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Preparation, Characterization and Application of Natural Zeolite from Tapanuli Indonesia Modified with KOH as Catalyst Support for Transesterification of Rice Bran Oil

Taslim*, Iriany, O. Bani, S.Z.D.M. Parinduri, P.R.W. Ningsih, and N. Taruna

Department of Chemical Engineering, Faculty of Engineering, Universitas Sumatera Utara, Medan 20155, Indonesia.

**(Corresponding author & ORCID : 0000-0003-0482-320X)*

Abstract:

An effort to increase the value of natural zeolite originating from Tapanuli had been conducted through its development as catalyst support in biodiesel production. Biodiesel is generally produced via transesterification, and a catalyst is utilized to enhance reaction rate. In this research methanol and rice bran oil (RBO) were used as feedstock. The objective of this work was to assess the effectiveness of natural zeolite modified by KOH as heterogeneous catalysts for transesterification of RBO. Natural zeolite was modified by impregnation at various KOH concentrations followed by drying and calcination. KOH/natural zeolite catalyst was characterized by Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM-EDX), and Fourier Transform Infrared (FTIR) Spectroscopy. It was then applied as heterogeneous catalyst in biodiesel production. Transesterification was conducted at 60ºC and 500 rpm. The transesterification was carried out at catalyst load of 2-4%, reaction time of 90-210 min, and methanol to RBO molar ratio (MTR) of 8:1-12:1. The maximum yield of 98.78% biodiesel was achieved at MTR of 10:1, reaction time of 120 min, and 2% catalyst load. The resulted biodiesel was then characterized for its physical properties such as density, viscosity and ester content. The biodiesel properties met the Indonesia standard (SNI). The results indicated that natural zeolite modified by KOH was applicable as a catalyst in the synthesis of biodiesel through transesterification from RBO.

Keywords: Catalyst support, KOH impregnation, natural zeolite, transesterification.

I. INTRODUCTION

Transesterification is a method often used in biodiesel production. During transesterification, triglycerides from vegetable oil or animal fats is reacted with alcohol with aid of catalyst to produce methyl esters or biodiesel. The catalyst used can be either a homogeneous catalyst or a heterogeneous catalyst. The use of heterogeneous catalysts has several advantages such as being more environmentally benign, easier to separate from liquid products, reusable, modifiable to increase activity and longer service life [1]. One source of heterogeneous catalysts that can be applied to transesterification reactions is natural zeolite. Natural zeolite is cheap, easy to get, and easy to modify by various methods. Zeolites are mesoporous compounds that contain a variety of metal oxides and can be used to support bases and transition metals [2]. Metal oxides, especially aluminosilicate compounds, has 3-dimensional solid crystalline structure with many pores. Due to these properties, zeolite has been used as an adsorbent, ion exchange, and catalyst [3]. The molecular structure of natural zeolites [4] are shown in Fig 1.

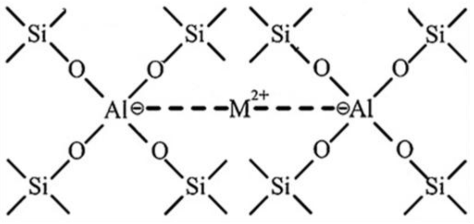

Fig 1. Natural zeolite framework

One method to increase the activity of natural zeolite is by acid or base impregnation. The use of solid base catalysts is better than solid acid catalysts, thus base impregnation is more suitable [5] for biodiesel synthesis. Base compounds that can be used to increase zeolite activity are KOH [6], NaOH [7] or K_2CO_3 [8]. Utilization of natural zeolite originating from Tapanuli as catalyst support had been carried out, but its detailed characteristics have never been reported. Therefore, this research aimed to evaluate the effectiveness of natural zeolite modified by KOH as heterogeneous catalysts, its characterization, and application in the RBO transesterification.

