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$K_2O/NbOPO_4$ solid acid catalyst for biodiesel production

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Abstract. Biodiesel production from palm oil and alcohol has been carried out using a $K_2O/NbOPO_4$ solid acid catalyst. $NbOPO_4$ catalyst was synthesized through the sol-gel method, followed by drying and calcination at a temperature of 800°C for 6 hours. The catalyst was further treated using K_2CO_3 with various concentrations of 15, 25, 35, 45 and 55% through the impregnation technique. Morphology and composition of the catalyst were evaluated by SEM, EDX and XRD instruments. The results showed that the catalyst has non homogeneous particles with size ranging between 1.86 μm to 25 μm, accompanied by the agglomeration. The results of the analysis also confirmed that the prepared catalyst contains potassium, niobium, phosphorus and oxygen with a composition of 10.15; 17.67; 6.11 and 41.83%, respectively. The catalytic activity was tested in the transesterification reaction for 3 hours, at a temperature of 65°C with the molar ratio of palm oil to alcohol of 12:1 and catalyst loading of 6%. The highest yield of 98.87% was obtained on the process using the catalyst impregnated with 35% K_2CO_3. The overall results show that there is a very promising potential of NbOPO4 catalysts for biodiesel production.

1. Introduction

The demand for fuel sourced from non-renewable fuels is currently increasing. This is caused by the increased utilization of fuel in daily life with the increasing growth of population [1, 2]. The impact caused by the continuous use of fuel sourced from fossils, especially in the field of transportation, induces concern about environmental and health damage [3]. The study on the utilization of vegetable materials as a substitute for fossil-sourced fuels continues to be explored. Of many renewable sources, palm oil can be an alternative material to produce renewable, sustainable and biodegradable biofuel [4-6].

There are several methods can be used to convert vegetable oils into biofuels such as transesterification, fermentation, thermal cracking, catalytic cracking, and hydro-processing. Each method has advantages and disadvantages [7]. The transesterification is a method commonly used to react triglycerides with alcohol to produce methyl esters and by-products in the form of glycerol. In general, biodiesel production uses a homogeneous base catalyst such as K or Na hydroxide in a transesterification reaction. However, the separation of homogeneous catalysts used and purification of the generated biodiesel is difficult due to saponification and emulsification [8-10]. In addition, the glycerol by-product can be easily contaminated by K or Na salts hence making it not possible to be

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directly used as a commodity [11]. The alternative approach of using heterogeneous catalysts continues to be studied to overcome the above problems. Some researchers have studied the characteristics of heterogeneous solid acid catalysts and it is reported that heterogeneous catalysts have good thermal stability, selectivity, catalyst performance and environmentally friendly [12-16]. Ion exchange organic resins, zeolite, and ZrO_2 have been used as solid acid catalysts [17]. However, some of these catalysts have limitations, such as low thermal stability, mass transfer resistance (diffusion limits which reduce reaction rates) or loss of acidic active sites in polar media [18].

The niobium metal transition has been reported as an interesting catalyst for various reactions [19-21]. Niobium as the main catalyst component has proven a very promising performance as a heterogeneous catalyst. The catalytic activity of commercial niobium to has been carried out by reacting diluted H_2SO_4 or H_3PO_4 solutions to obtain strong acid active sites. Phosphate compounds in niobic acid will form niobium phosphate which acts as an active catalytic site. The glassy morphology of $NbOPO_4$ can expose the Nb^{5+} Lewis acid site at low temperatures, which is strong with a high tendency to absorb oxygen from triglycerides [22]. There was a report that potassium salts (such as K_2CO_3) as support and have shown high catalytic activity in transesterification reactions. In this study, $NbOPO_4$ catalyst was synthesized and modified with potassium (K) for application in biodiesel production through transesterification reactions. The effect of potassium loading was studied in detail on the characteristics of the catalyst, as well as the yield and quality of biodiesel.

2. Experimental

2.1. Material

The main material used for the synthesis of the solid acid catalyst was $NbCl_2$. The citric acid (Merck, Germany) was used as a solvent. Phosphoric acid (85% pure H_3PO_4), Ammonia (25% NH_3 solution), and methanol (99.8%) were all supplied from Merck, Germany. Palm oil obtained from the PT. Socfindo Nagan Raya Aceh District, Indonesia was used as source of biodisel.

