

RICE HUSK SILICA SUPPORTED OIL PALM FRUIT ASH AS A CATALYST IN THE TRANSESTERIFICATION OF WASTE FRYING OIL

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ABSTRACT

An investigation was conducted on palm oil palm fruit ash (OPFA), OPFA supported by rice husk silica (RHS), and potassium-OPFA-RHS as catalysts for methyl esters production through transesterification process using waste frying oil. The catalysts showed longer lasting activity than the homogeneous alkali catalysts. The optimum conditions for the process were: OPFA and K-OPFA-RHS catalyst amount 3 %; OPFA-RHS catalyst amount 5 %; methanol to oil molar ratio 9:1; and a reaction duration is 2 h. The process was able to trans esterify oil to methyl esters at 96.6–98.2 % conversion at 65 °C for all series. The catalysts were easily separated from the reaction mixture by filtration and able to be reused. Reusability up to 5 cycles is feasible with ME content above 83 %. The final product met selected biodiesel fuel properties in accordance with European Standard EN 14214.

KEYWORDS: *Biodiesel; solid catalyst; oil palm fruit ash; rice husk silica; waste frying oil.*

1.0 INTRODUCTION

The growing awareness concerning the environmental issues on energy supply and usage have recently been the topic of interest in research. Among the various alternative energy discovered, biodiesel is one of the promising blended fuel to substitute petroleum derived diesel which offers friendly and sustainable environment. However, operational cost of feedstock (about 80%) exerts the major impact on the overall production cost of biodiesel (Gulsen, et al., 2014). The other issues are utilizing edible oil for biodiesel that competes with food needs and has a definite impact on global food security and agricultural land. One of the ways to counter this issue is to use waste oil (Canakci & Gerpen, 2001), which is abundant in supply, relatively inexpensive and the utilization offers benefits on environmental conservation (Nurfitri, et al., 2013). Currently homogeneous catalyst is utilized to catalyze the transesterification process. The production of biodiesel via transesterification process by homogeneous catalyst has few drawbacks. The homogeneous catalyst is likely to form soap through the saponification process during the transesterification of alcohol and oil, thus causes loss of time in separating and the purifying of product (Lim, et al., 2009).

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In addition, the isolating of homogeneous catalyst from the reaction mixture is difficult (Ebiura, et al., 2005; Oku et al., 2012). Recently, the production of biodiesel by transesterification method using solid catalysts has become more favorable and has been scaled up to industrial level. Therefore, a process using solid catalysts has been developed which has a positive impact on environment and the cost. Many types of heterogeneous catalysts, such as $\text{KF}/\text{Ca}_x\text{Al}_2\text{O}_{(x+3)}$, transition metal oxide, and functionalized carbon nanotubes (Oku, et al., 2012; Shuit, et al., 2013; Tao, et al., 2012). In addition, the exploitation of waste sources as catalysts in transesterification, i.e. egg shell, boiler ash, cockle shell and nano-sized solid acid synthesized from rice hull ash has become very attractive (Boey, et al., 2011a; Boey, et al., 2011b; Chakraborty, et al., 2010; Zeng, et al., 2014). On the other hand, the demand of biomass is in increasing trend globally, and an overview in Malaysia, the world's second largest producer of palm oil which contributes 39% of the world's total palm oil production (MPOC, 2014), at total of 19.22 million metric tons of palm oil produced in 2013, with a total of 5.3 million hectares planted with oil palm trees (MPOB, 2014). There are approximately 421 palm oil mills with a total of 100.8 million tons of fresh fruit bunch (FFB)/year (19.02 tons/ha x 5.3 million ha) in 2013 (MGGS, 2014). Malaysia generates about 95 million tons of biomass in 2012, approximately 5% of boiler ash (BA) is produced upon the burning of dry EFB, fiber (OPFA) and shell in boiler (Tangchirapat, et al., 2007). Meanwhile, the oil palm ash (OPA) is rich in SiO_2 , K_2O , CaO and others minerals (Evbomwan, et al., 2005).

