## Performance of K$_2$O/Nb$_2$O$_5$ as a heterogeneous catalyst for biofuel production

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**Abstract.** The objective of this study was to investigate K$_2$O/Nb$_2$O$_5$ as a new potential heterogeneous catalyst for biofuel production. The catalyst was prepared through an impregnation method using K$_2$CO$_3$ and Nb$_2$O$_5$. The K$_2$O/Nb$_2$O$_5$ was analyzed by scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX). The catalyst was tested for biodiesel production. Transesterification was conducted using vegetable oil and methanol on the predetermined operating condition. The highest yield of biofuel was the reach of 98.5% at K$_2$O loading of 50% on Nb$_2$O$_5$ and the catalyst loaded of 4 wt.% to oil. In the increasing of potassium loading on Nb$_2$O$_5$ shows increasing the activity of the catalysts. Potassium, as an active site, plays a vital role in the reaction of vegetable oil and methanol to produce biodiesel. It is a major component and enhance selectivity of the catalyst. Niobium was able to interact well with potassium, and it enhanced the crystallinity and stability of the catalyst. The characteristics of biodiesel, such as density and viscosity, are evaluated to confirm the purpose of catalyst function. The biodiesel characterization showed in the range with SNI standard.

### 1. Introduction

Biofuels, a renewable fuel produced from plant materials, animal waste, or microorganisms, that can be converted directly or indirectly. Biodiesel is one of two secondary biofuel’s generation and can be used as a petroleum diesel mixture and industrial process. It has a high cetane number and good lubrication in vehicles. As the most reliable biofuels, biodiesel production has been developed commercially in some countries, especially Indonesia [1-4]. Vegetable oil and alcohol are reacted through transesterification reaction in the presence of catalyst. The conventional method of biodiesel production usually uses homogeneous catalysts such as KOH and NaOH. This method causes a complicated separation process and so much washing waste. The use of heterogeneous catalysts is now an option. It offers advantages such as simple separation step and higher yield. Heterogeneous catalyst types can be prepared from various biomass sources; for example, clam ash utilizes CaO content to produce 87.4% of biodiesel [5-7].

Potassium significantly contributes to produce high biodiesel yield. It can be obtained from KOH or K$_2$CO$_3$, which is added to a carrier material with certain characteristics through several methods, such as impregnation or precipitation. The impregnation method is more effective, controllable, and inexpensive; the stability of the catalyst for reuse is also more secure [8]. Husin et al. experimented with
K₂CO₃ and produced a biodiesel yield of 75% [9]. Fitriana et al. even used KOH of 25% into zeolite through impregnation method to form K₂O/zeolite catalyst, but it did not effective [10]. With the same method, Yani et al. added K₂CO₃ to water hyacinth ash, which naturally contains potassium oxide, reached biodiesel yield of 97.57% [11].

The selection of materials support must be needed to obtain a catalyst with certain advantages and produce high-quality biodiesel. Niobium is one of the transition metal that was developed in the manufacture of a heterogeneous catalyst. Nb₂O₅ is an acid material with good interaction ability [12,13]. Imported CaO to Nb₂O₅ reached a biodiesel yield of 98% but with higher calcination temperature [14,15]. It spends a lot of energy. Therefore, preparing or operating friendly material modification is needed. The purpose of this study is to determine the ability of a new K₂O/Nb₂O₅ catalyst. It formed through the combination of K₂O and niobium pentoxide over the impregnation method with varied of mass K₂O given to Nb₂O₅. Catalyst ability for transesterification reaction of vegetable oil and alcohol into biodiesel will be proved. Glycerol also produced as a byproduct of this process. Characteristics of K₂O/Nb₂O₅ catalyst, such as morphology, composition, and crystallinity, will be evaluated using SEM + EDX. Biodiesel product also characterized to SNI standard.

2. Materials and methods

2.1. Materials
K₂CO₃ (99.9%) and Niobium(V)Oxide that used for the preparation of catalyst preparation and also methanol for transesterification reaction was purchase at the Merck (Germany), vegetable oil was bought from the market.

2.2. Preparation of K₂O/Nb₂O₅ catalyst
K₂CO₃ mass was varied od 10%, 20%, 30%, 40%, and 50% based on determine potassium amount to Nb₂O₅ support. K₂CO₃ was weighed and loaded into beaker glass. Aquadest was dropped until K₂CO₃ is sufficiently dissolved. Nb₂O₅ of 3 grams is added little by little until the mixture thickened. Mixture sturret at room temperature for 6 hours. After impregnation process, wet catalyst dried on the oven at 110°C for 24 hours to remove water content and to crystallize salt in the surface. The solid mixture calcined at 300°C for 3 hours to vaporize CO₂ component from K₂CO₃ bound and increase surface area of K₂O/Nb₂O₅ catalyst.

2.3. Catalyst characterization
Scanning Electron Microscopy (SEM) + Energy-Dispersive X-Ray spectroscopy (EDX) provide high-resolution images to evaluate morphology and chemical composition of part of surface area.

2.4. Transesterification reaction
The transesterification reaction using K₂O/Nb₂O₅ catalyst was carried out by molar ratio of methanol to oil 10:1 and catalyst loading of 4%wt. 30 grams of oil and 14.2 ml of methanol added into a batch reactor which equipped with a water hose condenser and hot plate. Reaction was conducted under constant operation condition at a temperature of 65°C for 90 minutes.

