Study of pH influences on the performance of Na-loaded NbOPO₄ solid acid catalyst for biofuel production

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Abstract. This study reports on the development, preparation, and performance test of NbOPO₄ solid acid catalyst for biofuel production from vegetable oil. NbOPO₄ catalyst was synthesized by sol-gel method using NbCl₅, H₂SO₄, and citric acid as the precursor solutions and chelating agent, respectively. Dependent variables in the study were calcination time of 5 h; NbOPO₄ loading of 2%; transesterification time of 3 h; reaction temperature at 65-70°C and oil mass of 30 g. Whereas, the catalyst pH of 2, 4, 6, 9, and Na impregnation ratio of 20-50% were set as independent variables. The catalyst morphology was analysed by Scanning Electron Microscopy, catalyst elements was detected by Electron Dispersive X-Ray and X-Ray Diffractometer was used to characterize the crystallinity degree of the catalyst. The performance of the catalyst was evaluated from a transesterification reaction for biofuel production. The highest biofuel yield of 98.5% was obtained in the reaction using catalyst with a pH of 4 and Na impregnation ratio of 30%. The density obtained was 0.860 gr/cm³ confirming that the produced biofuel complies with the SNI. It can be concluded that Na-loaded NbOPO₄ can be a promising alternative catalyst in biofuel production.

1. Introduction

Increased energy needs due to human life activities result in diminishing source of petroleum reserves, whereas the needs of fuel increase rapidly with increasing population. The decline of petroleum raw materials causes an increase in the price of petroleum-based fuels [1]. According to the International Energy Agency (IEA), world energy demand is expected to increase by more than 55% from 2005-2030, especially in the field of transportation [2]. One of the solutions to address this issue is by developing alternative renewable energy such as hydrogen [3], bioethanol [4], biodiesel [5], etc.

Vegetable oil-based biofuels are the most promising fuel alternative right now. Generally, it is known that vegetable oils are bio- and completely-degradable (more than 90% in 21 days) than petroleum fuels (around 20% within 21 days). In addition, the use of vegetable oil as fuel raw material is expected to benefit economically in the agriculture field [6].

The most common method for synthesizing biofuel is transesterification of vegetable oils or animal fats with short-chained alcohols [7]. Conventionally, production of renewable-sourced fuel is by using homogeneous strong base catalysts such as sodium or potassium hydroxide, and carbonates or alkoxides due to their high performance in milder conditions and low cost [8]. However, the use of homogeneous catalysts such as NaOH/KOH for the process has several disadvantages, for instances, causing corrosion
to the equipment, raw material requires processing because the presence of free fatty acids and water causes saponification reactions during transesterification of triglycerides [9]. This situation has a disadvantage not only because of the high consumption of catalysts but also the process of refining biofuel will be difficult, thereby increasing production costs [10].

The use of heterogeneous catalysts such as alkaline earth metal oxides, alkali metals [11], can be an alternative to overcome this problem with more merits such as easier catalyst separation and product purification which generate high purity glycerol and avoids neutralization of alkali catalysts [12]. According to research on biofuel production [13], there are several must-have traits for catalysts to achieve good catalytic performance like high porosity, high acid concentration, and sensitivity to water. Solid acid catalyst possesses most of these traits, and it has a very important role in the esterification of carboxylic acid due to the low cost of raw materials with a high concentration of free fatty acids (FFA) and no glycerin formation [14]. In addition, the solid acid catalyst is capable to esterify FFA free fatty acids and transesterify vegetable oil, simultaneously [15].

