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Characterization of Fly Ash Catalyst Using XRD Method for Biofuel Production from Used Cooking Oil

Dina Eka Pranata[1], Aida Syarif[2*], and Muhammad Yerizam[3]

[1] Applied Master of Renewable Energy Engineering, Politeknik Negeri Sriwijaya, Jl. Srijaya Negara, Bukit Besar, Ilir Barat I, Palembang 30139, Indonesia
[2] Chemical Engineering Department, Renewable Energy Engineering Study Program, Politeknik Negeri Sriwijaya, Jl. Srijaya Negara, Bukit Besar, Ilir Barat I, Palembang, South Sumatera 30139
[3] Chemical Engineering Department, Politeknik Negeri Sriwijaya, Jl. Srijaya Negara, Bukit Besar, Ilir Barat I, Palembang, South Sumatera 30139

*Corresponding Author: *aida_syarif@yahoo.co.id*

Abstract

The purpose of this study was to determine the characteristics of the fly ash catalyst and to test the catalyst in the production of biofuels from used cooking oil. Fly ash catalyst which has been activated using 1M NaoH was analyzed using XRD at an angle of $2\theta = 15° - 80°$ with a wavelength (λ) of X-rays of 0.15406 nm. From the results of the analysis, the compound $NaO_{2}6Si_{6}Y_{9}$ was obtained with a hexagonal structure. Furthermore, the results of the XRD analysis that can be obtained in the form of wavelength, intensity, 2θ and FWHM values will be substituted into the Debye Scherrer Equation to calculate the crystal structure size of the Fly Ash catalyst. So that obtained Crystal Size (D) of 8.1942 nm. Crystal size is an important factor for the catalyst because it is related to the number of active catalyst sites and the surface area of the catalyst. In addition, the larger the crystal size, the greater the surface area of the catalyst so that the greater the surface energy it has. In testing the fly ash catalyst in the process of cracking used cooking oil into biofuel, the optimum condition of the catalyst was 10% and the volume of biofuel produced was 615 mL.

Keywords: Fly Ash, XRD, NaOH, Debye Scherrer, Crystal

Abstrak (Indonesian)

Tujuan penelitian ini adalah untuk mengetahui karakteristik dari katalis fly ash dan menguji katalis tersebut pada pembuatan biofuel dari minyak jelantah. Katalis fly ash yang sudah di aktivasi menggunakan NaoH 1M dianalisa menggunakan XRD pada sudut $2\theta = 15° - 80°$ dengan panjang gelombang (λ) sinar X sebesar 0,15406 nm. Dari hasil Analisa tersebut di dapat senyawa $NaO_{26}Si_{6}Y_{9}$ dengan bentuk struktur hexagonal. Selanjutnya hasil Analisa XRD yang di dapat berupa nilai panjang gelombang, intensitas, 2θ dan FWHM akan di substitusikan kedalam Persamaan Debye Scherrer untuk menghitung ukuran struktur kristal dari katalis Fly Ash. Sehingga didapatkan Ukuran Kristal (D) sebesar 8,10942 nm. Ukuran kristal merupakan salah satu faktor penting bagi katalis karena berkaitan dengan jumlah situs katalis aktif dan luas permukaan katalis. Selain itu, semakin besar ukuran kristal maka semakin besar luas permukaan katalis sehingga semakin besar energi permukaan yang dimilikinya. Pada pengujian katalis fly ash dalam proses perengkahan minyak jelantah menjadi biofuel didapat kondisi optimum katalis sebesar 10% dan volume biofuel yang dihasilkan 615 mL.

