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Biodiesel Production from Castor Oil Using Heterogeneous Catalyst KOH/Zeolite of Natural Zeolite Bandung Indonesia

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Abstract. Biodiesel production from Castor (*Ricinus communis*) oil was carried out through transesterification using heterogeneous KOH/zeolite catalyst. The aim of this study was to determine the optimum condition of the reaction. The synthesis of the catalyst was initiated through chemical activation of zeolite, followed by the synthesis of KOH/zeolite through ultrasound-assisted method and calcination at 450 °C. Transesterification of castor oil was performed at a temperature of 55, 60 and 65°C; 5, 6, 7 h contact times; and 50, 60, 70% of catalyst concentration. The result of XRD analysis on natural zeolite indicated the zeolite belong the group mordenite. The addition of KOH to the activated zeolite gave rise to new peaks at 2θ: 31, 36, and 38. In addition, the data from XRF analysis indicated there is an increase of potassium (K) amount in KOH/zeolite compared to the activated one. Based on the GC-MS data of biodiesel produced through transesterification, the optimum yield of methyl ricinoleate was achieved at 55 °C, 7 h contact time and 70 % catalyst concentration. A number of physical properties such as water content and density are reported to have not yet met the SNI standard.

INTRODUCTION

Castor oil which is produced out of castor beans (*Ricinus communis*) has long been considered as a commodity with high economical value. Castor oil can be processed further to produce biodiesel oil as a substitute of fossil fuels. It holds many advantages over petroleum-based diesel due to its renewable, biodegradable, low toxicity and non-corrosive nature. It also has low emissions of unburnt hydrocarbons compared to the fossil fuel predessor [1-4]. The use of castor oil is preferred because of the presence of poisonous ricinoleic acid in it, so it will not affect the production of edible oil. The ricinoleic acid content in castor oil is extremely high [5-7]. The constituent free fatty

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acids in castor (*Ricinus communis*) oil is composed of 84.2% ricinoleic, 7.3% linoleic, 5.5% oleic, 1.3% palmitic and 1.2% stearic [8].

In general, the reaction rate of transesterification is affected by several variables including temperature, catalyst, methanol to oil molar ratio and reaction time [9-11]. The study on the effect of reaction time to the yield of biodiesel-conversion was evaluated as the reaction progressed from 1 to 6 h, the optimum result of biodiesel conversion was obtained at 6 h reaction time. The amount of yield produced after 6 h using KOH/Al_2O_3 catalyst was around 87.5% [12].

Kusumaningsih *et al.* [13] studied the transesterification reaction on biodiesel at the temperature of 55 and 65 °C, revealed that castor oil conversion into methyl ester approaches optimum along with the increasing of temperature. The addition of catalyst varied in concentration, which ranged from 0,2–0,9 g and the optimum result was obtained using 0,4 g of catalyst addition. The study concluded that if the concentration of catalyst is too high (> 0.4 g) too many nucleophiles will be activated compared to the number of existing reagents, which led to the formation of fatty acid.

The use of heterogeneous KOH/zeolite catalyst assists the separation process of biodiesel product after the transesterification reaction completes. Heterogeneous catalysts are easily separated, regenerated and reused for the further cycle during the transesterification process and thus known as an environmentally friendly process. A heterogeneous catalyst is widely applied in the industry due to its improved selectivity and is easily separated from the reaction mixture. Kusuma *et al.* [14] produced an optimum biodiesel conversion yield of 96.44% at 60 °C for 2 h, 1: 7 methanol to oil molar ration and 3% catalyst concentration of palm oil mass as a sample.

EXPERIMENTAL DETAILS

Tools and Materials

The tools required for this study are a set of laboratory glassware, a set of reflux, hotplate, oven, stopwatch, analytical balance, separatory funnel, pycnometer, ostwald's viscometer, burette and statif, and GC-MS (QP-2010S/Shimadzu) instrumentation. The materials required are Bandung natural zeolite, castor oil, methanol, aquadest, KOH (Merck), HCl (Merck), aluminium foil, filter paper, phenolphthalein indicator, 95% of ethanol, petroleum ether, oxalic acid solution, anhydrous Na_2SO_4 and acetone.

