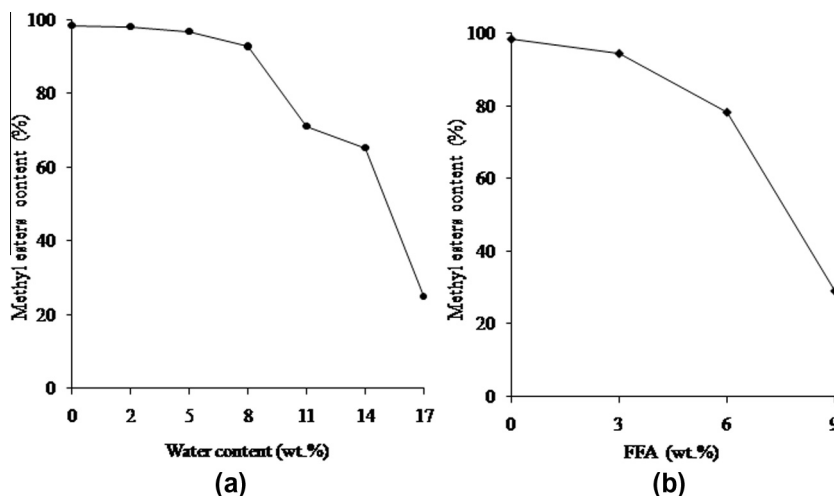


Fig. 7. Effect of (a) water content and (b) FFA toward the methyl esters content (reaction conditions: catalyst concentration 3%; temperature 55 °C; MeOH:oil molar ratio, 9:1).

Table 3
Properties of biodiesel from waste cooking oil.

Parameters	Unit	Na-sponge catalyst	Biodiesel specification EN14214
Ester content	wt.%	98.4 ± 0.4	96.5 (min)
Density	kg m ⁻³	874	860–900
Viscosity	mm ² s ⁻¹	3.8	3.5–5.0
Acid value	mg KOH g ⁻¹	0.3	0.5 (max)

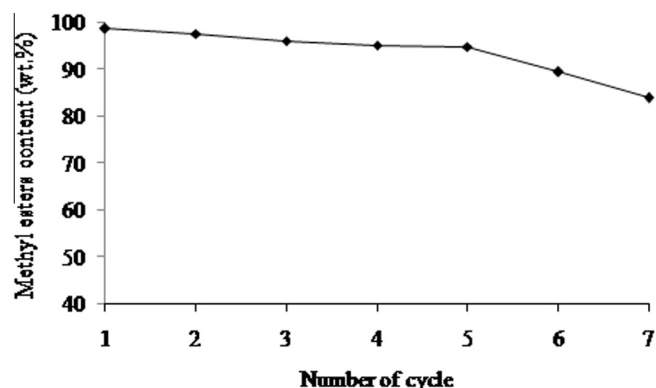


Fig. 8. Reusability of the catalyst (reaction conditions 3% catalyst; MeOH:oil molar ratio (9:1); 30 min at 55 °C).

washing using hexane and can be directly reused for subsequent reactions. This experiment shows that a simple regeneration method could recover the active sites of the catalyst and the activity of regenerated catalyst has a good reproducibility.

3.7. Biodiesel properties

EN 14214 as used in order to assess the quality of the final product (Table 3). The result of the evaluation shows that the final product meets all the tested parameters (ester content, density, viscosity, and acid value). The ester content catalyzed by SWSS (3 wt.%) is recorded the highest value of 98.4 ± 0.4%. The output of GC analysis proved that waste cooking oil mainly comprises of ME of myristic acid 0.92%, palmitic acid 34.46% followed by 0.91% palmitoleic, 3.95% stearic, 46.40% oleic, and 12.34% linoleic and traces of other acids. Although many other parameters need to be analyzed in order to confirm the final product as a fuel, these four parameters can serve as preliminary indicators of the product to be used as a fuel.

4. Conclusion

In this work, silica waste sponge with sodium (SWSS) was successfully utilized as a low-cost feedstock to produce ME (biodiesel) via ultrasound aided in situ transesterification. The highest ME content of 98.4 ± 0.4 wt.% was obtainable in an hour reaction time at 55 °C. Optimization of reaction parameters revealed that MeOH:oil, 9:1; catalyst, 3 wt.% and reaction duration 30 min as the optimal reaction conditions. The catalyst is tolerant toward FFA and water at 6% and 8%, respectively. The catalyst can be reused seven cycles maintaining 86.3% content. The use of ultrasound undoubtedly assisted in achieving this remarkable result in less than 1 h reaction time with the activation energy of 33.45 kJ/mol. Materials derived from waste sources, as used in this work, should be given a priority for a sustainable biodiesel production.

