

Biodiesel production from rice bran oil by transesterification using heterogeneous catalyst natural zeolite modified with K_2CO_3

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Abstract. In the present study, an effort had been made to use natural zeolite from Tapanuli Utara, North Sumatera as a potential catalyst for biodiesel production. Biodiesel production is usually through transesterification, and a catalyst is employed to improve reaction rate and yield. In this research rice bran oil (RBO) was used as feedstock. The objective of this work was to discover the effectiveness of natural zeolite modified by K_2CO_3 as catalysts in biodiesel production from RBO. K_2CO_3 /natural zeolite catalyst modification was by impregnation method at various K_2CO_3 concentrations followed by drying and calcination. Transesterification was conducted at 65°C and 500 rpm. Effect of process variables such as the amount of catalyst, reaction time, and the molar ratio of methanol to RBO was investigated. The maximum yield of 98.18% biodiesel was obtained by using 10:1 molar ratio of methanol to RBO at a reaction time of 3 hours in the presence of 4 w% catalyst. The obtained biodiesel was then characterized by its density, viscosity and ester content. The biodiesel properties met the Indonesia standard (SNI). The results showed that natural zeolite modified by K_2CO_3 was suitable as a catalyst in the synthesis of biodiesel through transesterification from RBO.

1. Introduction

Biodiesel is usually synthesized by transesterification of oil or fat with the aid of a catalyst. While the catalyst can either be homogeneous or heterogeneous catalysts, the later have some advantages over the other, such as less corrosive, easier to handle and separate, reusable and generating less amount of toxic wastes [1,2].

Natural zeolite is a potential catalyst for biodiesel production due to its abundance and low cost. Zeolite is a crystalline aluminosilicate with 3-dimensional structures that form uniform pore size [3]. Because of its physical and chemical properties, it has been utilized as absorbent, ion-exchange resin, and catalyst with high activity [4,5,6]. It can be modified to further increase its activity to enable higher biodiesel yield. Zeolite modification can be by acid or base impregnation. Based on previous research, impregnation with base is better than acid [7].

The use of KOH for natural zeolite modification had been reported in literature [8], however there is no study on K_2CO_3 usage for natural zeolite modification used as a catalyst in biodiesel production through transesterification. Therefore, this research aimed to assess the effect of K_2CO_3 in biodiesel synthesis from methanol and RBO as well as evaluating the properties of biodiesel produced and comparing it with existing standards.



2. Materials and Methods

2.1. Materials

Natural zeolite was obtained from Tapanuli Utara, North Sumatera, Indonesia. Before usage, natural zeolite was pulverized using ball mill, then treated with 30%(v/v) hydrogen peroxide solution under manual stirring for several minutes to remove impurities. Afterward, the solution was separated by heating in a water bath till dried. The zeolite was then washed with aqua dest and oven dried for 24 h at 110°C [8]. Dried zeolite was milled with mortar (micro hammer mill) to produce natural zeolite powder at 140 meshes. Refined rice bran oil (RBO) was purchased from local market, while analytical grade methanol and potassium carbonate were obtained from Rudang Jaya, Medan. The standard fatty acid methyl ester for FAME analysis was purchased from Sigma Aldrich.

2.2. Characterization of RBO

In this work, determination of density and kinematic viscosity was according to SNI-04-7182-2006. Analysis of free fatty acid content and fatty acid composition was according to SNI-01-0018-2006.

2.3. Catalyst preparation

Prepared natural zeolites were impregnated in K_2CO_3 solution. Solution concentration was varied from 15/60 to 55/60 (g K_2CO_3 /ml aqua dest). The process was carried out in a three-neck flask equipped with condenser reflux, thermometer, and magnetic stirrer at fixed mass ratio of natural zeolite to the K_2CO_3 solution of 1:4 at 60°C for two h. Afterward, the mixture was oven dried at 60°C for 24 h. The modified catalyst was then separated from the K_2CO_3 solution by vacuum filtration. Next, the catalyst was dried in an oven at 110°C for 24 h to remove the water, then calcined in a furnace at 450°C for four h [8]. After calcination, it was refined with a mortar to 140 meshes then stored for later use. The catalyst was characterized for its potassium content by using Atomic Absorption Spectroscopy (AAS).