II. MATERIALS AND METHODS

II.I. MATERIALS

In this study, natural zeolite was obtained from Tapanuli, North Sumatera, Indonesia. It was pretreated by pulverizing using ball mill, then stirred in 30% (v/v) hydrogen peroxide (H_2O_2) solution for several min to remove impurities. The mixture was heated in a water bath till dried. Afterward, the zeolite was washed with aqua dest and oven dried for 24 h at 110ºC [6]. Dried zeolite was milled with micro hammer mill to give natural zeolite powder at 140 meshes.

Refined rice bran oil (RBO) was supplied from local market, while analytical grade methanol (CH_3OH) and potassium hydroxide (KOH) were purchased from Rudang Jaya, Medan. RBO used in this study has characteristics as follows: free fatty acid content, the kinematic viscosity and the density at 25ºC respectively as follow: 0.20%; 42 mm2/s, 891 kg/m^3. The composition of fatty acid of RBO used in this research as follows: oleic 42.45%, linoleic 32.21%, palmitic 20.85%, stearic 2.02%, linoleic 1.22%, eicosenoic 0.51%, myristic 0.29%, palmitoleic 0.26%, arachidic 0.05%, lauric 0.01%.

II.II. CATALYST PREPARATION

KOH solution was prepared at concentration ranging from 75/100 to 175/100 (g KOH/ml distilled water) for zeolite impregnation. The impregnation was conducted at fixed mass ratio of natural zeolite to the KOH solution of 1:4 at 60°C for 120 min in a three-neck flask equipped with magnetic stirrer, reflux condenser, and thermometer. The product mixture was then oven dried at 60°C for 24 h. The modified catalyst obtained was then separated from the KOH solution through vacuum filtration. Water was removed by drying catalyst in an oven at 110°C for 24 h, followed by zeolite calcination in a furnace at 450°C for four h [6,8]. Calcinated zeolite was refined with a mortar to 140 meshes then stored in sealed plastic box for later use. The catalyst was analyzed for its potassium content by using Atomic Absorption Spectroscopy (AAS). Catalyst with highest potassium content was then analyzed using Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-EDX), and Fourier Transform Infrared (FTIR) Spectroscopy. Henceforth, this catalyst was used in the transesterification process.

II.III. TRANSESTERIFICATION

Transesterification procedures followed those of previous studies [6,8]. Methanol to RBO molar ratio (MTR) of 8: 1; 10:1; 12:1, and KOH/natural zeolite catalyst at 1 – 4 %w, were prepared. The methanol and catalyst were introduced into a three-neck flask on a hot plate and heated to 60°C at 500 rpm. Afterward, 125 ml RBO was added slowly into the flask and reaction carried on for 2 – 4 h. After reaction, catalyst was separated from the reaction mixture by vacuum filtration, and the filtrate was placed in a separating funnel for 24 h to form 2 layers. The lower layer was removed, and the upper (biodiesel/methyl ester) was washed with distilled water at 60°C till the washing water was clear to remove impurities and remaining catalysts. The remaining water in biodiesel was removed by heating at 105°C. Afterward, obtained biodiesel was weighed and analyzed.

III. RESULTS AND DISCUSSION

III.I. CATALYST CHARACTERIZATION

III.I.I. AAS analysis

AAS analysis was conducted to determine the potassium content absorbed in natural zeolite after impregnation with KOH solution at various concentrations. Table 1 shows the results of the potassium content analysis after impregnation. The highest potassium content was achieved at 36.2% at KOH concentration of 75 g/100 ml distilled water. At greater concentrations (100-175 g/100 ml distilled water), potassium content decreased. At high KOH concentrations, KOH solution is saturated or oversaturated. This phenomenon leads to incomplete KOH dissolution in aqua dest, reducing K$^+$ dissociation in KOH solution and thereby, also reducing K$^+$ absorption on natural zeolite surface during impregnation.

During impregnation, K$^+$ from KOH replaces Al or Si in natural zeolite to form Al-O-K or Si-O-K bonds as seen in the natural zeolite structure. During this ion exchange, a reverse reaction may occur if cation equilibrium is reached [9]. Therefore, higher KOH concentration decreases potassium content in natural zeolite.

