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Ms. Ref. No.: JESTCH-D-14-00001

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

Engineering Science and Technology: an International Journal

Dear Gaanty Pragas Maniam, Ph.D,

The reviewers have commented on your above paper. They indicated that it is not acceptable for publication in its present form.

However, if you feel that you can suitably address the reviewers' comments (included below), I invite you to revise and resubmit your manuscript.

Please carefully address the issues raised in the comments.

If you are submitting a revised manuscript, please also:

a) outline each change made (point by point) as raised in the reviewer comments

AND/OR

b) provide a suitable rebuttal to each reviewer comment not addressed

To submit your revision, please do the following:

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I look forward to receiving your revised manuscript.

Yours sincerely,

Erol ARCAKLIOGLU, Dr.

Editor in Chief

Engineering Science and Technology: an International Journal

Reviewers' comments:

Reviewer #1: The submitted manuscript described alkaline rice husk silica as a potential catalyst in

transesterification reaction for biodiesel production. Overall, the experimental works in the present study are not complete and lack of novelty. The results attained are rather expected as using alkaline heterogeneous catalyst in transesterification has been widely reported in literature. In addition, the prepared catalyst is highly sensitive towards free fatty acid (FFA) that further limits the application of the catalyst for other low quality feedstock.

Specific comments:

1. Introduction - The introduction is too long. Please minimize the content.
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.
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.
4. Line 99 - any reason why powdered ash is washed with HCl?
5. Line 105 - how to measure the molar of Si in rice husk ash? Please describe in detail.
6. Line 107 - Optimization work on calcination temperature of catalyst should be performed. Why select 500oC?
7. Line 122 - Effect of reaction temperature should be performed.
8. Line 141 - Please check the equation. Is it referred to FAME conversion or FAME content? Reference to the equation should be included.
9. Line 145-146 - Please include the concentration and volume used for internal standard.
10. 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.
11. 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.
12. 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.
13. Line 232 - Process study for raw rice husk ash silica should be included as a comparison study.
14. Line 247 - why increasing the catalyst concentration could resulted to saturated vacancy compared to low catalyst concentration?
15. Line 248-251 - Not clear. Atomic size could affect the reaction rate? Why strong interaction of active sites to support could lower the catalytic activity? Please clarify properly.
16. 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.
17. 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.
18. 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?

19. Line 296 - Not clear, especially "...and water almost immediately".

20. 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:

The authors have studied trans-esterification of waste cooking oil using alkali metal supported silica obtained from rice husk. From my vision the paper might be published in Engineering Science and Technology: an International Journal (JESTCH) but it will require a major revision of some aspects commented below.

- 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?
- I am concerned about the novelty of the work reported in the manuscript. Please explain the novelty and significance in the introduction.
- 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?
- 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?
- Please support FTIR comments using existing literature.
- 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.
- Surface morphology was observed using SEM. But a SEM image of rice husk silica alone was not provided. It is necessary for comparison purpose.
- 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.
- 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.
- Conclusion section should be re-written. What is learnt from this study in terms of catalytic effect, mechanism understanding and/or process?

Reviewer #4:

The following observations are requested for the needed revision.

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)

R1-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	<p>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 SiO₂) 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).</p> <p>Included in section 3.6</p>
7.	Line 122 - Effect of reaction temperature should be performed.		It is FAME content as in EN 14103. The term 'ME content' was used throughout the manuscript
8.	Line 141 - Please check the equation. Is it referred to FAME conversion or FAME content? Reference to the equation should be included.	Line 119 Line 270	Included in section 2.5
9.	Line 145-146 - Please include the concentration and volume used for internal standard.	Line 133	Included in section 3.1
10.	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 141	Discussion more scientific is added
11.	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 154 (FTIR) Line 168 (XRD) Line 177 (FESEM) Line 202 (basicity)	Discussion is revised
12.	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 168-176 Line 183	

13.	Line 232 - Process study for raw rice husk ash silica should be included as a comparison study.		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 247 - why increasing the catalyst concentration could resulted to saturated vacancy compared to low catalyst concentration?	Line 202	May because of the surface vacancies of support material (RHS) were filled with metals of catalysts, observed by (Ma et al., 2008)
15.	Line 248-251 - Not clear. Atomic size could affect the reaction rate? Why strong interaction of active sites to support could lower the catalytic activity? Please clarify properly.	Line 240	Clarified. The sentences have been rephrased for clear argument.
16.	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 242-244	From the experiment observation, it is obvious at the end of reaction
17.	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 252-255	Removed
18.	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		Explanation No.3 The FFA level of oil can be determine using acid value of oil after addition FFA (oleic acid)

