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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}

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

Response to Reviewer

No.	Comment Reviewer	Line no. in revised Manuscript	Response to Reviewer
1.	Reviewer #1: Unclear in certain section of the discussion whether the sodium silicate synthesis is silica waste sponge impregnated with sodium or a synthetic SiO ₂ support was used. i.e. line 134 "The FTIR spectra of silica waste sponge and sodium silicate synthesis". It might be better to use the same name when referring to the silica waste sponge, with and without sodium, throughout the manuscript	200-209	The term has been standardize throughout the manuscript

2.	Fig. 1: The symbols used for designation of peaks needs correcting. Same square symbol was used for Si-O-Si-Na ⁺ -O and Si-O-Si, diamond and open circle symbol are not explained in the caption, and filled circle symbol for Si-O is missing. Perhaps it might be clearer to denote on the graphs the different vibrational bonds?	205	The symbol have been corrected
3.	Fig. 2: (a) and (b) needs to be switched around to match discussion on page 7(lines145-150) or references in discussion needs to be corrected. Axis title for x axis for (a) and (b) is required. The peaks in (a) should be labelled with the angle or Miller index rather than triangle symbol.	216	The axis (a) and (b) were labeled, the peak (a) labeled with the Miller index.
4.	Line143-145: "X-ray diffraction (XRD) was used to determine the crystal structure of the sponge supported sodium was obtained by impregnation method, which is shown in Fig. 2." Sentence needs to be revised for English.	211	The sentence in revised manuscript has been improved for its clarity
5.	Line 146: What do you mean by "hump of 2"? Also Do you mean "the presence of a large reflection" instead of "the present large reflection" ?	212	The sentence corrected as "showed a hump at 2θ ranging from 16° to 40°, and the presence of large reflection at 22.45°, indicating the amorphous state of silica particles"
6.	Line 148: "which shows strong BOARD peaks", do you mean BROAD instead of BOARD? Also the English of this sentence needs fixing.	221	Yes, it is broad, corrected for English
7.	Line 156 on Fig. 2c, what is the decrease in the mass below 100°C attributed to? The weight	228	The weigh loss and the respective temperature range has been corrected and

	<p>loss described in the manuscript does not match the results shown in Fig. 2c. From 100 - 175oC, the weight dropped from approx. 97.2% to about 95.7%, and from 200-360oC the weight dropped from 95% to 91%. This weight change between 200-360oC is more than just "a little weight loss" as stated in the discussion. Also from 650- to 850oC the graph shows a decrease in weight remaining from approx. 88% to 81%. This change of only 7% is a lot less than the 16.3% quoted in the manuscript. The authors need to be clear as to the exact temperature range and corresponding weight loss or perhaps the authors have inserted a different TGA graph?</p>		<p>rephrased for the clear description.</p>
8.	<p>Line 163-165: "The BET surface area and pore volume decrease from 11.77 to 5.08m²/g and the pore volume from 0.15-0.08 cm³/g of the waste sponge and sodium silica, respectively." This sentence needs to be revised as it seems to state that the decrease from 11.77 to 5.08m²/g is for the waste sponge and 0.15-0.08 cm³/g is for the sodium silica. Perhaps the authors meant to say "The loading of the Si-sponge with sodium resulted in a decrease in both the BET surface area and pore volume from 11.77 to 5.08m²/g and 0.15-0.08 cm³/g, respectively.</p>	231	<p>The sentences have been rephrased for clear argument</p>
9.	<p>Fig. 3: The SEM image of Si-sponge with Na (Fig. 3b) is magnified ten times more compared to the SEM image for Si-sponge without Na(Fig. 3a). If the authors want to show the differences in porosity, the same magnifications should be</p>	233	<p>The same magnification for Si-waste sponge and Si-waste sponge with Na has been added in section 3.1, Figure 3a and b</p>

	used.		
10.	<p>Line 168-169: Also I do not understand what the authors mean by "The surface of catalyst creates porous materials(Fig. 3b)"</p> <p>Also the sentences that follows doesn't make sense: "The morphology shows the homogenous spherical catalyst, having a smooth surface and similar to each other increases the surface area.There are branches in the bundles of spicules which give the sponge its porous structures"</p> <p>-This also contradicts the BET surface area results. The authors state that the smooth surface of the spherical catalyst increases the surface area, but the BET results show a decrease in the surface area for Na loaded Si-sponge.</p>	109	The sentences have been rephrased to match with the micrograph
		240	
		259	
11.	-Also, the authors say there are branches in the bundles, I do not see these branches in the SEM image. The needle shaped spicules look rather smooth.		Revised
12.	<p>What is the stirring speed used for methyl ester conversion? If the authors want to compare mechanical stirring and sonication, the effect of stirring speed on methyl ester conversion needs to be studied. Or choose a stirring speed that gives the same mechanical energy as the ultrasound power used. This can be done by measuring the calorimetric power.</p> <p>Fig. 4a was discussed in section 3.2 and then Fig. 4b was discussed in section 3.3. It is</p>	112	<p>The similar mechanical energy is produced at about 300 rpm. Additional study has been carried out at 300 rpm and reported in section 2.4</p> <p>The figures have been separated</p>

	<p>better to separate these two graphs into Fig. 4 and Fig. 5 if they are going to be in different sections.</p>		
13.	<p>Also the caption is incorrect, (a) should be reaction duration on ME conversion and (b) should be catalyst amount. Also the wt% of catalyst used in the reaction duration should be stated in the caption. Similarly, the duration used in the variation of catalyst amount should be stated in the figure caption.</p>	276	<p>The caption has been corrected. The implementations of catalyst amount and reaction duration have been added.</p>
14.	<p>Also it is unclear was the catalyst used the Na loaded Si-sponge?</p>	112	<p>Yes the catalyst is Na impregnated in waste sponge (Na-waste sponge) and labelled as SWSS in revised manuscript</p>
	<p>The authors does not state how temperature was controlled. It is stated the reaction temperature was 55 °C, however sonication of greater than 10min will increase the temperature significantly more than mechanical stirring.</p>	151	<p>Included in section 2.4, therefore the temperature was controlled and maintained at the desired level (± 0.1 °C) by water circulating from a thermostated bath by means of a pump.</p>
	<p>Discussion on Fig.4b in section 3.3: The authors claim that the reasons for the ME conversion to remain unaffected at catalytic material above 3% were due to "higher power consumption required to compensate for an adequate stirring speed and the solution becoming more viscous." Does the viscosity vary with increasing catalytic material? It is unclear why more material will require higher stirring speed? The plateau is also reached at 3wt% for the sonicated system. Does that mean there is insufficient mixing for ultrasound when there is too much material?</p>	62	<p>Obviously there will be some effect on stirring of too much material is used.</p>
		79	