Preparation and Modification of KOH/Zeolite Catalyst

The zeolite that gets through the 230 mesh sieve was immersed in 200 mL HCl 6 M for 4 h with continuous stirring. The mixture was then filtered and washed with distilled water until the pH of the filtrate was neutral, and dried in an oven at 120ºC for 4 h. The modification process was carried out by dissolving KOH into 50 mL of distilled water with varying concentrations of 50, 60, and 70 % of zeolite weight. Exactly 50 g of zeolite were immersed in KOH solution, the synthesis process was assisted by ultrasonic waves at 43 kHz for 10 min. After that came the multi-level calcination at 110 °C for 24 h and then, again, at 450 °C for 4 h [15]. The zeolite after activation and KOH / zeolite were characterized using XRD and XRF.

Transesterification Reaction of Castor Oil Using Heterogeneous KOH/Zeolite Catalyst with Variations of Contact Time, Temperature and Catalyst Composition

KOH / Zeolite heterogeneous catalyst of 50% concentration was measured about 17% of oil mass and then mixed with methanol in beaker glass. The castor oil was added subsequently. The oil to methanol molar ratio here was to 1:15. The mixture was put into the reactor and stirred. The reaction was carried out at a temperature of 60 °C with variation in reaction times; 5, 6 and 7 h. The results were separated through vacuum filtration and placed in separating funnel. The upper layer (methyl ester) was washed using distilled water, and then added with petroleum ether and anhydrous Na_2SO_4. Afterward, it was analyzed using GC-MS.

Analysis of water content in castor oil methyl ester was conducted in the gravimetric method. The analysis of free fatty acids (FFA) in samples required NaOH, while the analysis of methyl ester density used pycnometer. The study on the effect of temperature to the transesterification reaction was carried out at 55 dan 65 ºC. KOH/zeolite catalysts of 60 and 70% were used to asses the effectivity of heterogeneous catalysts for castor oil transestrification reactions,

RESULT AND DISCUSSION

Modification of KOH/zeolite

The preparation of zeolite preceding the activation process resulted in the enlarging of zeolite surface area. Zeolite activation using acid (HCl) caused dealumination and decationization, where Al and other metal cations are released and led to the increasing of Si/Al ratio. Furthermore, acid activation has caused a decrease in Ca and Mn impurities concentration which would enhance zeolite catalytic ability in castor oil transesterification reactions.

TABLE 1. XRF analysis results of natural activated and modified zeolite

Element	Natural zeolite (%)	Activated zeolite (%)	Modified zeolite (%)
Al	8,4	7,2	-
Si	56,9	52,9	40,7
K	8,75	11,3	38,7
Ca	10,5	9,31	8,02
Ti	0,90	1,2	1,0
V	0,04	0,05	0,02
Cr	-	0,069	0,058
Mn	0,41	0,39	0,27
Fe	12,0	14,1	10,2
Ni	-	0,858	-
Cu	0,11	0,21	0,11
Zn	0,03	0,04	-
Sr	1,0	1,2	0,45
Ba	0,1	-	0,2
Eu	0,2	-	0,3
Zr	-	0,7	-
Re	0,2	-	-

The modification of zeolite by mixing with 50% KOH has increased the K^+ ion content of Bandung natural zeolite (Table 1). This result can be considered as confirmation for successful impregnation of K^+ ion to zeolite surface. The success of KOH impregnation to zeolite surfaces was also supported by the XRD results (Fig. 1). The diffractogram indicated that the natural zeolite is indeed a mordenite. This is based on the presence of peaks in compliance with the standard at 2θ (°) = 13.4; 19,6; 22.2; 25; 6; 26.2; 27.6; and 30.8. The addition of KOH to Bandung natural zeolite was exhibited to have an effect on the XRD diffractogram pattern. The diffractogram of modified zeolite showed a decrease in the crystallinity of the zeolite structure. The decrease in its intensity is caused by the addition of KOH which attaches to the surface of zeolite active side.

New peaks at 2θ (°) = 31, 34, and 38 which correspond to the peak of standard KOH (ICSD no. 61047) give enough indication on the success of KOH/zeolite modification. Furthermore, this was supported by the increase in peak intensity at 2θ (°) = 23 and 27.5. The desired result was for KOH to be oxidized to K_2O in the calcination process. However, the K_2O peak does not appear on the diffractogram, which is presumably because of insufficient temperature in the calcination process of zeolite modification.

