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## Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst

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### ABSTRACT

Investigation was conducted on three alkali metals (Li, Na, and K) supported by rice husk silica as catalysts for methyl esters production. A simple pseudo-heterogeneous transesterification process of used cooking oil with methanol was conducted to produce methyl esters using calcined alkali metal supported rice husk silica as a solid catalyst. Alkali metal silicate catalysts showed longer lasting activity than the traditional alkali catalysts. The optimum conditions for the process were: alkali metals silicate calcination temperature 500 °C, time 3 h; catalyst amount 3%; methanol to oil molar ratio 9:1; and a reaction temperature of 65 °C. The process was able to transesterify oil to methyl esters in the range of 96.5–98.2% in 1 h for all series. The catalyst is able to tolerate free fatty acid and moisture up to 1.25% and 1.75%, respectively. The catalyst was easily separated from the reaction mixture by filtration and able to reuse six times. The final product met the selected biodiesel fuel properties in accordance with European Standard (EN) 14214.

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### 1. Introduction

The global oil consumption in 2010 grew by 2.7 million barrels per day (b/d), or 3.1%, to reach a record level of 88 million b/d, while the fossil fuel reserve is depleting [3]. Furthermore, petroleum-based activities are one of the main causes of carbon dioxide (CO<sub>2</sub>) emission to the atmosphere. The transportation and industrial sector are almost entirely dependent on petroleum-derived fuels, which accounted for respectively 12.2 and 4.6 million b/d of oil consumption in January 2012 [8]. This scenario has driven the EU, the USA, Brazil, and parts of Asia to import renewable energy.

Biodiesel is one of the energy sources that can be used as an alternative fuel for diesel engines. Such data demonstrates the global awareness of the limitations of the fossil fuel and the quest for new energy alternatives. The common feedstocks for biodiesel are vegetable oils and animal fats. Thus, it can be said that the major lipid for biodiesel production comes from edible oils. However, as feedstock accounts for approximately 80% of the operational cost

[9], the feedstock price has a huge effect on the overall production cost. In addition, consuming edible oil for biodiesel competes with food supply and has a definite impact on global food security and land.

One way to reduce the production cost is by utilizing used cooking oil (UCO). The source is abundant supply, relatively inexpensive and the utilization offers benefits on environmental conservation [25]. In addition, it is low in price in terms of its operational cost and feedstock, and recycling technology can be applied during the process. However, the UCO contains free fatty acid (FFA) and moisture. FFA content in waste oil should be as low as possible for alkali-catalysed transesterification and alkali catalysts will readily react with FFA to form soap if FFA content above 2.5% present in the reaction media [2]. This reaction is highly unfavourable because it will deactivate the catalyst from accelerating the transesterification reaction. Furthermore, too much soap in the product can drastically reduce the methyl esters (ME) yield and inhibit the subsequent purification process of biodiesel, including glycerol separation and water washing. Recently, the production of biodiesel by transesterification method using solid catalysts has become more favourable compared to others and has been scaled up to industrial level. Solid base catalysts bring several advantages, such as the catalyst can easily be separated from the reaction mixture, no washing is required, easy regeneration, less

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corrosive character of the product, low in cost and it is a more environment friendly approach.

There is a very limited work on comparing alkali metals supported by silica from rice husk ash (RHA) as a catalyst in transesterification. RHA was utilized as a catalyst support for Li in transesterification of soybean oil [6]. RHA as biomass has promising role with high silica content (87–99%) and available abundantly, being a low cost waste source as amorphous silica precursors [24]. Each tonne of rice produces 200 kg of rice husk, and with the complete combustion will be generated 40 kg of RHA [21]. Recently, about 146 million tonnes of RHA was produced annually worldwide [10] and efforts are being made to overcome this environmental issue by utilization this material as support. Accordingly, in this study RHA is used as a supporting material for alkali metals (Li, Na, K), which are considered as strong base catalysts. The base catalysts are prepared using a simple impregnation method. The effect of a catalyst structure on alkali metal silicate and reaction parameters (catalyst amount, methanol to oil molar ratio, reaction duration and reaction temperature) on the ME content will be investigated. Furthermore, their tolerance towards water and FFA will also be discussed.

## 2. Material and methods

### 2.1. Materials

The raw material used in this work is UCO, (acid value was found to be  $3.54 \pm 0.05$  mg KOH/g, equivalent to 1.77% FFA (as oleic acid) and  $0.28 \pm 0.04$  of moisture content), which was collected from a local restaurant. RHA was collected from rice mills in Kedah, Malaysia. The chemicals purchased from Sigma–Aldrich (Switzerland) including sodium hydroxide, lithium hydroxide, potassium hydroxide all were of 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,  $\geq 99.8\%$ ), sulphuric acid (95–97%), and hexane (anhydrous,  $\geq 99.8\%$ ) were supplied by Hamburg (Germany), hydrochloric acid (37% HCl) and  $CDCl_3$  for NMR was purchased from Merck and Cambridge Isotope Laboratories, Andover, MA (USA), respectively.

### 2.2. Preparation of rice husk silica

RHA was macerated with a porcelain mortar and sieved with a 200 mesh sieve. Then, 10 g of powdered ash was washed with 60 mL of  $0.1 \text{ mol L}^{-1}$  HCl for 1 h, and neutralized with deionized water. The washing step is to remove the trace of minerals/metal (Al, Ca, K, Mg, Mn and Na) contained in RHA [14,19] and organic compounds. Finally, the clean ash was dried in an oven at  $105^\circ\text{C}$  for 2 h. The purified RHA is labelled as rice husk silica (RHS).

### 2.3. Preparation of alkali metal silicate and acid silica catalysts

Alkali metal silicates were prepared using the wet impregnation method. Amorphous RHS was suspended in water as a first step. An aqueous solution of alkali metal (sodium hydroxide, lithium hydroxide, or potassium hydroxide) was then slowly added to the suspension. All reactions were performed at  $M^+OH:SiO_2$  molar ratio of 2:1 (stoichiometrical ratio) [11]. The obtained mixture was then stirred and heated at  $90^\circ\text{C}$  for 2 h. Lastly, the mixture was dehydrated at  $200^\circ\text{C}$  for 30 min, and then calcined at 200, 500 and  $700^\circ\text{C}$  for 3 h.

Acid silica catalyst was prepared by impregnation method as follows: Two grams of RHS was added into 25 mL of  $0.2 \text{ M H}_2\text{SO}_4$  solution. The mixture was stirred vigorously at room temperature

for 2 h before drying at  $100^\circ\text{C}$  for 2 days. The obtained dry powder was ground followed by calcination at  $500^\circ\text{C}$  for 7 h. The samples were labelled as  $SO_4$ -silica [17].