2.2. Preparation of $K_2O/NbOPO_4$

The synthesis of $NbOPO_4$ was carried out by following the procedure of a number of references from previous studies [1, 15, 18, 19]. $NbCl_2$ was dissolved in a citric acid solution dropwise with continuous stirring for 1 hour. After that, H_2PO_4 and NH_3 5% were added as pH regulators. The solution was heated at a temperature of 70 - 80^oC, stirring continued until a clear solution was obtained. The process was stopped after the gel was formed and then put in the oven at 80^oC for 24 hours to remove the water content. Following that, the formed gel was put into the furnace at 800^oC for 6 hours to stabilize the crystalline phase. Introduction of K_2CO_3 onto the $NbOPO_4$ catalyst was conducted by wet impregnation process. K_2CO_3 with varied concentration (15%, 25%, 35%, 45%, and 55%) was impregnated on $NbOPO_4$ for 6 hours, then put into the furnace for 4 hours at 200^oC.

2.3. Catalyst characterization

To study the characteristics of the prepared catalysts, the analysis was done through several techniques. Composition analysis was carried out using an X-ray diffractometer (XRD) instrument which was recorded using Cu Kα radiation on a D/max-2500 diffractometer, the diffractogram reading was carried out at an angle of 2θ. The morphology and structure were studied by scanning electron microscopy (SEM). Each element of the catalyst has a unique atomic structure and was identified by the spectrum of electromagnetic emissions using EDX.

2.4. Vegetable oil characterization

The suitability of vegetable oil as a fuel for diesel engines depends on its physical chemistry characteristics. Therefore, several tests were carried out, such as evaluation on the kinematic viscosity which greatly influences the friction and flow rate of biodiesel at a certain temperature. In addition, the density and fatty acid composition were also determined.

2.5. Transesterification reaction

Production of biodiesel (methyl ester) was conducted through the transesterification process using a three-neck round-bottom flask reactor equipped with stirring motor and thermometer. Palm oil and methanol were weighed with methanol to oil weight ratio of 12:1, it was then put into the flask with $K_2O/NbOPO_4$ catalyst as much as 2% (of oil weight). The transesterification process was carried out for 3 hours with continuous stirring at a constant temperature of 65°C. The reactor used was equipped with a condenser to avoid the evaporation of methanol during the transesterification process. After completion, the separation was carried out using filter paper and a separating funnel. During separation, the used catalyst was attached to the filter paper. The separated oil was left for 48 hours until 2 layers of liquid were formed, namely the upper layer in the form of methyl ester/biodiesel and the bottom layer in the form of glycerol. The washing process was then carried out on biodiesel using hot water (50°C) [22]. During washing, emulsions occurred between biodiesel and water. To achieve perfect separation, the unreacted methanol was removed and the remaining residual impurity/glycerol emulsion solution was left for 24 hours. The biodiesel yield was calculated based on Equation (1).

$$\%\, Yield = \frac{Mass\ of\ biodiesel}{Mass\ of\ oil}\ x\ 100\ \% \qquad (1)$$

3. Results and discussion

3.1. Characterization of the catalyst by XRD

The crystalline phase of the synthesized catalyst was identified by XRD analysis and results are given in Figure 1. Figure 1 shows that there are two broad peaks of 2Θ angle readings which are in the range 15–40◦ and 40–60◦. The broad pattern (d = large) and low intensity indicate the amorphous character of $NbOPO_4$ [11, 19, 20]. There is no detectable crystalline phase from $NbOPO_4$ and/or Nb_2O_5 in the sample. Moreover, based on the diffractogram pattern there is no K diffraction peak observed which is presumably because the K content in the catalyst is in the size of very small nanoparticles and had spread evenly [11, 19]. A similar finding was also reported for the characteristics of the Ru metal transition on the $NbOPO_4$ solid catalyst used for cellulose conversion to sorbitol [19].

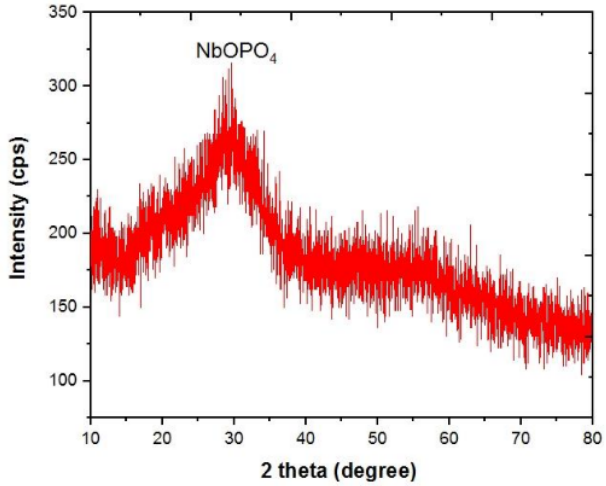

Figure 1. XRD diffractogram of $K_2O/NbOPO_4$ catalyst

3.2. Characterization of $K_2O/NbOPO_4$ catalyst by SEM -EDX

To determine the morphology and particle size of the synthesized $K_2O/NbOPO_4$ catalyst, SEM analysis was carried out. Figure 2 presents the results of the SEM microphotograph of $K_2O/NbOPO_4$ catalysts recorded at 5000x magnification, the image shows the presence of micro grains of different magnitudes and macro pores between these micro grains. The porous structure on the micrometric scale is illustrated in Figure 2.