The most often used solid acid catalyst for esterification is ion exchange organic resin, zeolite [16], silica supported heteropolyacid (HPA/silica) and ZrO₂ [17]. However, some of these catalysts have shortages, such as low thermal stability, limitation of mass transfer, and weak acidic active sites in polar media [14]. Niobia-based materials have great potential as catalysts for application in biofuel production. In some cases, this catalyst shows better catalytic performance in the esterification of free fatty acids in comparison to some zeolites [12]. Niobium materials have been proven to be a very promising heterogeneous catalyst, either as the main catalyst component or when added in small loading into the catalyst. Various efforts have also been made in developing new applications of niobium catalyst for chemical processes [14]. Some researchers suggested that the addition of a phosphate group to niobic acid forms niobium phosphate which acts as an active catalytic site [18]. Involvement of Nb-based solid acid catalyst in biofuel production has been reported in a few research literature, however, the information regarding its performance parameters is still considered limited especially in regards to its performance under different pH conditions.

In this study, the alkali metal sodium is combined with transition metal niobium as solid acid compounds. The catalyst was synthesized via the sol-gel method with several pH variations. The effects of pH were studied on the characteristics of the catalyst in terms of chemical composition, morphology, also its performance in the transesterification process in terms of biofuel yield.

2. Materials and methods

2.1. Materials

Niobium Chloride (NbCl₅, Merck) was used as the main catalyst material, Sodium Hydroxide (NaOH, Merck), citric acid (Merck) as a solvent and chelating agent, H₃PO₄ (85%) which purchased from Merck as a source of phosphorus, and NH₃ (25%, Merck) as pH regulator. Vegetable oil which acquired from local market and methanol (Merck) were employed in the transesterification process.

2.2. Preparation of Na/NbOPO₄

The NbOPO₄ catalyst was synthesized by adapting procedures of earlier reports [19,20]. In detail, NbCl₅ was dissolved in citric acid solution in a dropwise manner with continuous stirring for 1 hour. After that, H₃PO₄ was added and followed by 5% of NH₃ to regulate the pH of the solution as desired (2; 4; 6; 9). The process was then proceeded to heating at a temperature of 70 - 80 °C with continuous stirring until a clear solution was obtained. The process was stopped once the solution turned into a gel, it was then put in an oven at a temperature of 110 °C for 24 hours to remove the water content. Following that, the formed gel was put into a furnace at 800 °C for 6 hours to stabilize the crystalline phase. The addition of co-catalyst Na into the NbOPO₄ system was carried out by wet impregnation process. A total of 30% Na was impregnated onto NbOPO₄ for 6 hours and the catalyst was then furnace for another 4 hours at 200 °C.
2.3. Catalyst characterization

To observe the characteristic of the prepared catalyst, a number of basic characterization was conducted. Chemical composition of catalyst was analysed by means of X-ray diffraction (XRD), the patterns were recorded on a Bruker diffractometer using radiation Cu Kα (λ = 0.154 nm) which operated at 40 kV and 100 mA. The diffractogram reading was done at a 2θ range of 10 – 60° with a scanning speed of 5° min [10]. In addition, the morphology and structure of the prepared catalyst were also studied by scanning electron microscopy (SEM) analysis. Whereas, EDX (Electron Dispersive X-ray) was used to detect the elements and surfaces in the sample through an electron conductor.

2.4. Catalytic reaction

The catalytic performance of the prepared catalyst was tested in biofuel production by transesterification of vegetable oil. The experiment was carried out in a three-neck rounded flask which equipped with stirring hotplate, thermometer, and condenser. Vegetable oil and methanol were weighed with a ratio of 1:12 and put into the flask. Afterward, the Na/NbOPO₄ catalyst with a loading of 2% of oil weight was also added. The transesterification process was carried out for 3 hours with continuous stirring at a constant operating temperature of 65 °C. Once done, the catalyst was separated from the oil by use of filter paper and a separating funnel. After removing the catalyst, the oil was left for 48 hours until 2 layers of liquids were formed, the upper layer was methyl ester or best known as biodiesel meanwhile the bottom layer was the side-product (glycerol). The biodiesel part was collected and washed using warm water (50 °C) [21]. During washing, emulsion occurred between biodiesel and water. This emulsion was left for another 24 hours to achieve perfect separation, remove the unreacted methanol and the residual impurity/glycerol. The yield of generated biodiesel was calculated by using Eq. (1):

\[
\text{% Yield} = \frac{\text{Mass of biodiesel produced}}{\text{Mass of Oil}} \times 100\% \tag{1}
\]