Kata Kunci: Fly Ash, XRD, NaOH, Debye Scherrer, Kristal

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INTRODUCTION

Most of the energy use in the world today comes from non-renewable natural resources, namely fossil fuels in the form of oil and natural gas. Consumption of fuel oil (BBM) which continues to rise every year, reported in 2030 will increase to reach 107 million kilo liters/year and about 50% or 55.64% of the fuel is fulfilled by imports. The limitations of fossil energy require diversification of energy resources to ensure energy availability. So the use of new and renewable energy must be increased [1]. Biomass is one of the renewable energy sources that has the potential to be developed because we can find it in almost all parts of Indonesia. One of them is used cooking oil which can be converted into biofuel. Biofuel can be produced using either homogeneous or heterogeneous catalysts. However, when using homogeneous catalysts, a separation process is required to recover the catalyst at the end of the process and additional equipment is required to purify the product from the crystals and increase the possibility of corrosion. Homogeneous catalysts are usually used solutions such as NaOH [2], CH_3ONa [3] and KOH [4]. Therefore, heterogeneous catalysts are currently being developed more than homogeneous catalysts.

Heterogeneous catalysts have many advantages including low cost, easy to separate [2], non-corrosive and potentially used many times [5]. In this study, the catalyst used is fly ash from PLTU Python and will be activated using 1M NaOH. According to Kurniasari et al (2011) the best operating conditions for activation with NaOH were obtained at a concentration of 1M [6]. Activation with NaOH also aims to remove certain ions from the catalyst framework and replace them with Na+ ions so that the catalyst has conditions that are closer to the homoionic form [7]. With the homoionic form, the molecules will have relatively the same pore size, so it is expected that their adsorption ability and selectivity to water vapor will also be better.

In this study, fly ash catalyst will be analyzed using X-Ray Diffraction (XRD). The working principle is that when monochromatic X-rays fall on a crystal, the X-rays will be scattered in all directions, but because there is a regularity in the position of the atoms in the crystal, in certain directions the scattering waves will have constructive interference and in other directions they will have destructive interference [8]. The atoms in a crystal can be viewed as elements that form a family of plane planes that have characteristic distances between planes [9]. The necessary condition for parallel beams when scattered crystal atoms will interfere constructively is to have a path distance difference of exactly nλ, where the difference in distance between 2 parallel beams is 2d sin , and fulfills the Bragg equation.

$$n\,\lambda = 2\,d\,\sin\theta \qquad (1)$$

where, λ = X-ray wavelength (Å)
d = distance between grids (Å)
θ = diffraction angle (degrees)
n = 1,2,3, etc. (order of diffraction)

Samples for XRD analysis can be powders, solids, thin films, or bands. The minimum number of samples required is only a few milligrams, but with large amounts (grams) better accuracy will be obtained. The XRD method is a non-destructive method, meaning that the sample is not damaged solidly when analyzed and can be used for other analyzes.

The results of the XRD analysis are in the form of a diffractogram in the form of an arrangement of lines or peaks with different intensities and positions that are specific to the material being analyzed. Each crystalline phase has a characteristic diffractogram arrangement, so it can be used as a fingerprint for identification tests [9]. Determination of the suitability of the crystal structure formed is done by matching each peak that appears on the diffractogram at a certain angle value of 2θ and d from the analysis with data from JCPDS (Joint Committee Powder Diffraction Standard) in order to obtain information on the orientation of the crystal planes formed. If all the orientations of the crystal planes are identified, it is certain that the crystal structure is in agreement.

MATERIALS AND METHODS

Waste Cooking Oil

The used cooking oil in this study is used cooking oil from waste from restaurants in the city of Palembang. One of the efforts to reduce the used cooking oil waste is to use it as a book material for making biofuels [10]. Used cooking oil has a long hydrocarbon chain that allows it to be used as biofuel The highest fatty acid composition in palm oil is oleic acid 32.192% and palmitic acid 14.939% [11]. To break the long chain compound molecules into low hydrocarbon fractions, a cracking process is needed. The prototype used in the used cooking oil cracking process can be seen in Figure 1.