Table 1. Potassium content in catalyst after KOH impregnation

KOH concentration (g/100 ml) distilled water	Potassium content (%)
0	1.2
75	36.2
100	32.3
125	18.1
150	12.2
175	09.4

In addition, the competition between K$^+$ and metal ions in natural zeolite, which increases with concentration, also limits K$^+$ absorption. Therefore, there is a decrease in potassium content in KOH/natural zeolite with higher KOH concentration. Modification of the catalyst by this impregnation process results in Al-O-K or Si-O-K bonding in the modified natural zeolite structure [4] as shown in Fig 2.

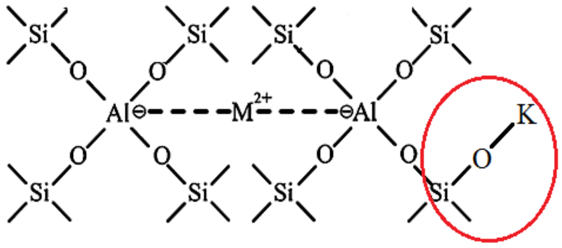

Fig 2. Modified zeolite framework

III.I.II. SEM-EDX analysis

Fig 3 depicts the results of SEM-EDX on catalyst morphology and composition both before and after impregnation with KOH solution at concentration of 75g/100 ml distilled water. Fig 3a presents the morphology of natural zeolites which are porous, have sharp edges with lots of empty space between particles.

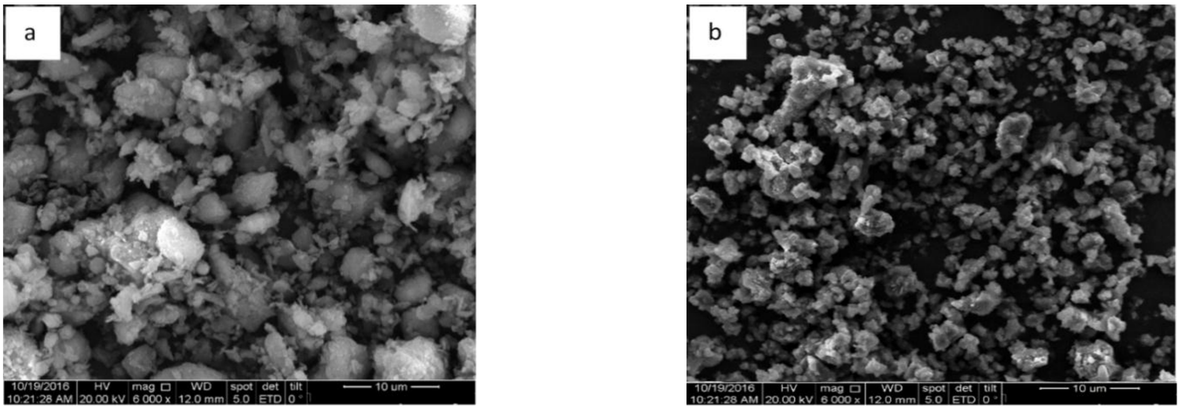

Fig 3. Morphology of (a) natural zeolite, (b) modified natural zeolite

Fig 3b shows that these pores and empty spaces are occupied by potassium during impregnation. K^+ is bound to negative ions from natural zeolite structure $(AlO_4)^{5-}$ or $(SiO_4)^{4-}$. The negatively charged oxygen in natural zeolite will bind to positively charged K to form a balanced chemical structure. As a result, a new group of Si-O-K or Al-O-K was formed.

According to Noiroj et al. [10] K attached to zeolite is oxidized to K_2O, this compound has a high catalytic activity and is suitable for transesterification. Modified natural zeolite has more potassium than natural zeolite without modification. This is confirmed by EDX results as shown in Table 2.