15.	<p>Other explanation for effect of ultrasound needs to be taken into account.</p> <p>a)Wetting of the pores within the catalytic material. Is the catalytic material fully hydrated? If not, then it is possible with ultrasound there is more wetting of the pores, hence more surface area is exposed to the reactant.</p>	249 253 254 278	The suggested explanation is added in section 3.3 (with a great appreciation to the reviewer)
16.	<p>b)Fig. 4a shows that a maximum ME reached for US is approx 98.4% and 87.9% for MS. This corresponds to the maximum reached in Fig. 4b. So perhaps at 3wt% catalyst the maximum ME has already been reached therefore further increase in the catalyst material will not increase ME?</p>	288 293 325	Agree
17.	<p>c)Increase in temperature by sonication can increase reaction rate if the temperature was not controlled.</p> <p>Description given in the start of section3.4 on kinetic studies should be given in a separate theory section or appendix and not in the results and discussion section.</p>	109	<p>The temperature was controlled</p> <p>Separated as section 2.6</p>
18.	<p>Section 3.5 estimation of energy consumption for process. This section is only a small paragraph and the authors only quoted what Gude et al. reported, that is transesterification using a hot plate requires much more energy than ultrasonic process. Either put this in introduction or combine with other section or measure the energy consumption used in the current study for US and MS.</p>	112 and 122 125	Section 3.5 is removed, and the reference (Gude et al.) was added in section 1.1 introduction
18.	The authors show that Na-		

<p>19.</p> <p>20.</p> <p>21.</p>	<p>sponge can tolerate up to 6% water content and FFA, but what % of water and FFA are usually present in waste liquids?</p> <p>English for the following phrases/sentences needs to be corrected: Line188: "The very difference conversion" Line193: " causing them to suspend each other easily" Line194: "will be strongly accelerating the reaction rate" Line 212: "the highest conversion of WCO under MS WAS observed WAS lower" English. Line 221: "with the presence catalyst" correct to "with the presence OF catalyst". Line273: "...which clearly shows that the reaction rate by US method higher than that of MS" Line 277: "...rate constant is depending strongly on temperature" Line 315: "...is usually considered known to inhibit the reaction"</p>	<p>79</p>	<p>The water and FFA content of the oil is mentioned in section 2.1</p> <p>The english sentences has been improved</p>
<p>22.</p>	<p>Reviewer #2: The efficiency of ultrasound irradiation or the attenuation effects on the cavitation activity depends on the reactor geometry, authors should describe the reactor in the experimental set up. Moreover, the amount of oil used for the experiments is too small (5 ml of oil in test tube). Data in a bigger scale at least 50 ml are necessary to imagine the feasibility of the protocol. Please mention previous papers (i.e. Cintas Ultrason. Sonochem. 2010, 17(6), 985-989)</p>	<p>79</p>	<p>The experimental set up include in section 2.4</p> <p>The sample size has been increased in bigger scale (section 2.4) The suggested reference has been added</p>

23.	The amount of the reactant used and also the conditions for reaction in US and MS reactors were different. US reactor was tested at 55°C while MS reactor at 65°C as mentioned in the experimental part. These data cannot be compared!	348	The temperature under both US and MS studied from 50 to 60 °C.
24.	The authors should remark the repeating times of the experiment and it would be better if the authors use the average value and the standard deviation to plot in the graph in Fig.4, 6 and 7 to show the accuracy of the results.		The data was repeated three times and the data in the manuscript is the average as mentioned in section 2.4. The graph in figure 4, 6 and 7 is average value from three time experiment and the standard deviation has been added in the revised manuscript
25.	<p>WCO was used as the raw material in this work. In general, the pretreatment step was performed before to eliminate the FFA in WCO resulting in the soap formation. However, the authors ignore this aspect, I would expect some problems in section 3.2 and 3.3?</p> <p>P.13 line 274, the unit of the rate constant is min⁻¹ but it is s⁻¹ in Table 2 what is the exactly unit of this value? and while it is not mentioned the rate constant from MS reactor obtained in this work in Table 2? Are there any details or more statements from other works that support the results from this work?</p> <p>P.15 1st paragraph, it has been mentioned that US reactor can reduce the energy consumption and this is a very important aspect to scale-up the process in the real application. It is mandatory to describe the energy consumption to produce biodiesel comparing the</p>		<p>The FFA content in our feedstock (WCO) is lower than 2.5%. The solid base catalyst still tolerates if the FFA is lower than 2.5% (Boro et al., 2012). As such pretreatment is not performed.</p> <p>The unit is corrected to min⁻¹</p> <p>The total energy consumption calculation according Cintas et al. (2010) Ultrason. Sonochem., 17, 985-989 and Liu et al.(2014) Ultrason.Sonochem., 20, 708-714: US: 80 Watt MS: 501 Watt</p>

	<p>conventional reactor?</p> <p>P.15 in the Tolerance towards water and FFA of Na-Sponge section. The effect of water and FFA on the activity of Na-Sponge was examined. Authors did the experiment by adding some percentage of water or FFA in the reactant (oil). Then, what's kind of oil in this part? is it the WCO as mentioned before? If it is, as we know that there are also some FFA in WCO so it should be better to mentioned this before. Otherwise, if it is another kind of oil it should be mentioned to avoid confusion.</p> <p>P.16 in the biodiesel section I read: "The result of the evaluation shows that the final product meets all the tested parameters (ester content, density, viscosity, and acid value)". However, it can be seen in Table 3 that the viscosity does not meet the standard value.</p>		<p>Yes, the oil in this part of experiment is waste cooking oil (FFA is 1.77%). The FFA content of WCO has been added in section 2.1</p> <p>The non-confirming viscosity value is for the unrefined biodiesel. However for the final product (after methanol has been stripped via rotary evaporator) the viscosity meets the specification. The error is much regretted.</p>
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Draft of the Revised Manuscript:

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

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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 (WCO) 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

(ME) 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 MeOH:oil, 9:1; catalyst, 3 wt.% and reaction duration of 30 min as optimum reaction conditions. The catalyst is able to tolerate free fatty acid (FFA) and moisture content up to 6% and 8%, respectively. In addition, the catalyst can be reused for seven cycles while maintaining the ME 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.

Keywords: Transesterification, Heterogeneous catalyst, Ultrasound, Waste cooking oil, Biodiesel

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 0.7–1.0M tonnes of waste oil, Turkey 0.35M tonnes and Canada 0.12M tonnes, 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].

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 of the 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 (SiO_2 , MgO, Al_2O_3 , and $\text{Mg}(\text{Al})\text{O}$) and they concluded that Li impregnation onto $\text{Mg}(\text{Al})\text{O}$ as the most active catalyst and generate higher conversion. Kumar et al. [10] successfully converted *Jatropha curcas* oil using Na/SiO_2 and ultrasonication reduced the reaction time comparing to the conventional batch processes and we found 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 [12,13,14] 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 methyl ester 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 assistant and with comparison of 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 $0.28\% \pm 0.04$ of moisture content). Waste sponge (WS) was collected from Tanjung Lumpur shore in Kuantan, Malaysia, and were cut into small pieces ($0.5\text{--}1.0$ cm³), cleaned with water several times and air-dried for 24 h. The WS fragment was then calcined at 500 °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 ($H_{\text{p}} = 8.2$), 2,4-dinitroaniline ($H_{\text{p}} = 15.0$) and 4-nitroaniline ($H_{\text{p}} = 18.4$), 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 °C for 2 h. Lastly, the mixture was dehydrated at 200 °C for 30 min, and then calcined at 500 °C for 3 h.

