

MODIFICATION OF BAYAH BANTEN NATURAL ZEOLITE AS HETEROGENEOUS CATALYST IN BIODIESEL PRODUCTION

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The purpose of this study was to produce a biodiesel through the reaction of waste cooking oil with methanol by using a modified Bayah Banten zeolite as catalyst. This catalyst was produced from its natural form by using potassium hydroxide (KOH) as a reactant in 100 ml of distilled water. The reaction to produce a biodiesel was performed at various temperature and time to get the optimum condition. The advantages of this catalyst were eco-friendly, easily separated after the reaction process, and can be reused as a catalyst. The molar ratio of waste cooking oil and methanol for transesterification process was 1:7. The yield of biodiesel at various optimum temperatures and times is 94% (50 gram of KOH/100ml), 87,8% (75 gram of KOH/100ml), and 86% (100 gram of KOH/100 ml). Biodiesel results were analyzed by GC Ester content and modified catalysts were characterized using XRD, FTIR, and SEM-EDX.

Key words: A modified bayah banten zeolite, ion exchange catalyst, waste cooking oil

INTRODUCTION

Biodiesel is a mixture of alkyl ester and long chain fatty acid which is derived from renewable natural resource such as vegetables oil, animal oil and waste cooking oil which are expected to replace the existing petroleum diesel both through esterification and transesterification process [1]. ASTM International defines biodiesel as the mixture of ester monoalkilic, the length of the chain from fatty acid from renewable resource to be used as fuel of diesel machine. The mixture of diesel fuel is shown as "BX" in which "X" is the percentage of biodiesel in the mixture. For example, "B5" shows the combination of 5% biodiesel and 95% of petro diesel, it means that B100 shows pure biodiesel.

Biodiesel has many advantages such as non-toxic with zero sulfur content, easily degraded, produces low carbon monoxide emissions, and non-combustible hydrocarbon binding agents [2]. Furthermore, biodiesels are renewable, biodegradable and have higher certain number than conventional diesels [3]. The oxygen content of biodiesel is higher than petro diesel where diesel engines denote to reduce of particulates emission, carbon monoxide, sulfur, polyaromatic, hydrocarbons, and smoke and noise [4].

Recently, the use of homogeneous catalysts is still dominant in biodiesel production; despite its limitation, problem of high cost, the difficulty of catalyst separation from the mixture, and high amounts of waste water produced occur during the purification of biodiesel [1]. The problem can be reduced by switching to the use of heterogeneous catalysts. It is more active, requiring lower temperatures, shorter reaction times and re-useable [3]. Heterogeneous catalyst is an alternative to homogeneous catalyst replacement because it is easy to separate and reuse. Heterogeneous catalyst shows a high potency, strong and long-lasting that can be used for utilizing free fatty acids

up to 40% [5]. Heterogeneous catalyst used is the Bayah Banten zeolite modified.

[1] Heterogeneous Zeolite LTA catalysts using NaOH could be used to produce biodiesel with a temperature of 62.9°C and reaction time of 146 minutes with yield of biodiesel yield (92.8 ± 4.0)%. [6] Meanwhile, utilization of Zeolite/chitosan/KOH produced 93% biodiesel at 1:7 molar ratios for 3 hours whereas. [2] Using natural impregnated zeolite by KOH as a heterogeneous catalyst to produce biodiesel, research was conducted at a temperature of 50°C, as long as two hours, yielded 96.7% biodiesel. [7] Another method is to using an impregnated NAX catalyst using a 16% KOH produced (95.2 ± 0.96%) biodiesel for 3 hours reaction and temperature 65°C. [8] Using lithium metasilicate and mixed with ABW zeolite as catalyst, produced biodiesel above 95% within one hour reaction time. Furthermore, the catalyst used can be recycled in three cycles in a row without deactivation. With the reduction of catalyst-to-oil loading up to 30% by weight, biodiesel yields can still be achieved. [9] using a heterogeneous synthesis of fly ash synthesis with Methanol and mustard oil to get the maximum conversion of 84.6% biodiesel, 5% catalyst weight a molar ratio (12:1) as long as 7 hours at 65°C. The catalyst is reused for three usage cycles. [10] Modification of FeCl₃ as a heterogeneous catalyst. Producing yield biodiesel 92%, molar ratio (10:1), catalyst content 8% at 90°C, reaction time 120 min. [11] transesterification of biodiesel using gram KOH/zeolite as a heterogeneous catalyst. Variation of KOH concentration to get the maximum yield of biodiesel is 95.09% on impregnation of 100 grams of KOH in 100 ml of aquadest for 2 hours, reaction temperature of 60°C and the molar ratio (1: 7), the catalyst used of 3% of palm oil. [12] Transesterification process of heterogeneous catalyst with methanol, with a molar ratio (15:1). Alumina catalyst with 35% KI for 3 hours at a fixed temperature was dried at 393 K for 16 hours