On the other hand, according to the Department of Statistics Malaysia, the paddy production is increased from 2.58 million tons in 2011 to 2.75 million tons in 2012 (Department of Statistics Malaysia, 2013). Land utilization in Malaysia for paddy production is at 692.3 hectares in 2012 (Monthly Statistical Bulletin Malaysia, 2013). It is reported that for each tons of rice produced, about 0.2 tons of rice husk is generated (533,000 tons rice husk ash (RHA) in 2011) (Liou, 2004). RHA as a biomass has a promising role as a support with high silica content (87-99%) abundant and being a low cost waste source as amorphous silica precursors (Noushad, et al., 2012). Accordingly, in this study, utilization of biomass from OPFA-RHS as a solid catalyst in transesterification reaction was investigated, with optimization of methanol/oil molar ratio, catalyst amount, reaction time and reusability.

2.0 MATERIALS AND METHOD

2.1 Materials

Waste frying oil (WFO), (acid value 3.54 ± 0.05 mg KOH/g, equivalent to 1.77% FFA (as oleic acid) and $0.28\% \pm 0.04$ of moisture content), was collected from local hawker in Gambang, Pahang, Malaysia. Oil palm fruit (OPF) was obtained from FELDA Lepar Hilir Palm Oil Mill, Gambang, Pahang, Malaysia; and the RHA was obtained from rice mills in Kedah, Malaysia. The chemicals purchased from Sigma-Aldrich (Switzerland) including potassium hydroxide, phenolphthalein ($H_c = 8.2$), 2,4-dinitroaniline ($H_c = 15.0$), 4-nitroaniline ($H_c = 18.4$) and methyl heptadecanoate as an internal standard of GC grades ($> 99.1\%$). Methanol (anhydrous, $\geq 99.8\%$), hydrochloric acid (37%), and hexane (anhydrous, $\geq 99.8\%$) were supplied by Hamburg (Germany). CDCl_3 for NMR was purchased from Cambridge Isotope Laboratories, Andover, MA (USA).

2.1.1 Catalyst Preparation and Characterization

The RHA was sieved to obtain a smaller ash with particle size of 200 mesh and dried overnight in an oven at 105 °C until constant weight. Then, 10 g of powdered RHA was washed with 60 mL of 0.1 mol L⁻¹ HCl for 1 h, and neutralized with deionized water. The resultant RHA is ready to be used as a catalyst support. Finally, the treated ash was dried in an oven at 105 °C for 2 h, after which it is rich in silica and labelled as rice husk silica (RHS). The OPF were washed with clean water, dried in the oven at 105 °C, and burnt in a furnace at 500, 600 and 700 °C, for 5 h. For activity studies, the treated ash at 700 °C was selected and designated as OPFA. The OPFA-RHS catalyst was prepared via wet impregnation method. The RHS (10g) was suspended in water and then OPFA (20g) was added to the suspension. The obtained mixture was then stirred and heated at 90 °C for 4 h. Lastly, the mixture was dehydrated at 200 °C for 30 min, and then calcined at 500 °C for 3 h. The potassium doping onto OPFA-RHS was carried out by heating 20g of OPFA-RHS with 5g of KOH in 44.56 ml deionized water to 90 °C till dryness. The dried reaction mixture was then kept in the oven at the same temperature for 12 h. Then the treated ash was ground into fine powder and calcined for 3 h at 500 °C. The KOH impregnated catalyst was designated as K-OPFA-RHS.

The catalysts and support were identified by X-ray diffraction (Rigaku) with Cu K α X-ray as a source. A FTIR (Perkin Elmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of catalyst and methyl esters at 400-4000 cm⁻¹ range. The morphology of catalyst was observed by SEM (Zeiss EVO50). The base strength of the catalyst (H₊) was determined 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 WFO was filtered to remove any visible solid material. The acid value of the oil was determined following the standard EN 14104; and the moisture content was analysed using Karl Fischer titration method (784 KFP Titrino, Metrohm).