2.3. Material characterization

The SWS and SWSS were identified by X-ray diffraction (Rigaku) with Cu $K\alpha$ X-ray as a source. FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of catalyst and support at $400\text{--}4000$ cm⁻¹ range. The catalyst was examined by thermogravimetric analysis (TGA) using Mettler Toledo TGA instrument, from 25 to 900 °C with 10 °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 °C and the adsorption of N₂ was measured at -196 °C. The size and morphology of the catalyst were observed by FE-SEM (JSM-7800F). The basicity of catalyst (H_{p}) was determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein ($H_{\text{p}} = 8.2$), 2,4-dinitroaniline ($H_{\text{p}} = 15.0$) and 4-nitroaniline ($H_{\text{p}} = 18.4$). 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 colour 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 loses of methanol due to the evaporation and thermocouple thermometer. The ultrasonic reaction was performed using Branson (USA) ultrasonic bath (42 kHz) with the power input 235 W and the exact power dissipation at 40 W determined calorimetrically [19,20,21]. The bath was filled with distilled water up to 1/3 of its volume. The temperature was controlled and maintained at the desired level (± 0.1 °C) by water

circulating from a thermostated bath by means of a pump. The constituent of 50 ml oil [22], desired amount of catalyst and methanol, the above mixture was immersed in an ultrasound (US) water bath. The effect of catalyst amount (1–9 wt.%), reaction duration (10–80 min), the addition of water (2–17%) and FFA (3–9%) on the conversion of triglycerides to biodiesel were investigated (in this study oleic acid was used to adjust the FFA content), with the temperature ranging from 50 to 60 °C. The conversion of WCO to 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 the liquid phase under atmospheric pressure, at temperature ranging from 50 to 60 °C with continuous stirring. After the transesterification, the reaction mixture was allowed to cool. Then, to further separate the product (methyl ester 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 x diameter 0.25 mm x film thickness 0.25 μm) using methyl heptadecanoate as an internal standard. Helium was used as the carrier gas with a linear velocity of 40 cm/s. The oven temperature was programmed at 190 °C, held for 2 min, then ramped at 10 °C per min until it reached 230 °C, and with a final hold time of 8 min. The sample volume of 0.6 μL 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 as following formula:

$$\text{Conversion (\% ME content (\%))} = \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{m} \times 100$$

Where

ΣA = total peak area of ME from C_{12:0} to C_{18:1}

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

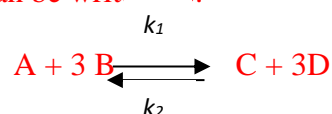
m = mass, in mg, of the sample

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

In order to examine the potential of catalytic utilization, 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 continue 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, methyl esters it 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 1 methanol; D is the methyl ester and C is the glycerol.

The rate determination step in transesterification reaction starts with the attacks on the carbonyl carbon atoms 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 methyl ester 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 methyl ester (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_f 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:

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

The transesterification model is based on the major assumptions above. The 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:

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

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

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

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

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

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

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

Where, k is the reaction rate constant. The rate constant 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 equation 9, x is the ME content, t is the reaction duration, and the rate constant (k) 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) shown in Fig. 1. The typical one, with the broadband at about 3410-3470 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) 1020-1100 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 503-687 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 impregnation of sodium and the silica shell was successfully bound.

The powder XRD pattern of SWS and SWSS is shown in Figure 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 and Proctor, (2000) [25] indicating the disordered structure mainly due to amorphous SiO_2 . In Fig. 2(b), the intense diffraction peaks found at 25.26° - 65.93° 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 the 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 $^\circ\text{C}$, 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 to 380 $^\circ\text{C}$ is attributed to the removal of organic compound from the SWS and the decomposition of sodium hydroxide (melting point: 318 $^\circ\text{C}$). The third endothermic region, the ranging from 650 to 850 $^\circ\text{C}$, has a weight loss of 8.81%. The 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 m^2/g and the pore volume from 0.15 to 0.08 cm^3/g of the SWS and SWSS, respectively. The morphology of SWSS shows the homogenous surface (Fig. 3b), having a smooth 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 colour from colourless to pink (phenolphthalein) and from yellow to mauve (2,4-dinitroaniline) but failed to change the colour of 4-nitroaniline. The basic strength SWSS is in the range: $15 < \text{H}_- < 18.4$. On the other hand, SWS was failed to change the colour of all Hammett indicators. Therefore, SWS does not have basic properties and suitable to be uses 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 10 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 $^\circ\text{C}$ ME content under US increased within the first 10 min. Further increase in the reaction time to 30 min, the content increased 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. The direct transesterification reaction using US is the most

efficient reaction (Fig. 4). On the other hand, it is noted that by using MS, the content, reached the peak ($87.7\pm 0.6\%$) at 80 min.

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 direct transesterification using ultrasound assistant. The ultrasound could affect the content ME on the short time reaction, 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. The reasons for the ultrasound being the most efficient technique were explained above.

3.3. Effect of catalyst amount

The amount of catalyst was varied in the range of 1-9 wt.%. As shown in the Fig. 5, a plot of catalyst amount vs. ME content for the 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 $55\text{ }^{\circ}\text{C}$, for 80 min). The transesterification depends on the amount of catalyst used. Increasing the amount of catalyst from 1 to 3% will increase ME content significantly. This is because the contact opportunity of the catalyst and the reactant, directly affect the reaction speed and the content. 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 a previous report 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 methyl esters and the separation of esters became difficult [28,29]. Another explanation is due to the wetting of the pores within the catalytic material, hence more surface area is exposed to the reactant. Therefore, the catalyst concentration is an influencing factor on the amount of methoxide ions formed. As a result, the larger the amount of catalyst, the faster the reaction proceeds. However, the highest ME yielded using MS ($87.9\pm 0.6\%$) is lower than that of US ($98.4\pm 0.4\%$) at 3 wt.% catalyst. By using ultrasound, it enhances the mass transfer between catalyst and reactants as well as maintains the required kinetic energy in the reaction media. Dispersion due to ultrasonic sound increases the surface area of catalyst available to the reactants [30,31]. 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 $60\text{ }^{\circ}\text{C}$ 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 content is achieved. The average overall reaction rate constant at different temperatures can be calculated according to 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 $55\text{ }^{\circ}\text{C}$, 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:

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

where Ea is the activation energy (J/mol), define as the minimum energy required to start a chemical reaction, R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), 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. The activation energy (Ea) and frequency factor determined from Fig. 6b. Accordingly, the values of Ea and A of ultrasound and mechanical stirring were determined as 33.45 kJ/mol ; $1.95 \times 10^4 \text{ min}^{-1}$ and 59.81 kJ/mol ; $9.70 \times 10^7 \text{ min}^{-1}$, respectively. Compared to the activation energy of acid and base catalysts catalyzed transesterification of soybean oil with mechanical stirring, which is in the range of $33\text{--}84 \text{ kJ/mol}$ [17]. The activation energy of 33.45 kJ/mol was suggesting a lower energy barrier was required for thus proposed reaction, and indicating that the reaction can be carried out under mild temperature and pressure conditions.