2.5. Separation and characterization of biodiesel
Catalyst was separate from the product using separating funnel and filter paper. In separating funnel, biodiesel and glycerol would be separated because of differences in density (where density of glycerol is greater than density of biodiesel). After being separated, biodiesel was dried by dry washing on oven at 80°C for 60 minutes. Biodiesel yield was calculated, density and viscosity also identified to confirm that the biodiesel product is accordance to SNI Standard.
3. Results and discussions

3.1. Characterization of K2O/Nb2O5 catalyst

The SEM analysis of the K2O/Nb2O5 catalyst can be seen in Fig. 1.

![Figure 1. High magnification SEM image of K2O/Nb2O5 catalyst.](image)

SEM observation results in figure 1 show the morphology at selected catalyst with a magnification of 5.00. It is visible the particle shape with a range of the width of 1.01-1.12μm and a range of lengths of 9-22.25μm. Pore in range of 0.3-1μm. Hexagonal shaped particles are interconnected with each other. Nb2O5 nano, combined with K2O, are well compounded. Potassium atoms are inserted into the catalyst to maintain the structure and expand layer between adjacent hexagonal tissue fields to form new porosity [16]. Besides to evaporate impurities, calcination also produced energy that helps Nb2O5 to interact well K2O and produce new excellent crystal structure [17]. Calcination could also change the phase structure, particle size, and morphology of the catalyst [11,18,19].

To determine the components and compositions, K2O/Nb2O5 catalyst was analyze with Energy-dispersive X-ray spectroscopy (EDX). The results can be seen in Table 1.

| Element     | Wt.% |
|-------------|------|
| Carbon      | 10.71 |
| Oxygen      | 37.69 |
| Potassium   | 40.01 |
| Niobium     | 11.58 |
| Total       | 100  |

Table 1. EDX Analysis of Elements.

The atomic percent of K2O on Nb2O5 was analyzed using the EDX instrument. The potassium remains a major component on the support. K2O enriched active site and increased catalyst selectivity of transesterification reaction. The carbonyl atom of triglycerides molecule was able to attract methoxide anions on the surface of potassium. Then it confirms the formation of tetrahedral ions on the alkyl chain and ultimately dissociates to form biodiesel. Niobium, as support, also plays an important role in K2O in carrying out the reaction. Niobium can interact with K2O and increase the crystallinity and stability of a collaborated compound [20].

3.2. Biodiesel production using K2O/Nb2O5 catalyst

3.2.1. Yield. The variation of K2CO3 mass impregnated on Nb2O5 was calculated based on the potassium amount that will be appropriated. The effect of K2CO3 impregnation loading of 10%, 20%, 30%, 40% and 50% on biodiesel acquisition can be seen in Figure 2.
Based on Figure 2, the yield of biodiesel increase with increasing of K$_2$CO$_3$ loading. The yield of biodiesel is 95.3%, 96.4%, 97.1%, 97.3%, and 98.5%, respectively. The amount of K$_2$O, which is embraced, influences the amount of active site. More active sites because of more K$_2$O effect the conversion of triglycerides into biodiesel. K$_2$O components could be act as a binder that can improve the mechanical properties and selectivity of the catalyst [21]. Based on data, good impregnation of K$_2$CO$_3$ to produce highest yield was 50%.

3.2.2. Density and viscosity of biodiesel. Biodiesel product was also analyze to identified its properties to SNI Standard and vegetable oil properties. There are given in Table 2.

| Parameter     | Unit | (a)SNI Standard | (b)Vegetable oil | Experiment |
|---------------|------|-----------------|------------------|------------|
| Density       | Kg/m$^3$ | 850-890         | 880              | 850-855    |
| Viscosity     | cSt   | 2.3-6.0         | 40.24            | 2.9-3.2    |

Density is an important parameter that affects the performance of biodiesel. In this research, it was 850-855 kg/m$^3$ and included in a range of SNI Standard. Changing value of vegetable oil densities become lighter shows the synthesis of biodiesel using K$_2$O/Nb$_2$O$_5$ catalyst was successfully through the conversion [22-23]. The high viscosity of vegetable oil also the one reason why vegetable oil cannot be used directly in diesel engines [24]. In addition, disrupting engine operations, high viscosity also results in poor atomization in the injection chamber. Kinematic viscosity was a measure of fluid resistance to flow without external force applied except gravity. The kinematic viscosity of biodiesel obtained from this study was 2.9-3.2cSt. The value was in the range of SNI Standard. Decrease of viscosity was the result of the transesterification reaction producing an alkyl ester and decreasing the viscosity of oil [25]. So, it shows the performance of the K$_2$O/Nb$_2$O$_5$ catalyst is appropriate to the reaction.

4. Conclusions
K$_2$O/Nb$_2$O$_5$ catalyst for the transesterification reaction has been successfully prepared. Potassium-rich and its function result in high catalyst selectivity in vegetable oil conversion. Potassium oxide collaboration with niobium produces very good interactions and has high crystallinity. The highest yield of biodiesel (98.47%) was obtained using K$_2$CO$_3$ impregnated to Nb$_2$O$_5$ of 50%. The characteristic of biodiesel in accordance to SNI Standard.
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