<p>19.</p> <p>20.</p> <p>21.</p> <p>22.</p> <p>23.</p> <p>24.</p>	<p>contradicted result was observed. How the authors adjust the FFA level in the oil?</p> <p>Line 296 - Not clear, especially "...and water almost immediately".</p> <p>Line 3.6 - Catalyst regeneration study (after 6 runs) and catalyst leaching test should be included to improve the novelty of the present work.</p> <p><u>Reviewer 3:</u></p> <p>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?</p> <p>I am concerned about the novelty of the work reported in the manuscript. Please explain the novelty and significance in the introduction.</p> <p>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?</p> <p>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?</p> <p>Please support FTIR comments using existing literature.</p>	<p>Line 283</p> <p>Line 291</p> <p>Line 312</p> <p>Line 1 Line 17 Line 25</p> <p>Line 68</p>	<p>Revised and rephrased</p> <p>Leachibility catalyst included in section 3.8</p> <p>WCO changes as waste cooking oil EN14214 is European standard</p> <p>Novelty has been added in the last paragraph of 1. Introduction</p> <p>Added in section 3.1</p> <p>Yes, the purity silica is 96.5% from XRF analysis</p> <p>Included in section 3.1</p>
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25.	The authors should mention that there is no any porosity for rice husk silica alone as its surface	Line 177	Included in section 3.1
26.	area is only about 13 m ² /g. Addition to alkaline metals leads to decrease the surface areas of prepared catalysts.	Line 181	
27.	Surface morphology was observed using SEM. But a SEM image of rice husk silica alone was not provided. It is necessary for comparison purpose.	Line 154	Included in section 3.1 Fig.3(a)
28.	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.	Line 189	From the experiment observation RHS cannot using as catalyst in transesterification.
29.	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 183	The unrelated reference is dropped. Other references have been rechecked for the corrections.
30.	Conclusion section should be re-written. What is learnt from this study in terms of catalytic effect, mechanism understanding and/or process?		Rephrased
31.	<p><u>Reviewer 4:</u></p> <p>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</p>	Line 329	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.

	following properties: cetane number (min) 51, iodine value (max) 120 g iodine/100g, flash point (min) 120C, and water content (mg/kg) 500	Line 322	
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Transesterification of **waste 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 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 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.

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 (CO₂) 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 ($H_p = 8.2$), 2,4-dinitroaniline ($H_p = 15.0$) and 4-nitroaniline ($H_p = 18.4$) and methyl heptadecanoate as an internal standard GC grades ($> 99.1\%$). Methanol (anhydrous, $\geq 99.8\%$) and hexane (anhydrous, $\geq 99.8\%$) were 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 $105 \text{ }^\circ\text{C}$ 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 $90 \text{ }^\circ\text{C}$ for 2 h. Lastly, the mixture was dehydrated at $200 \text{ }^\circ\text{C}$ for 30 min, and then calcined at $500 \text{ }^\circ\text{C}$ for 3 h.

2.4. Material characterization

The alkali metal silicate was identified by X-ray diffraction (Rigaku) with Cu K α 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 N₂ 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 μ m) 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 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:

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

Where

$\sum A_{\text{ME}}$ = 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.

¹H-NMR is used to verify the ME content, in addition to GC. ¹H-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 CDCl₃ 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 $\text{M}^+\text{-O}$ 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 ($\text{M}^+=\text{Li, Na, K}$) 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 ($\text{C}_{12:0}$) 0.86%, methyl myristate ($\text{C}_{14:0}$) 1.27%, methyl palmitate ($\text{C}_{16:0}$) 30.24% followed by 3.54% methyl palmitoleate ($\text{C}_{16:1}$), 4.67% methyl stearate ($\text{C}_{18:0}$), 40.82% methyl oleate ($\text{C}_{18:1}$), 17.55% methyl linoleate ($\text{C}_{18:2}$), and 1.05% methyl linolenate ($\text{C}_{18:3}$). 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 ($-\text{CH}=\text{CH}-$). 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 ($-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$) of the unsaturated fatty acid chain. The quartet at δ 2.28 ppm represents the α -methylene protons to ester ($-\text{CH}_2-\text{CO}_2\text{Me}$). The α -methylene protons to double bond ($-\text{CH}_2-\text{C}=\text{C}-$) appear as a doublet at δ 2.01 and 2.05 ppm. The β -methylene protons to ester ($\text{CH}_2-\text{C}-\text{CO}_2\text{Me}$) 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 ($\text{C}-\text{CH}_3$) 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 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. 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.