3. Results and discussions

3.1. Analysis of catalyst chemical components

With the aim to identify the chemical components in the prepared catalyst, XRD characterization was conducted and its pattern is shown in Fig. 1. It can be seen that there is only one broad peak at a 2θ range of 15–40° which denotes the presence of NbOPO₄. Other than that, no diffraction from either crystalline Nb₂O₅ or NbOPO₄ was detected, which suggests that the prepared niobium phosphate catalyst has a mesoporous structure. Moreover, the presence of co-catalyst Na is not observed in the XRD patterns, presumably because the loading of Na is quite low, or the Na particles are very small and have spread evenly on the catalyst surface [22].

![Figure 1. XRD pattern of the Na/NbOPO₄ catalyst.](image-url)
Besides XRD pattern, EDX analysis is also provided further confirm the chemical components of the catalyst in terms of atomic composition and percentage. As given in Table 1, it appears that the prepared Niobium catalyst is mainly composed of Niobium, Sodium, Phosphorus and Oxygen with a total of 17.67%; 0.69%; 6.11% dan 36.94%, respectively.

![EDX analysis of Na/NbOPO$_4$ catalyst.](image)

**Figure 2.** EDX analysis of Na/NbOPO$_4$ catalyst.

| Element   | Weight (%) | Atom (%) |
|-----------|------------|----------|
| Carbon    | 28.35      | 42.77    |
| Oxygen    | 36.94      | 41.83    |
| Sodium    | 0.69       | 0.32     |
| Aluminum  | 0.11       | 0.07     |
| Phosphor  | 6.11       | 3.57     |
| Potassium | 10.15      | 8.00     |
| Niobium   | 17.67      | 3.45     |
| Total     | 100        | 100      |

**Table 1.** Spectrum acquisition catalyst.

3.2. **Analysis of catalyst morphology**

The morphological observation of Na-doped NbOPO$_4$ catalyst is based on the imaging result from SEM analysis as shown in Fig. 2. From the SEM image, it is seen that the Na/NbOPO$_4$ catalyst has a morphology with nonuniform particle size ranging from 1.86 µm to 25 µm. The particles are also seen agglomerated which indicates that the catalyst particle has a mesoporous structure with a low degree of crystallinity [22]. The relatively small particle size is attributed to the presence of impregnated Na doping which reduces the size of NbOPO$_4$ catalyst and provides higher specific surface area [23].
3.3. pH influences on the performance of Na/NbOPO₄

pH is often used to monitor reactions, especially in an aqueous solution where one of the reactants or products is acidic or basic [24]. The effect of catalyst pH on the biofuel yield was tested in the transesterification reaction and results can be seen in Fig. 4. From Fig. 4, it is clearly seen that the transesterification process using NbOPO₄ catalyst with pH 4 generated the highest biofuel yield of 98.5%. This result indicates that the Niobium catalyst reacts well at this pH condition. Gil and research team reported that at pH 4 NbOPO₄ catalyst has a strong Bronsted acid site which improves its performance after the addition of H₃PO₄ [14]. However, a marginal yield decline is seen at a process using a catalyst with pH 6. It is presumably because pH 6 is close to neutral and the Bronsted acid site is not as strong in this condition. Interestingly, the biofuel yield increases slightly from 90% to 90.71% at the use of catalyst with a pH of 8. It can be concluded that the standard pH according to this reaction is acid or base.

