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Synthesis of K₂O/Zeolite catalysts by KOH impregnation for biodiesel production from waste frying oil

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Abstract. K₂O/Zeolite compounds were successfully synthesized using KOH as starting material and natural zeolite as support. The catalysts were calcined at 500ºC for 3 h and then characterized by X-Ray Diffractometer (XRD) and Scanning Electron Microscopy (SEM). The SEM images reveal that the zeolite and K₂O/zeolite particles are irregular in shape (100 to 400 nm). The independent variables were impregnated amounts of KOH (15 - 25%), catalyst to oil ratios of 1.0 - 6.0 wt.%, and reaction time of 2 h. The highest biodiesel yield of 95% was produced from the reaction with 2.1 wt.% catalyst of 25% KOH impregnated. The properties of produced biodiesel complied with SNI. The catalytic stability test showed that the 25% KOH impregnated catalyst was stable.

1. Introduction

Petroleum fuels sources that use as energy sources are currently depleted, while the needs for fuels increase rapidly with increasing population. Reduced petroleum feedstock causes increasing the price of petroleum fuel [1-5]. Biodiesel is one of the types of renewable energy of biofuels that can replace the fuel oil of diesel without requiring engine modifications and produce cleaner emissions. In general, the properties of biodiesel are very similar to diesel, the difference is that biodiesel has a higher cetane number than diesel and high flash point it can be degraded easily (biodegradable), does not contain sulfur (or very low, if exist), and aromatic compounds so that the resulting combustion emissions are more environmentally friendly than diesel fuel [6-9].

The homogenous catalyst is more widely used in biodiesel production processes, such as KOH and NaOH. The use of these homogeneous catalysts raises another problem in the resulting product. The resulting biodiesel still containing the catalyst so it supposed to separated and also can cause side reactions like saponification reactions that affected the process of biodiesel production. Heterogeneous catalysts have the advantage of separating products from the catalyst more easily and simply, which can be separated by filtration or precipitation [10-12].

In this work, the potassium was impregnated on natural zeolite materials (KOH/Zeolite) for producing biodiesel from waste vegetable oil. Waste vegetable oil is one of the raw materials for making biodiesel, because the material still containing triglycerides, aside of free fatty acids. The

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availability is quite abundant, causing the oil to be a waste that has a potential to pollute the environment such as rising levels of COD (Chemical Oxygen Demand) and BOD (Biology Oxygen Demand) in the waters, also cause the smell of decay due to biological degradation [13]. During producing biodiesel process catalysts heterogeneous have lower yields, so recent studies have focused more on developing potassium-solid catalysts support into zeolite to obtain optimal yield. Several type of solid based catalysts have been reported in recent years, such as metal oxides, CaO, MgO, K_2CO_3/MgO, KNO_3/Al_2O_3, KOH/Al_2O_3, and NaY zeolite solid based catalyst shown a great activity of catalytic in biodiesel production [14].

This paper discusses the influence of active phase content in KOH/zeolite catalysts and the catalyst performance on the biodiesel production yield. The prepared catalyst was characterized by XRD and SEM methods. The effect of catalyst preparation conditions and various reaction variables on biodiesel yield were investigated. The catalyst reusability is also investigated for several consecutive runs as it represents a key advantage for industrial biodiesel production.

2. Materials and methods

2.1. Preparation of K_2O/Zeolite
Prior to use, the crushed natural zeolite was placed into the oven to reduce the water content. Then various KOH solutions (15%, 20%, and 25%) were impregnated into the natural zeolite mixed with aquadest and stirred at room temperature. The purpose of this method was to fill the pores using a metal salt solution of a certain concentration. After impregnation, the catalyst was dried in an oven at 110 °C for 24 h. The purpose of drying was to reduce the water content and crystallize the salt on the surface of the pores. Then the solids were calcined for 3 h at 500 °C which is aimed to enhance the contact surface area and to obtain K_2O on the catalyst with zeolite as support. The KOH as a source of potassium oxide which added to the zeolite structure during calcination will be converted to K_2O.

2.2. Catalyst characterization
The calcined catalyst was characterized by X-ray diffractometer (XRD) to identify the crystal phase of the sample. In the XRD method, the samples were analysed using Bruker diffractometer with Cu-Kα radiation (λ = 0.154 nm) operating at 40 kV and 100 mA. The diffractograms were recorded in the 2θ ranges of 10 – 60º at a scanning speed of 5º min^{-1}. The shape and size of the catalyst was recorded by Scanning Electron Microscopy (SEM).