2.1.2 Transesterification of waste frying oil

Transesterification of WFO using various catalysts, OPFA, OPFA-RHS and K-OPFA-RHS, was carried out in a 250 ml two-neck round bottom flask equipped with a reflux condenser, thermometer on a magnetic hotplate. The transesterification experiment was carried out at temperature 65 °C. Several reaction parameters, catalyst amount (0-5%), methanol/oil molar ratio (6:1-21:1), reaction time (0-5 h), reusability and leaching of catalysts were investigated. At the end of the reaction, the reaction mixture was allowed to cool to room temperature. Methyl esters (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 was repeated three times in order to reflect the precision and errors of the results. The ME content in biodiesel was determined using GC-MS method. 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.

3.0 RESULT AND DISCUSSION

3.1 Characterization of Catalyst

The major chemical groups present in RHS and catalysts (OPFA, OPFA-RHS and K-OPFA-RHS) are identified by the FTIR spectra as shown in Figure 1. In the typical peak, with the broad band at about 3460 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, et al., 2000). Band at 1635 cm^{-1} shows the presence of bending vibration of water molecules bound to the catalyst and support matrix (Rafiee et al., 2012). 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 $Si-O-M^+$ or bond of $Si-O-M^+$ (M^+ may indicate Si, Al, Mg) are shown at 1013 cm^{-1} and 1403 cm^{-1} . The stretching of O-Si-O is shown at 805 cm^{-1} and the peak at 1096 and 1119 cm^{-1} are attributed to the Si-O stretching vibrational modes (Saengprachum, et al., 2013). Peaks were not found between 2800 and 3000 cm^{-1} , deducing that there were no organic compounds in the silica after the treatment.

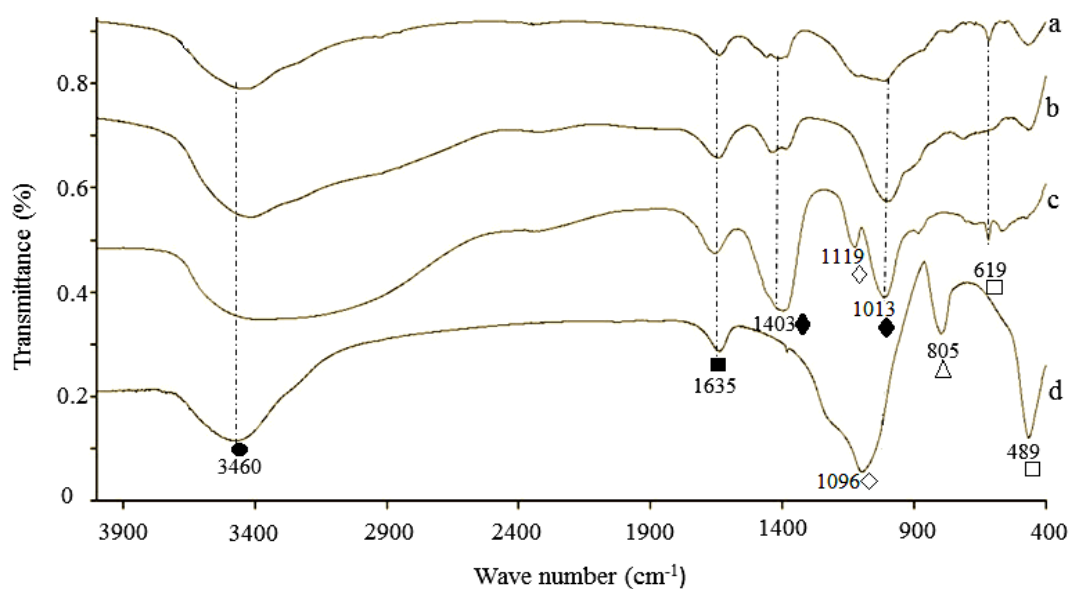


Figure 1. FTIR spectra of (a) K-OPFA-RHS, (b) OPFA-RHS, (c) OPFA and (d) RHS (all after calcined; □: M^+-O ; ▲: O-Si-O; ◆: deformation (Si-O-Si)-(M-O); ◇: Si-O; ■: O-H vibration from water molecules; ●: O-H bending and stretching)