These findings are consistent with those reported in the study done by other researchers. For instance, Martinez et al investigated the effect of catalyst pH on the photocatalytic degradation performance of TiO₂ on the 2,4-D substrate and Ametryne at pH 5, 7, 9. They found that the best operating conditions for TOC removal using 2,4-D was at pH 5 with a catalyst concentration of 0.6 g/L [25]. Meanwhile, for ametryne substrate, the best results were achieved at pH 9 with a catalyst concentration of 0.6 g/L. These results indicate that the 2,4-D degradation is more effective at acidic pH, and ametryne is more effective at basic pH. In another work, the effect of catalyst pH and zinc content on the immobilization of the anthrax virus was studied. They reported that the enzymatic activity of proteins significantly decreases below pH 6 and almost completely disappears at pH 4 [26].

3.4. Characteristic of biofuel

Several basic tests have been conducted to evaluate the physical and chemical characteristics of biofuel produced from the transesterification process using Na/NbOPO₄ catalysts with pH variations and 30% co-catalyst Na loading. Results of characterization are presented in Table 2.

Table 2. Characteristics of biofuel in this research dan the standard according to SNI 7182: 2015.

| Parameter           | Unit      | This Research | SNI     |
|---------------------|-----------|---------------|---------|
| Kinematic Viscosity | mm²/s (cp)| 4.72 – 5.55   | 2.3 – 6.0|
| Density             | Kg/m³     | 860 - 890     | 850 - 890|

Kinematic viscosity is a measure of resistance to fluid flow caused by the internal friction of one part of the fluid moving over the other. In general, fuel with too high viscosity is not preferable as it worsens the fuel atomization. Hoekman et al resumed that high viscosity is unwanted as it causes the formation of the larger size of fuel droplets, poor evaporation, narrower angle of injection spray, and bigger fuel
spray in-cylinder penetration [27]. The kinematic viscosity obtained in this study is 4.72 - 5.55 cp. This value is in the range SNI standard, namely 2.3 - 6.0 cp.

Density property of fuel has a vital impact on the performance of the engine. The bigger or smaller amount of injected fuel is dependent on its density because meter fuel is not pumped by mass of fuel injection, but by its volume. Therefore, the ratio of air to fuel as well as the energy content in the combustion chamber is affected by the density of the fuel [27]. The results of the density measurements in this study are 860-890 kg/m³ which is in accordance with SNI standard, namely in the range 850-890 kg/m³. It has been reported that the density of biofuel is also influenced by long chains of the methyl ester, the longer the chain the lower the density [28]. At last, it can be concluded that the transesterification process using Na/ NbOPO₄ solid acid catalyst can produce biofuel which quality is in accordance with Indonesian National Standards.

4. Conclusion
This study proposed the application of Na/NbOPO₄ as a heterogeneous solid acid catalyst for biofuel production. The catalyst was prepared with different pH condition to study the influence of pH on the catalytic performance. The XRD analysis reveals that the prepared catalyst has glassy properties of mesoporous niobium phosphate. EDX analysis confirmed that the Na/NbOPO₄ is composed of 36.94% oxygen, 17.67% Niobium, 10.15% Sodium, and 6.11% phosphorus. Na/NbOPO₄ catalyst shows morphology with non-homogeneous particle size accompanied by agglomeration. It was found that catalyst with a pH of 4 produced the highest yield of biofuel of 98.5%. The density and viscosity characteristics confirmed that the generated biofuel has a quality which complies with the Indonesian National Standards (SNI). From overall results, it can be concluded that Na/NbOPO₄ is a promising solid acid catalyst for the transesterification process of vegetable oil. Moreover, it is important to control the pH condition of the Na/NbOPO₄ solid acid catalyst to obtain a high yield of biofuel production.

Acknowledgments
This research was funded by the Ministry of Higher Education and Technology under the Master Thesis Research grant.