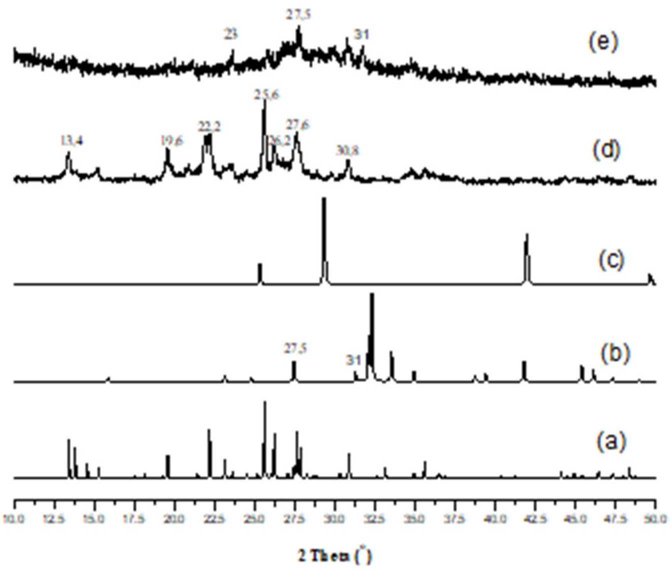

FIGURE 1. XRD diffractogram of (a) standard of mordenite zeolite (commission structure of international zeolite association, 2001) (b) standard of KOH (ICSD no. 61047) (c) standard of K_2O (ICSD no. 641282) (d) natural zeolite (e) modified KOH / zeolite

The Effectivity of Heterogeneous Catalysts KOH/Zeolite in Castor Oil Transesterification Reactions

Based on the GC chromatogram, the product of the castor oil transesterification reaction at least contains 8-9 possible compounds indicated by the number of peaks. Compounds with the highest intensity appear at retention time (Rt) between 35.7-36.7. This compound is in compliance with the characteristic of methyl ricinoleic, the largest component in castor oil. Identification of compounds can be carried out using mass spectra data by estimating the fragmentation patterns of each peak. Take one example of the ricinoleic methyl ester mass spectra. A number of the estimated mass spectra of compounds contained in biodiesel produced through transesterification reaction of castor oil are shown in Fig. 2.

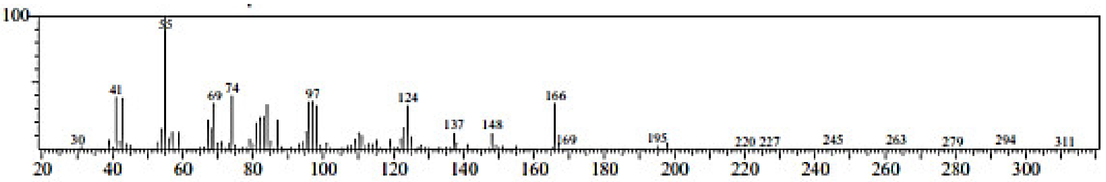

FIGURE 2. Mass spectra of ricinoleic methyl ester

Figure 2 showed spectra of compounds contained in biodiesel, one of them has retention time (Rt) between 35.7–36.7 which has similar base peak with standard methyl ricinoleic at m/z 55. The characteristic of methyl ricinoleate fragmentation is the presence of high-intensity peaks at m/z 166 and 55. The peak at m/z 74 appeared due to Mc Lafferty's rearrangement. The presumed fragmentation pattern of this compound is given in Fig. 3.

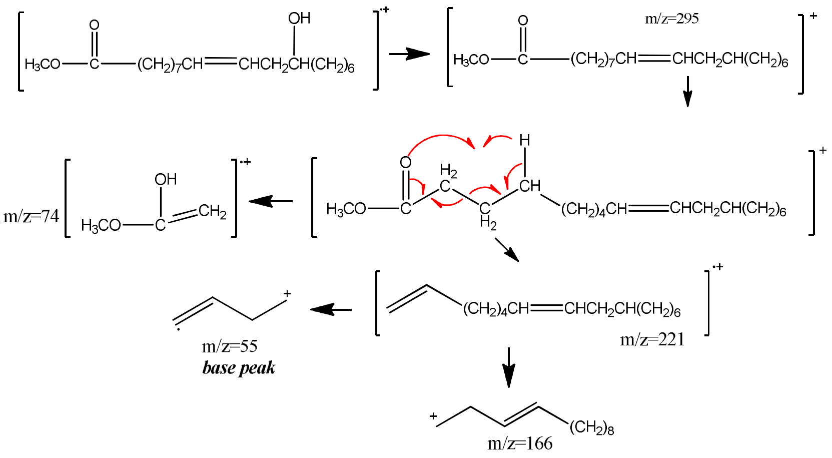

FIGURE 3. The presumed fragmentation pattern of methyl ricinoleate, the largest component in castor oil