Ultrasound is one of the factors that increase the collisions in the reaction process. Ultrasound increases the frequency of collisions between reactant molecules that accelerate the reaction to occur perfectly. In accordance with Arrhenius equation, greater the collisions, the greater the reaction rate constant values, so as in this case, US is very essential since oil and methanol are not readily miscible solutions. Methyl ester content and Ea that were reported from previous studies are presented in Table 2 [32,33,34,35,36,37,38,39]. 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 Ea is observed in the previous study using US. However, the work utilization of NaOH as a homogeneous catalyst has a lower Ea , whereas in our work, we used heterogeneous catalyst. Moreover, much higher Ea is observed in mechanical stirring with different catalyst was used. 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 to reduce 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 methyl esters separation thereby lowering the content. In order to examine the effect of water and FFA on the activity of SWSS, 2–17 wt.% water and 3–9 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 ($92.8 \pm 0.5 \%$) 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 H_2O 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 $78 \pm 0.5\%$, however, at 9% FFA content reduced to about $29 \pm 0.6\%$ (This observation indicated 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. 7,

show that the SWSS can be used up to seven cycles with maintaining the activity at considerable ME content (86.3%). After the transesterification reaction is completed, the SWSS was decanted with simple 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 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 used cooking oil mainly comprises of methyl esters of myristic acid 0.92%, palmitate acid 28.00% followed by 1.91% palmitoleic, 3.95% stearic, 35.50% oleic, and 12.34% linoleic. 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 for the purpose as a fuel.

4. Conclusion

In this work, silica waste sponge with sodium (SWSS) was successfully utilized as a low-cost feedstock to produce methyl ester (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 with 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.

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Figure captions

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

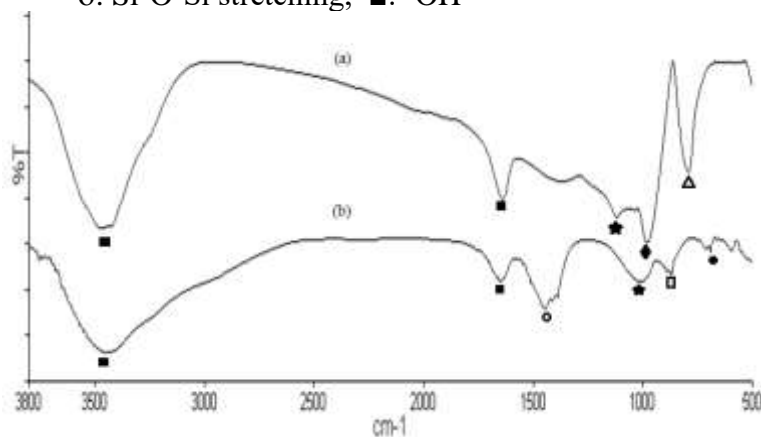


Fig. 2. XRD pattern of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium; (c). DTG/TGA of silica waste sponge with sodium.

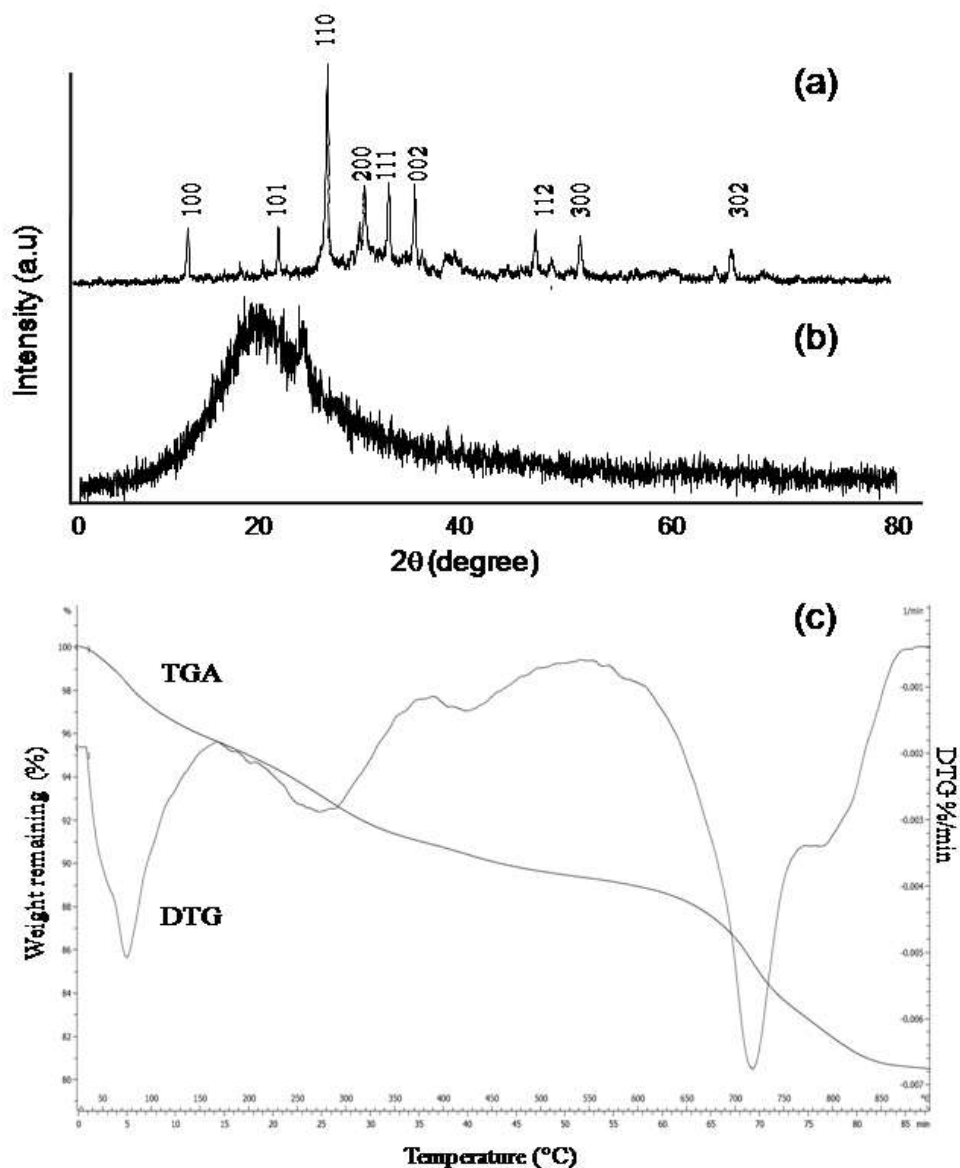


Fig. 3. SEM micrograph of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium.