In order to obtain the optimal calcinations conditions, OPFA were calcined at $500\text{ }^{\circ}\text{C}$, $600\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$ for 5 h. From XRD results (Figure 2a-c), it was found that at $500\text{ }^{\circ}\text{C}$ the OPFA is not a clear crystal structure and with the increasing of calcination temperature (600 – $700\text{ }^{\circ}\text{C}$), the sharp peaks were intensified and amorphous peaks were seen at much lower intensity. The calcination treatment enhances the intensity of few diffraction peaks, as illustrated by the crystalline phase of the catalyst to become more regular. Hence the best calcination temperature, $700\text{ }^{\circ}\text{C}$, is chose as the optimal calcination temperature. The major peaks of OPFA patterns were potassium calcium silicate ($K_4CaSi_3O_9$ and $K_{9.6}Ca_{1.2}Si_{12}O_{30}$). The presence of $K_4CaSi_3O_9$ is indicated by

2-theta (θ) at 28.6, 31.3, 31.9, 32.3, 40.7, 41.9, 50.4, 66.1°, while for $K_{9.6}Ca_{1.2}Si_{12}O_{30}$ by 2θ at 29.9, 39.8, 58.9, 73.9°. The diffractograms of RHS (Figure 2d) 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 previous study (Kalapathy, et al., 2000), indicating the disordered structure of amorphous SiO_2 . The intense diffraction peaks of OPFA-RHS (Figure 2e) is found at 28.65° to 76.48° and the intense peaks at 23.77° to 46.81° is found for K-OPFA-RHS (Figure 2f). The most intense and sharp peak was at 28.65° and 31.90° are confirmed to be potassium calcium silicate and potassium silicate, respectively.

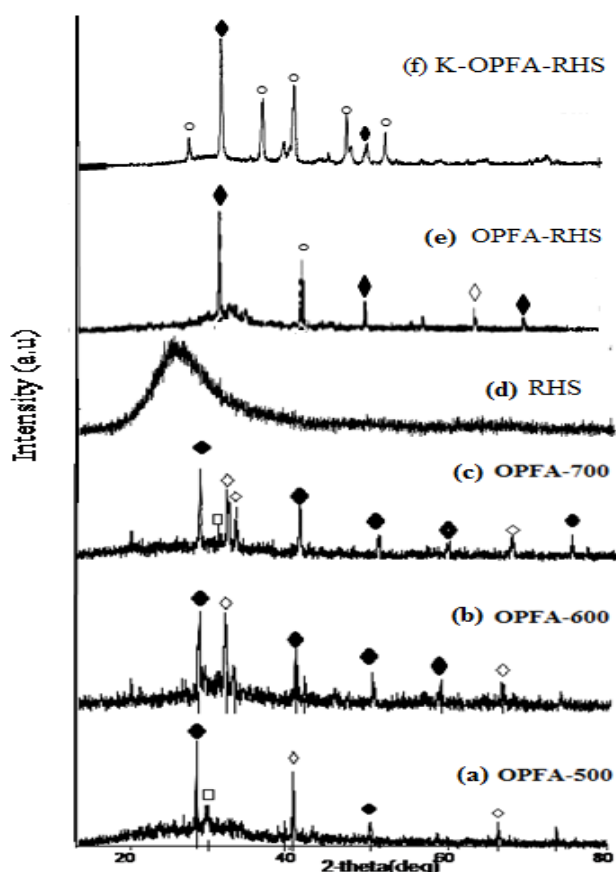


Figure 2. XRD pattern of catalysts at different calcination temperatures ($\circ K_2SiO_3$; $\blacklozenge K_{9.6}Ca_{1.2}Si_{12}O_{30}$; $\diamond K_4CaSi_3O_9$; $\square KAlO_2$)

The micrograph of the RHS, OPFA, OPFA-RHS, and K-OPFA-RHS demonstrated the crystal morphology (Figure 3a-d). The RHS was showing a spherical shape and heterogeneous surface morphology. The micrographs of OPFA was shown spongy and porous, as was reported elsewhere (Boey, et al., 2011; Chin, et al., 2009). The morphology of OPFA-RHS and K-OPFA-RHS catalysts were in the form of regular and spherical shaped particle. The basicity of the catalyst was estimated using the Hammett indicator. The basic strength of OPFA and K-OPFA-RHS is in the range: $15 < H_- < 18.4$. Therefore, the catalyst 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 OPFA-RHS in this study are in the range: $8.2 < H_- < 15.0$ because it failed to change the colour of 2,4-dinitroaniline.