### 2.4. Material characterization

The alkali metal silicate was identified by X-ray diffraction (Rigaku) with  $Cu K\alpha$  X-ray as a source. A FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of alkali metal silicate at  $400\text{--}4000 \text{ cm}^{-1}$  range. Surface analysis of the catalyst was examined by using Micro-meritics ASAP 2000. Prior to the analysis, all the samples were degassed at  $105^\circ\text{C}$  and the adsorption of  $N_2$  was measured at  $-196^\circ\text{C}$ . The size and morphology of catalyst was observed by FE-SEM (JSM-7800F). X-ray fluorescence (XRF) analysis was performed on Bruker S8 Tiger using the pressed-pellet (pressure at 8.0 Pa) method. The base strengths of the catalyst ( $H_L$ ) were 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 25 mg of catalyst was shaken with 5.0 mL of a solution of Hammett indicator diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the colour change of the solution was noted. The UCO was filtered to remove visible solid materials. The acid value of the oil was determined following the standard EN 14104; and the moisture content was analysed using Karl Fischer titration method (784 KFP Titrino, Metrohm).

### 2.5. Transesterification

The content of UCO to ME was performed in a 50 ml 2-neck round bottom flask equipped with a reflux condenser and magnetic stirrer. The transesterification reaction between oil and methanol was carried out in the liquid phase under atmospheric pressure, at  $65^\circ\text{C}$  for 1 h with continuous stirring. The effect of the molar ratio of methanol to oil (6:1–20:1 wt.%), catalyst amount (1–4 wt.%), reaction duration (0.5–5.0 h), reaction temperature ( $35\text{--}75^\circ\text{C}$ ) and the addition of water and FFA (0.25–7 wt.%) on the reaction were investigated. After the transesterification, the reaction mixture was allowed to cool to room temperature. ME was isolated by centrifugation to further separate the layers (ME, glycerol and catalyst), and then the excessive amount of methanol and water was evaporated before the chromatographic analysis. The reaction were carried out three times in order to reflect the precision and errors of the results. The concentration of ME in the sample was determined by following the European regulation procedure EN 14103 [4]. 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  $0.25 \mu\text{m}$ ) using methyl heptadecanoate as an internal standard. Helium was used as the carrier gas with a linear velocity of  $40 \text{ cm/s}$ . The oven temperature was programmed at  $190^\circ\text{C}$ , held for 2 min, then ramped at  $10^\circ\text{C}$  per min until it reached  $230^\circ\text{C}$ , and with a final hold time of 8 min. The sample volume of  $0.6 \mu\text{L}$  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  $C_{12:0}$  to  $C_{18:1}$

$A_{\text{ISTD}}$  = peak area of methyl heptadecanoate

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

$V_{\text{STD}}$  = volume, in mL, of the methyl heptadecanoate solution.  
 $m$  = mass, in mg, of the sample.

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

$^1\text{H}$  NMR is used to verify the ME content, in addition to GC.  $^1\text{H}$  NMR spectrum of ME was obtained using a Bruker (Billerica, MA) AV-500 spectrometer operating at 500 MHz with a 5-mm broadband inverse Z-gradient probe in  $\text{CDCl}_3$  as a solvent and reference.

In order to examine the potential reutilization of the catalyst, the used catalyst was tested to assess its catalytic activity. For reuse experiments, the used solid catalyst recovered by decanting it after a simple washing using methanol and *n*-hexane. The dried used catalyst was directly used as a catalyst for the repeated reactions. The quality of the ME was tested for viscosity, acid number, free fatty acid (FFA) and density, water content, iodine value and flash point following the EN 14214 method.

### 3. Results and discussion

#### 3.1. Characterization of alkali metals silicate

The major chemical groups present in RHS and alkali metals silicate are identified by the FTIR spectra as shown in Fig. 1. The characteristic absorption peaks at  $486\text{--}619\text{ cm}^{-1}$  are attributed to the vibration of the  $\text{M}^+\text{--O}$  bond structure, and the characteristic absorption band from deformation of  $\text{M}^+\text{OH}$  become  $\text{Si--O--M}^+$  are shown at  $858$  and  $981\text{ cm}^{-1}$ ,  $\text{O--Si--O}$  stretching are shown at  $794$  and  $1101\text{ cm}^{-1}$ . The predominant absorbance peak at  $1381\text{ cm}^{-1}$  is due to siloxane bonds ( $\text{Si--O--Si}$ ) [15]. In the typical peak, with the broadband at about  $3500\text{ cm}^{-1}$ , the band can be attributed to the  $\text{O--H}$  bending and stretching of the associated water molecules. In agreement with previous report, the broadband between  $2800$  and  $3750\text{ cm}^{-1}$  is attributed to silanol OH groups and adsorbed water [14]. Band at  $1641\text{ cm}^{-1}$  shows the presence of bending vibration of water molecules bound to the silica matrix [26,28]. Peak were not found between  $2800$  and  $3000\text{ cm}^{-1}$ , deducing that there were no organic compounds in the silica after the treatment. Summarizing the FTIR results, it can be concluded that the impregnation of alkali metal ( $\text{M}^+ = \text{Li, Na, K}$ ) in silica matrix was successful.

The diffractograms of RHS (Fig. 2a) showed a hump at  $2\theta$  ranging from  $16^\circ$  to  $40^\circ$ , and the presence of large reflection at  $22.45^\circ$ , indicating the amorphous state of silica particles, in agreement with Kalapathy et al. [14]; Madrid et al. [19]; and Mansha et al. [20]; indicating the disordered structure of amorphous  $\text{SiO}_2$ . The XRD demonstrated that RHS can be a promising support material for alkali metals (Li, Na, and K). In order to obtain the optimal calcination conditions, alkali metals silicates were prepared at  $200^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $700^\circ\text{C}$  for 3 h. From XRD results, it was found that at  $200^\circ\text{C}$  the catalysts structure are not a clear crystal structure and with the temperature increase ( $500\text{--}700^\circ\text{C}$ ) the catalysts structure are in clear crystalline stage. The calcination treatment causing enhancement in intensity of some diffraction peaks, as illustrated by the crystalline phase of the catalyst became more regular as calcination temperature increases. Hence the lowest best calcination temperature,  $500^\circ\text{C}$ , is chose as the optimal calcination temperature, as well as saves energy as compared to at  $700^\circ\text{C}$ . The intense diffraction peaks from at  $23.77\text{--}46.81^\circ$  are confirmed to be potassium silicate (Fig. 2a). The intense diffraction sharp peaks from  $25.26^\circ$  to  $65.93^\circ$  are related to sodium silicate (Fig. 2b). The most intense and sharp diffraction peaks at  $18.93\text{--}38.55^\circ$  are attributed to  $\text{Li}_2\text{SiO}_3$  and the smaller peaks at  $16.70^\circ$ ,  $22.24^\circ$ ,  $28.16^\circ$ ,  $34.82^\circ$ ,  $49.28^\circ$ , and  $60.78^\circ$  are correspond to  $\text{Li}_4\text{SiO}_4$  (Fig. 2c). The amorphous structure of the acid silica after the acid treatment and calcination steps was shown in Fig. 2d. No peaks that is corresponding to the acid was observed on the XRD diffractograms, indicating that acid was highly dispersed on the surface of silica or incorporated into the framework.