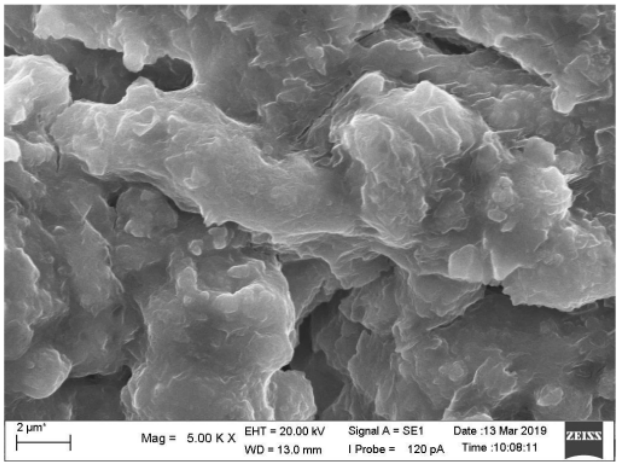

Figure 2. SEM image of synthesized $K_2O/NbOPO_4$ catalyst with 35% K_2CO_3

It can be seen that the catalyst has the nonhomogeneous particles which size ranging from 1.86 - 25 µm accompanied by the phenomenon of agglomeration. It was found that morphological and mesopore structures were more or less dependent on potassium loading on the surface of $NbOPO_4$ [5]. EDX is an analysis technique to identify the elements contained in a sample. The impregnation of potassium onto $NbOPO_4$ solid acid catalyst was successful, as shown in Table 1. As depicted from Table 1, the catalyst consists of oxygen, phosphorus, potassium and niobium. The quantity of potassium and niobium were obtained of 0,91% and niobium 9,41%, respectively.

Table 1. Elements contained in the catalyst

Element	Weight (%)	Atom (%)
Oxygen	52.24	80.54
Phosphorus	11.33	9.14
Potassium	1.42	0.91
Niobium	35	9.41
Total	100	100

3.3. Effects of K_2CO_3 and catalyst loadings on the biodiesel yield

The effect of K_2CO_3 concentration on the performance of $K_2O/NbOPO_4$ catalysts was evaluated in the transesterification process of palm oil into biodiesel. The yield of biodiesel obtained regarding the concentration of K_2CO_3 used for impregnation process are shown in Figure 3. It can be seen that yield of biodiesel proportional to the loading of potassium. For example, yield of biodiesel reached of 92.89% and 94% at the potassium loading of 15 and 25% K_2CO_3, respectively. Catalysts which impregnated with 35% K_2CO_3 showed the best performance indicated by a high generated yield of 98.87%. It is believed that the distribution of potassium on the surface of $NbOPO_4$ acts as a buffer for the active phase. However, an increase in K_2CO_3 loading up to 55% causes a decrease in catalyst performance as seen from the reduced yield of biodiesel by 2% compared to the results using 35% $K_2O/NbOPO_4$. The effect of adding K_2CO_3 above 35% results in poor or too thick K scattering, causing distribution problems on the $NbOPO_4$, this can cause the closure of active sites [21, 22]. Other researchers mentioned that the excessive presence of active phases on the surface of the catalyst is not desirable [12]. In other words, biodiesel conversion is reduced due to decreased catalytic performance.