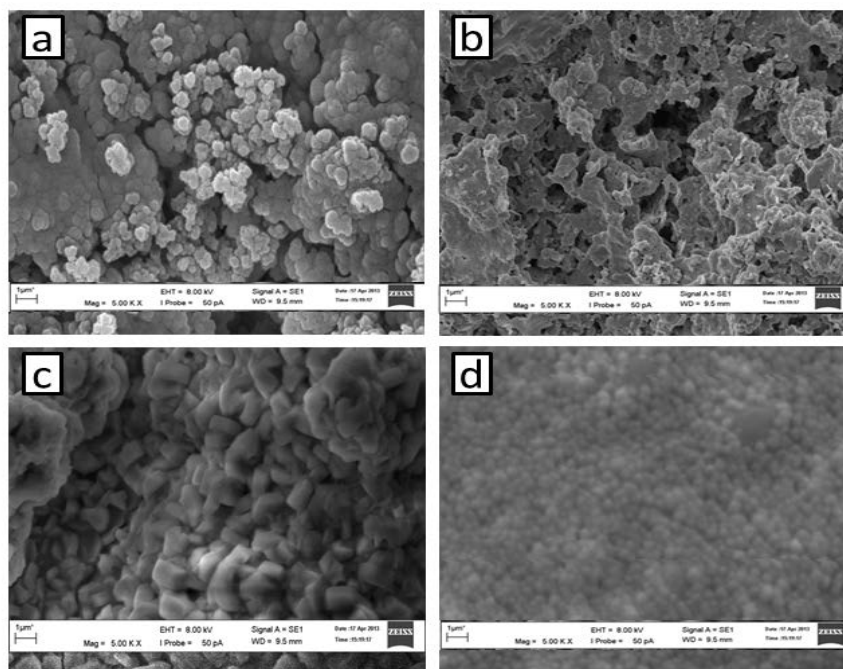


Figure 3. SEM micrographs of calcined (a) RHS, (b) OPFA, (c) OPFA-RHS and (d) K-OPFA-RHS

3.2 Transesterification of WFO

3.2.1 Effect of catalyst amount

The amount of catalyst was varied in the range of 0 to 5 wt.%. The reaction was carried out with a methanol to oil molar ratio of 9:1 and reaction temperature of 65 °C for 2 h. As shown in Figure 4a, ME conversion is dependent on the amount of catalyst used (0-2%), with the increasing of catalyst amount increases ME content significantly. The maximum conversions about $97.4 \pm 0.5\%$ and $98.2 \pm 0.3\%$ for OPFA and K-OPFA-RHS, respectively, was achieved at 3% catalyst. As for OPFA-RHS, $96.6 \pm 0.4\%$, conversion is achieved at 5% catalyst. The increase in ME content is due to the contact opportunity of the catalyst and the reactant, directly affect the reaction speed. Furthermore, the addition of a large amount of catalytic material had lead to an increase in ME content. The excess solid catalyst reacted with the oil, resulting in emulsion formation, thus leading to low yields of ME and the separation of esters became difficult (Hindryawati & Maniam, 2015; Hingu, et al., 2010). Therefore, the catalyst concentration is an influencing factor on the amount of methoxide ions formed to reaching the equilibrium of reaction.