EDX profile of RHS (Fig. 3a) contains predominantly the elements of O, Si and C (76.36, 21.06, 2.58% atomic, respectively). Both Si and O peaks correspond to the silica and the signal of carbon is originated from carbon coating in the FESEM-EDX analysis. From the XRF results, the metal content in RHS are  $\text{SiO}_2$  (96.5%),  $\text{MgO}$  (1.10%),  $\text{K}_2\text{O}$  (1.01%),  $\text{CaO}$  (0.44%),  $\text{MnO}$  (0.42%),  $\text{Al}_2\text{O}_3$  (0.31%),  $\text{Na}_2\text{O}$  (0.20%),  $\text{Fe}_2\text{O}$  (0.02%). It is evident that the silica (96.5%) is the predominant compound in RHS and a small amount of other elements. The micrograph of the RHS and alkali metals silicate demonstrated the crystal morphology. FESEM micrograph of RHS showing a porous surface morphology, with a high surface area ( $13.243\text{ m}^2/\text{g}$ ). Fig. 3(b–d) shows the alkali metals ( $\text{Li}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SiO}_3$ ,

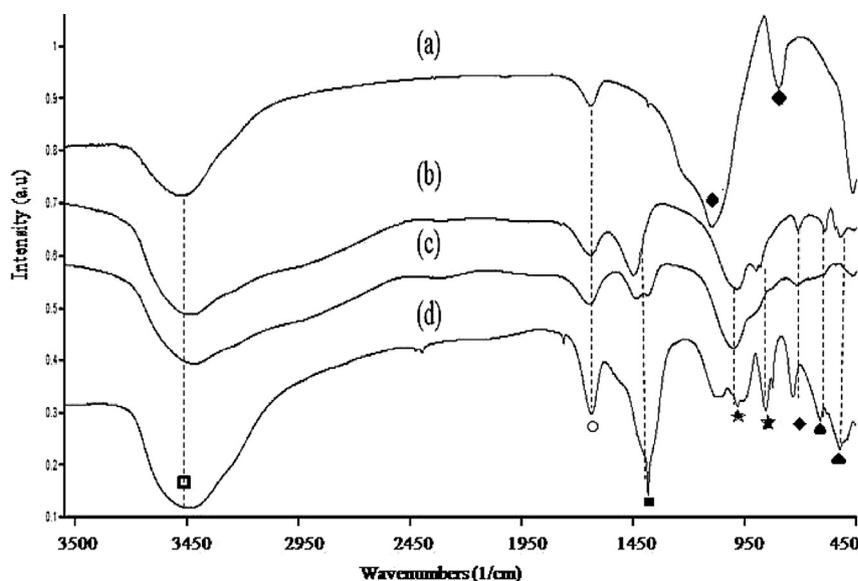


Fig. 1. FT-IR spectra of (a) RHS, (b)  $\text{K}_2\text{SiO}_3$ , (c)  $\text{Na}_2\text{SiO}_3$ , (d)  $\text{Li}_2\text{SiO}_3$ ;  $\blacktriangle$ :  $\text{M}^+\text{--O}$ ;  $\blacklozenge$ :  $\text{O--Si--O}$ ;  $\star$ : deformation ( $\text{Si--O--Si}$ )-( $\text{M--O}$ );  $\blacksquare$ :  $\text{Si--O--Si}$  stretching;  $\circ$ :  $\text{O--H}$  vibration from water molecules;  $\square$ :  $\text{O--H}$  bending and stretching (after calcined at  $500^\circ\text{C}$ ).

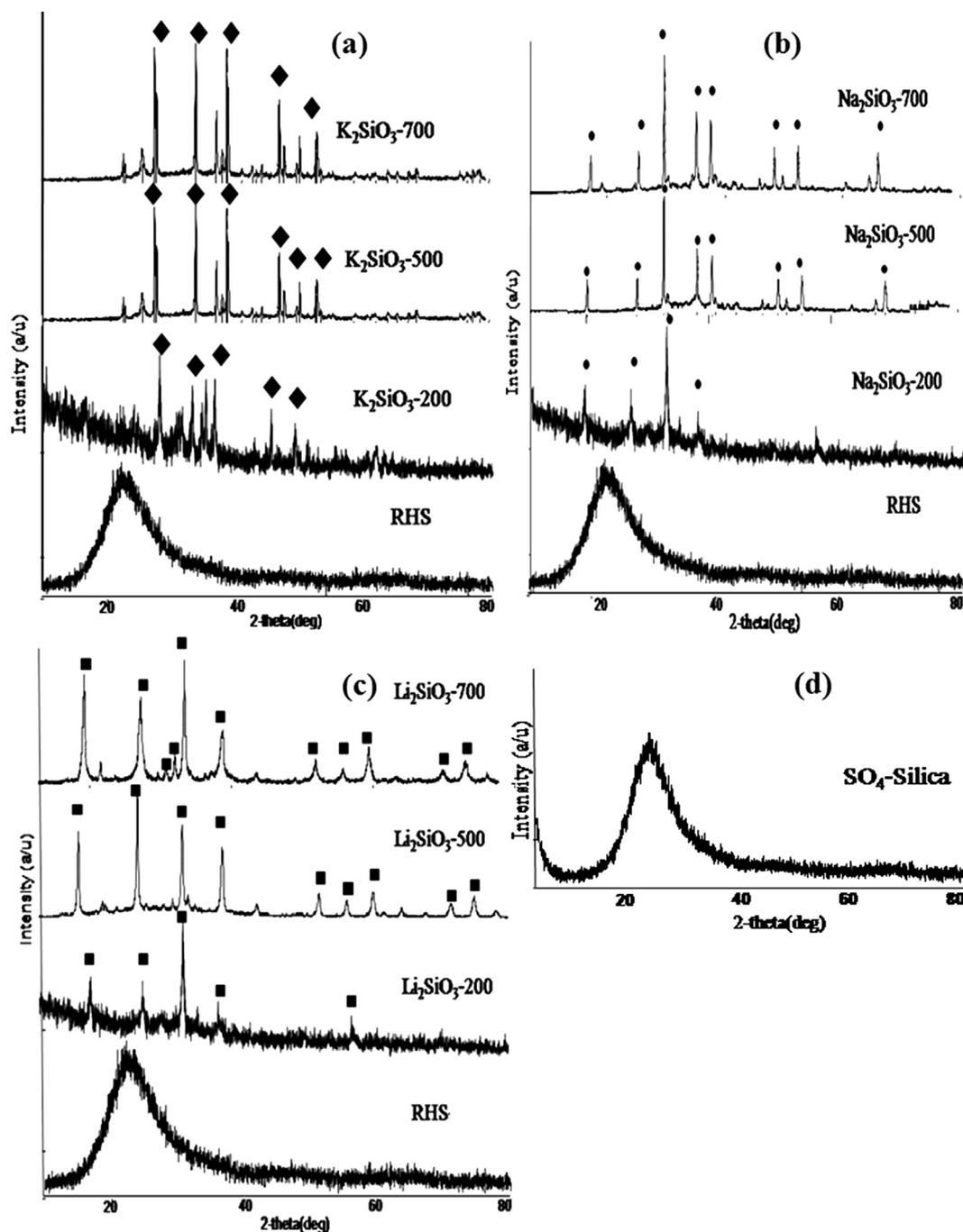


Fig. 2. XRD pattern of alkali metals silicate: (a)  $\blacklozenge$   $K_2SiO_3$ ; (b)  $\bullet$   $Na_2SiO_3$ ; (c)  $\blacksquare$   $Li_2SiO_3$  (after calcined at 200–700 °C) and (d)  $SO_4$ -RHS.

and  $K_2SiO_3$ ) particles on the surface of amorphous silica, with few spherical crystals and obvious agglomeration with a rough surface. The series of alkali metal silicate with a primary particle size of around 10–22, 25–38, and 30–50 nm range for  $Li_2SiO_3$ ,  $Na_2SiO_3$ , and  $K_2SiO_3$ , respectively.