2.4. Transesterification

Transesterification adopted procedures reported by Kusuma et al. [8]. Methanol, at a molar ratio of RBO to methanol of 1:8; 1:10; and 1:12, and K_2CO_3 /natural zeolite catalyst, at 2 – 4 %w, were prepared. The methanol and catalyst were mixed in a three-neck flask on a hot plate and heated to 65°C at 500 rpm. Afterward, 125 ml RBO was added slowly into the flask and reaction carried on for 2 – 4 h. At the end of the reaction, the catalyst was separated from the reaction mixture by vacuum filtration, and the filtrate was placed in a separating funnel for 24 hours to form 2 layers. The lower layer (glycerol) was removed, and the upper (methyl ester/biodiesel) was washed with aquadest at 60°C till the washing water was clear to remove impurities and remaining catalysts. The resulting biodiesel was heated to 105°C to remove residual water. Obtained biodiesel was then weighed and analyzed.

3. Results and Discussion

3.1. Characteristic of RBO

The results of RBO characterization were as follow: the density at 25°C was 890 kg/m³, the kinematic viscosity was 43 mm²/s, and free fatty acid content was 0.22%. The chemical composition of RBO was analyzed using gas chromatography (GC), and the results are presented in Table 1.

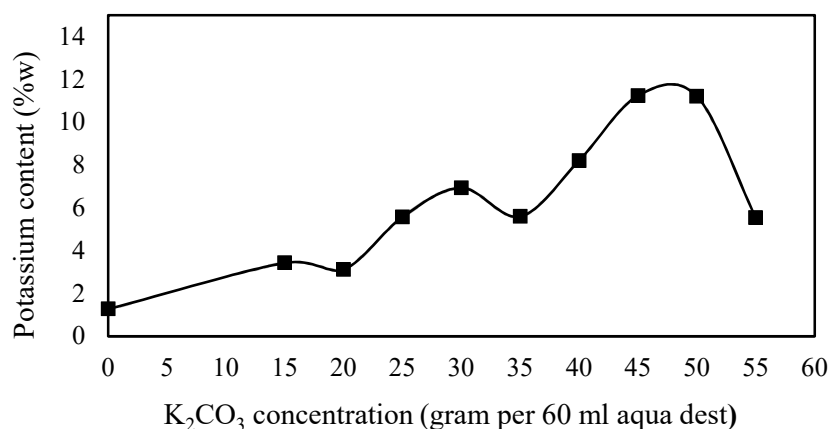
3.2. Catalyst characterization

Preparation of K_2CO_3 /natural zeolite catalyst was performed with nine variations of K_2CO_3 solution concentration to obtain highest potassium content in the catalyst. Figure 1 shows the potassium content in natural zeolite analyzed by AAS. The binding of potassium to the main skeleton of natural zeolite is illustrated in Figure 2.

Table 1. Fatty acid composition of RBO.

Fatty Acid	Composition (%)
Lauric acid (C12:0)	0.0114
Myristic acid (C14:0)	0.3912
Palmitic (C16:0)	20.8620
Palmitoleic acid (C16:1)	0.2638
Stearic Acid (C18:0)	2.0197
Oleic acid (C18:1)	42.4643
Linoleic acid (C18:2)	32.2081
Linolenic acid (C18:3)	1.2199
Arachidic acid (C20:0)	0.0522
Eicosenoicacid (C20:1)	0.5074

From Figure 1, potassium content in modified natural zeolite increased with the K_2CO_3 concentration of impregnating solution till K_2CO_3 concentration of 45 g per 60 ml aquadest, which reached 11.24%. The potassium content in this K_2CO_3 /natural zeolite catalyst is less than that of KOH/natural zeolite by Kusuma et al. [8] which peaked at 45.34%. The lower potassium content is because K_2CO_3 is not a strong base which can fully ionize, and its alkaline properties are below KOH base properties. At concentration beyond 45/60 (w/v), potassium content decreased to 5.54%. This decrease is possibly caused by close to the saturation condition of the K_2CO_3 solution at higher concentration.

