

Biodiesel synthesis from refined bleached and deodorized palm oil (RBDPO) by transesterification using durian shell based carbon modified with KOH as heterogeneous catalyst

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Abstract. In this study, an attempt had been made to use durian shell as carbon source for catalyst support for transesterification reaction. In this research, refined bleached and deodorized palm oil (RBDPO) and methanol were used as feedstock. The aim of this work was to evaluate the capability of durian shell based carbon as heterogeneous catalysts in transesterification of RBDPO. Carbonization of durian shell was conducted at 600°C for 2 h. The carbon resulted was modified by impregnation with potassium hydroxide (KOH) followed by drying and calcination. The modified activated carbon was characterized by Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDS). This heterogeneous catalyst was utilized in transesterification of RBDPO. Transesterification of RBDPO was performed at 60°C and 500 rpm. Effect of process variables such as the load of catalyst and reaction time was investigated. The highest yield of 97.29% biodiesel was obtained by using 12:1 molar ratio of methanol to RBDPO at a reaction time of 90 minutes in the presence of 3 w% catalysts. The resulted biodiesel was then characterized for its ester content, density, and viscosity. The biodiesel properties met the Indonesia standard (SNI). The results confirmed that activated carbon from durian shell modified with KOH is suitable as a heterogeneous catalyst in the synthesis of biodiesel.

1. Introduction

The shell of durian (*Durio zibhetius*) contains cellulose, hemicellulose, lignin and other extractive substances. The shell carbon content is over 40% on dry basis [1]. It can be converted to activated carbon, although the resulting carbon cannot be directly used as catalyst due to lack of active ingredient. However, the carbon may still be use as catalyst support by slight modifications [2]. Generally, activated carbon has inert bonds which do not interfere with trans esterification. It also has many micro pores which allow for high adsorption capability of metal compounds such as NaOH or KOH, and is stable at high temperatures. Furthermore, activated carbon is relatively inexpensive and abundant [3].

Activated carbon can be produced by pyrolysis. The carbon obtained is called bio-char which is a by-product of the pyrolysis. The main products of pyrolysis are bio-oil and bio-gas. Pyrolysis can be carried out using CO₂ or N₂ [4, 5]. Pyrolyzed biomass will form a deeper pore layer so that K compounds and the like can adhere well. Activation of carbon catalyst using the KOH impregnation method is the easiest way. KOH activity in activated carbon is able to improve internal porosity [6].

The use of heterogeneous catalysts in biodiesel synthesis has several advantages such as easier separation of catalysts from liquid products, reusable, and more environmentally benign. Through modification, heterogeneous catalyst may have better selectivity and activity, and extended life span [7]. Previous studies on the use of activated carbon from biomass as catalyst support in the transesterification of vegetable oil have been published in several literature, but are limited to those derived from waste pomelo peel [5], candlenut shell [8], flamboyant pods [9], palm shell [10], waste date pits [11], and shea nut shell [12], with biodiesel yield reaching 90% or more. However, the use of activated carbon as catalyst support from durian shell has never been conducted. Therefore, this research aimed to evaluate durian shell as a carbon source for catalyst support, modify it with KOH, apply it to transesterification of RBDPO to produce biodiesel, and compare it with existing standards.

2. Materials and Methods

2.1. Materials

Durian was obtained from Medan, Indonesia. Before usage, durian shell was washed with water, and crushed using a commercial blender until it becomes mush, then filtered. The shell was dried in an oven at 120°C for 5 h. After drying, it was reduced to 2-3 mm, and then milled to 100 meshes using a ball mill [1]. Powdered durian shell was stored in a closed container.

Analytical grade KOH and methanol were obtained from Rudang Jaya, Medan. RBDPO was obtained from a local supplier. The characteristics of RBDPO used in this study were as follows: the kinematic viscosity was 40 mm²/s, the density at 25°C was 890 kg/m³, the free fatty acid content was 0.05%, and the water content was 0.03%.

2.2. Catalyst preparation

Durian shell powder was pyrolyzed in a stainless steel pipe reactor for 2 h at 600°C under gaseous nitrogen flow of 200 L/min. Upon reaching room temperature, 10 g bio-char was collected and washed with 0.1M HCl to remove impurities, then neutralized until the pH approaches 7 using distilled water. Afterwards, bio-char was dried in the oven for 12 h at 110°C then cooled to room temperature. The dried bio-char was impregnated with KOH for 3 h [8] at a mass ratio of 1:4 in 250 ml water. Then it was dried in an oven at 110°C for 24 h. The impregnated bio-char was then calcined in a pipe reactor at 500°C for 3 h. After being cooled to the room temperature, the bio-char was stored in a closed container, and ready to be used as a catalyst in transesterification.