2.3. Waste frying oil characterization
Kinematic viscosity of frying oil is determined using the Oswald viscometer. The density of used cooking oil is determined using a pycnometer. The acid number is determined by the method of acid base titration analysis.

2.4. Esterification reaction
The 50 g of waste vegetable oil is put into a two-neck flask. Then, methanol was added with a mole ratio oil-to-methanol of 1:8 and 1% of 0.1 N HCl as a catalyst. The two-neck flask was then assembled on the tool set. The reaction was carried out at 60 °C for 2 h then after the esterification process completed, the solution was poured into the separating funnel and precipitated for 24 h. Finally, oils were dried in the oven to remove water.

2.5. Transesterification reaction
The reaction took place in a two-neck flask in where 1- 6 % of the catalyst were placed in the reactor and mixed with 50 g esterified waste vegetable oil and methanol with the ratio of oil-to-methanol of 1: 8 [15]. After that, the reactor was closed and then heated to a temperature of 60 ºC and stirred using a magnetic stirrer with varying time for 2, 4, and 6 h. During the process, the operating temperature was kept constant. After the reaction, stirring and heating were stopped. Then the result was inserted into

the separation funnel and allowed for 12-24 h to achieve a perfect separation between two phases. The separation/purification process of the methyl ester layer needed to be resumed by drying it in an oven at 100 °C for 3 h to evaporate methanol remaining in methyl ester product. The yield of biodiesel was calculated by using the equation given in the literature.

$$\% \, Yield = \frac{Weight \; of \; biodiesel \; produced}{Weight \; of \; oil \; used} \; x \; 100\%$$

(1)

A mixture of K_2O/Zeolite catalyst with methanol was filtrated in a vacuum condition. A rotary evaporator was used to separate the excess methanol from the filtrate. The residue was then centrifuged for 20 minutes to separate the biodiesel from glycerol. The used catalyst was filtered, heating at 500 °C and then fed to the next run.

3. Results and discussion

3.1. Characterization of waste frying oil
The characteristic data of waste frying oil are demonstrated in Table 1.

Table 1. Properties of waste frying oil.

Parameter	Value
Kinematic viscosity, at 40 °C (cSt)	17.24
Density ($g.cm^{-3}$)	0.9166
Acid number (mg $KOH.g^{-1}$)	2.92

The result of the analysis of waste frying oil showed acid number reach 2.92 mg $KOH.g^{-1}$, kinematic viscosity of 17.24 at 40 °C (cSt) and density 0.9166 $g.cm^{-3}$. The high acid number in the frying oil requires the esterification process to reduce the acid number and the transesterification process to decrease the viscosity so that it can produce the final product in the form of biodiesel that meets the quality of SNI. 04-7182-2006. The acid number of waste frying oil decrease of 0.83 mg $KOH.g^{-1}$ after esterification process.

3.2. Characterization of natural zeolite and K_2O/zeolite catalyst by XRD
The XRD pattern of synthesized catalyst is shown in Figure 1. The natural zeolite exhibits a very
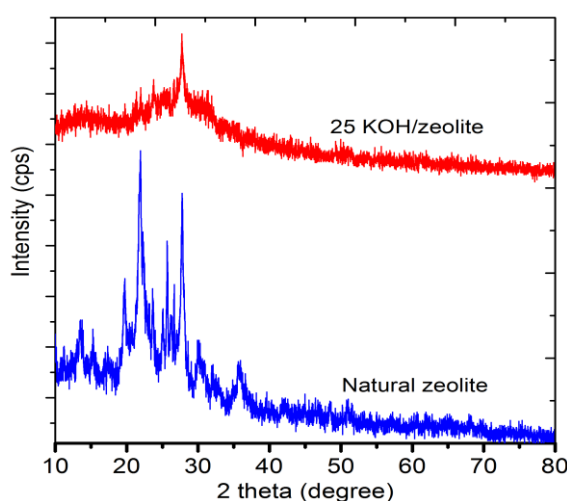

Figure 1. XRD patterns of natural zeolite and 25KOH/zeolite.

intense diffraction peak in the XRD pattern indicating a high crystallinity of the support.The diffraction peaks of the 20 wt.% KOH/zeolite sample are less intense than those of the support indicating that the zeolite crystallinity decreased upon KOH impregnation. These results are in accordance with previous study [16]. Moreover, no KOH or K_2O diffraction peaks are observed on the XRD patterns of the prepared catalysts. This might be due to the presence of highly dispersed and/or amorphous K_2O particles [17-19].