Based on the summarization of GC-MS results given in Table 2, methyl ricinoleate produced at 7 hours reaction time was around 86.14%, while at a reaction time of 5 and 6 h were 77.14 and 82.63%, respectively. Longer contact time between heterogeneous KOH/zeolite catalysts in transesterification reaction resulting in higher methyl ricinoleic production (%). The progression was evaluated at 5, 6 and 7 h reaction time and the optimum methyl ricinoleic conversion (%) was at 7 h. In previous researches, variations in reaction time 1, 2 and 3 h were conducted combined with the same treatment, but there were no layers of methyl ester and glycerol present after castor oil transesterification reaction.

TABLE 2. Major methyl ester content produced through castor oil transesterification reaction

Test	Methyl Palmitic (%)	Methyl Linoleic (%)	Methyl Oleic (%)	Methyl Stearic (%)	Methyl Ricinoleic (%)*
Reaction times					
5 h	2,83	-	16,11	2,37	77,14
6 h	2,27	-	12,05	1,99	82,63
7 h	2,28	4,45	3,20	3,22	86,14**
Temperatures					
55 °C	2,26	1,76	1,48	1,99	91,41**
60 °C	2,28	4,45	3,20	3,22	86,16
65 °C	1,97	-	10,51	1,83	84,36
Catalysts (%)					
50%	2,28	4,45	3,20	3,22	86,14
60%	6,97	-	38,5	8,19	45,65
70%	2,15	1,33	1,20	2,09	92,11**

*reference for determining optimum conditions **optimum conditions

The optimum % area of methyl ricinoleic was found at a reaction temperature of 55°C which is around 91.41%, while the % area 60 and 65°C were 86.16 and 84.36%. These results indicated that the increase in temperature hold significant effect on the reduction of % area of methyl ricinoleate. The use of 70% KOH/zeolite catalyst resulted in the highest % area of methyl ricinoleate at 92.11%. Meanwhile, the % area of methyl ricinoleate in the addition of 50 and 60% catalyst were 86.14 and 45.65%. It can be concluded that increasing the amount of KOH ratio to natural zeolite affected the result of castor oil transesterification reaction, significantly.

The Determination of Water Content, Free Fatty Acids, and Density of Biodiesel Product

A number of physical characteristic assessments were performed on the biodiesel product including water content, free fatty acids and density measurement. These characteristics will directly affect engine performance and are presented in Table 3.

TABLE 3. The physical quality of biodiesel product

Test	Water content (%)	Free fatty acid (mg-NaOH/g)	Density (Kg/m^3)
Standard	**0,05**	**Max 0,8**	**850-890**
Reaction Time			
5 h	0,08	0,37	952
6 h	0,06	0,42	944
7 h	0,03	0,37	961
Temperatures			
55 °C	16,4	0,16	955
60 °C	3	0,64	961
65 °C	5,2	0,32	966
Catalysts			
50%	0,04	0,04	952
60%	0,25	0,06	993
70%	0,05	0,06	961

Table 3 showed the effect of reaction time, reaction temperature and the amount of KOH addition on heterogeneous KOH/zeolite catalysts on castor oil transesterification. The water content of biodiesel produced from the treatment of reaction temperature variations exceeded the standard of SNI 04-7182-2006. It is accounted for by the difficulty of methyl ester to be separated from the remaining water. It was attempted in this study to add anhydrous Na_2SO_4 to methyl ester to the extent of saturation, but the gravimetric analysis results of water content were still above the standard. On the contrary, the free fatty acids concentration in the product of all three treatments have met SNI standard for the acid value (max. 0.5 mg-KOH/g). However, the density of biodiesel produced through all three treatments also exceeded the standard SNI, which was around 850-890 (Kg/m^3).

SUMMARY

It can be concluded from the study that methyl ester production from castor oil using heterogeneous catalyst KOH/natural zeolite of Bandung reached optimum at high temperature and contact time, which was accomplished at 55ºC and 7 h contact time. The higher the amount of KOH added to the production of heterogeneous KOH/zeolite catalysts, namely 70%, the more significant its effect on methyl ester production from castor oil. This was indicated by the increasing amount of methyl ricinoleic as the main free fatty acid composition of castor oil. The physical properties of the products have not yet met the standard of SNI.

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