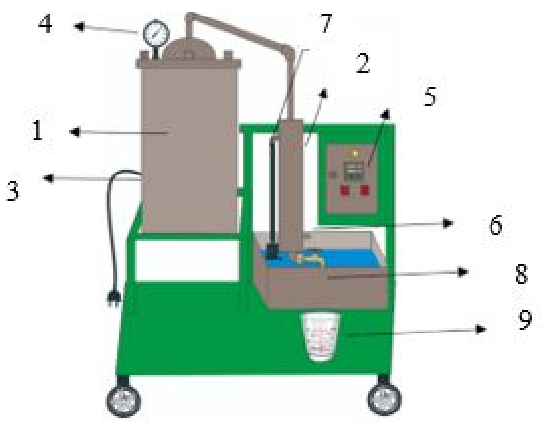

Figure 1. Thermal Catalytic Cracking Reactor

where:
1. Thermal catalytic cracking reactor,
2. Condenser,
3. Preheater (heater),
4. Pressure control,
5. Themo Control,
6. Cooling water (inlet),
7. Cooling water (outlet),
8. Product output pipe,
9. Beaker Glass for biofuel

Catalyst Activation

Fly ash is a material that has a fine grain size, is grayish in color and is obtained from burning coal. In this experiment, fly ash from the Pyton PLTU was used. The fly ash used is activated first using sodium hydroxide with a concentration of 1 M. as in Figure 2 below

Figure 2. Activated Fly Ash Catalyst

Fly Ash is sieved with 100 mesh size. Then soaked with aquadest for 24 hours and filtered. Fly Ash is heated using an oven for 3 hours at a temperature of 120ºC. Then this material is used as a Prior to characterization using XRD, the catalyst was first activated to increase its ability to accelerate the reaction. such as catalyst activation using high temperatures to expand the surface area and increase the amount of iodine in fly ash [12]. In addition, catalyst activation can use alkaline activator to remove heavy metal compounds by adsorption using nanosilica [13].

In this study, the activation of fly ash using alkaline activator to remove impurities and expand surface area. Fly Ash measuring 100 mesh is mixed into NaOH 1M solution with a 1: 4 ratio. then the mixture is heated on a hot plate using a temperature of 110 ° C while stirring with a magnetic stirrer for 3 hours. Fly Ash solution is filtered and washed with distilled water until a neutral pH. Fly Ash is dried in an oven at a temperature of 110 °C for 3 hours. then fly as was calcined at 500 °C for 3 hours [14]. The higher the NaOH content in the mixture during the smelting process, the more Na+ ions will react with the alumina and silica contained in the fly ash so that there will be more sodium silicate and sodium aluminate products [15]. Activated fly ash catalyst will be analyzed using *X-Ray Diffraction* (XRD).

Analysis Data

Characterization of fly ash catalyst using XRD at an angle of 2θ = 15 ° - 80 ° with a wavelength (λ) of X rays of 0.15406 nm. The results of XRD analysis are in the form of a diffractogram which will be processed to obtain the crystal size using the Debye Scherrer equation [16]:

$$D=\frac{K.\lambda}{\beta \text{ Cos } \theta} \qquad (2)$$

The modified Debye Scherrer equation was used to determine one crystal size value [17]. Debye Scherrer's modification equation is formulated as follows:

$$\ln \beta = \ln\frac{K.\lambda}{\beta \text{ Cos } \theta} = \ln\frac{K.\lambda}{D} + \ln\frac{1}{\text{Cos } \theta} \qquad (3)$$

where:
D = Crystal Size
K = 0.9
λ = Wavelength of x rays (0.15406)
β = FWHM (Rad)
θ = peak position (rad)

RESULTS AND DISCUSSION

Characteristic of Fly Ash as Catalyst

The catalyst that has been produced is then analyzed using the X-ray diffraction method. This XRD test is carried out to identify the presence of a crystalline phase in the material, and to analyze the structural properties (such as the composition of the crystal orientation) of each phase [18]. The results of the XRD test were matched with the data on the mercury application to obtain a 3D shape from the crystal form of the fly ash catalyst