All samples were measured for specific surface area using BET, using nitrogen gas sorption at liquid nitrogen temperature ( $-196\text{ }^\circ\text{C}$ ). Table 1 shows the surface area of the rice husk silica as  $13.243\text{ m}^2/\text{g}$ . Upon impregnation and calcination of alkali metals, the BET surface area decreases, thereby reflecting the reduction of the pore volume and pore size. The decrease is probably due to the penetration of catalyst into pores and surface of rice husk silica [13]. The nitrogen adsorption–desorption isotherm of alkali metal

silicate synthesized catalyst shows the typical Type II isotherm, indicating that the alkali metal ( $Li^+$ ,  $Na^+$ ,  $K^+$ )-rice husk silica is multilayer sorption and in the microporous range. The pore distributions of the material in this study are relatively narrow. Sodium and potassium silicate 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 of sodium silicate and potassium silicate are in the range:  $15 < H_- < 18.4$ . Lithium silicate could change the colour from colourless to pink (phenolphthalein) but failed to change the colour of 2,4-dinitroaniline. The basic strength of lithium silicate in this study is in the range:  $8.2 < H_- < 15.0$ . On the other hand, RHS was failed to change the colour of all Hammett

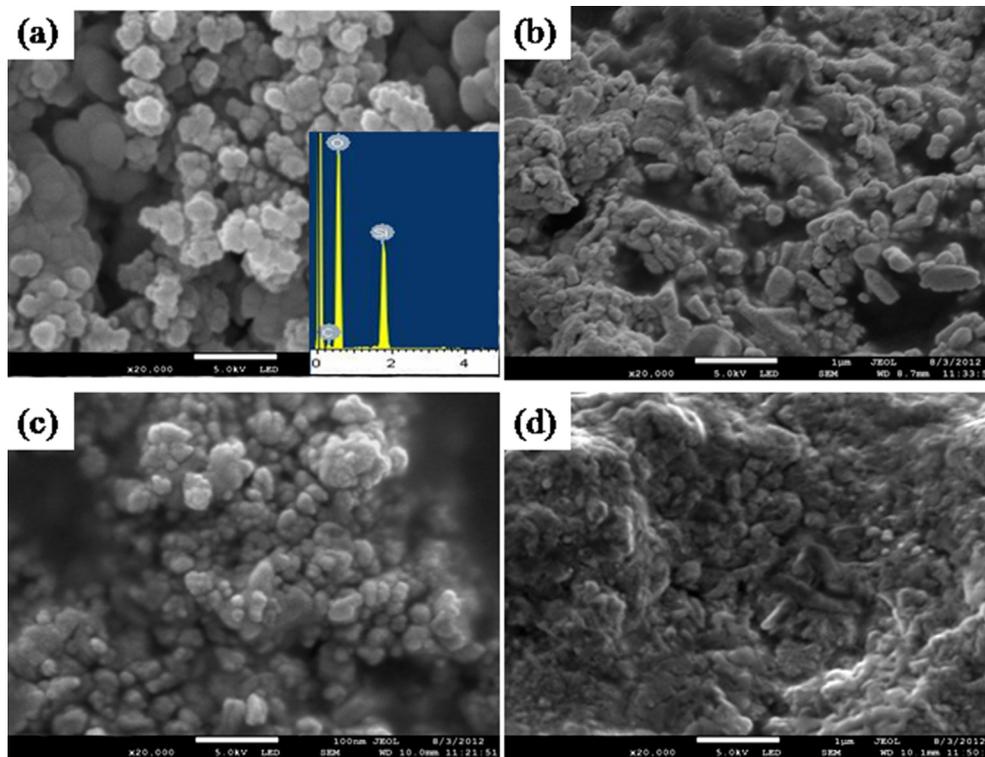


Fig. 3. FESEM micrographs of (a) RHS, (b) K<sub>2</sub>SiO<sub>3</sub>, (c) Na<sub>2</sub>SiO<sub>3</sub>, (d) Li<sub>2</sub>SiO<sub>3</sub> (after calcined at 500 °C).

indicators. Therefore, RHS does not have basic properties and suitable to be used as a support material.

### 3.2. Characterization of methyl esters

Higher ME content of 96.6%, 97.6%, 98.2% was recorded for Li<sub>2</sub>SiO<sub>3</sub>, K<sub>2</sub>SiO<sub>3</sub>, and Na<sub>2</sub>SiO<sub>3</sub>, respectively. Fatty acid profile of the ME prepared from UCO was determined by GC–MS analysis (Fig. 4a). The output of GC analysis proved that UCO mainly comprises of ME of methyl laurate (C<sub>12:0</sub>) 0.86%, methyl myristate (C<sub>14:0</sub>) 1.27%, methyl palmitate (C<sub>16:0</sub>) 30.24% followed by 3.54% methyl palmitoleate (C<sub>16:1</sub>), 4.67% methyl stearate (C<sub>18:0</sub>), 40.82% methyl oleate (C<sub>18:1</sub>), 17.55% methyl linoleate (C<sub>18:2</sub>), and 1.05% methyl linolenate (C<sub>18:3</sub>). Fig. 4a presents chromatogram of ME from UCO and the internal standard (methyl heptadecanoate). The oleic acid is the major fatty acid followed by palmitic acid and linoleic acid. Methyl esters of stearic, palmitoleic, myristic, linolenic and lauric were present as minor constituents.

The <sup>1</sup>H NMR spectrum of ME from UCO is shown in Fig. 4b. The triplet at δ 5.31–5.36 ppm represents the olefinic protons (–CH=CH–). A signal at δ 3.66 ppm is representing methoxy protons of the ester functionality of the biodiesel. The doublet at δ 2.78 ppm indicates the bis-allylic protons (–C=C–CH<sub>2</sub>–C=C–) of the unsaturated fatty acid chain. The quartet at δ 2.28 ppm represents the α-methylene protons to ester (–CH<sub>2</sub>–CO<sub>2</sub>Me). The α-methylene

protons to double bond (–CH<sub>2</sub>–C=C–) appear as a doublet at δ 2.01 and 2.05 ppm. The β-methylene protons to ester (CH<sub>2</sub>–C–CO<sub>2</sub>Me) also appear as a singlet at δ 1.62 ppm. The triplet signals at δ 1.26–1.31 ppm are expected for the protons of backbone methylenes of the long fatty acid chain. The terminal methyl protons (C–CH<sub>3</sub>) at δ 0.88–0.89 ppm appear as a doublet. From the NMR data it could be verified that ME content was quite complete.

