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

Noor Hindryawati[a,c], Gaanty Pragas Maniam[a,b*], Md. Rezaul Karim[a], Chong Kwok Feng[a]
[a]Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia
[b]Central Laboratory, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia
[c]Faculty of Mathematic and Natural Sciences, Mulawarman University, Gunung Kelua, 75113 Samarinda, East Borneo, Indonesia

*Corresponding author. Tel.: +60 16 4110236; fax:+60 9 549 2766
E-mail address: gaanty@hotmail.com

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 heterogeneous transesterification process of waste 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 tolerant 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.

Keywords: Waste cooking oil, Transesterification, Alkali metal, Rice husk silica, Heterogeneous catalyst, Methyl ester.

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 (BP.Statistical, 2012). Furthermore, petroleum-based activities are one of the main causes of carbon dioxide (CO_2) 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 (EIA, 2012a). 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 (EIA, 2012b), 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 waste cooking oil (WCO). The source is abundant supply, relatively inexpensive and the utilization offers benefits on environmental conservation (Nurfitri et al., 2013). 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 WCO contains free fatty acid (FFA) and moisture. FFA content in waste oil should be as low as possible for alkali catalysts, because alkali catalysts will readily react with

FFA to form soap. 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 heterogeneous catalysts has become more favourable compared to others and has been scaled up to industrial level. Heterogeneous base catalysts bring several advantages, such as the catalyst can easily be separated from the reaction mixture, no washing is required, easy regeneration, less 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 (Chen et al., 2013). 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 (Noushad et al., 2012). Each tonne of rice produces 200 kg of rice husk, and with the complete combustion will be generated 40 kg of RHA (Memon et al., 2011). Recently, about 146 million tonnes of RHA was produced annually worldwide (FAO, 2013) 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 WCO, (acid value was found to be 3.54±0.05 mg KOH/g, equivalent to 1.77% FFA (as oleic acid) and 0.28% ±0.04 of moisture content), 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 ($H\_$= 8.2), 2,4-dinitroaniline ($H\_$= 15.0) and 4-nitroaniline ($H\_$= 18.4) and methyl heptadecanoate as an internal standard GC grades (> 99.1%). Methanol (anhydrous, ≥ 99.8%) and hexane (anhydrous, ≥ 99.8%) were supplied by Hamburg (Germany), and $CDCl_3$ for NMR was purchased from Cambridge Isotope Laboratories, Andover, MA (USA).

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 mol L^{-1} HCl for 1 h, and neutralized with deionized water. The washing step is to remove the trace of minerals/metal (Al, K, Na, Mn, Mg and Ca) contained in RHA (Kalapathy and Proctor, 2000; Madrid et al., 2012) and organic compounds. The purified RHA have higher silica content (higher by 8.22%). Finally, the clean ash was dried in an oven at 105 °C for 2 h. The purified RHA is labelled as rice husk silica (RHS).

2.3. Preparation of alkali metal silicate powder

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) (Foletto et al., 2009). The obtained mixture 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.

2.4. Material characterization

The alkali metal silicate was identified by X-ray diffraction (Rigaku) with Cu Kα X-ray as a source. A FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of alkali metal silicate at 400-4000 cm^{-1} range. 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 N_2 was measured at –196 °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_) were determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein (H_= 8.2), 2,4-dinitroaniline (H_= 15.0) and 4-nitroaniline (H_= 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 WCO 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 analyzed using Karl Fischer titration method (784 KFP Titrino, Metrohm).

2.5 Transesterification

The content of WCO 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 °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 (35-75 °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. 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 formula:

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

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.

^{1}H-NMR is used to verify the ME content, in addition to GC. ^{1}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 $CDCl_3$ 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 486–619 cm^{-1} are attributed to the vibration of the M^{+}–O bond structure, and the characteristic absorption band from deformation of $M^{+}OH$ become Si–O–M^{+} are shown at 858 and 981 cm^{-1}, O–Si–O stretching are shown at 794 and 1101 cm^{-1}. The predominant absorbance peak at 1381 cm^{-1} is due to siloxane bonds (Si-O-Si) (Le et al., 2013). In the typical peak, with the broadband at about 3500 cm^{-1}, the band can be attributed to the O-H bending and stretching of the associated water molecules. In agreement with previous report, the broad band between 2800 and 3750 cm^{-1} is attributed to silanol OH groups and adsorbed water (Kalapathy and Proctor, 2000). Band at 1641 cm^{-1} shows the presence of bending vibration of water molecules bound to the silica matrix (Rafiee et al., 2012; Vasconcelos et al., 2007). Peak were not found between 2800 and 3000 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 (M^{+}= Li, Na, K) in silica matrix was successful.