References
[1] Fitriana N, Husni H, Yanti D, Pontas K, Alam P N, Ridho M and Iskandar 2018 IOP Conf. Ser. Sci. Eng. 334 012011
[2] Vam A 2013 Kinetics of The Hydro-deoxygenation of Stearic Acid over Palladium on Carbon Catalyst in Fixed-Bed Reactor for the Production of Renewable Diesel (Ohio: OhioLINK) p 10
[3] Husin H, Adisalamun, Sy Y, Asnawi T M and Hasfita F 2017 AIP Int. Conf. Eng. Sci. Nan. 1788 030073
[4] Shruti A, Byadgi and Kalburgi P B 2016 Procedia Environ. Sci. 35 555–562
[5] Zuhra, Husin H, Hasfita F and Rinaldi W 2015 Agritech 35 69–77
[6] Sari E, Kim M, Salley S O and Ng K Y S 2013 Applied Catal. A Gen 467 261-269
[7] Buyukkaya E 2010 Fuel 89 3099–3105
[8] Camilia O, Pereira, Marcio F, Portilho, Cristiane A, Henriques and Zotin F 2014 J. Braz. Chem. Soc. 25 2409–2416
[9] Song C, Liu Q, Ji N, Deng S, Zhao J, Li S and Kitamura Y 2016 Bioresour. Technol. 214 747–754
[10] Husin H, Asnawi T M, Husaini H, Ibrahim I and Hasfita I 2018 IOP Conf. Ser.:Mater. Sci. Eng. 358 012008
[11] Husin H, Abubakar, Ramadhan S, Sijabat C F B and Hasfita F 2018 Matec Web Conf. 197 09008
[12] Aranda D A G, Goncalves J D A, Peres J S, Ramos A L D, Melo C A R, Antunes O A C, Furtado N C and Taft C A 2009 J. Phys. Org. Chem. 22 709-716
[13] Rade L L, Lemos C O T, Barrozo M A S, Ribas R M, Monteiro R S and Hori C E 2019 Renew.
Energy 131 348-355

[14] Bassan I A L, Nascimento D R, Gil R A S, Silva M I P, Moreira C R, Gonzalez W A, Faro A C, Onfroy T and Lachter E R 2018 Fuel Process Technol. 106 619-624

[15] Tesser R, Casale L, Verde D, Serio M D and Santacesaria E 2010 Chem. Eng. Sci. 157 539–550

[16] Shruti G, Chopade, Kulkarni K S, Kulkarni A D and Topare N S 2012 Acta Chim. Pharm. Indica 2 8-14

[17] Mongkolbovornkij P, Champreda V, Sutthisripok W and Laosiripojana N 2010 Fuel Process Technol. 91 1510–1516

[18] Polica M D, Rivaldi J D, Castro H F D and Carneiro L M 2016 Engineering Journal: IJOER 10 175–184

[19] Xi J, Zhang Y, Ding D, Xia Q, Wang J, Liu X, Lu G and Wang Y 2014 Applied Catal. A, Gen. 469 108–115

[20] Sørensen D R, Nielsen U G and Skou E M 2014 J. Solid State Chem. 219 80–86

[21] Nisar J, Razaq R, Farooq M, Iqbal M, Khan R A, Sayed M, Shah A and Rahman I U 2017 Renew. Energy 101 111–119

[22] Li J, Lv X, Wang Y, Li Q and Hu C 2018 ACS Omega 3 4836–4846

[23] Wang X, Song Y, Huang C and Wang B 2018 Sustain Energ. Fuels 2 1530-1541

[24] Clark W M, Medeiros N J, Boyd D J and Snell J R 2013 Bioresour. Technol. 136 771-774

[25] Machuca-martínez F and Colina-márquez J A 2011 Ing. Investig. Desarro. 29 1106

[26] Montpellier L H and Siemann S 2013 FEBS Lett. 587 317–321

[27] Hoekman S K, Broch A, Robbins C, Ceniceros E and Natarajan M 2012 Renew. Sustain. Energy Rev. 16 143–169

[28] Refaat A A 2009 Int. J. Environ. Sci. Tech 6 677–694