Acknowledgments

The authors acknowledge MTUN CoE Grant (RDU 121207 and RDU 121208), MTUN Showcase (RDU 131202), RAGS Grant (RDU

121402) and GRS Grant (PRGS 130303) from the Ministry of Education Malaysia and Universiti Malaysia Pahang for funding the research project, the Government of East Borneo, Indonesia for the scholarship (N. Hindryawati).

References

- [1] Today's Zaman. Recycling of waste cooking oil into biodiesel protects water resources. <http://todayszaman.com/newDetail_getNewsById.action?newId=277470> [accessed September 2013].
- [2] K.T. Tan, K.T. Lee, A.R. Mohamed, Potential of waste palm cooking oil for catalyst-free biodiesel production, *Energy* 36 (2011) 2085–2088.
- [3] A. Abbaszadeh, B. Ghobadian, M.R. Omidkhah, G. Najafi, Current biodiesel production technologies: a comparative review, *Energy Convers. Manage.* 63 (2012) 138–148.
- [4] P.D. Patil, V.G. Gude, H.K. Reddy, T. Muppaneni, S. Deng, Biodiesel production from waste cooking oil using sulfuric acid and microwave irradiation processes, *J. Environ. Prot.* 3 (2012) 107–113.
- [5] P.-L. Boey, G.P. Maniam, S.A. Hamid, D.M.H. Ali, Crab and cockle shells as catalyst for the preparation of methyl esters from low free fatty acid chicken fat, *J. Am. Oil Chem. Soc.* 88 (2011) 283–288.
- [6] A.K. Endalew, Y. Kiros, R. Zanzi, Heterogeneous catalysis for biodiesel production from *Jatropha curcas* oil (JCO), *Energy* 36 (2011) 2693–2700.
- [7] J.A. Melero, L.F. Bautista, J. Iglesias, G. Morales, R. Sánchez-Vázquez, Zr-SBA-15 acid catalyst: optimization of the synthesis and reaction conditions for biodiesel production from low-grade oils and fats, *Catal. Today* 195 (2012) 44–53.
- [8] K.-T. Chen, J.-X. Wang, Y.-M. Dai, P.-H. Wang, C.-Y. Liou, C.-W. Nien, J.-S. Wu, C.-C. Chen, Rice husk ash as a catalyst precursor for biodiesel production, *J. Taiwan Inst. Chem. Eng.* 44 (2013) 622–629.
- [9] C.S. Castro, C. Ferreti, J.I. Di Cosimo, J.M. Assaf, Support influence on the basicity promotion of lithium-based mixed oxides for transesterification reaction, *Fuel* 103 (2012) 632–638.
- [10] D. Kumar, G. Kumar, Poonam, C.P. Singh, Ultrasonic-assisted transesterification of *Jatropha curcas* oil using solid catalyst, Na/SiO₂, *Ultrason. Sonochem.* 17 (2010) 839–844.
- [11] F. Guo, N.-N. Wei, Z.-L. Xiu, Z. Fang, Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate, *Fuel* 93 (2012) 468–472.
- [12] I. Choedkiatsakul, K. Ngaosuwana, G. Cravotto, S. Assabumrungrat, Biodiesel production from palm oil using combined mechanical stirred and ultrasonic reactor, *Ultrason. Sonochem.* 21 (2014) 1585–1591.
- [13] N. Gharat, V.K. Rathod, Ultrasound assisted enzyme catalyzed transesterification of waste cooking oil with dimethyl carbonate, *Ultrason. Sonochem.* 20 (2013) 900–905.
- [14] P.-L. Boey, S. Ganesan, G.P. Maniam, D.M.H. Ali, Ultrasound aided in situ transesterification of crude palm oil adsorbed on spent bleaching clay, *Energy Convers. Manage.* 52 (2011) 2081–2084.
- [15] V.G. Gude, P.D. Patil, G.E. Grant, S. Deng, Sustainable Biodiesel Production, in: *Proceedings of the 2nd World Sustain. Forum*, 1–30 November 2012; Sciforum Electronic Conference Series 2.
- [16] H. Ehrlich, H. Worch, Sponges as natural composites: from biomimetic potential to development of new biomaterials, in: L.-H.G. Custódio MR, Hajdu E, Muricy G (Eds.), *Porifera research: Biodiversity, innovation and sustainability* (eds) Série Livros 28. Museu Nacional, Rio de Janeiro. pp. 303–312, ISBN 978-85-7427-023-4, 2007.
- [17] B. Freedman, R.O. Butterfield, E.H. Pryde, Transesterification kinetic of soybean oil, *J. Am. Oil Chem. Soc.* 63 (1986) 1375–1380.
- [18] H. Nouredini, D. Zhu, Kinetics of transesterification of soybean oil, *J. Am. Oil Chem. Soc.* 74 (1997) 1457–1463.
- [19] V.L. Gole, P.R. Gogate, Intensification of synthesis of biodiesel from nonedible oil using sonochemical reactors, *Ind. Eng. Chem. Res.* 51 (2012) 11866–11874.
- [20] T. Sivasankar, A.W. Paunekar, V.S. Moholkar, Mechanistic approach to enhancement the yield of a sonochemical reaction, *AIChE J.* 53 (2007) 1132–1143.
- [21] D. Liu, E. Vorobiev, R. Savoie, J.-L. Lanoiselle, Comparative study of ultrasound-assisted and conventional stirred dead-end microfiltration of grape pomace extracts, *Ultrason. Sonochem.* 20 (2013) 708–714.
- [22] P. Cintas, S. Mantegna, E.C. Gaudino, G. Cravotto, A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel, *Ultrason. Sonochem.* 17 (2010) 985–989.
- [23] M. Balat, H. Balat, Progress in biodiesel processing, *Appl. Energy* 87 (2010) 1815–1835.
- [24] I.N. Levine, *Physical Chemistry*, 6th ed., McGraw Hill Higher Education, New York, 2002, pp. 515–539.
- [25] U. Kalapathy, A. Proctor, J. Shultz, A simple method for production of pure silica from rice hull ash, *Bioresour. Technol.* 73 (2000) 257–262.
- [26] A. Kalva, T. Sivasankar, V.S. Moholkar, Physical mechanism of ultrasound-assisted synthesis of biodiesel, *Ind. Eng. Chem. Res.* 48 (2009) 534–544.
- [27] Z. Wei, C. Xu, B. Li, Application of waste eggshell as low-cost solid catalyst for biodiesel production, *Bioresour. Technol.* 100 (2009) 2883–2885.
- [28] S.M. Hingu, P.R. Gogate, V.K. Rathod, Synthesis of biodiesel from waste cooking oil using sonochemical reactors, *Ultrason. Sonochem.* 17 (2010) 827–832.