The diffractograms of RHS (Fig. 2 a) 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, in agreement with Kalapathy and Proctor, (2000); Madrid et al., (2012); and Mansha et al., (2011), indicating the disordered structure of amorphous SiO_2. The XRD demonstrated that RHS can be a promising support material for alkali metals (Li, Na, and K). The intense diffraction peaks from at 23.77° to 46.81° are confirmed to be potassium silicate (Fig.2 b). The intense diffraction sharp peaks from 25.26° to 65.93° are related to sodium silicate (Fig.2 c). The most intense and sharp diffraction peaks at 18.93° to 38.55° are attributed to Li_2SiO_3 and the smaller peaks at 16.70°, 22.24°, 28.16°, 34.82°, 49.28°, and 60.78° are correspond to Li_4SiO_4 (Fig. 2 d).

EDX profile of RHS (Fig. 3 a) 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 SiO_2 (96.5%), MgO (1.10%), K_2O (1.01%), CaO (0.44%), MnO (0.42%), Al_2O_3 (0.31%), Na_2O (0.20%), Fe_2O (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 m^2/g). Figure 3 (b-d) shows the alkali metals (Li_2SiO_3, Na_2SiO_3, 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 °C). Table 1 shows the surface area of the rice husk silica as 13.243 m^2/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 (Islam et al., 2013). 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 indicators. Therefore, RHS does not have basic properties and suitable to be uses as a support material.

3.2 Characterization of Methyl Esters

Higher ME content of 96.6%, 97.6%, 98.2% was recorded for Li_2SiO_3, K_2SiO_3, and Na_2SiO_3, respectively. Fatty acid profile of the ME prepared from WCO was determined by GC-MS analysis (Fig.4 a). The output of GC analysis proved that WCO mainly comprises of ME of methyl laurate ($C_{12:0}$) 0.86%, methyl myristate ($C_{14:0}$) 1.27%, methyl palmitate ($C_{16:0}$) 30.24% followed by 3.54% methyl palmitoleate ($C_{16:1}$), 4.67% methyl stearate ($C_{18:0}$), 40.82% methyl oleate ($C_{18:1}$), 17.55% methyl linoleate ($C_{18:2}$), and 1.05% methyl linoleneate ($C_{18:3}$). Figure 4a presents chromatogram of ME from WCO 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 is present as minor constituents.

The ^1H NMR spectrum of ME from WCO is shown in Figure 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 ($-C=C-CH_2-C=C-$) of the unsaturated fatty acid chain. The quartet at δ 2.28 ppm represents the α-methylene protons to ester ($-CH_2-CO_2Me$). The α-methylene protons to double bond ($-CH_2-C=C-$) appear as a doublet at δ 2.01 and 2.05 ppm. The β-methylene protons to ester (CH_2-C-CO_2Me) 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 ($C-CH_3$) 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^+, Na^+, K^+) 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 68.8–96.6, 69.4–98.2, 80.4–97.6 (wt.%) for Li_2SiO_3, Na_2SiO_3, and K_2SiO_3, 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 (Molaei and Ghasemi, 2012; Noiroj et al., 2009) or may because of the surface vacancies of support material (RHS) were filled with metals of catalysts, observed by Ma et al. (2008). In Fig. 5 a, when the Li_2SiO_3 amounts are 1% and 2%, the content of ME is lower. Perhaps the Li^+ cation with smaller atomic size (compared to Na^+ and K^+) bonded strongly with SiO_2 and forms a stable compound. As noted by Castro et al. (2012), stable compounds resulting lower catalyst activity.

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_2SiO_3, Na_2SiO_3 and K_2SiO_3, 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_2SiO_3, Na_2SiO_3 and K_2SiO_3, 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 (Eevera et al., 2009).

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 WCO requires 3 moles of methanol for each mole of oil (3:1), and excess methanol shifts the equilibrium 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 (Molaei and Ghasemi, 2012). Therefore, it can be concluded that a methanol to oil ratio of 9:1 is the preferred amount for a higher content ME.