Table 2. Results of EDX Analysis

No.	Element	Natural zeolite (%)	Modified natural zeolite (%)
1.	P	0.10	-
2.	Na	0.75	-
3.	Mg	0.07	-
4.	Al	7.69	5.61
5.	Si	38.17	29.88
6.	K	1.20	36.20
7.	Ca	0.10	0.09
8.	Ti	0.14	0.13
9.	Fe	0.36	0.20
10.	O	51.42	27.89

III.I.III. FTIR Analysis

FTIR analysis on impregnated natural zeolite is conducted on zeolite with highest potassium (K) content of 36.2%, which is the result of impregnation with KOH solution at concentration of 75/100 ml distilled water. FTIR analysis is useful to determine the presence of K-O groups on natural zeolite heterogeneous catalysts that have been modified with KOH and to compare with the groups in natural zeolite without modification. Fig 4 presents the FTIR characterization of natural zeolite and KOH modified natural zeolite. FTIR results showed that O-H group was evidenced in natural zeolite at 3433.3 cm^{-1} while in the KOH modified natural zeolite, it was evidenced at 3371.6 cm^{-1}. In addition, the bonded H_2O at 1631.8 cm^{-1} in natural zeolite appeared to have a decreased percentage of transmittance in KOH modified natural zeolite at 1647.2 cm^{-1}. This is due to the impregnation and calcination in which H_2O molecules are separated from natural zeolite structure and replaced with K. Therefore, there is a decrease in the bonding of H_2O molecules adsorbed in natural zeolites.

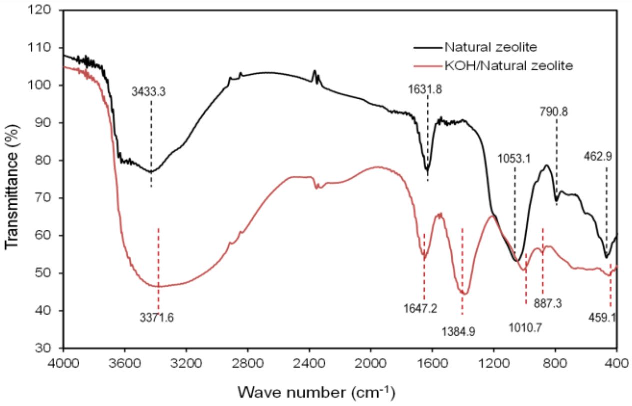

Fig 4. FTIR analysis of natural zeolite and modified natural zeolite

In natural zeolites, symmetrical stretching of Si bonds in the form of T-O-T was evidenced at 1053.1 cm^{-1} whereas on KOH modified zeolite, the symmetrical stretching of Si bond was evidenced at 1010.7 cm^{-1}. T-O bending vibration absorption is in the range of 500-420 cm^{-1}. The peaks at 462.9 cm^{-1} and 459.1 cm^{-1} on natural zeolites and KOH modified natural zeolites indicated the bending vibrations of T-O (Si-O or Al-O) bonds. This peak is an interpretation of the internal fabric in the natural zeolite framework. Basically the natural zeolite structure and the modified natural zeolite structure are not much different. The intensity of some spectral peaks of KOH modified natural zeolite also decreased. This is because during impregnation, decationization occurs as result of desylication and loss of crystallinity [7].

The peak of natural zeolite at 790.8 cm^{-1} was evidenced of a symmetric stretching vibration of metal oxide. For KOH modified natural zeolite, the vibration was observed at a different peak, 887.3 cm^{-1}. The metal was suspected to be potassium, as a result of natural zeolite impregnation in KOH solution. Thus, in natural zeolites and KOH modified natural zeolites there was potassium oxide (K-O). Peaks at 800-600 cm^{-1} were evidenced of bonds due to cation exchange [7]. Therefore, the peak of this absorption indicated that there is a group of K^+ cations that bind to the main framework of natural zeolites, either as Si-O-K or Al-O-K. The presence of this peak in natural zeolites became an important part of the catalytic activity of natural zeolites as catalysts in reactions. In addition, KOH modified natural zeolites had a more intense peak at 887.3 cm^{-1}, which indicates potassium group, compared to unmodified natural zeolite. This suggests that potassium content in KOH modified natural zeolite is greater than natural zeolite without modification.