- [29] C. Stavarache, M. Vinatoru, R. Nishimura, Y. Maeda, Fatty acids methyl esters from vegetable oil by means of ultrasonic energy, *Ultrason. Sonochem.* 12 (2005) 367–372.
- [30] W. Guo, H. Li, G. Ji, G. Zhang, Ultrasound-assisted production of biodiesel from soybean oil using Brønsted acidic ionic liquid as catalyst, *Bioresour. Technol.* 125 (2012) 332–334.
- [31] L.T. Thanh, K. Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda, H. Bandow, Ultrasound-assisted production of biodiesel fuel from vegetable oils in a small scale circulation process, *Bioresour. Technol.* 101 (2010) 639–645.
- [32] V.G. Deshmane, Y.G. Adewuyi, Synthesis and kinetics of biodiesel formation via calcium methoxide base catalyzed transesterification reaction in the absence and presence of ultrasound, *Fuel* 107 (2013) 474–482.
- [33] A.P. Vyas, J.L. Verma, N. Subrahmanyam, Effects of molar ratio, alkali catalyst concentration and temperature on transesterification of *Jatropha* oil with methanol under ultrasonic irradiation, *Adv. Chem. Eng. Sci.* 1 (2011) 45–50.
- [34] J.M. Avramovic, O.S. Stamenkovic, Z.B. Todorovic, M.L. Lazic, V.B. Veljkovic, Empirical modeling of ultrasound-assisted base-catalyzed sunflower oil methanolysis kinetics, *Chem. Ind. Chem. Eng. Q.* 18 (2011) 115–127.
- [35] L. Zhang, B. Sheng, Z. Xin, Q. Liu, S. Sun, Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst, *Bioresour. Technol.* 101 (2010) 8144–8150.
- [36] M.K. Jha, A.K. Gupta, V. Kumar, Kinetics of transesterification on *Jatropha curcas* oil to biodiesel fuel, in: *Proceedings of the World Congress on Engineering and Computer Science, WCECS*, 24–26 October 2007, San Francisco, USA.
- [37] A. Birla, B. Singh, S.N. Upadhyay, Y.C. Sharma, Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell, *Bioresour. Technol.* 106 (2012) 95–100.
- [38] D. Kumar, A. Ali, Nanocrystalline K–CaO for the transesterification of a variety of feedstocks: structure, kinetics and catalytic properties, *Biomass. Bioenerg.* 46 (2012) 459–468.
- [39] S. Yan, M. Kim, S.O. Salley, K.Y.S. Ng, Oil transesterification over calcium oxides modified with lanthanum, *Appl. Catal. A* 360 (2009) 163–170.
- [40] P.-L. Boey, S. Ganesan, S.-X. Lim, S.-L. Lim, G.P. Maniam, M. Khairuddean, Utilization of BA (boiler ash) as catalyst for transesterification of palm olein, *Energy* 36 (2011) 5791–5796.