Acknowledgement

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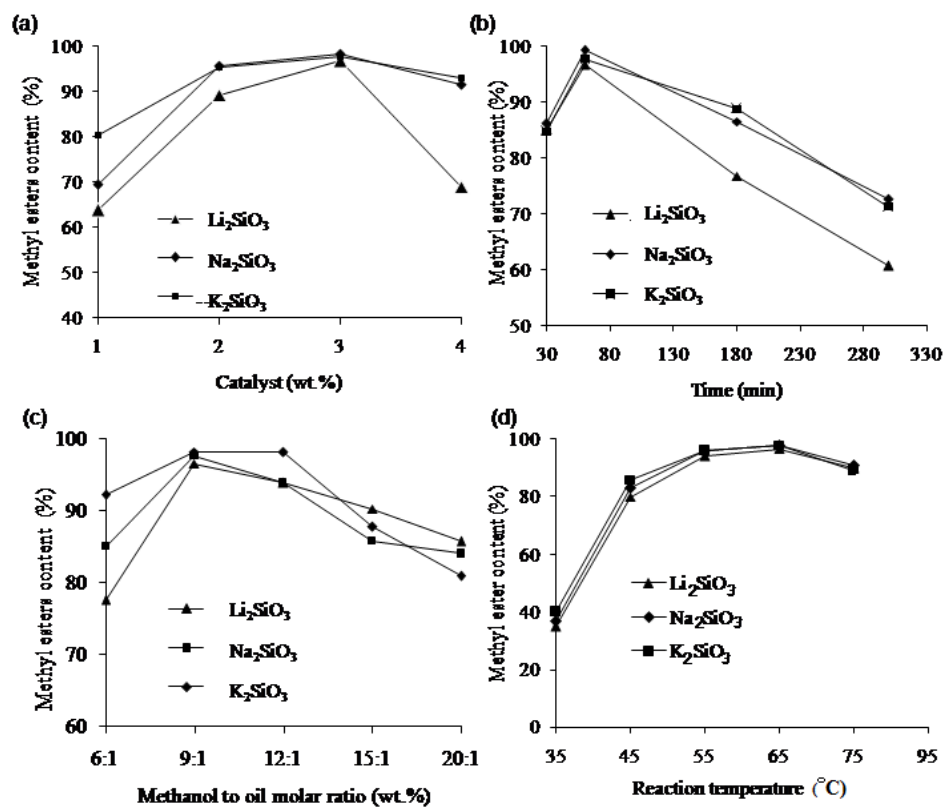
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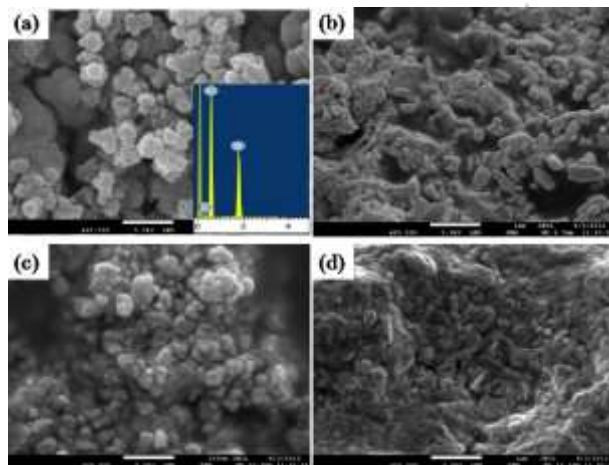
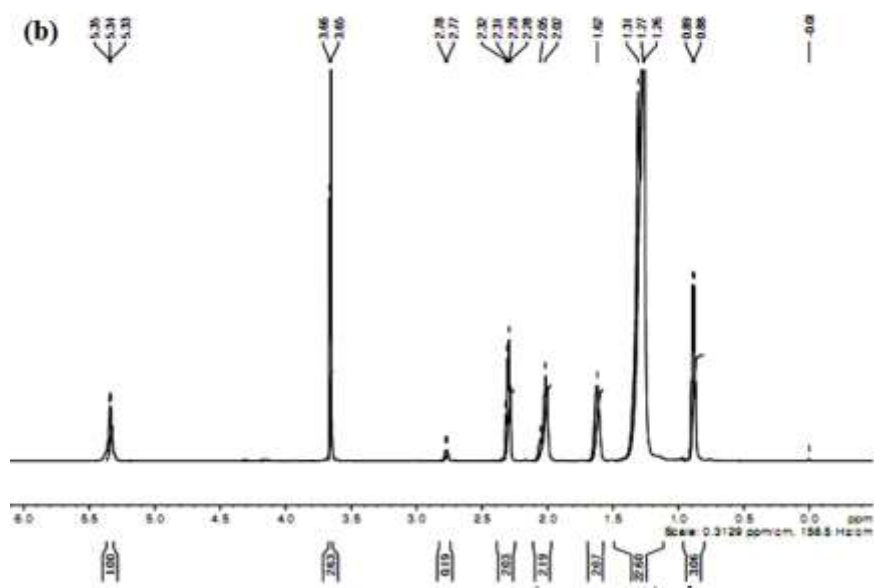
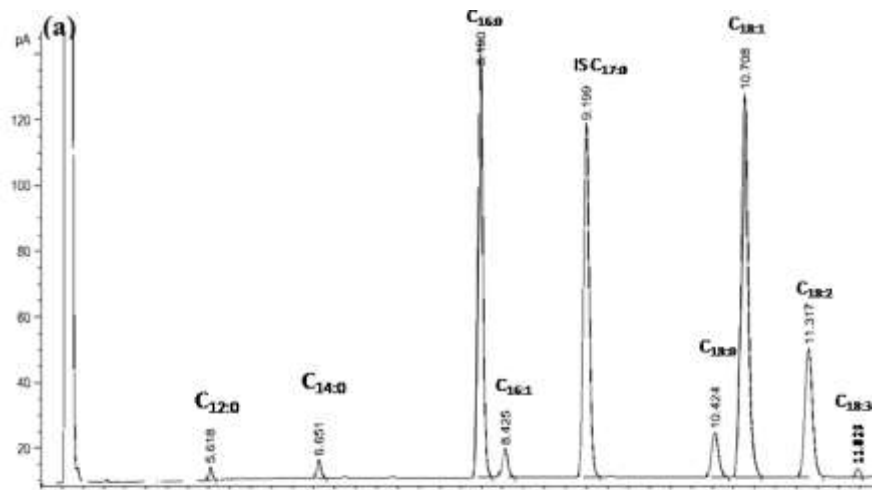
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Figure captions:

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) SiO_2 ; (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) 1H 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 leachability towards ME content (reaction conditions: catalyst amount 3%; methanol to oil molar ratio 9:1; 1 h and at 65°C).





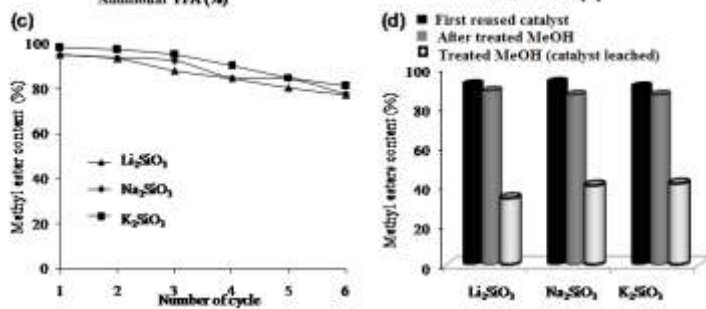
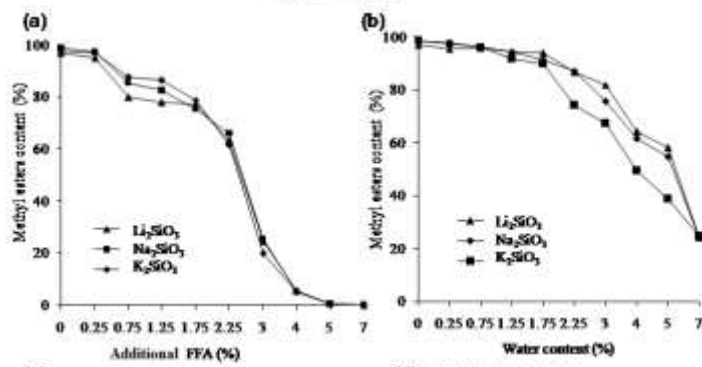
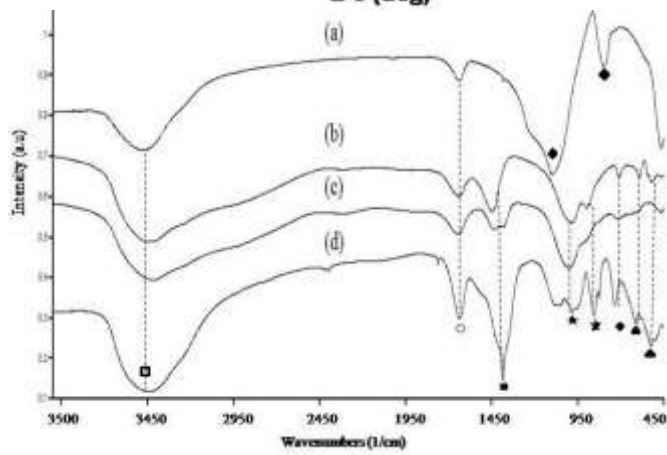
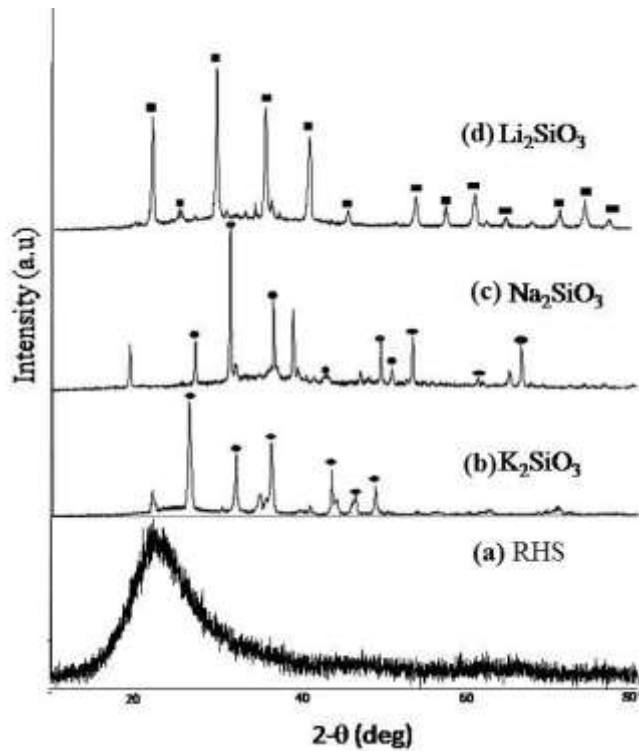