3.3. Morphology of catalyst by SEM

In order to elucidate the morphology and particle sizes of prepared sample, the SEM measurement of ash catalysts was also performed. The SEM morphologies of zeolite and KOH/zeolite are shown in Figure 2 & 3. The zeolite and KOH/zeolite catalyst were previously calcined in a muffle furnace at 500 °C for 4 h. Both zeolite and KOH/zeolite particles seem to agglomerate. The KOH/zeolite prepared samples show a difference in the morphology, as illustrated in Figure 3. KOH particles highly dispersed in the structure of zeolite support are nearly undistinguished with K_2O particles. The SEM images reveal that the zeolite and KOH/zeolite particles are irregular in shape (100 to 400 nm), as shown in Figure 2 & 3. The catalyst in nanosizes is able to increase the catalyst surface area significantly.
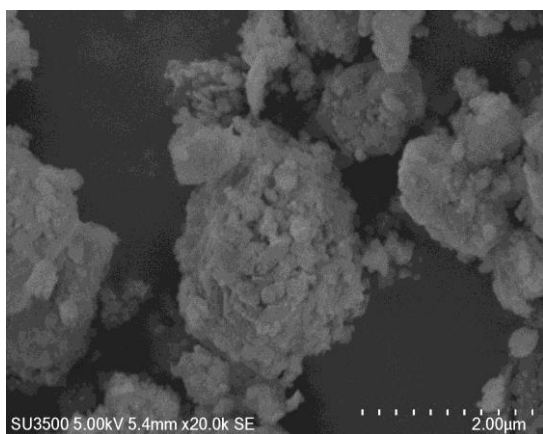

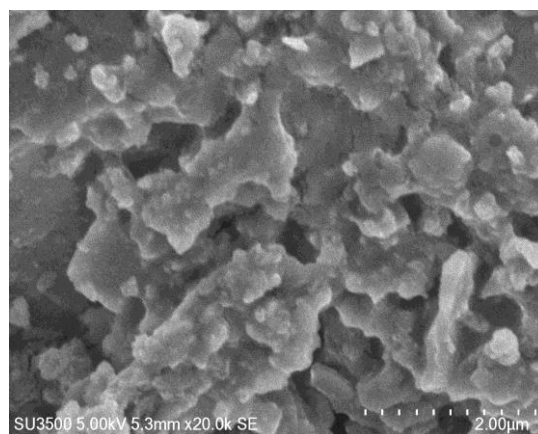**Figure 2.** SEM Images of natural zeolite.

Figure 3. SEM images of K_2O/Zeolite.

3.4. Effect of mass KOH on zeolite and catalyst to oil ratio

Figure 4 is a plot of the influence of the amount of impregnated KOH and catalyst to oil ratio on the yield of biodiesel. All transesterification reaction conditions were carried out with a methanol to oil ratio of 8:1, temperatures at 65 °C, reaction time of 2 h, and various catalysts to oil ratio (1.0 - 6.0, wt.%). The transesterification reactions were carried out with the zeolite support, 15KOH/zeolite, 20KOH/ zeolite and 25KOH/zeolite catalysts. As can be seen in Figure 4, the amount of KOH loaded on zeolite affected the conversion of waste frying oil into biodiesel. The zeolite support used alone is inactive in the transesterification reaction. However, by increasing the loading amount of KOH from 15 wt.% to 25 wt.%, a significant increase in biodiesel yield was observed. For instance, by varying the loading amount of KOH from 15 wt.% to 25 wt.%, the biodiesel yield increased from 54,02% to 75% by using a catalyst to oil ratio of 1.0 wt.%. This increase in biodiesel yield is attributed to the higher K_2O active phase content in the catalyst [16]. The possible reason is that enough KOH with good dispersion on the surface and in pores of zeolite is needed for the catalysis of transesterification reaction [20].

The effect of catalyst amount on biodiesel yield is demonstrated in Figure 4. As seen in Figure 4, the biodiesel yield on 35% KOH/zeolite is raised from 75.0% to the maximum yield of 95% with catalyst amount increasing from 1.0 to 2.5 wt.%. However, biodiesel yield dropped to 94% as the

catalyst amount further increased to 4.0 wt.%. The reasons for yield decrease is that when the solid catalyst was excessive, the slurry (mixture of solid catalyst and reactants) was too viscous, therefore leading to a problem of mass transfer [21].
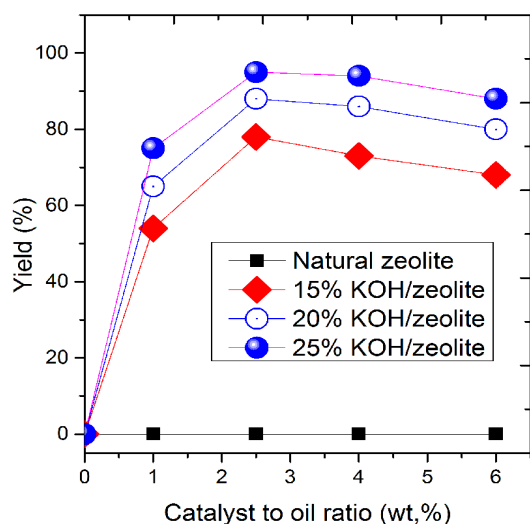