### 3.3. Effect of catalyst amount and reaction duration

This study investigated the effect of the catalyst amount and the effect of the reaction duration for all the alkali metal silicate. The amount of catalyst was varied in the range 1–4 wt.%. The reaction was carried out with a methanol to oil molar ratio of 9:1 and reaction temperature of 65 °C for 1 h. Fig. 5a shows the results regarding the effect of the alkali metal silicate (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) amount on the catalytic activity. The transesterification was dependent on the amount of catalyst used in this study. By increasing the amount of catalyst from 1 to 3%, the content of ME increased from 68.8 to 96.6, 69.4–98.2, 80.4–97.6 (wt.%) for Li<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, and K<sub>2</sub>SiO<sub>3</sub>, respectively. The ME content reaches an optimal value when the catalyst amount reaches 3%. This is because the contact opportunity of the catalyst and the reactant, directly affect the reaction speed and the content. Furthermore, increasing the amount of catalyst did not affect the content profoundly. This is probably because of the demand of higher power consumption for an adequate stirring speed and the solution becoming more viscous [22,23] or may because of the surface vacancies of support material (RHS) were filled with metals of catalysts, observed by Ma et al. [18]. In Fig. 5a, when the Li<sub>2</sub>SiO<sub>3</sub> amounts are 1% and 2%, the content of ME is lower. Perhaps the Li<sup>+</sup> cation with smaller atomic size (compared to Na<sup>+</sup> and K<sup>+</sup>) bonded strongly with SiO<sub>2</sub> and forms a stable compound. As noted by Castro et al. [5]; stable compounds resulting lower catalyst activity.

**Table 1**  
BET surface area, pore volume and pore size of RHS and alkali metals silicate.

No	Sample	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)
1	Rice husk silica (RHS)	13.243	0.085	221.57
2	Li <sub>2</sub> SiO <sub>3</sub> –RHS	1.745	0.014	84.85
3	Na <sub>2</sub> SiO <sub>3</sub> –RHS	2.781	0.050	28.60
4	K <sub>2</sub> SiO <sub>3</sub> –RHS	0.172	0.003	18.74

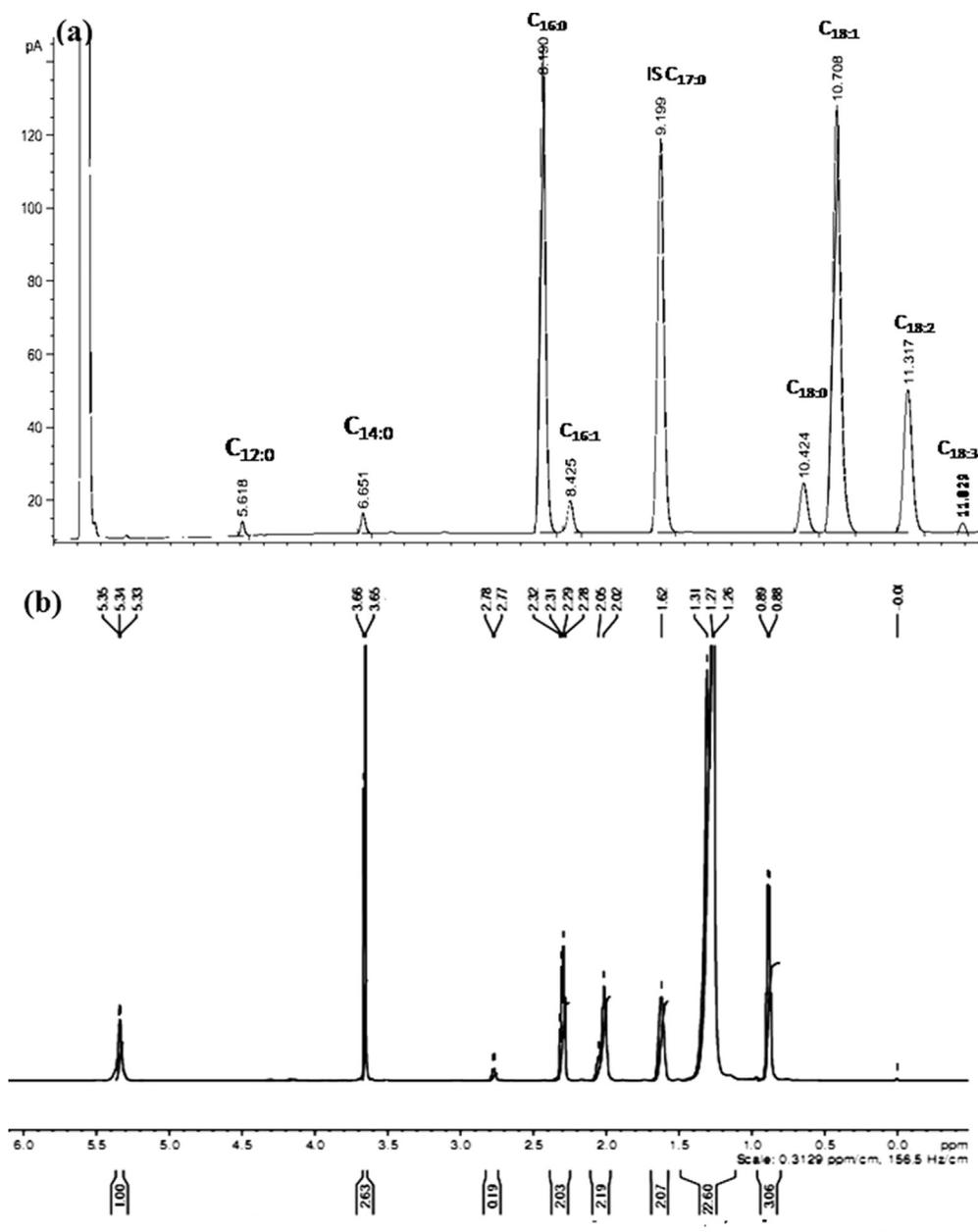


Fig. 4. (a) Gas chromatogram and (b) <sup>1</sup>H NMR spectrum of ME from used cooking oil.

The effect of the reaction duration is shown in Fig. 5b. All the alkali metal silicate seemed to have the similar ability to be a catalyst for the reaction. The reaction duration was varied from 30 to 300 min. From Fig. 5b, it can be seen that for the catalyst amount of 3 wt.%, the ME content increased within the first 30 min and reached as high as 85.0%, 86.1% and 84.6% for Li<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub>, respectively. Further, with an increase in the reaction duration more than 30 min, the ME content increased and remained almost constant as a result of near equilibrium conditions at 96.6%, 98.2%, 97.6% for Li<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub> and K<sub>2</sub>SiO<sub>3</sub>, respectively. Moreover, it is interesting to note that for a longer reaction duration the ME content decreases, possibility due to the reverse reaction, since transesterification, is a reverse reaction resulting in a loss of esters as well as causing more fatty acid to form soap [7].