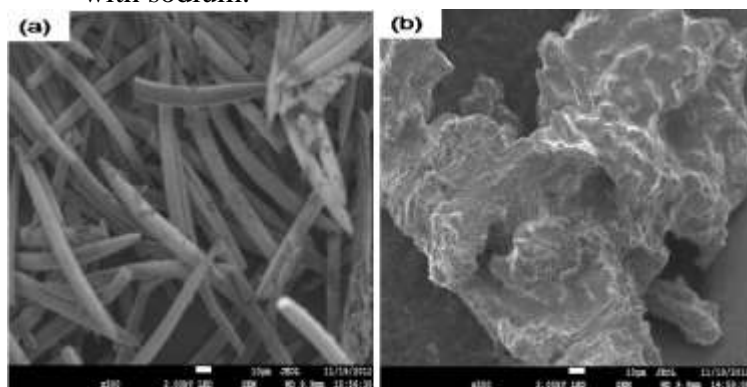


Fig. 4. Effect of reaction duration (10–80 min) on methyl ester content (reaction conditions: catalyst amount, 3 wt.%; MeOH:oil molar ratio, 9:1; reaction temperature 55 °C).

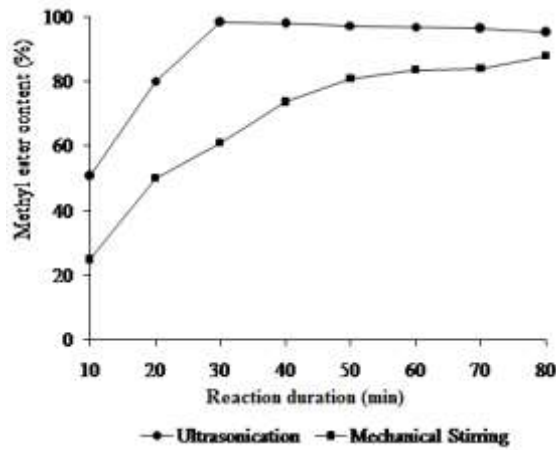


Fig. 5. Effect of catalyst amount (1–9 wt.%) on methyl ester content (reaction conditions: MeOH:oil molar ratio, 9:1; reaction duration 80 min ; reaction temperature 55 °C).

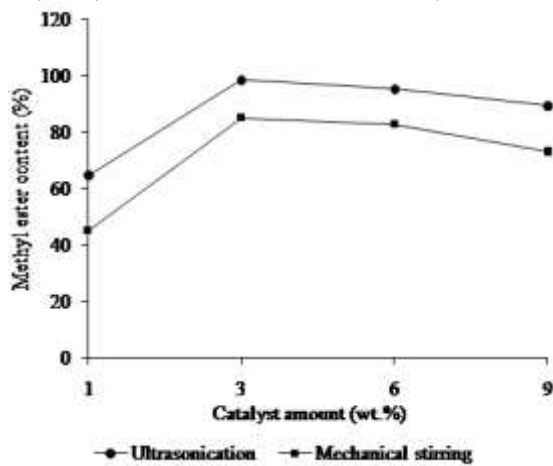


Fig.6. (a) $-\ln(1-x)$ vs. time plot for the ultrasound, (b) $-\ln(1-x)$ vs. time plot for the mechanical stirring, (c) Arrhenius plot $\ln k$ vs. $1/T \times 10^{-3}$ for ultrasound, (d) Arrhenius plot $\ln k$ vs. $1/T \times 10^{-3}$ for mechanical stirring (reaction conditions: catalyst concentration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

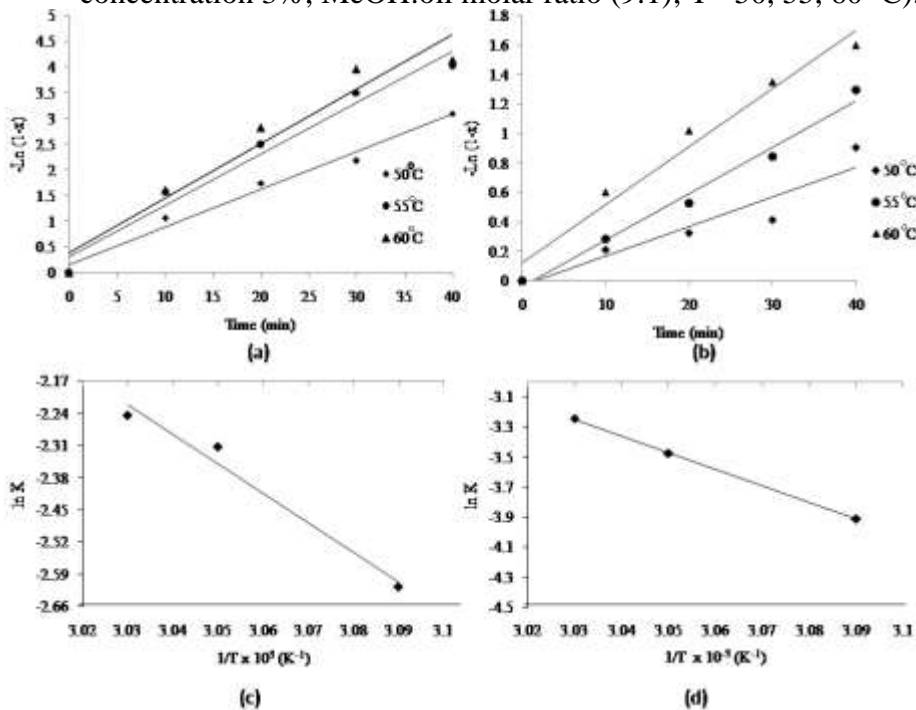


Fig. 7. Effect of (a) water content and (b) FFA toward the methyl ester content (reaction conditions: catalyst concentration 3%; temperature 55 °C; MeOH:oil molar ratio, 9:1).