3.2.2 Effect of methanol to oil molar ratio

The effect of methanol to oil molar ratio is one of the important variables that affect in the transesterification reaction. As observed from Figure 4b, molar ratios of methanol to oil 6:1, 9:1, 12:1, and 20:1 were used. The reaction was carried out with a catalyst

amount of 3% and reaction temperature of 65 °C for 2 h. The maximum ME content was achieved 97.4±0.5%, 98.2±0.3% at 9:1 ratio using OPFA and K-OPFS-RHS, respectively. As for OPFA-RHS, 90.8±0.5 %, conversion is achieved at 12:1 ratio. Further increase in molar ratio did not cause any appreciable change in the reaction activity. This may due to the high ratio is too large and can retard the separation of methyl esters and glycerol as well as complicates the methanol removal process (Molaei & Ghasemi, 2012). The lower ME content for OPFA-RHS, is due to the lower basicity of OPFA-RHS as compared to other catalysts (as indicated by Hammett indicators).

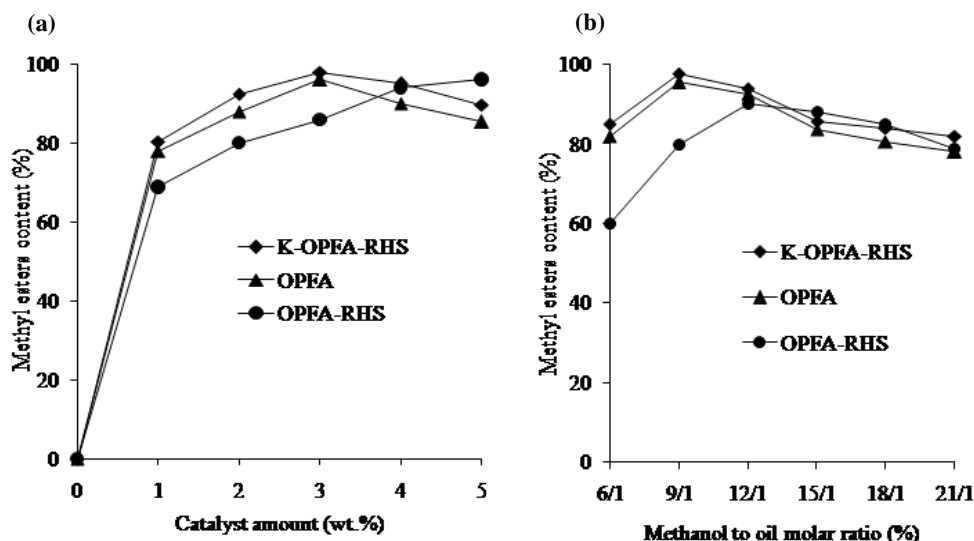


Figure 4. (a) various catalysts amount (0-5 wt.%), and (b) methanol to oil molar ratio (6:1 – 21:1) on methyl esters content

3.2.3 Effect of reaction duration

The effect of the reaction duration is shown in Figure 5a. OPFA and K-OPFA-RHS catalysts seemed to have similar ability. The reaction duration was varied from 0 to 5 h. The reaction was carried out with catalyst amount of 3% and methanol to oil molar ratio 9:1 at 65 °C. From Figure 5a, it can be seen that the ME content increased within the first 30 min and reached as high as 80%, 65% and 61% for OPFA, K-OPFA-RHS and OPFA-RHS, respectively. 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 at 97.5±0.5 %, 98.2±0.4% and 93.5±0.5% for OPFA, K-OPFA-RHS and OPFA-RHS, respectively. Figure 5a shows the best reaction duration for OPFA and K-OPFA-RHS is 2 h, furthermore, OPFA-RHS are at 3 h reaction duration. It is interest to note that for longer reaction duration the conversion decreases, which may due to the reversible reaction, resulting in a loss of esters as well as causing more fatty acid to form soap.

3.2.4 Reusability

Reusability is one of the factors in economical application of heterogeneous catalyst. The catalyst was reused without any further activation. At the end of reaction, the OPFA, OPFA-RHS, and OPFA-K-RHS catalysts were decanted with simple washing

with methanol followed by hexane and directly used again for subsequent reaction under the optimum condition. After 5 cycles, the ME content was above 83% for OPFA, K-RHS and OPFA-RHS (Figure 5b). This experiment shows that a simple regeneration method could recover the active sites of the catalyst.