**Figure 1.** Effect of K_2CO_3 concentration on potassium content (%w) in catalyst.

K_2CO_3 solubility in water at 30°C is 113.7 g in 100 ml water [9]. In water, K_2CO_3 will ionize, and K^+ will be absorbed in the natural zeolite. As in Figure 2, K^+ ions bind to the negative side of the natural zeolite structure (SiO_4)⁴⁻ or (AlO_4)⁵⁻. The negatively charged oxygen (O) binds to positively charged potassium (K) resulting in an equilibrated chemical structure of natural zeolites [10]. The chemical structure of natural zeolite modified with K_2CO_3 will possess more potassium (K) than the chemical structure of natural zeolite without modification. Also, a new group of Si-O-K or Al-O-K is formed.

Impregnation will lead to ion exchange. In this ion exchange, a counter-reaction may occur because of equal cations [9]. This phenomenon is due to competition between K_2CO_3 ions in high concentration K_2CO_3 solution which renders the ions unable to compete with free ions or to reform K_2CO_3 and cause potassium in natural zeolite to decrease.

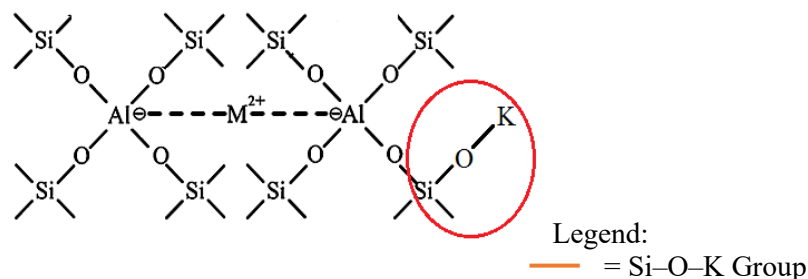


Figure 2. Main skeletal structure of natural zeolite [10].

3.3. Transesterification

3.3.1. Effect of amount of catalyst on biodiesel yield

Based on the AAS analysis of K_2CO_3 /natural zeolite catalyst, the catalyst with highest potassium concentration was employed for the rest of this experiment. Figure 3 presents the effect of the amount of catalyst on biodiesel yield. Within the observed range, increasing the amount of catalyst increased in biodiesel yield. This trend is also observed by other researchers [11,12]. In this research, biodiesel yield increased from 79.05% to 98.18% as the amount of catalyst from 2% to 4%. A greater amount of catalyst led to increasing of catalyst active side, resulting in higher yield of biodiesel [13]. Kusuma et al. [8] reported that the yield of biodiesel could reach 95% at 3% catalyst usage. However, their study did not vary the amount of catalyst. Also, they used a natural zeolite derived from Pacitan East Java and impregnated with KOH solution.