From the comparison of alkali metals and acid catalyst reported in Fig. 5b, one can observe that the rate of ME content for alkali

catalyst is faster than that of acid catalyst. At 1 h reaction time, the ME content reached the maximum (96–98%) for alkali catalyst as compared to only 16% for acid catalyst. Furthermore, the reaction duration under acid catalyst is always longer as compared to the alkali catalyst. This is probably because of the reaction under alkali metals catalyst reaching the equilibrium faster. Therefore, it can be concluded that the alkali metals silicate show potential to be used as catalysts for the transesterification of UCO with FFA content 1.77%.

#### 3.4. Effect of methanol-to-oil molar ratio

The molar ratio of methanol and oil is one of the important variables that affect the transesterification reaction. Stoichiometrically, the transesterification of UCO requires 3 mol of methanol for each mole of oil (3:1), and excess methanol shifts the equilibrium

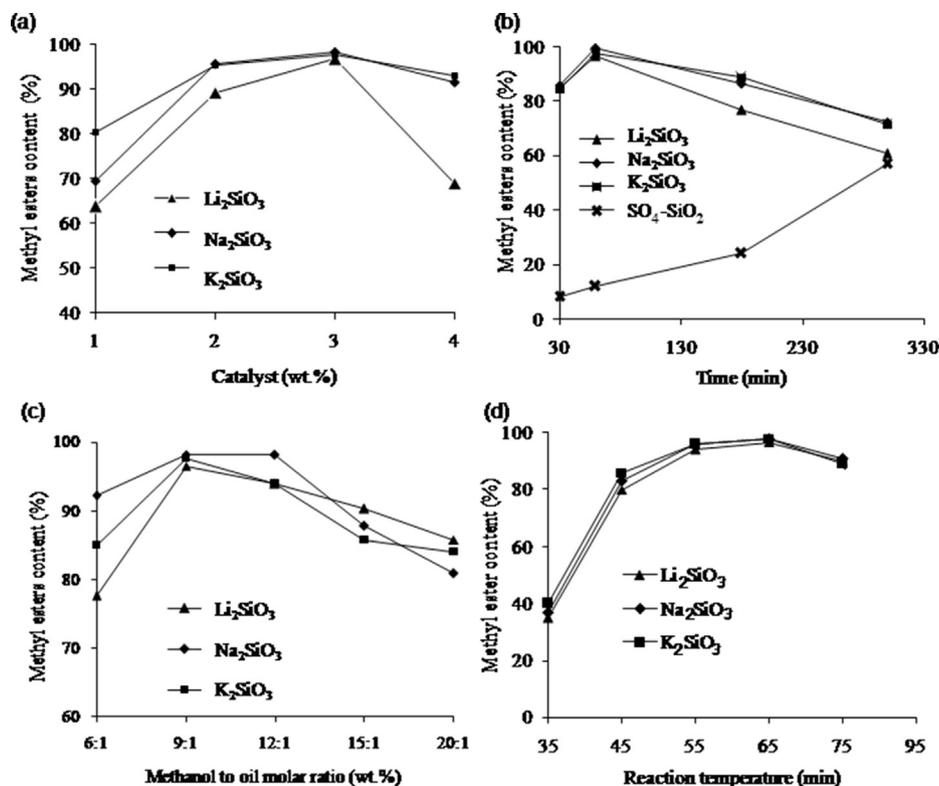


Fig. 5. Effect of (a) catalysts amount, (b) reaction duration, (c) methanol to oil molar ratio (d) reaction temperature in transesterification using alkali metals silicate as catalysts.

towards the direction of ME production. Unfortunately the excess of methanol could be increasing the recycling cost of production; nevertheless the methanol is usually recovered and reused in the industrial process after purification. Therefore, the choice of an optimal molar ratio has to take the increase in process expense into consideration. As observed from Fig. 5c, molar ratios of methanol to oil 6:1, 9:1, 12:1, and 15:1 are commonly used. The content of ME is increased when the methanol to oil ratio is raised to 9:1. A further increase in the methanol amount does not increase the content of ME any further. Probably the high ratio is too large and can cause the difficult separation of ME and glycerol as well as complicate the methanol removal process [22]. Therefore, it can be concluded that a methanol to oil ratio of 9:1 is the preferred amount for a higher content ME.

### 3.5. Effect of reaction temperature

The reaction rate of transesterification is also influenced by reaction temperature. The reaction temperature was varying from 35 to 75 °C. As seen in Fig. 5d, increase temperature reaction, almost linearly with increasing of ME content. The maximum ME content were obtained at temperature between 55 and 65 °C (at molar ratio of 9:1 and catalyst amount of 3%) mainly due to the fact that the range is at the boiling point of methanol. Further increase above 65 °C, the ME content seems to decline. Furthermore, the higher temperature, the higher will be the production cost.

### 3.6. Tolerance towards water and free fatty acid of catalyst

The presence of water and free fatty acid (FFA) in base-catalysed transesterification is usually considered known to inhibit the reaction by promoting saponification. Triglyceride hydrolyses into free fatty acid (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. Practically any value below 2.5% is acceptable for basic catalyst system [2,16]. In order to examine the effect of water and FFA value on the activity of catalyst, the addition of 0.25–7 wt.% water and FFA (oleic acid), respectively were added to the existing FFA of 1.77% FFA and the results were recorded. The effect of addition FFA on ME content using various catalysts is shown in Fig. 6a. It was found with increasing amount of FFA, the ME content is decreasing. For the oil with addition 1.25% of FFA, the content of ME still at 79.7, 85.4, 87.6%, respectively for  $\text{Li}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SiO}_3$  and  $\text{K}_2\text{SiO}_3$ . However increasing addition of FFA to 2.25% the ME content reduced to 63.2, 61.5, 66.0%, respectively for  $\text{Li}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SiO}_3$  and  $\text{K}_2\text{SiO}_3$ . At this point the FFA has reacted immediately with the catalyst to form soap and water. Soap formation complicated the mixing and product separation processes, meanwhile water accelerated formation of FFA from the remaining triglycerides [1]. Fig. 6b indicates that addition of water slightly decreased the content of ME. Furthermore, when 1.75% of water was added the ME content still high (93.7, 91.0 and 89.6%, respectively for  $\text{Li}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SiO}_3$  and  $\text{K}_2\text{SiO}_3$ ). The result indicates that catalyst has a remarkable tolerance to water in the transesterification of UCO, indicates that  $\text{H}_2\text{O}$  up to 1.75% has little effect on the total basicity of the catalyst.