3.6. Effect of reaction temperature

The reaction rate of transesterification is also influenced by reaction temperature. The reaction temperature was varying from 35-75 °C. As seen in Fig. 5 d, increase temperature reaction, almost linearly with increasing of ME content. The maximum ME content were obtained at temperature between 55-65 °C (at molar ratio 12:1 and catalyst amount 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.

3.5. Tolerance towards water and free fatty acid of catalyst

The presence of water and free fatty acid (FFA) in base-catalyzed transesterification is usually considered known to inhibit the reaction by promoting saponification. Triglyceride hydrolyzes 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 (Boro et al., 2012; Leung et al., 2010). In order to examine the effect of water and FFA value on the activity of catalyst, the addition of 0.25–7wt.% 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. 7a. 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 Li_2SiO_3, Na_2SiO_3 and K_2SiO_3. However increasing addition of FFA to 2.25 % the ME content reduced to 63.2, 61.5, 66.0 %, respectively for Li_2SiO_3, Na_2SiO_3 and K_2SiO_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 (Boey et al., 2011). Fig. 7b 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 Li_2SiO_3, Na_2SiO_3 and K_2SiO_3). The result indicates that catalyst has a remarkable tolerance to water in the transesterification of WCO, indicates that H_2O up to 1.75 % has little effect on the total basicity of the catalyst.

3.6 Reusability and leaching 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. 7 c, 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 methanol then n-hexane, and can be directly reused for the transesterification reaction. A ME content between 87–90% could be obtained even after the third cycle. 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. 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 (Taufiq-Yap et al., 2011; Wang et al., 2012) due to the reduction in the number of active sites.

In order to assess the leachibility 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. 7d, 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.

3.7 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, and acid value, water content, iodine value, flash point and cetane number) in accordance with EN 14214, for all the alkali metal silicate. The ester content catalyzed by Na_2SiO_3 (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 analyzed 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_2SiO_3, Na_2SiO_3, and K_2SiO_3) 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 96.5–98.2% 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

Boey, P.-L., Ganesan, S., Lim, S.-X., Lim, S.-L., Maniam, G.P., Khairuddean, M., 2011. Utilization of BA (boiler ash) as catalyst for transesterification of palm olein. Energy. 36, 5791-5796.

Boro, J., Deka, D., Thakur, A.J., 2012. A review on solid oxide derived from waste shells as catalyst for biodiesel production. Renew. Sust. Energ. Rev. 16, 904-910.

BP.Statistical, 2012. Statistical Review of Production and Consumption Energy in The World US Securities and Exchange Commission, 201<www.bp.com/statisticalreview>(August 2012).

Castro, C.S., Ferreti, C., Di Cosimo, J.I., Assaf, J.M., 2012. Support influence on the basicity promotion of lithium-based mixed oxides for transesterification reaction. Fuel. 103, 632-638.

Chen, K.-T., Wang, J.-X., Dai, Y.-M., Wang, P.-H., Liou, C.-Y., Nien, C.-W., Wu, J.-S., Chen, C.-C., 2013. Rice husk ash as a catalyst precursor for biodiesel production. J. Taiwan Inst. Chem. Eng. 44, 622-629.

Eevera, T., Rajendran, K., Saradha, S., 2009. Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental conditions. Renew. Energy. 34, 762-765.

EIA, 2012a. Energy Information Administration. US Energy Information Administration, <http://205.254.135.7/totalenergy/data/monthly/>. (April 2012).

EIA, 2012b. Monthly Biodiesel Production Report, Energy Information Administrator (EIA), US Department of energy 1000 Independence Ave., SW Washington DC 20585. <http://www.eia.gov/biofuels/biodiesel/production/> (April 2012).

FAO, 2013. FAO rice market monitor. Food and Agriculture Organization of the United Nations. <http://www.fao.org/economic/est/publications/rice-publications/rice-market-monitor-rmm/en/> (January 2013).

Foletto, E.L., Gratieri, E., Oliveira, L.H.d., Jahn, S.L., 2009. Conversion of rice hull ash into soluble sodium silicate. Mater. Res. 9, 335-338.