Figure 4. Effect of KOH loaded on zeolite and catalyst amount on biodiesel yield. Reaction condition: methanol: oil ratio = 8:1, T =65 $^{\circ}$C, P = 1 atm, t = 2 jam.
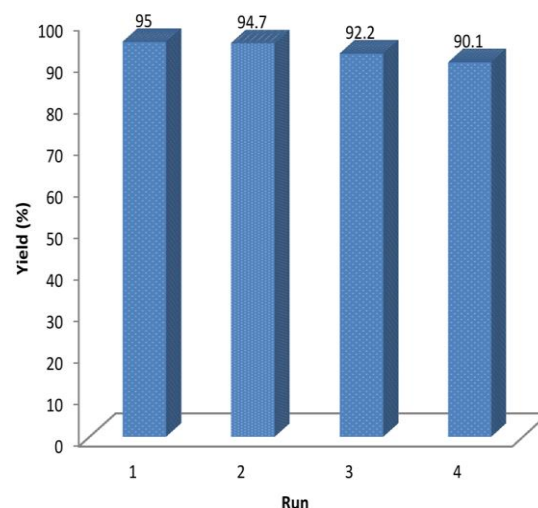
Figure 5. Reuse of the catalyst: Reactionn condition: Catalyst 2.5 wt.%, over the 25KOH/zeolite catalyst, methanol: oil ratio = 8:1, T =65 $^{\circ}$C, P = 1 atm.

3.5. Reusability Catalyst

In this case, reusability of KOH with loading of 25%, 3% catalyst ratio and a reaction time of 2 h was investigated by obtaining and reusing the catalyst in four consecutive runs. Figure 5 shows the biodiesel yield with four successive runs. After four experiments, a catalyst with a 25KOH/zeolite shows good stability in maintaining its catalytic performance, where the yield of biodiesel decreased by only 2.8%. The decrease of catalytic activity after the four recycling was caused by the loss of catalyst during the process of filtration, activation, and the morphology change of used catalyst. The other reason is heating process would developed crystals agglomeration which decreasing catalyst surface area and subsequently suppressed nanocatalyst reactivity and lead to decline biodiesel yield [19].

3.6. Characteristic of biodiesel

To study the physicochemical properties, the transesterification reaction was carried out in the presence of the catalyst under calcined at 500 $^{\circ}$C. The characteristics of the biodiesel sample were shown in Table 2.

Table 2. Characteristic of biodiesel of this work, SNI standard.

Parameter	This work	SNI
Kinematic viscosity, at 40 $^{\circ}$C (cSt)	2,6 – 3,8	2,30 – 6,00
Density (g.cm^{-3})	0,886 – 0,873	0,85 – 0,89
Acid number (mg KOH.g^{-1})	0,21 – 0,42	max 0,80

As listed in Table 2, the fuel properties of the prepared biodiesel have been found to comply with the SNI standards. Refer to Table 2, its can be seen that the kinematic viscosity of biodiesel is ranging

from 2.6 - 3.8cSt. The density of biodiesel is ranging from 0.866 - 0.873 g.cm^{-3} and the acid number is ranging from 0.21 - 0.42 mg KOH.g^{-1}. These values are also in compliance with SNI standards.

4. Conclusions

Preparation and the use of zeolite impregnated with KOH as heterogeneous catalysts for the transesterification of waste frying oil with methanol has been evaluated. The higher the number of KOH impregnations and the more catalysts used, the higher the yield of biodiesel. The optimum condition was obtained at 25% KOH impregnation indicated a very high catalytic activity (95.0% biodiesel yield) with the optimum reaction conditions determined: the molar ratio of methanol to oil by 8:1, the amount of catalyst by 2.5%. Reusability of a 25% KOH load catalyst demonstrates good stability in maintaining its catalytic performance, in which the heterogeneous catalyst is able to remain stable for 4 consecutive runs. Characteristics of the biodiesel, such as kinematic viscosity, density and acid number are sufficient in accordance with the requirements of SNI.

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