Table 1

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

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

Table 2

Properties of biodiesel from waste cooking oil

Parameters	Unit	Catalysts			Biodiesel specification EN14214
		Li ₂ SiO ₃	Na ₂ SiO ₃	K ₂ SiO ₃	
Ester content	wt. %	96.6±0.03	98.2±0.04	97.6±0.02	96.5 (min)
Density	kg m ⁻³	887	873	895	860 – 900
Viscosity	mm ² s ⁻¹	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)

Ms. Ref. No.: JESTCH-D-14-00001

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

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

Due date revision: 13 April 2014

Response to Reviewer

No.	Comment Reviewer	Response to Reviewer
1.	<p>Reviewer #1: Comment 2: It is still not addressed properly. Since the authors were using waste cooking oil as the feedstock, high free fatty acid (FFA) is expected and alkaline catalyst is definitely not a suitable option (Line 49-54). Based on the rebuttal from authors, it seems that the reaction time is more important than the FFA content; however, it is actually contradicting to the information presented in the Introduction. In addition, the negative effect of FFA towards FAME content when using alkaline catalyst also presented in Figure 6 (a). Why heterogeneous acid is not developed to overcome the problem of FFA? Again, it is suggested to add in the preparation of acid-RHS to improve the novelty of the present work.</p>	<p>Line 49-54 in the introduction address the homogeneous alkali catalyst (base) ex. NaOH, KOH. These types of homogeneous alkali catalyst are not tolerance toward the presence of FFA (>2.5%) in the feedstock of biodiesel.</p> <p>Therefore, in line 54-59 we informed that the heterogeneous alkali catalyst has more tolerance towards the FFA. In this manuscript we impregnate alkali metals into RHS in order to create a pseudo-heterogeneous alkali substance and also more tolerance toward FFA in feedstock.</p> <p>Heterogeneous acid catalyst was included in section 3.2</p>
2.	<p>Comment 3: "Practically any value below 2.5 % is acceptable for basic catalyst" - however, normally, waste cooking oil contains high FFA as mentioned in the introduction. If the FFA is below 2.5 %, I would consider the oil is still in good condition (refined) and not totally "waste" cooking oil. In biodiesel production, if "waste cooking oil" is used as the feedstock, the FFA content is definitely more than 2.5 % and acid catalyst is required to pretreat the FFA. Proper revision is still required to address the contradict information presented in the</p>	<p>Waste cooking oil change as used cooking oil (UCO)</p> <p>The sentences have been rephrased for clear argument (Line 49-51).</p> <p>Figure 7 change as Figure 6.</p>