Islam, A., Taufiq-Yap, Y.H., Chu, C.-M., Ravindra, P., Chan, E.-S., 2013. Transesterification of palm oil using KF and $NaNO_3$ catalysts supported on spherical millimetric γ-Al_2O_3. Renew. Energy. 59, 23-29.

Kalapathy, U., Proctor, 2000. A simple method for production of pure silica from rice hull ash. Bioresour. Technol. 73, 257-262.

Le, V.H., Thuc, C.N.H., Thuc, H.H., 2013. Synthesis of silica nanoparticles from Vietnamese rice husk by sol–gel method. Nanoscale Res. Lett. 8, 3-10.

Leung, D.Y.C., Wu, X., Leung, M.K.H., 2010. A review on biodiesel production using catalyzed transesterification. Appl. Energy. 87, 1083-1095.

Ma, H., Li, S., Wang, B., Wang, R., Tian, S., 2008. Transesterification of Rapeseed oil for synthesizing biodiesel by K/KOH/Al_2O_3 as heterogeneous base catalyst. J. Am. Oil Chem. Soc. 85, 263-270.

Madrid, R., Nogueira, C.A., Margarido, F., 2012. 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.

Mansha, M., Javed, S.H., Kazmi, M., Feroze, N., 2011. Study of rice husk ash as potential source of acid resistance calcium silicate Adv. Chem. Eng. Sci. 1, 147-153
Memon, S.A., Shaikh, M.A., Akbar, H., 2011. Utilization of rice husk ash as viscosity modifying agent in self compacting concrete. Construc. Build. Mater. 25, 1044-1048.
Molaei,D. A., Ghasemi, M., 2012. Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. Fuel Process.Technol. 97, 45-51.
Noiroj, K., Intarapong, P., Luengnaruemitchai, A., Jai-In, S., 2009. A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. Renew. Energy. 34, 1145-50.
Noushad, M., Rahman, I.A., Husein, A., Mohammed, D., Ismail, A.R., 2012. A simple method of obtaining spherical nanosilica from rice husk. IJASEIT. 2, 28-30.
Nurfitri I, Maniam GP, Hindryawati N, Yusoff MM, Ganesan S. 2013. Potential of feedstock and catalysts from waste in biodiesel preparation: A review. Energy Convers Manage.74, 395-402.
Rafiee, E., Shahebrahimi, S., Feyzi, M., Shaterzadeh, M., 2012. Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material). Inter. Nano Lett. 2, 1-8.
Taufiq-Yap, Y.H., Lee, H.V., Yunus, R., Juan, J.C., 2011. Transesterification of non-edible Jatropha curcas oil to biodiesel using binary Ca–Mg mixed oxide catalyst: Effect of stoichiometric composition. Chem. Eng. J. 178, 342-347.
Vasconcelos, D.C.L., Oréfice, R.L., Vasconcelos, W.L., 2007. Processing, adhesion and electrical properties of silicon steel having non-oriented grains coated with silica and alumina sol–gel. Mater. Sci. Eng.: A. 447, 77-82.
Wang, J.-X., Chen, K.-T., Wu, J.-S., Wang, P.-H., Huang, S.-T., Chen, C.-C., 2012. Production of biodiesel through transesterification of soybean oil using lithium orthosilicate solid catalyst. Fuel Process. Technol. 104, 167-173.

Figure captions:

1. Fig. 1. FT-IR spectra of (a) RHS, (b) K_2SiO_3, (c) Na_2SiO_3, (d) Li_2SiO_3: ▲:M^+-O; ♦:O–Si–O; ✭ : deformation (Si-O-Si)-(M-O); ■: Si-O-Si stretching; ○: O-H vibration from water molecules; □: O-H bending and stretching (after calcined at 500 °C).
2. Fig. 2. XRD pattern of alkali metals silicate: (a) SiO2; (b) ♦ K_2SiO_3; (c) ● Na_2SiO_3 and (d) ■ Li_2SiO_3 (after calcined at 500 °C)
3. Fig. 3. FESEM micrographs of (a) RHS, (b) K_2SiO_3, (c) Na_2SiO_3, (d) Li_2SiO_3 (after calcined at 500 °C)
4. Fig. 4. (a) Gas chromatogram and (b) ^{1}H NMR spectrum of ME from waste cooking oil
5. 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
6. Fig. 6. Effect of (a) adding FFA (initial FFA= 1.77%) and (b) adding water content (c) catalyst reusability, and (d) catalyst leachibility towards ME content (reaction conditions: catalyst amount 3%; methanol to oil molar ratio 9:1; 1 h and at 65°C).