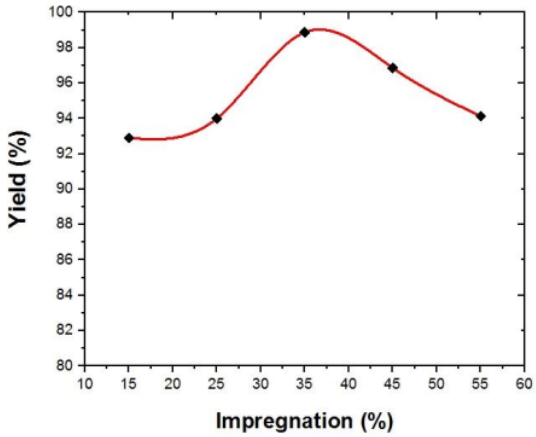

Figure 3. Effect of % K_2CO_3 on biodiesel yield (%)

3.4. Characteristic of biodiesel

Several tests were carried out to determine the characteristics of the produced biodiesel. Table 2. shows the results obtained in the physicochemical characterization of the palm oil biodiesel produced in this study. The physicochemical characteristics of biodiesel were only analyzed on that sample produced from the transesterification process using $K_2O/NbOPO_4$ catalyst with 35% K_2 loading as it showcased the highest yield. The quality of biodiesel in terms of density and viscosity are given in Table 2. It can be explained that the density, and kinematic viscosity are in accordance with the specifications of the Indonesian National Standard (SNI) which emphasized that the catalyst synthesized in this study has the potential to be applied in the production of palm oil into biodiesel.

Table 2. Characteristics of biodiesel produced in this study

Test Parameters	Unit	Research Results	SNI
Kinematic Viscosity	mm^2/s (cst)	4,72 – 5,55	2,3 – 6,0
Density	Kg/m^3	860 - 890	850 - 890

Figure 4 depicts the chromatogram profile from GCMs analysis of biodiesel produced in the transesterification process using 35% $K_2O/NbOPO_4$ catalyst. In Fig. 4, there is the appearance of some peaks that represent the fatty acid components contained in biodiesel. In detail, the data on fatty acid contents of biodiesel can be seen in Table 3. It can be seen that the produced biodiesel mainly consists of Palmitic acid, Linoleic acid, and Oleic acid. Figure 4 also shows that peaks 1 and 2 with an area of 48815069 representing palmitic acid appear at the retention time of 20-21 with the highest composition of 56.92%. Furthermore, peak 3 represents lenoleic acid and and peaks 4.5 are marking the presence of oleic acid with a composition of 3.52% and 39.57% respectively.

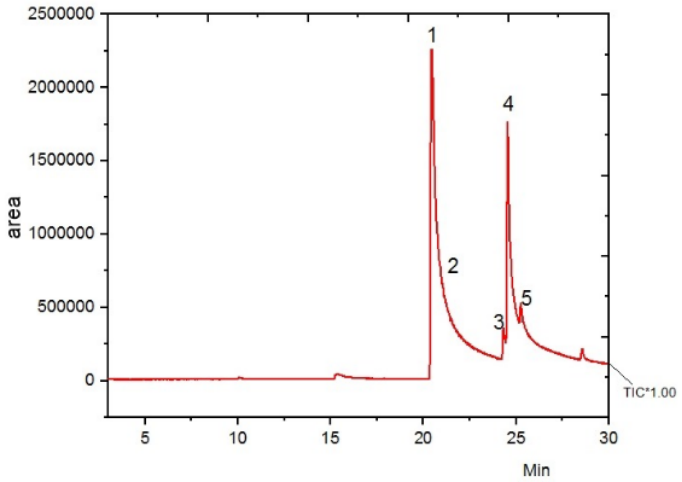

Figure 4. Chromatogram profile of biodiesel

Table 3. Composition (%) of biodiesel

Peak	Fatty Acid	Name	Composition (%)
1,2	Palmitic Acid	Hexadecanoic acid	56.92
3	Linoleic Acid	Octadecanoic acid	3.52
4,5	Oleic Acid	Octadecanoic acid	39.57

4. Conclusion

This study reports the loading effect of K_2 impregnation on the characteristics and performance of $K_2O/NbOPO_4$ as a heterogeneous solid acid catalyst for the biodiesel production. XRD analysis shows an amorphous character of mesoporous niobium phosphate catalyst. The results of SEM analysis stated that the size of the $K_2O/NbOPO_4$ catalyst particles is not homogeneous accompanied by the phenomenon of agglomeration. EDX analysis shows that the $K_2O/NbOPO_4$ catalyst is composed of potassium and niobium with a percent atom is 0,91% and 9,41%, respectively. From the results obtained, the loading of K_2 has a significant effect on the performance of $NbOPO_4$ catalysts in the process of transesterification of palm oil into biodiesel. The highest biodiesel yield was obtained as much as 98.87% in the reaction using the $NbOPO_4$ catalyst which impregnated with 35% of K_2CO_3. The

produced biodiesel has qualities that are in accordance with SNI. According to the obtained results, this developed $K_2O/NbOPO_4$ catalyst can be considered as an attractive alternative to heterogeneous catalysts for biofuel production.

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