2.4. Transesterification

Transesterification followed procedures from several researchers [8, 13, 14] with slight modification. Methanol at a molar ratio of 12:1 to RBDPO, and biochar catalyst, at 2-4 wt. %, were prepared. The methanol and catalyst were introduced into a three-neck flask equipped with a thermometer, reflux condenser and magnetic stirrer. Then the flask was placed on a hot plate operated at 65°C and 500 rpm. Afterward, RBDPO was added to the flask and reaction proceeded for 60-150 min. Upon completion, product was separated from the catalyst by vacuum filtration, and the filtrate was placed in a separating funnel for 18 h to form 2 layers. The lower layer was removed and the upper (crude methyl ester) was washed by adding 80°C water, followed by violent shaking, and then left for 5 min to form two layers. The lower layer was removed again from the separation funnel. The washing process was repeated until the washing water became clear. To remove residual water, the top layer was heated at 105°C

while stirred on a hot plate equipped with magnetic stirrer. The methyl ester (biodiesel) obtained was then weighed and analyzed. The biodiesel yield was calculated using the following equation [14, 15].

$$\text{Yield of biodiesel} = \frac{\text{weight of biodiesel} \times \% \text{FAME}}{\text{weight of oil}} \times 100\% \quad (1)$$

Where % FAME in the equation (1) is the concentration fatty acid methyl ester obtained by gas chromatography analysis.

3. Results and Discussion

3.1 Catalyst characterization

Surface morphology analysis was carried out using SEM-EDS for raw durian shell, durian shell after pyrolysis at 600°C for 2h (bio-char), and bio-char impregnated in 40 g KOH/250 ml aqua des for 24 h. Figure 1 shows the results of SEM-EDS analysis. In figure 1(a), the surface of durian shell has few pores. This suggests that raw durian shell has small surface area. In figure 1(b), bio-char has larger surface area due to pore formation. Formation of pores in bio-char was due to the release of gas products at high temperatures. During pyrolysis, durian shell which contains cellulose, hemicellulose and lignin undergo decay reaction, forming gas products such as CO, CO₂, H₂, CH₄, C₂H₂, C₂H₆, benzene and their derivatives; liquid products in form of high molecular weight hydrocarbons (bio-oil); and solid products in form of carbon (bio-char) [1]. These pores play an important role in potassium absorption during KOH impregnation.

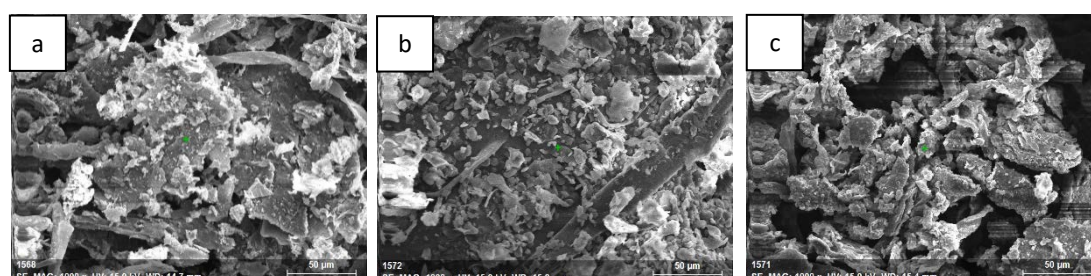


Figure 1. Morphology of (a) durian shell, (b) bio-char, (c) bio-char impregnated with KOH

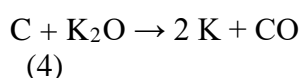
In figure 1(c), potassium was dispersed and penetrated into the pore channel, causing it to cover the pore surface. Similar findings were also reported in some literatures [8, 9, 10, and 11]. Further calcination was carried out to vaporize volatile matters, and enhance metal absorption bio-char surface.

Table 2. Elemental composition of durian shell, bio-char and bio-char impregnated with potassium hydroxide (KOH)

No .	Element	Durian shell (%)	Bio-char (%)	Bio-char impregnated with KOH (%)
1.	C	41.27	72.69	48.54
2.	O	46.72	26.72	33.90

3.	P	8.41	0.00	0.00
4.	Al	1.64	0.00	0.00
5.	Mg	0.30	0.00	0.00
6.	Si	0.14	0.00	0.00
7.	Ca	1.52	0.59	0.00
8.	K	0.00	0.00	17.56

The EDS results as found in table 1 shows that there is a change of elemental composition (in weight percent) in durian shell, bio-char, and bio-char impregnated with KOH. In the durian shell, the dominant elements are carbon and oxygen. In bio-char, the carbon content increases from 41.27% to 72.69%, because during pyrolysis carbon atoms will coalesce and form more stable bonds, while other compounds will evaporate or break the bonds [8]. After impregnation, the carbon content in bio-char decreases, while oxygen increases. During impregnation, carbon can react with KOH and form micropores on the carbon surface [12] and possible reactions [16] are given by equation (2) - (4). Potassium carbonate and potassium oxide are suspected as active substances responsible for catalyzing transesterification in biodiesel synthesis.