	<p>introduction with materials and methods & results and discussion. From the rebuttal by authors, there is no "Figure 7" in the revised manuscript. It should be Figure 6. Please check the "Figure 7" mentioned in text throughout the revised manuscript.</p>	
3.	<p>Comment 4: Why HCl will not wash out the Si? From line 90, the silica content is "more than 8.22 %" (why not mention the exact value?) - based on this value, the silica content is actually very low compared to the value mentioned in Introduction (line 63). However, in line 182, the authors again mentioned the silica content in RHS was 96.5 %. It is very confusing.</p>	<p>Acid wash is to remove the organic and trace elements (metal) and HCL does not wash out Si because strong bond of Si-O-Si, creates a strong framework. Therefore it is hard/difficult for HCL to wash out Si in the cleaning/washing process.</p> <p>Line 86 (the silica content is 8.22 %.) is removed. The explanation in line 86 that unpurified RHS has silica content 88.28% and after the washing (with HCl) the silica content increases to 96.5% (line 181). The sentences have been rephrased for clear argument.</p>
4.	<p>Comment 6: Why the XRD result for catalyst calcined at 500-700 °C is not found in the revised manuscript to justify the rebuttal by authors? Why not calcine the catalyst from 200-700 °C? The mentioned two references also not included in the revised manuscript.</p>	<p>The RHS calcinations between 200-700 °C was added in section 3.1</p>
5.	<p>Comment 7: Why methanol:oil molar ratio of 12:1 was selected, but not the optimum ratio 9:1 (line 266)? Please check the numbering of each subtitle. This minor mistake should not occur in the revised manuscript.</p>	<p>Revised</p>
6.	<p>Comment 8: The reference is still not provided in the revised manuscript. Please check.</p>	<p>References were already provided, but we did not mark them in red ink. However, now we did put it in red ink.</p>
7.	<p>Comment 10: Caption for Figure 2 (a) should change to RHS instead of SiO₂.</p>	<p>Revised</p>
8.	<p>Comment 20:</p>	<p>Regeneration of catalyst is added in section 3.6</p>

	<p>It is obvious that a lot of active sites were leached out from the catalyst (33-40 % of FAME content is considered very high under reaction without catalyst!). Catalyst regeneration is not included in the revised manuscript and not addressed by the authors in the rebuttal.</p>	
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The Revised Manuscript For R2 :

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 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: Used cooking oil, Transesterification, Alkali metal, Rice husk silica, Pseudo-heterogeneous catalyst, Methyl ester.

5. 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 (CO₂) 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 used cooking oil (UCO). The source is abundant supply, relatively inexpensive and the utilization offers benefits on environmental conservation (Nurfritri 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 UCO contains free fatty acid (FFA) and moisture. **FFA content in waste oil should be as low as possible for alkali-catalyzed transesterification and alkali catalysts will readily react with FFA to form soap if FFA content above 2.5% present in the reaction media (Boro et al., 2012).** 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 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.

6. Material and Methods

2.1 Materials

The raw material used in this work is UCO, (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), 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 ($H_c = 8.2$), 2,4-dinitroaniline ($H_c = 15.0$) and 4-nitroaniline ($H_c = 18.4$) and methyl heptadecanoate as an internal standard GC grades ($> 99.1\%$). Methanol (anhydrous, $\geq 99.8\%$), sulfuric 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.

6.2. 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, Ca, K, Mg, Mn and Na) contained in RHA (Kalapathy and Proctor, 2000; Madrid et al., 2012) and organic compounds. Finally, the clean ash was dried in an oven at $105 \text{ }^\circ\text{C}$ for 2 h. The purified RHA is labelled as rice husk silica (RHS).

6.3. 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 $\text{M}^+\text{OH}:\text{SiO}_2$ molar ratio of 2:1 (stoichiometrical ratio) (Foletto et al., 2009). The obtained mixture was then stirred and heated at $90 \text{ }^\circ\text{C}$ for 2 h. **Lastly, the mixture was dehydrated at $200 \text{ }^\circ\text{C}$ for 30 min, and then calcined at 200, 500 and $700 \text{ }^\circ\text{C}$ 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 $100 \text{ }^\circ\text{C}$ for 2 days. The obtained dry powder was ground followed by calcination at $500 \text{ }^\circ\text{C}$ for 7 h. The samples were labeled as SO_4 -silica (Ling et al., 2008).

6.4. Material characterization

The alkali metal silicate was identified by X-ray diffraction (Rigaku) with $\text{Cu K}\alpha$ 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 Micromeritics ASAP 2000. Prior to the analysis, all the samples were degassed at $105 \text{ }^\circ\text{C}$ and the adsorption of N_2 was measured at $-196 \text{ }^\circ\text{C}$. The size and morphology of 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 ($\text{H}_+ = 8.2$), 2,4-dinitroaniline ($\text{H}_+ = 15.0$) and 4-nitroaniline ($\text{H}_+ = 18.4$). 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 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 analyzed 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 $65 \text{ }^\circ\text{C}$ 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 ($35\text{--}75 \text{ }^\circ\text{C}$) 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. 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 $^{\circ}\text{C}$, 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 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:

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

Where

ΣA = total peak area of ME from $\text{C}_{12:0}$ to $\text{C}_{18:1}$

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.