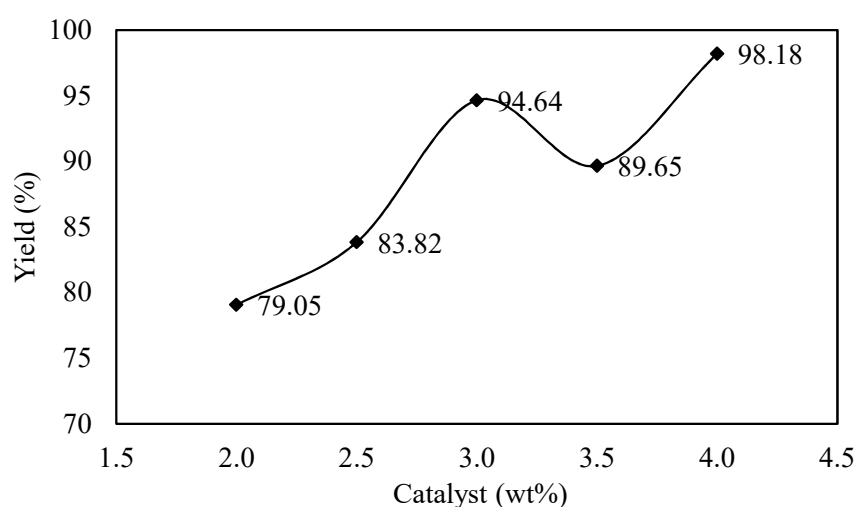


Figure 3. Effect of catalyst amount on biodiesel yield at reaction temperature of 65°C, RBO to methanol molar ratio of 10:1, and reaction time of 3 h.

In this study, biodiesel was also produced by transesterification of RBO using natural zeolite catalyst without K_2CO_3 impregnation, which yielded 3.94% biodiesel. This yield is well below those obtained using a modified natural zeolite catalyst.

3.3.2. Effect of reaction time on biodiesel yield

To observe the effect of reaction time on biodiesel yield, the experiment was conducted by varying the reaction time at fixed amount of catalyst, reaction temperature, and reactant molar ratio. Figure 4 depicts the effect of reaction time on biodiesel yield. The biodiesel yield increased with reaction time in the time range of 2-3 h. However, after 3 hours, biodiesel yield decreased. Initially, the reaction proceeded slowly due to mixing and dispersion of methanol in oil. After that, the reaction continued

until it reached maximum conversion. Transesterification is a reversible reaction. Once the optimum yield is achieved, additional reaction time will not affect the yield and even result in reverse reaction to form fatty acid, decreasing methyl ester yield [14].

In this study, for a reaction time of 2 hours, the yield of biodiesel produced was 85.86%. After 2.5 hours biodiesel yield increased to 91.56%. At a reaction time of 3 hours, biodiesel yield was highest at 98.18%. The same phenomenon was also reported by Noiroj et al. [7], but they used palm oil as raw material with KOH/NaY modified catalysts.

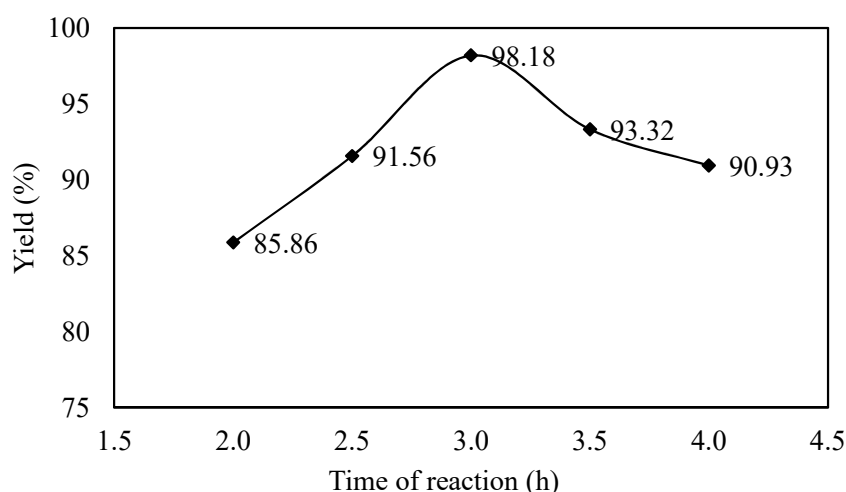


Figure 4. Effect of reaction time on biodiesel yield at 65°C, 4% catalyst, and methanol to RBO molar ratio of 10:1.

3.3.3. Effect of methanol to RBO molar ratio on biodiesel yield

Figure 5 illustrates the effect of methanol to RBO molar ratio on biodiesel yield at various amount of K_2CO_3 / natural zeolite catalyst.