In table 1, the potassium content of bio-char impregnated with KOH reached 17.56%. This result is higher than those reported from previous researchers, where potassium content reached 11.62% for carbon originating from candlenut shell [8], and 10.26% for carbon originating from flamboyant pods [9]. This finding proves that the absorption of potassium on the bio-char surface has been going well.

3.3. Transesterification

Figure 2 presents the effect of reaction time on biodiesel yield, at methanol to RDBPO molar ratio of 12:1, reaction temperature of 60°C, and various amount of catalyst. The reaction was initially slow for the first 60 min, due to mixing and dispersion of methanol into oil. After that the reaction took place faster to reach the highest yield of 97.29% in the next 30 min. Further time addition resulted in reduced biodiesel yield. Similar results were also reported by several researchers [8, 9, 14]. The decrease is due to the nature of transesterification which is a reversible reaction. Once the optimum yield is achieved, excessive reaction time leads to reverse reaction to form fatty acids, decreasing biodiesel yield [18].

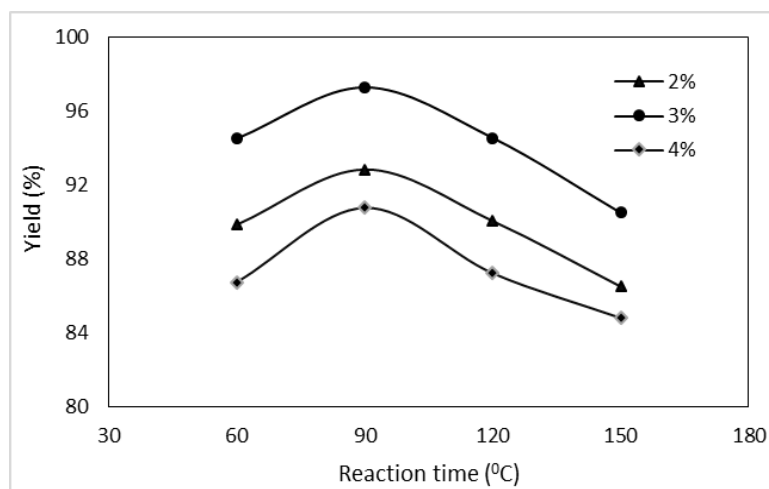


Figure 2. Effect of reaction time on biodiesel yield at 60°C, methanol to RBDPO ratio 12:1, and 3% catalyst loading

Figure 2 also shows that catalyst loading affects biodiesel yield. The biodiesel yield increased with catalyst loading in the catalyst range of 2-3%, but using more than 3% catalyst decreased biodiesel yield. At 2% catalyst load, biodiesel yield was only 92.85% for 90 min reaction time. This suggests that catalyst load is insufficient to convert RBDPO (triglycerides) into methyl esters. Using more catalysts up to 3% provided more active sides, enabling a biodiesel yield of 97.29% at 90 min reaction time. Using 4% catalyst load decreased biodiesel yield to 90.77%. This yield reduction is related to mass transfer resistance due to greater viscosity of reaction mixture and formation of catalyst clumps. The same phenomenon was also reported in several literatures [8, 14, 17, and 19].

The yield of biodiesel generated from this study is greater than that reported by some researchers, in which highest yield of 96.65% was reported for carbon catalysts derived from candlenut shell [8], and 89.81% for carbon catalysts derived from flamboyant pods [9]. This suggests that carbon from durian shell is suitable for use as a heterogeneous catalyst support in biodiesel synthesis.

3.3. Biodiesel properties

Table 2 presents the physical properties of biodiesel and the Indonesian National Standards (SNI). In table 2, bbiodiesel produced from this study has met existing standards. This further confirms that the durian shell derived bio-char impregnated with KOH is suitable to be used as a heterogeneous catalyst in biodiesel synthesis.

Table 2. Comparison of the physical properties of biodiesel produced from RBDPO with bio-char catalyst with Indonesia Standard (SNI-04-7182-2006).

Properties	Biodiesel produced	SNI
Methyl Ester content, %	96.9-99,2	>96,5
Density at 15 °C, g/ml	0.87-0,89	0.86-0.90
Kinematic viscosity at 40 °C, mm ² /s	4.2-5.1	1.9-6.0
Flash point, °C	149-150	>100

4. Conclusion

The durian shell is acceptable as carbon source for catalyst support on biodiesel synthesis. The potassium carbonate and potassium oxide compounds formed on carbon after impregnation with KOH. These compounds are the active ingredient responsible for catalyzing a transesterification process. The carbon modified with KOH can be used as a heterogeneous catalyst in the synthesis of biodiesel from RBDPO. At a methanol to RBDPO molar ratio of 12:1, 60°C reaction temperature, 90 min reaction time, and 3% catalyst load, the biodiesel yield was highest at 97.29%. From the assessment on the physical properties, biodiesel produced in this study has met the SNI.

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