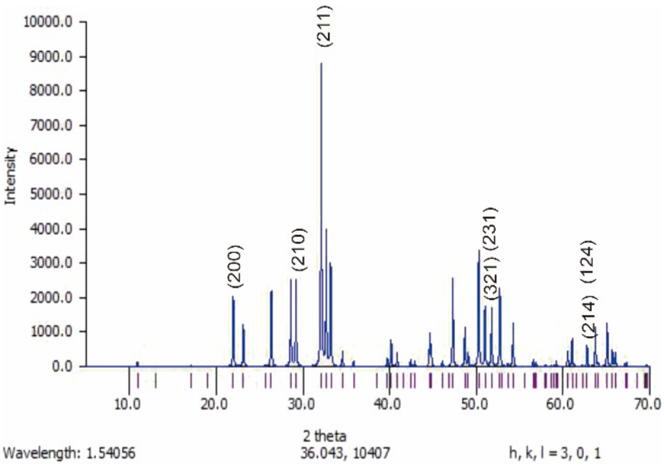

Figure 3. Fly ash catalyst diffractogram

Figure 3 shows the diffractogram of a Fly Ash catalyst. The peaks that appear are all identified and are in accordance with standard data from the Joint Committee on Powder Diffraction Standard (JCPDS) 00-009-0432 which indicates that the polycrystalline structure of the Fly Ash catalyst is in the crystal plane orientation (200), (210), (211), (321)) (231), and (214) (124).

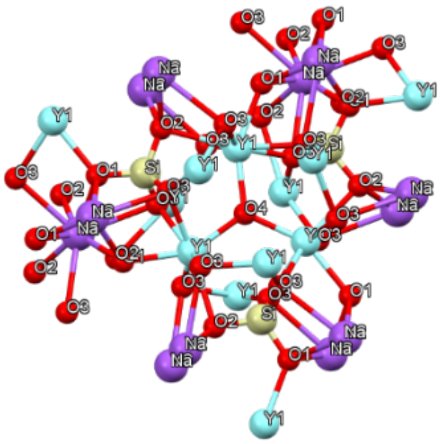

Figure 4. Hexagonal crystal structure of Fly Ash catalyst using mercury application

The appearance of the distribution of the orientation of the crystal plane shows that the Fly Ash catalyst is composed of 4 O atoms and one Si atom with a clinoptilolite (Na-Y) structure and has a hexagonal structure as shown in Figure 4. Nasikin and Lubad (2002) the zeolite framework is formed from four atoms. O with one Si atom with a clinoptilolite structure [19]. The crystal data that is formed can be seen in Table 1.

Table 1. Fly Ash Catalyst Crystal Data

Parameter	Value
Material name	$NaO_{26}Si_6Y_9$
Formula Name	$NaO_{26}Si_6Y_9$
Crystal Form	Hexagonal
Density (g/cm^3)	4.573
Intensity	958.66
FWHM (deg)	0.32
λ (nm)	0.15406
2.θ angle at highest peak (deg)	27.0
θ angle at highest peak (deg)	13.5

The crystal size of the Fly Ash catalyst can be calculated using the Debye Scherrer equation with the wavelength, intensity, 2θ, and FWHM values that have been generated from XRD analysis.

The calculation of the values of ln (1 / cos θ) and ln (β) results of the XRD analysis of the Fly Ash catalyst at all crystalline plane orientations is shown in table 2. From the modified Debye Scherrer equation in table 2 a graph of the relationship between ln (1 / cos θ) is made as axis x and ln β as the y axis so that the value of the intercept is obtained as shown in Figure 4. From the intercept value obtained from the graph equation it can be substituted into equation 3 to determine the crystal size (D).

Table 2. XRD Analysis of Fly Ash Catalyst

2θ	θ	1/cos θ	β	ln(1/cos θ)	ln(β)
20.30	10.15	1.01	0.11	0.01	-2.20
27.0	13.50	1.03	0.01	0.03	-5.19
32.34	16.17	1.04	0.01	0.04	-4.40
54.0	27.0	1.12	0.03	0.12	-3.52
64.1	32.05	1.18	0.07	0.16	-2.66