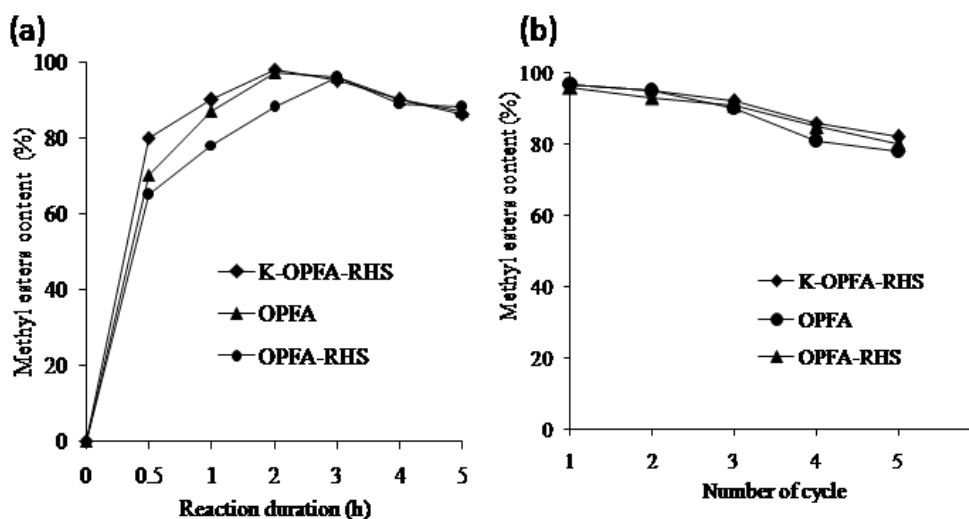


Figure 5. (a) Effect of reaction duration (0-5 h) on ME content from WFO; (b) reusability of catalyst (reaction condition for reaction duration: 3% catalyst; methanol to oil molar ratio (12:1))

3.2.5 Methyl esters properties

In order to assess the quality of the final product, it was evaluated according to EN-14214 (Table 1). It was found that the final product meets all the tested parameters (ester content, density, viscosity, water content, flash point, iodine value and acid value) in accordance with EN 14214, for all the catalysts. The ester content catalyzed by OPFA and K-OPFA-RHS recorded the highest ME content of 98.2%, and 97.5% at 2 h. Although many other parameters need to be analyzed in order to confirm the final product to be used as a fuel, these seven parameters can serve as preliminary indicators for the purpose.

Table 1. Biodiesel Properties Prepared Under Different Catalysts

Parameters	Unit	Catalysts			Biodiesel specification EN14214
		OPFA	OPFA-RHS	K-OPFA-RHS	
Ester content	wt. %	97.4±0.4	96.6±0.3	98.2±0.5	96.5 (min)
Density	kg m ⁻³	887	885	873	860 – 900
Viscosity	mm ² s ⁻¹	4.0	4.1	3.8	3.5 – 5.0
Water content	mg/kg	200	300	200	500 (max)
Flash point	°C	155	156	154	101 (min)
Iodine value	g I ₂ /100 g	102	103	102	120 (max)
Acid value	mg/g KOH	0.3	0.4	0.3	0.5 (max)

4.0 CONCLUSION

Oil palm fruit ash and potassium hydroxide catalysts supported on rice husk silica used in this work showed remarkable to produce methyl esters from waste frying oil. According to the result of catalysts characterization, the formed $K_4CaSi_3O_9$, $K_{9.6}Ca_{1.2}Si_{12}O_{30}$ and K_2SiO_3 should be the main active components for the catalytic activity. The optimum reaction conditions were: catalyst amount 3% for the OPFA and K-OPFA-RHS, while 5% for OPFA-RHS with methanol to oil molar ratio of 9:1 for 2 h at 65 °C with a constant stirring which able to produce ME between 96.6–98.2%. The catalyst exhibited relatively good reusability, where up to 5 cycles were feasible with ME higher than 83%.

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