$^1\text{H-NMR}$ 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 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.

7. 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 $\text{M}^+\text{-O}$ 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 ($\text{M}^+ = \text{Li, Na, K}$) in silica matrix was successful.

The diffractograms of RHS (Fig. 2a) showed a hump at 2θ 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 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). **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 (500-700 °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 °C, is chose as the optimal calcination temperature, as well as saves energy as compared to at 700 °C. The intense diffraction peaks from at 23.77° to 46.81° are confirmed to be potassium silicate (Fig. 2a). The intense diffraction sharp peaks from 25.26° to 65.93° are related to sodium silicate (Fig. 2b). 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. 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 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 UCO was determined by GC-MS analysis (Fig.4a). The output of GC analysis proved that UCO mainly comprises of ME of methyl laurate ($\text{C}_{12:0}$) 0.86%, methyl myristate ($\text{C}_{14:0}$) 1.27%, methyl palmitate ($\text{C}_{16:0}$) 30.24% followed by 3.54% methyl palmitoleate ($\text{C}_{16:1}$), 4.67% methyl stearate ($\text{C}_{18:0}$), 40.82% methyl oleate ($\text{C}_{18:1}$), 17.55% methyl linoleate ($\text{C}_{18:2}$), and 1.05% methyl linolenate ($\text{C}_{18:3}$). Figure 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 ^1H NMR spectrum of ME from UCO is shown in Figure 4b. The triplet at δ 5.31–5.36 ppm represents the olefinic protons ($-\text{CH}=\text{CH}-$). 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 ($-\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}-$) of the unsaturated fatty acid chain. The quartet at δ 2.28 ppm represents the α -methylene protons to ester ($-\text{CH}_2-\text{CO}_2\text{Me}$). The α -methylene protons to double bond ($-\text{CH}_2-\text{C}=\text{C}-$) appear as a doublet at δ 2.01 and 2.05 ppm. The β -methylene protons to ester ($\text{CH}_2-\text{C}-\text{CO}_2\text{Me}$) 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 ($\text{C}-\text{CH}_3$) 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 be because of the surface vacancies of support material (RHS) were filled with metals of catalysts, observed by Ma et al. (2008). In Fig. 5a, 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).

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 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 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.

3.5. 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 0.25–7 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 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. 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 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 UCO, indicates that H_2O up to 1.75% has little effect on the total basicity of the catalyst.

3.6 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 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. 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 or **the activity declined due to the ion-exchange between M^+ and H^+ as the hydrolysis reaction is reversible (Guo, et al, 2012).**

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 M^+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.

3.7 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.

8. 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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Figure captions:

- Fig. 1. FT-IR spectra of (a) RHS, (b) K₂SiO₃, (c) Na₂SiO₃, (d) Li₂SiO₃: ▲: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).
- Fig. 2. XRD pattern of alkali metals silicate: (a) RHS; (b) ◆ K₂SiO₃; (c) ● Na₂SiO₃ and (d) ■ Li₂SiO₃ (after calcined at 200-700 °C)
- Fig. 3. FESEM micrographs of (a) RHS, (b) K₂SiO₃, (c) Na₂SiO₃, (d) Li₂SiO₃ (after calcined at 500 °C)
- Fig. 4. (a) Gas chromatogram and (b) ¹H NMR spectrum of ME from used cooking oil
- 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
- 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).
- Fig.7. ME content in the transesterification of UCO with methanol using regenerated alkali metal silicate.

The New Revised Figure in R2

- Figure 2. Fig. 2. XRD pattern of alkali metals silicate: (a) RHS; (b) ◆ K₂SiO₃; (c) ● Na₂SiO₃ and (d) ■ Li₂SiO₃ (after calcined at 200-700 °C)