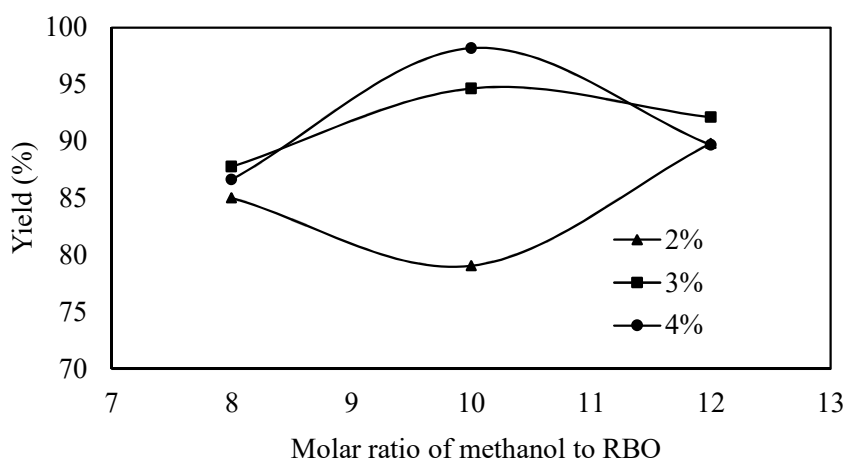


Figure 5. Effect of methanol to RBO molar ratio on biodiesel yield at reaction temperature of 65°C and 3 h reaction time.

As in Figure 5, biodiesel production at 2% catalyst followed different trend than those at 3% and 4% catalyst. For 3% and 4% catalyst, biodiesel yield increased from methanol to oil molar ratio of 8:1 to 10:1, then decreased at 12:1. This decrease is because adding methanol will cause the oil concentration to drop, resulting in a low reaction rate and shifting the reaction equilibrium [14]. Also,

excess glycerol as a byproduct blocks the reaction between methanol with oil and catalyst. Decreasing biodiesel yield is also due to the polar hydroxyl group in methanol which acts as an emulsifier and complicates product separation [13].

At a molar ratio of methanol to oil of 10: 1, the reaction formed a lot of methyl ester with little glycerol. This result indicates that the ratio is particularly suitable for biodiesel production. In other words, the best reaction condition is at methanol to oil molar ratio of 10:1 with a yield of 98% biodiesel. The results obtained are greater than those reported by Kusuma et al. [8] with the highest yield of 95.09% at 7:1 molar ratio using palm oil and KOH/ natural zeolite catalyst from Pacitan, East Java, Indonesia.

3.4. Biodiesel Properties

Table 2 lists several biodiesel properties resulting from this study and their comparison with the SNI-04-7182-2006 standard. From the test results of some biodiesel properties, the synthesized biodiesel met the established standards. The results suggest that modified K_2CO_3 /natural zeolite catalyst can be used as a heterogeneous catalyst in the manufacture of biodiesel from RBO.

Table 2. Comparison of the properties of biodiesel produced from RBO with K_2CO_3 /zeolite catalyst with Indonesia Standard (SNI-04-7182-2006).

Properties	Biodiesel produced	SNI
Methyl Esther content, %	98.82	>96,5
Density at 15 °C, g/ml	0.87	0.86-0.90
Kinematic viscosity at 40 °C, mm ² /s	4.22	1.9-6.0
Flash point, °C	150.00	>100

4. Conclusion

The natural zeolite modified with K_2CO_3 can be used as a heterogeneous catalyst in the manufacture of biodiesel from RBO and gives a much higher biodiesel yield compared to natural zeolite without modification. At a methanol to RBO molar ratio of 10:1, 3 hour reaction time, and 4% catalyst, the biodiesel yield was highest at 98.18%. From the test results, the biodiesel properties (purity, density, viscosity, and flash point) met the SNI Standard.

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