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> Engineering Science and Technology, an International Journal (JESTECH) Editorial
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Response to Reviewer

No.	Comment Reviewer	Line no. in revised Manuscript	Response to Reviewer
	<u>Reviewer 1</u>		
1.	Introduction - The introduction is too long. Please minimize the content.	Line 29	The content of introduction has been minimized
2.	Line 46-54 - Why alkaline catalyst was prepared in the present work since the authors are aware of the sensitivity of alkaline catalyst towards FFA? Why not acid heterogeneous catalyst? It is suggested to the authors to add in the preparation of acid rice husk silica (together with process study) to improve the novelty of the present work.	Line 49-59	Since the rate of reaction base catalyst is high, by Alkali loaded in RHS become more efficient. However, using acid-RHS in process will take long reaction time.

3.	Line 90 - Please indicate the unit of acid value. By referring to the acid value of 3.54 or equivalent to 1.77 % FFA, the prepared catalyst should be sensitive to FFA as observed in Figure 7 (a). Why the authors could still obtain high biodiesel conversion as observed in Figure 5 (a)-(c)? Contradicted result is observed and the reviewer is doubted on the experimental procedures and analytical method.	Line 76 Line 120 Line 283	Unit for acid value is added in section 2.1. Practically any value below 2.5% is acceptable for basic catalyst (Boro et al., 2012; Leung et al., 2010). In Fig. 7(a), the value is the additional FFA value to the existing FFA of 1.77%. Accordingly caption for Fig.7 has been amended to add the term ‘additional FFA’.
4.	Line 99 - any reason why powdered ash is washed with HCl?	Line 88	The washing step is to remove the trace minerals/metal (Al, K, Na, Mn, Ca and Mg) and organic compounds prior to the silica extraction from RHA.
5.	Line 105 - how to measure the molar of Si in rice husk ash? Please describe in detail.	Line 96	We can calculate the M^+OH/SiO_2 ratio of the system the following reaction: $2\ M^+OH + SiO_2 \rightarrow M_2SiO_3 + H_2O$ From the equation above, the molar ratio $M^+OH : SiO_2 = 2 : 1$. From the known value of M^+OH, molar ratio of Si can be calculated
6.	Line 107 - Optimization work on calcination temperature of catalyst should be performed. Why select 500°C?	Line 98	From XRD result, it was found that at 500-700 °C the catalysts structure was in clear crystalline stage whereas above that it started to be cristobalite (phase of SiO_2) and decrease the basicity. As such we chose 500 °C as the optimal condition. These observations were supported by two literatures (Guo et al., 2010; Saceda et al., 2011).
7.	Line 122 - Effect of reaction temperature should be performed.	Line 119 Line 270	Included in section 3.6
8.		Line 133	It is FAME content as in EN 14103. The term ‘ME content’

			was used throughout the manuscript
9.	Line 141 - Please check the equation. Is it referred to FAME conversion or FAME content? Reference to the equation should be included.	Line 141	Included in section 2.5
10.	Line 145-146 - Please include the concentration and volume used for internal standard.	Line 154 (FTIR) Line 168 (XRD) Line 177 (FESEM) Line 202 (basicity)	Included in section 3.1
11.	Line 3.1 - Characterization (FT-IR, XRD, SEM and basicity) for raw rice husk ash silica before impregnation should be included as a comparison study.	Line 168-176	Discussion more scientific is added
12.	Line 169-182 - There is no need to mention all the location of diffraction peaks. Please add in more scientific discussion of the XRD result.	Line 183	Discussion is revised
13.	Line 186 - the SEM images are not clear. The images did not show the catalysts are "homogeneous spherical" (not really the same size and not all are spherical shape) with "smooth surface" (agglomerated with rough surface is observed). Please revise the discussion properly.	Line 202	Reaction with raw RHS showed no conversion at all. RHS can be used as support material; it does not have basic properties as confirmed by Hammett indicator test (no colour changes).
14.	Line 232 - Process study for raw rice husk ash silica should be included as a comparison study.	Line 240	May because of the surface vacancies of support material (RHS) were filled with metals of catalysts, observed by (Ma et al., 2008)
15.	Line 247 - why increasing the catalyst concentration could resulted to saturated vacancy compared to low catalyst concentration?	Line 242-244	Clarified. The sentences have been rephrased for clear argument.
	Line 248-251 - Not clear. Atomic size could affect the		