### 3.7. Reusability, leaching and regeneration of catalyst

Reusability is one of the factors in the economical application of alkali metal silicate as the heterogeneous base catalyst. The catalyst was reused without any further activation. The results provided in Fig. 6c, show that the alkali metal silicate can be used more than once by keeping the activity until six cycles with considerably high ME content. After the transesterification reaction was completed, the alkali metal silicate was decanted with simple washing using

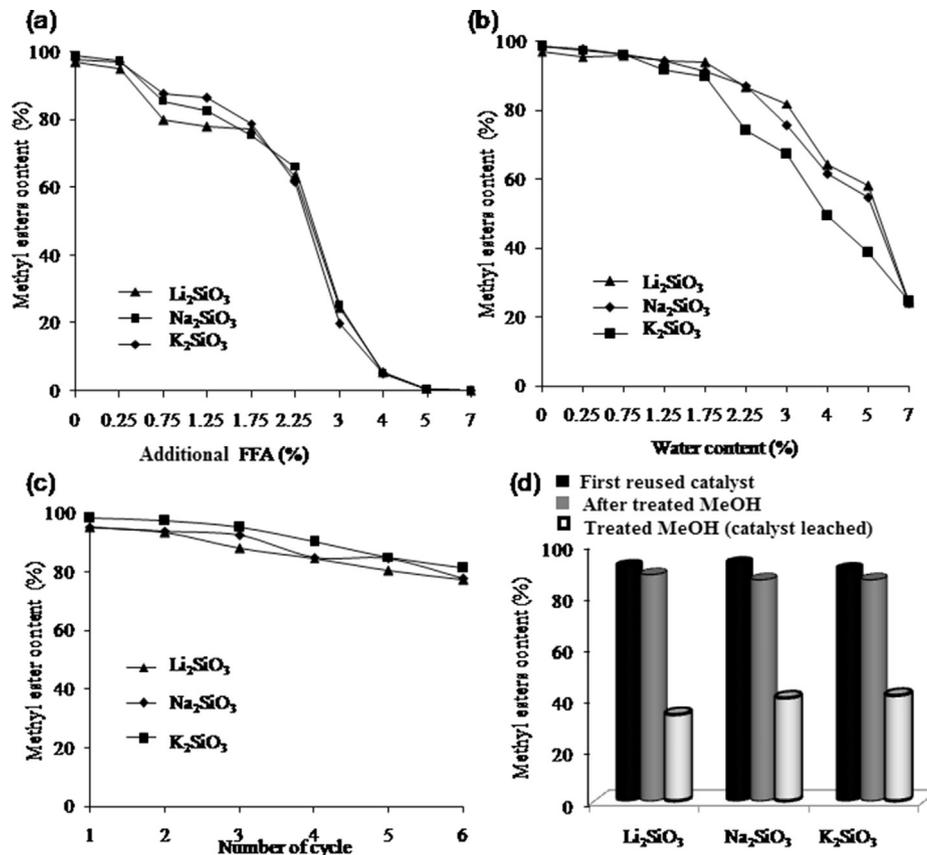


Fig. 6. Effect of (a) adding FFA (initial FFA = 1.77%) and (b) adding water content (c) catalyst reusability, and (d) catalyst leachability towards ME content (reaction conditions: catalyst amount 3%; methanol to oil molar ratio 9:1; 1 h and at 65 °C).

methanol then *n*-hexane, and can be directly reused for the transesterification reaction. A ME content between 87 and 90% could be obtained even after the third cycle. The ME content was further reduced to 77–86% when alkali metal silicate was reused for four to six cycles, which might be due to the leaching from the catalyst, thus it will reduce the ME content during the next run of the reaction [27,29] due to the reduction in the number of active sites or the activity declined due to the ion-exchange between  $\text{M}^+$  and  $\text{H}^+$  as the hydrolysis reaction is reversible [12].

In order to assess the leachability of the catalysts, those catalysts were stirred with methanol for 1 h (without feedstock). Then the reacted catalyst and the treated methanol was separated. The methanol-reacted solid catalysts were subjected to transesterification under the optimal conditions. Similarly, the treated methanol was also subjected to transesterification but without any catalyst. As seen in Fig. 6d, under methanol-reacted solid catalyst, a considerable ME content were achieved (86–89%), whereas under the treated methanol (without any catalyst), a very low ME content (33–40%) was observed for all catalyst. The observation proves that there is no complete leaching of the alkali metals into methanol during reaction.

After six cycles, the catalyst activity can be recovered by activated the alkali metals silicate with  $\text{M}^+\text{OH}$  and calcined at 500 °C for 3 h. The regenerated catalyst was then reused for transesterification of UCO with methanol, and the results were given in Fig. 7. Regenerated catalyst performed excellently in catalytic activity, and biodiesel yield of 96.6–97% was achieved. As the regenerated catalyst was reused for three times, ME yield was still maintained at more than 91%. This study shows that the simple regeneration method could recover the active sites well,

and catalytic activity of regenerated catalysts have good reproducibility.

### 3.8. Methyl esters properties

In order to assess the quality of the final product, it was evaluated according to European biodiesel standard (EN) 14214 (Table 2). It was found that the final product meets all the tested parameters (ester content, density, viscosity, water content, flash point, iodine value and acid value in accordance with EN 14214, for all the alkali

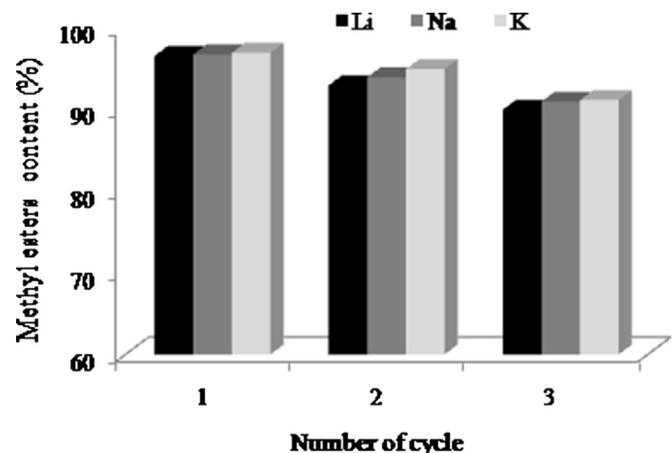


Fig. 7. ME content in the transesterification of UCO with methanol using regenerated alkali metal silicate.

**Table 2**  
Properties of biodiesel from waste cooking oil.

	Unit	Catalysts			Biodiesel specification EN 14214
		Li <sub>2</sub> SiO <sub>3</sub>	Na <sub>2</sub> SiO <sub>3</sub>	K <sub>2</sub> SiO <sub>3</sub>	
Ester content	wt.%	96.6 ± 0.03	98.2 ± 0.04		97.6 ± 0.02
96.5 (min)					
Density	kg m <sup>-3</sup>	887	873	895	860–900
Viscosity	mm <sup>2</sup> s <sup>-1</sup>	3.1	3.2	4.4	3.5–5.0
Water content	mg/kg	300	200	200	500 (max)
Flash point	°C	160	158	156	101 (min)
Iodine value	g iodine/100 g	102	103	102	120 (max)
Acid value	mg/g KOH	0.4	0.3	0.4	0.5 (max)

metal silicate. The ester content catalysed by Na<sub>2</sub>SiO<sub>3</sub> (3 wt.%) recorded the highest value of 98.2%. All the alkali metal silicate catalysts had good catalytic activity with content above 96.5%. Although many other parameters need to be analysed in order to confirm the final product as a fuel, these seven parameters can serve as preliminary indicators for the purpose as a fuel.