III.II. TRANSESTERIFICATION

Based on the AAS analysis of KOH modified natural zeolite catalyst, the catalyst with the highest potassium concentration was employed for the rest of this experiment. Fig 5 depicts the effect of catalyst loading on biodiesel yield at various MTR. At catalyst load of 1-2%, biodiesel yield increased due to an increase in the active catalyst side. Further addition of catalyst caused the biodiesel yield to decrease. The use of 1% catalyst is not enough to convert much RBO into methyl ester, as the result biodiesel yield was low. The use of 3-4% catalyst rendered the reaction mixture more viscous, thus increasing the tendency to form lumps that can inhibit the reaction and reduce biodiesel yield. The same condition was also reported in the literature [11,12].

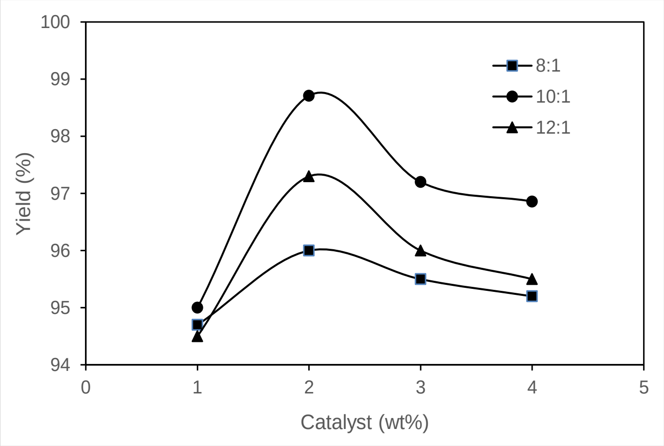

Fig 5. Effect of catalyst load on biodiesel yield at reaction temperature of 60°C, and reaction time of 2 h.

Fig 5 also presents the effect of MTR on biodiesel yield. At constant catalyst load, an increase in MTR from 8: 1 to 10: 1 increased biodiesel yield. Increased MTR induces contact between methanol and RBO, thus biodiesel yield increased. However, further increase in MTR may hinder separation of methyl ester and glycerol, because glycerol is soluble in excess methanol [13]. At MTR of 10:1, biodiesel yield was greater than those at MTR of 8:1 and 12:1. These results are similar to those reported in previous studies [8,14]. In this research, the highest biodiesel yield of 98.78% was obtained at 2% catalyst load, and MTR of 10:1. Kusuma et al. [6] reported that biodiesel yield reached 95% at 3% catalyst load, and MTR of 7:1. However, they used natural zeolite originating from Pacitan, East Java, Indonesia.

III.III. BIODIESEL PROPERTIES

Table 3 lists several biodiesel properties resulting from this study and the SNI-04-7182-2006 standard. Based on some biodiesel properties, the synthesized biodiesel had met the established standards. The results prove that KOH modified natural zeolite catalyst can be used as a heterogeneous catalyst in the production of biodiesel from RBO.

Table 3. Comparison of biodiesel properties produced from RBO with KOH modified natural zeolite catalyst with Indonesia Standard (SNI-04-7182-2006).

Properties	Biodiesel produced	SNI
Methyl ester content, %	98.62	>96,5
Density at 40 °C, kg/m^3	0.87	850-890
Kinematic viscosity at 40 °C, mm^2/s	4.22	1.9-6.0
Flash point, °C	150.00	>100

IV. CONCLUSION

The natural zeolite from Tapanuli Indonesia modified with KOH can be used as a catalyst in the production of biodiesel from RBO. At MTR of 10:1, reaction time of 2 h, and catalyst load of 2%, the biodiesel yield was highest at 98.78%. From the assessment on its properties (purity, density, viscosity, and flash point), the biodiesel had met the Indonesian National Standard (SNI).

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