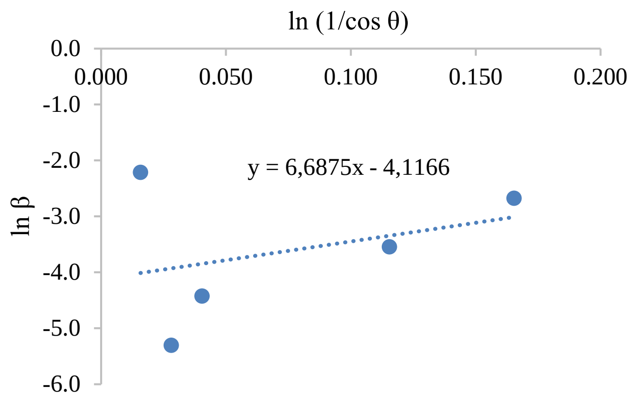

Figure 5. Graph of the relationship between ln (1/cosθ) and ln β

From the graph in Figure 5, the intercept value obtained is – 4.1166 and the value of K = 0.9 and λ = 0.15406 nm. From the relationship between the value of the intercept, the value of K, and λ, the crystal size can be calculated. The relationship between crystal size, intercept value, K and λ is shown by the equation below:

$$\text{crystal size (D)} = \frac{K \times \lambda}{e^{\text{Intercept value}}}$$

$$= \frac{0.9 \times 0.15406}{e^{-4.1166}}$$

$$= \frac{0.1386}{0.0163}$$

$$= 8.5064 \text{ nm}$$

Crystal size is one of the important factors for the catalyst because it is related to the number of active catalyst sites and the surface area of the catalyst [20]. In addition, the larger the crystal size, the greater the surface area of the catalyst so that the greater the surface energy it has [21].

Analysis of Catalyst and Temperature variations on the volume of biofuel produced

In this study, the sample base used was 5 liters of used cooking oil which was put into the Thermal Catalytic Cracking reactor with a temperature range of 250-300°C with a catalyst amount of 0% ,5%, 10%, 15% and 20%. The effect of temperature and catalyst on the volume of oil produced is shown in Figure 5.

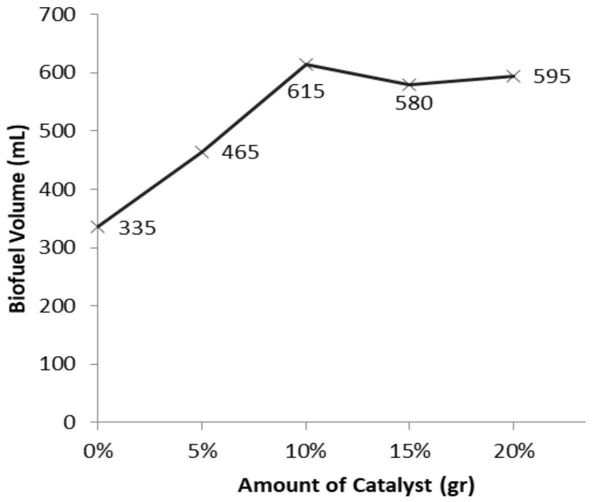

Figure 5. Fly ash catalyst analysis on biofuel volume

In Figure 5 it can be seen that the volume of biofuel will increase as the catalyst is added. This shows that the addition of fly ash catalyst plays a role in increasing biofuel products. At 0% catalyst concentration, 335 mL of biofuel was obtained, 5% biofuel catalyst obtained increased to 465 mL, and 615 mL of 10% biofuel was obtained. While the 15% biofuel catalyst obtained decreased to 580 mL and the 20% catalyst decreased the product to 595 mL. From the graph, we can conclude that the optimum catalyst point is obtained when 10% catalyst is added. according to Zhang et al. (2009) the increase in the number of products will decrease, even to the point that there is no increase at all in the addition of a certain amount of catalyst [22]. In this study, the increase in biofuel yield was not followed when the catalyst was added as much as 10%. Excessive use of catalyst also causes the formation of relatively large residues [23]. Another factor that is thought to affect the percentage increase in the product is the formation of coke which can cover the surface of the catalyst thereby reducing the active substance.

CONCLUSION

1. Based on the diffractogram obtained from the XRD analysis results, it indicates that the catalyst used has a hexagonal crystal structure.
2. The results of the calculation of crystal size fly ash catalyst produces a crystal size of 8,1094 nm.
3. The optimum point for adding catalyst in the cracking process is 10% with a volume of 615 mL biofuel

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