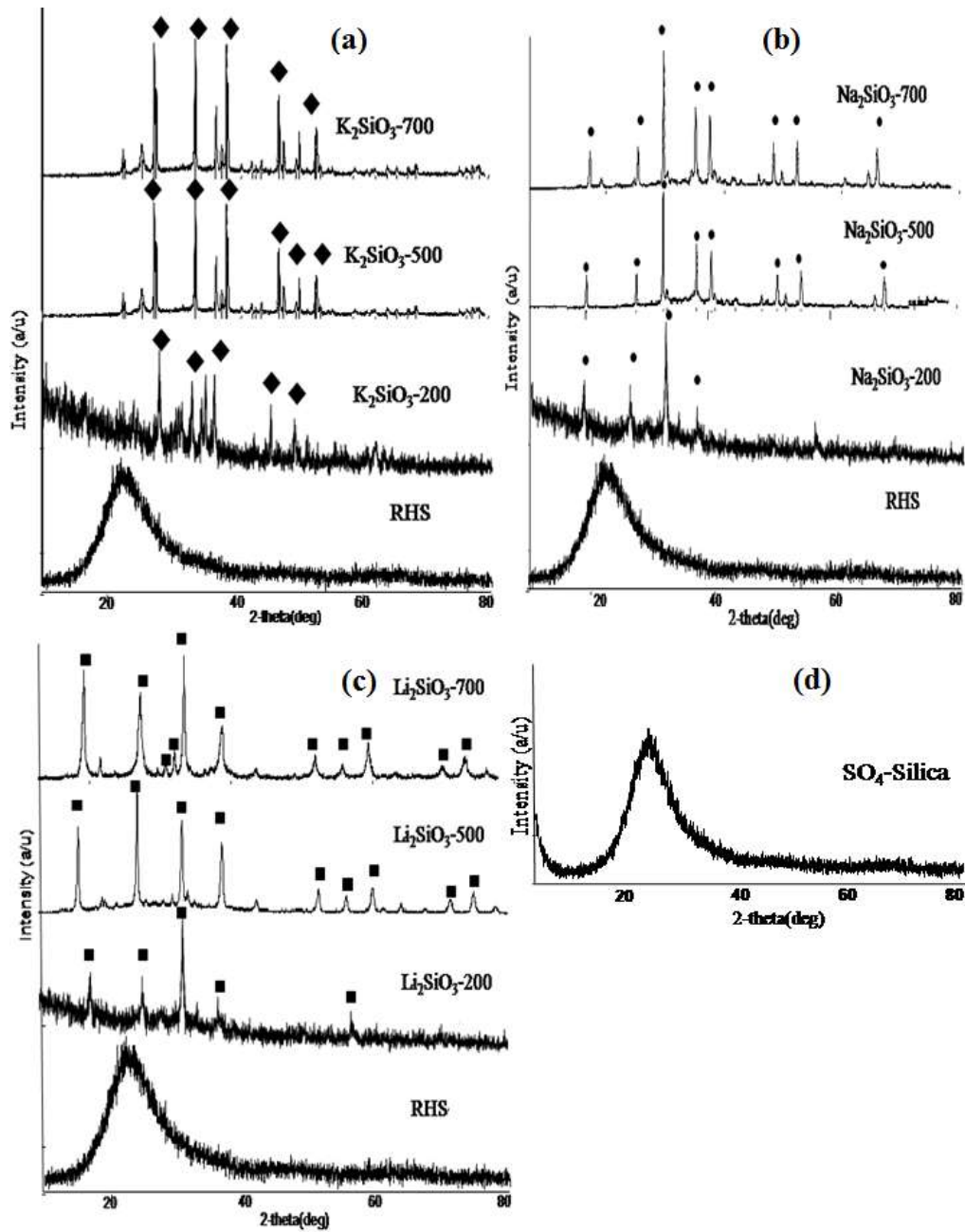
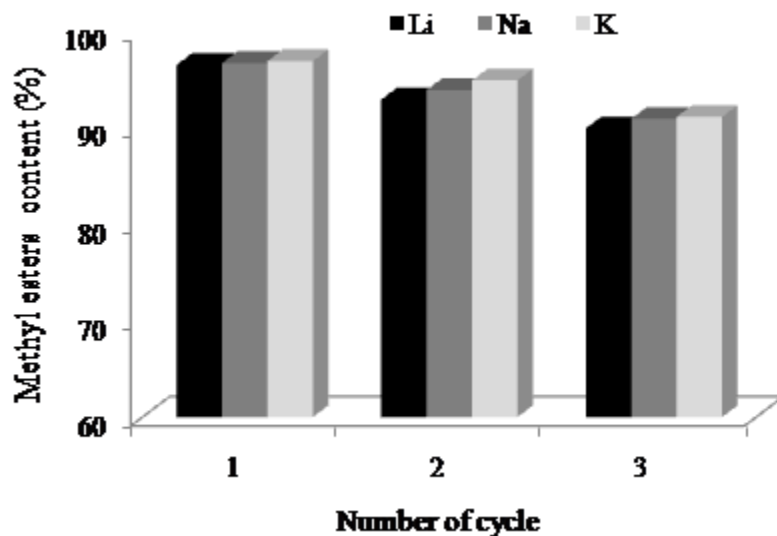


Figure 7. ME content in the transesterification of UCO with methanol using regenerated alkali metal silicate.



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