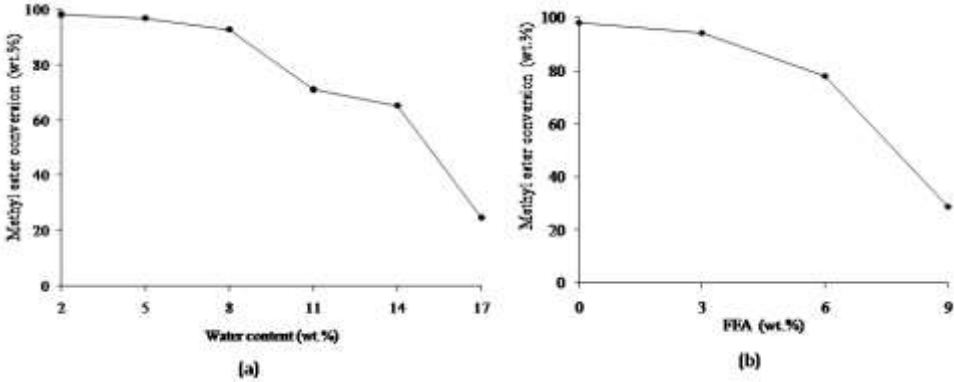
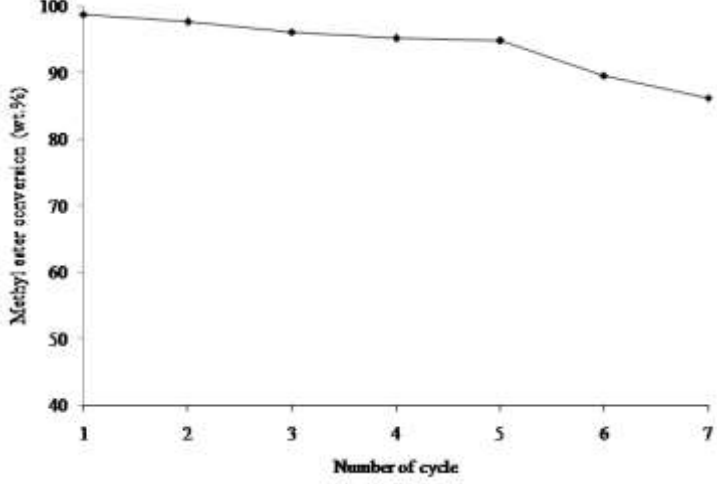


Fig. 8. Reusability of the catalysts (reaction conditions 3% catalyst; MeOH:oil molar ratio (9:1); 30 min at 55 °C).



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

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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 MeOH:oil, 9:1; catalyst, 3 wt.% and reaction duration of 30 min as optimum reaction conditions. The catalyst is able to tolerate 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.

Keywords: Transesterification; Heterogeneous catalyst; Ultrasound; Waste cooking oil; Biodiesel

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].

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 $0.28\% \pm 0.04$ of moisture content). Waste sponge (WS) was collected from Tanjung Lumpur shore in Kuantan, Malaysia, and were cut into small pieces ($0.5\text{--}1.0$ cm³), cleaned with water several times and air-dried for 24 h. The WS fragment was then calcined at 500 °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 ($H_{\text{L}} = 8.2$), 2,4-dinitroaniline ($H_{\text{L}} = 15.0$) and 4-nitroaniline ($H_{\text{L}} = 18.4$), and methyl heptadecanoate (as an internal standard) GC grades (>99.1%). Methanol (anhydrous, ≥99.8%), and hexane (anhydrous, ≥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 Na⁺:Si molar ratio of 2:1. The mixture obtained was then stirred and heated at 90 °C for 2 h. Lastly, the mixture was dehydrated at 200 °C for 30 min, and then calcined at 500 °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 400–4000 cm⁻¹ range. The catalyst was examined by thermogravimetric analysis (TGA) using Mettler Toledo TGA instrument, from 25 to 900 °C with 10 °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 °C and the adsorption of N₂ was measured at 196 °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 ($H_{\text{L}} = 8.2$), 2,4-dinitroaniline ($H_{\text{L}} = 15.0$) and 4-nitroaniline ($H_{\text{L}} = 18.4$). 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 loses 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 (± 0.1 °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 to 60 °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 to 60 °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 × diameter 0.25 mm × film thickness 0.25 μ 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 °C, held for 2 min, then ramped at 10 °C per min until it reached 230 °C, and with a final hold time of 8 min. The sample volume of 0.6 μ 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

ΣA = 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

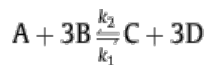
m = mass, in mg, of the sample

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; ~~D is the ME and C is the glycerol~~; 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 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:

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

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:

$$r = -\frac{d[A]}{dt} = k[A] \tag{2}$$

$$\frac{d[A]}{[A]} = -kdt \tag{3}$$

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

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

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

$$\ln [A_0](1-x) \Big|_0^x = -kt \Big|_0^t \tag{6}$$

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

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

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

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

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 3410–3470 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) 1020–1100 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 503–687 cm^{-1} are attributed to the vibration of the Na⁺–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.

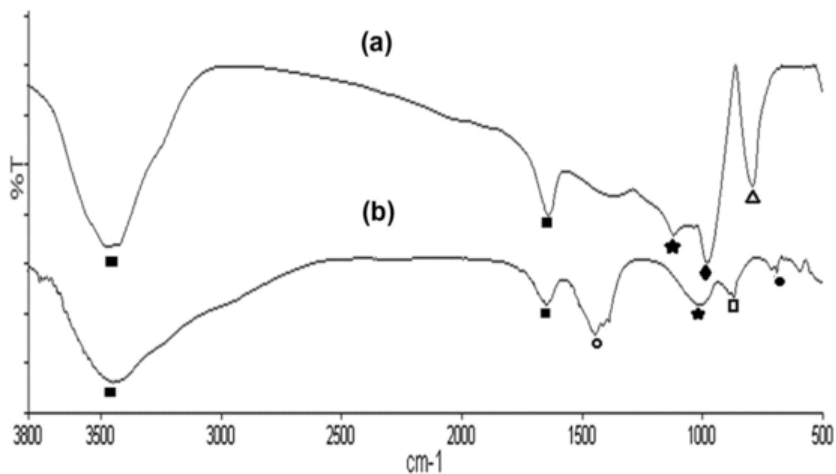


Fig. 1 FTIR spectra of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium; ●: Na–O, △: O–Si–O, □: (Si–O–Si)–(Na+–O), ◇: Si–O, ★: Si–O–Si bending, ○: Si–O–Si stretching, ■: –OH.

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 Kalapathy et al. and Proctor [25] indicating the disordered structure mainly due to amorphous SiO₂. In Fig. 2b, the intense diffraction peaks found at 25.26°–65.93° correspond to the Miller indexes (1 0 0),

(1 0 1), (1 1 0), (2 0 0), (1 1 1), (0 0 2), (1 1 2), (3 0 0) and (3 0 2) were confirmed as Na₂SiO₃ (SWSS).