#### 4. Conclusions

Alkali metal silicates (Li<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, and K<sub>2</sub>SiO<sub>3</sub>) were prepared by the impregnation of alkali hydroxide on RHS. The FTIR and XRD results proved that the impregnation of alkali metals on silica is a success. The morphology shows that the homogenous spherical crystals with typical microporous and the pore distributions are relatively narrow. The optimum reaction conditions were: alkali metal silicate calcinated at 500 °C for 3 h; catalyst amount 3%; methanol to oil molar ratio 9:1; reaction temperature 65 °C with a constant stirring were able to transesterify with ME content between 96.5 and 98.2% in 1 h for all series. The catalyst was easily separated from the reaction mixture by filtering off the reaction solution and could be reused for six times. The ME met several key specifications of European biodiesel standard (EN) 14214.

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#### References

- [1] P.-L. Boey, S. Ganesan, S.-X. Lim, S.-L. Lim, G.P. Maniam, M. Khairudean, Utilization of BA (boiler ash) as catalyst for transesterification of palm olein, *Energy* 36 (2011) 5791–5796.
- [2] J. Boro, D. Deka, A.J. Thakur, A review on solid oxide derived from waste shells as catalyst for biodiesel production, *Renew. Sustain. Energy Rev.* 16 (2012) 904–910.
- [3] BP Statistical, Statistical Review of Production and Consumption Energy in the World US Securities and Exchange Commission, 201, August 2012, [www.bp.com/statisticalreview](http://www.bp.com/statisticalreview).
- [4] British-Adopted European Standard, Fat and Oil Derivatives – Fatty Acid Methyl esters (FAME) – Determination of Free and Total Glycerol and Mono-, Di-, Triglyceride Contents (Reference Method), BS EN 14105:2003, 2003.
- [5] 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.
- [6] 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.
- [7] T. Eevera, K. Rajendran, S. Saradha, Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions, *Renew. Energy* 34 (2009) 762–765.
- [8] EIA, Energy Information Administration, US Energy Information Administration, April 2012. <<http://205.254.135.7/totalenergy/data/monthly/>>.
- [9] EIA, Monthly Biodiesel Production Report, Energy Information Administrator (EIA), US Department of Energy, 1000 Independence Ave., SW Washington DC 20585, April 2012. <<http://www.eia.gov/biofuels/biodiesel/production/>>.
- [10] FAO, FAO Rice Market Monitor, Food and Agriculture Organization of the United Nations, January 2013. <<http://www.fao.org/economic/est/publications/rice-publications/rice-market-monitor-mmm/en/>>.
- [11] E.L. Foletto, E. Gratieri, L.H.d. Oliveira, S.L. Jahn, Conversion of rice hull ash into soluble sodium silicate, *Mater. Res.* 9 (2009) 335–338.
- [12] 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.
- [13] A. Islam, Y.H. Taufiq-Yap, C.-M. Chu, P. Ravindra, E.-S. Chan, Transesterification of palm oil using KF and NaNO<sub>3</sub> catalysts supported on spherical millimetric γ-Al<sub>2</sub>O<sub>3</sub>, *Renew. Energy* 59 (2013) 23–29.
- [14] U. Kalapathy, A. Proctor, J. Shultz, A simple method for production of pure silica from rice hull ash, *Bioresour. Technol.* 73 (2000) 257–262.
- [15] N. Thuadaj, A. Nuntiya, Preparation of nanosilica powder from rice husk ash by precipitation method, *Chiang Mai J. Sci.* 35 (2008) 206–211.
- [16] D.Y.C. Leung, X. Wu, M.K.H. Leung, A review on biodiesel production using catalyzed transesterification, *Appl. Energy* 87 (2010) 1083–1095.
- [17] L.S. Ling, H. Hamdan, Sulfated silica–titania aerogel as a bifunctional oxidative and acidic catalyst in the synthesis of diols, *J. Non-Cryst. Solids* 354 (2008) 3939–3943.
- [18] H. Ma, S. Li, B. Wang, R. Wang, S. Tian, Transesterification of rapeseed oil for synthesizing biodiesel by K/KOH/Al<sub>2</sub>O<sub>3</sub> as heterogeneous base catalyst, *J. Am. Oil Chem. Soc.* 85 (2008) 263–270.
- [19] R. Madrid, C.A. Nogueira, F. Margarido, Production and Characterisation of Amorphous Silica from Rice Husk Waste, Proceedings 4th International Conference on Engineering for Waste and Biomass Valorisation, September 10–13, 2012 – Porto, Portugal 4, 2012.
- [20] M. Mansha, S.H. Javed, M. Kazmi, N. Feroze, Study of rice husk ash as potential source of acid resistance calcium silicate, *Adv. Chem. Eng. Sci.* 1 (2011) 147–153.
- [21] S.A. Memon, M.A. Shaikh, H. Akbar, Utilization of rice husk ash as viscosity modifying agent in self compacting concrete, *Constr. Build. Mater.* 25 (2011) 1044–1048.
- [22] D.A. Molaei, M. Ghasemi, Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts, *Fuel Process. Technol.* 97 (2012) 45–51.
- [23] K. Noiroj, P. Intarapong, A. Luengnaruemitchai, S. Jai-In, A comparative study of KOH/Al<sub>2</sub>O<sub>3</sub> and KOH/NaY catalysts for biodiesel production via transesterification from palm oil, *Renew. Energy* 34 (2009) 1145–1150.
- [24] M. Noushad, I.A. Rahman, A. Husein, D. Mohammed, A.R. Ismail, A simple method of obtaining spherical nanosilica from rice husk, *IJASEIT* 2 (2012) 28–30.
- [25] I. Nurfitri, G.P. Maniam, N. Hindryawati, M.M. Yusoff, S. Ganesan, Potential of feedstock and catalysts from waste in biodiesel preparation: a review, *Energy Convers. Manag.* 74 (2013) 395–402.
- [26] E. Rafiee, S. Shahebrahimi, M. Feyzi, M. Shaterzadeh, Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material), *Inter. Nano Lett.* 2 (2012) 1–8.
- [27] Y.H. Taufiq-Yap, H.V. Lee, R. Yunus, J.C. Juan, Transesterification of non-edible *Jatropha curcas* oil to biodiesel using binary Ca–Mg mixed oxide catalyst: effect of stoichiometric composition, *Chem. Eng. J.* 178 (2011) 342–347.
- [28] D.C.L. Vasconcelos, R.L. Oréfice, W.L. Vasconcelos, Processing, adhesion and electrical properties of silicon steel having non-oriented grains coated with silica and alumina sol–gel, *Mater. Sci. Eng. A* 447 (2007) 77–82.
- [29] J.-X. Wang, K.-T. Chen, J.-S. Wu, P.-H. Wang, S.-T. Huang, C.-C. Chen, Production of biodiesel through transesterification of soybean oil using lithium orthosilicate solid catalyst, *Fuel Process. Technol.* 104 (2012) 167–173.