16. 17. 18. 19. 20. 21. 22.	reaction rate? Why strong interaction of active sites to support could lower the catalytic activity? Please clarify properly. Line 259 - 261 - Why soap is not formed at the initial of the experiment and only formed during reaction reached equilibrium? It is somehow contradicted as affinity to form soap is much higher than transesterification since soap formation reaction is spontaneous. Line 261 - 268 - It is not necessary to include the discussion of reaction mechanism for Figure 5. Figure 6 is not necessary as it does not truly reveal the fast reaction rate of using base catalyst. Instead, fast or slow of a reaction should be revealed through kinetic study and catalytic activation energy. Line 292 - 1.25 % FFA could reduce the conversion of biodiesel. However, the original feedstock contains 1.77 % FFA and yet the authors could achieve high biodiesel conversion as observed in Figure 5. Why contradicted result was observed. How the authors adjust the FFA level in the oil? Line 296 - Not clear, especially "…and water almost immediately". Line 3.6 - Catalyst regeneration study (after 6 runs) and catalyst leaching test should be included to improve the novelty of the present work. **Reviewer 3:**	Line 252-255 Line 283 Line 291 Line 312 Line 1 Line 17 Line 25 Line 68	From the experiment observation, it is obvious at the end of reaction Removed Explanation No.3 The FFA level of oil can be determine using acid value of oil after addition FFA (oleic acid) Revised and rephrased Leachibility catalyst included in section 3.8 WCO changes as waste cooking oil EN14214 is European standard

23.	Title: The authors should use full words instead of abbreviation not only in the title but also in Abstract. Please remove WCO and include waste cooking oil. What is EN 14214 in abstract?	Line 177	Novelty has been added in the last paragraph of 1. Introduction
24.	I am concerned about the novelty of the work reported in the manuscript. Please explain the novelty and significance in the introduction.	Line 181	Added in section 3.1
25.	Alkali metal supported catalysts were prepared at the concentration of 2 :1 (metal silica molar ratio) . This is the theoretical ratio. What is the real amount of metal content in the silica? Did the authors check the real metal content in the silica using either XRF or ICP-MS?	Line 154	Yes, the purity silica is 96.5% from XRF analysis
26.	Silica content of rice husk varies depending upon the source of rice husk. As far as I understood from the experimental section, authors pretreated rice husk and then used as a silica. Did the authors check the purity of silica?	Line 189	Included in section 3.1
27.	Please support FTIR comments using existing literature.	Line 183	Included in section 3.1
28.	The authors should mention that there is no any porosity for rice husk silica alone as its surface area is only about 13 m2 /g. Addition to alkaline metals leads to decrease the surface areas of prepared catalysts.		Included in section 3.1 Fig.3(a)
29.	Surface morphology was observed using SEM. But a SEM image of rice husk silica alone was not provided. It is necessary for comparison purpose.		From the experiment observation RHS cannot using as catalyst in transesterification.

	Authors give properties of biodiesel from waste cooking oil in Table 2. It is necessary to provide a run with only rice husk silica and give properties of biodiesel in order to check whether or not alkaline supported metals are work.		
30.	Some references do not refer to the sentence. For instance, " The protons from the cation were transferred to diglyceride anions to generate diglyceride (Balat and Balat, 2010)." There is no any similar comment in the paper reported by Balat and Balat, 2010, Appl. Energy. 87, 1815-1835). I suggest removing unrelated references and providing the proper and relevant citations to the paper.	Line 329	The unrelated reference is dropped. Other references have been rechecked for the corrections.
31.	Conclusion section should be re-written. What is learnt from this study in terms of catalytic effect, mechanism understanding and/or process?	Line 322	Rephrased
	Reviewer 4: For my opinion, The final product does not met fuel properties for methyl esters in accordance with EN 14214. (in Table 2); because table 2 does not contain the following properties: cetane number (min) 51, iodine value (max) 120 g iodine/100g, flash point (min) 120C, and water content (mg/kg) 500)		Included in Table 2. As added in section 3.7. The listed seven (7) properties can serve as a good indicator for the purpose as fuel.