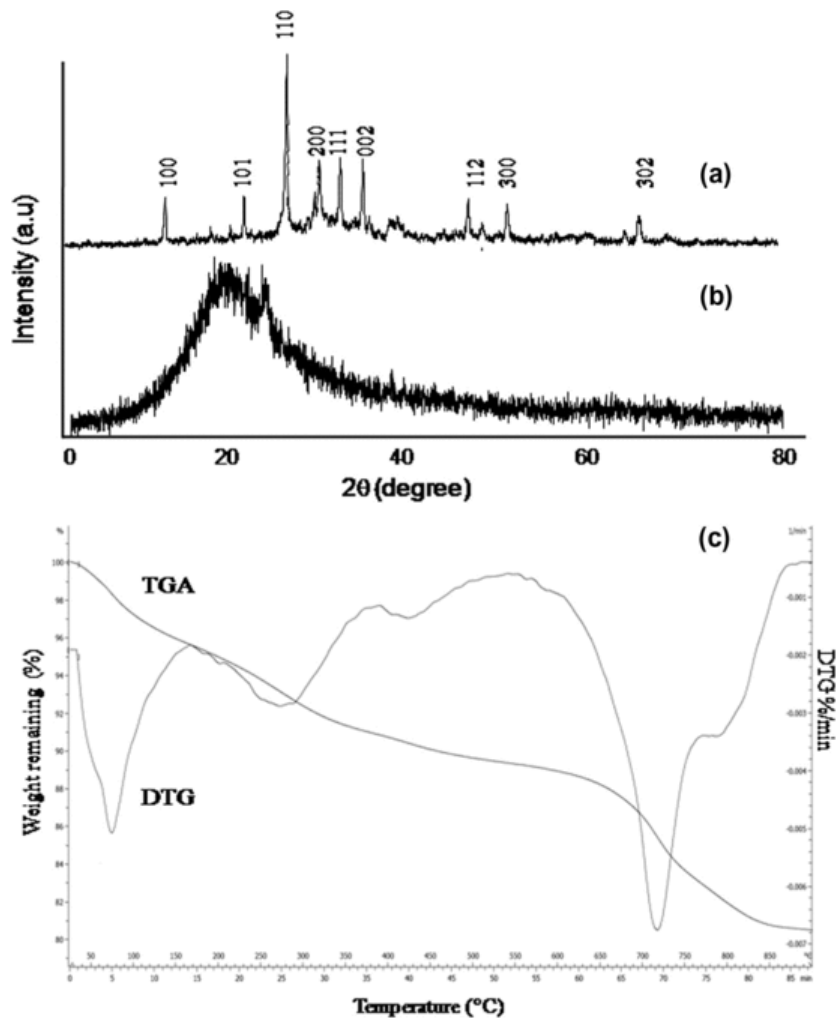


Fig. 2 XRD pattern of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium; (c). DTG/TGA of silica waste sponge with sodium.

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 Na₂SiO₃ particles. The second region, the weight loss (4.66%) at temperature around 180 to 380 °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 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 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 of 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.

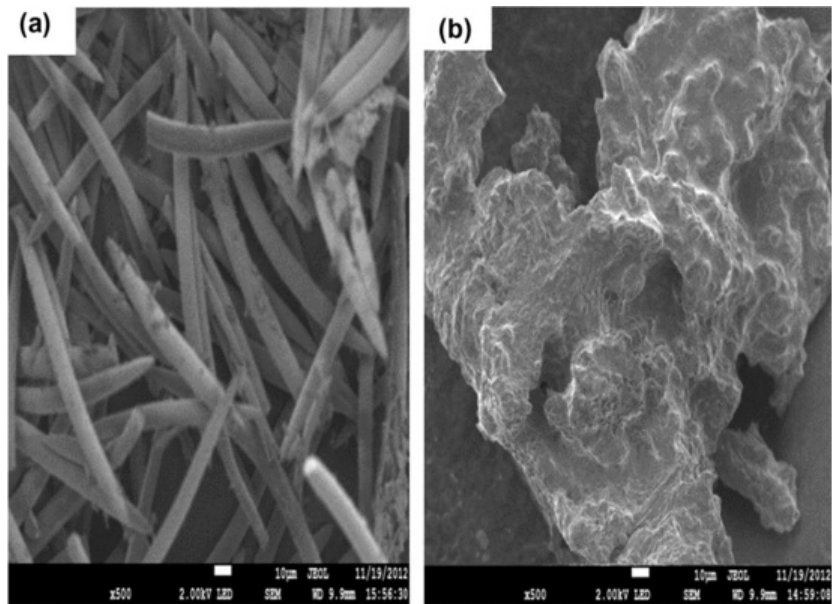


Fig. 3 SEM micrograph of (a) silica waste sponge without sodium and (b) silica waste sponge with sodium.

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.

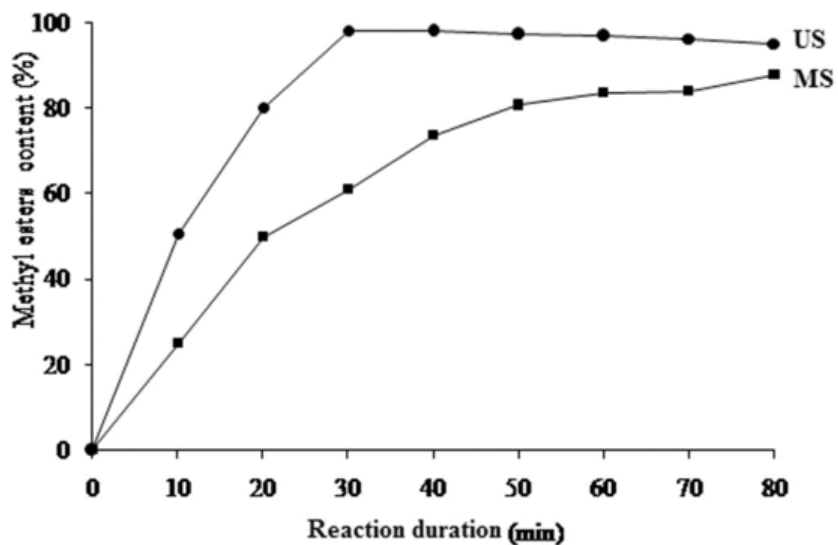


Fig. 4 Effect of reaction duration (0–80 min) on methyl esters content (reaction conditions: catalyst amount, 3 wt.%; MeOH:oil molar ratio, 9:1; reaction temperature 55 °C; US: ultrasound, MS: mechanical stirring).

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 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.

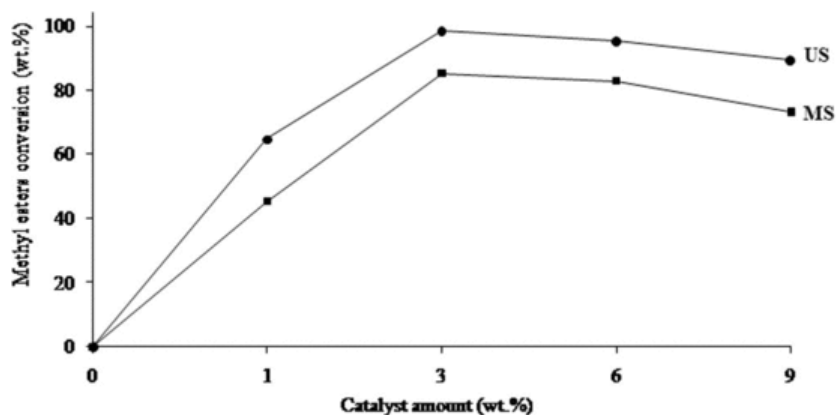


Fig. 5 Effect of catalyst amount (0–9 wt.%) on methyl esters content (reaction conditions: MeOH:oil molar ratio, 9:1; reaction duration 80 min; reaction temperature 55 °C; US: ultrasound, MS: mechanical stirring).

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 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.

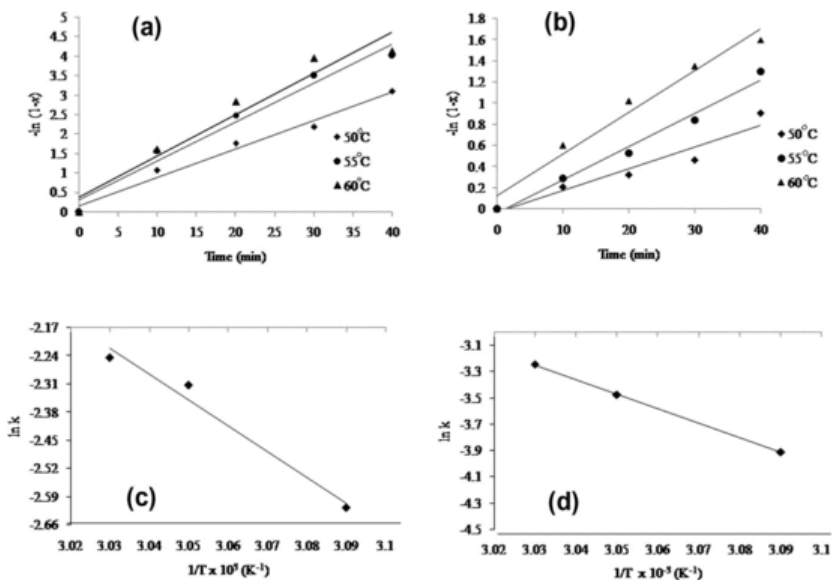


Fig. 6 (a) Plot of $-\ln(1-x)$ vs. time plot for the ultrasound, (b) Plot of $-\ln(1-x)$ vs. time plot for the mechanical stirring, (c) Arrhenius plot of $\ln k$ vs. $1/T \times 10^{-3}$ for ultrasound, (d) Arrhenius plot of $\ln k$ vs. $1/T \times 10^{-3}$ for mechanical stirring (reaction conditions: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

Table 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 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:

$$k = Ae^{-\frac{E_a}{RT}}$$

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 ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), 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 ; $1.95 \times 10^4 \text{ min}^{-1}$ and 59.81 kJ/mol ; $9.70 \times 10^7 \text{ min}^{-1}$, respectively. The result under heterogeneous catalyst is comparable to E_a of homogeneous catalysts under mechanical stirring, ranging from 33 – 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.

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.

Table 2 Comparative study in activation energy and reaction rate from different technique in the optimum condition for methyl ester formation 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	CaOMeCa(OCH ₃) ₂	1	9:1	90	60	0.0033	71.25	>90	[24][32]
	Jatropha	NaOH	1	9:1	30	50	0.0910	16.95	>93	[25][33]
	Sunflower	KOH	0.7	7.5:1	50	40	–	46.20	>90	[26][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	[27][35]
	Jatropha	NaOH		21:1	60	105		152	>80	[28][36]
	Waste frying	CaO	2	6.03:1	480	60		79	99.5	[29][37]
	Waste cooking	K/CaO	7.5	12:1	70	65	0.0620	54	98	[30][38]
	Soybean	CaO–La ₂ O ₃	5	20:1	60	58		49.3	94.4	[31][39]

^a Conv = methyl ester conversion.

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].

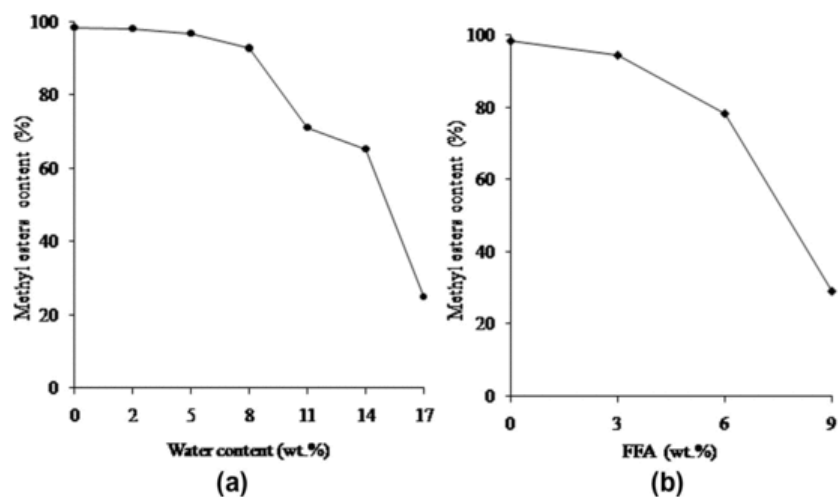


Fig. 7 Effect of (a) water content and (b) FFA toward the methyl esters content (reaction conditions: catalyst concentration 3%; temperature 55 °C; MeOH:oil molar ratio, 9:1).

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 Fig. 7, 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 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 $98.4 \pm 0.4\%$. The output of GC analysis proved that waste cooking oil mainly comprises of ME of myristic acid 0.92%, palmitate palmitic acid 28.9934.46% followed by 40.91% palmitoleic, 3.95% stearic, 35.5046.40% 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 (Fig. 8).

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	$\text{mm}^2 \text{s}^{-1}$	3.8	3.5–5.0
Acid value	mg KOH g^{-1}	0.3	0.5 (max)

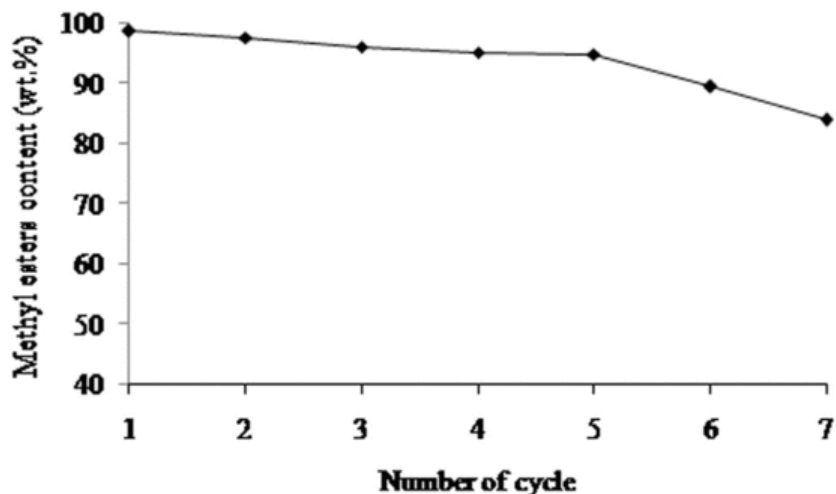


Fig. 8 Reusability of the catalyst (reaction conditions 3% catalyst; MeOH:oil molar ratio (9:1); 30 min at 55 °C).

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 $98.4 \pm 0.4 \text{ wt.}\%$ 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.

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Highlights

- Sponge as a potential waste-derived catalyst support.
- Ultrasound-aided transesterification for 98.4% conversion in 30 min.
- Na-supported sponge was successfully used as a catalyst.

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