(KI / Al_2O_3) and calcined at 773K for 3 hours, (1-5%) the weight of the catalyst used, the biodiesel produced at optimum conditions is 95.2%. [5] By using Chlorosulfonic-Circonia catalyst ($HClSO_3-ZrO_2$) as a heterogeneous catalyst for making biodiesel with methanol and rice bran oil with free fatty acids (FFA) content (20-50%). 92% conversion was resulted at 120°C, molar ratio (12:1), for 12 hours and 6% by weight of catalyst. [13] Al_2O_3 is modified MgZnO catalyst as catalyst (MgZnAlO) activated and studied for transesterification of vegetable oil with methanol to produce biodiesel. The effect of parameters such as molar ratio, catalyst weight, reaction time and temperature was studied. Catalysts were reused for five cycles. The conversion of biodiesel produced was 98%. [14] Heterogeneous catalysts used zeolite NaX and KOH to produce biodiesel using soybean oil. The best results were obtained by loading zeolite NaX at 10% KOH at 24 hours impregnation. 339K temperature was dried for 3 hours. The yield of biodiesel was 85.6% at molar ratio (10:1), reaction time of 8 hours and, the catalyst used as much as 3% by weight of soybean oil. [15] Biodiesel production using various zeolite heterogeneous catalysts between ZSM-5 (MFI), Modernite (MOR), Faujasite (FAU), beta (BEA) zeolite and silica at the ratio of Si / Al molar ratio (25,10,3,13). The best conversion results on HMFI (25) and HMOR (10). Optimum conversion produced 80% at 60°C.

The heterogeneous catalyst in this study comes from the area of lebak Banten that is natural zeolite which has a three-dimensional frame structure which is a crystalline silica alumina. The natural zeolite used has huge amount but the distribution is uneven and the crystallinity is poor. To improve it, the activation and modification was conducted to increase its activation as a catalyst [16]. This study focused on the modification process of Bayah Banten natural zeolite with the impregnation method using KOH and the calcination process to produce the catalyst. The catalyst produced was then reacted with waste cooking oil to produce biodiesel by transesterification process. The effect of concentration, temperature and reaction time was observed.

MATERIAL AND METHODS

Material preparation

Natural Zeolite was derived from nature of Bayah Banten, Banten Province, Indonesia. The existing zeolite was crushed firstly by using a hammer to obtain a size from 50 to 60 meshes. Waste cooking oil was obtained from Cilegon restaurant which had been used for three times. KOH was Made in Germany with index- No.019-002-00-8, Brand KGA, 6427 / Darmstadt Germany, Tel +49 (6) 615172-2440 EMD Millipore Corporation. Methanol Pro Analyse was made in Germany.

Preparation of a modified Bayah Banten zeolite catalyst

The zeolite was from the natural zeolite of Bayah Banten through the crushing stage, and then sieved (Screening) to get the desired diameter size. Activation of zeolite in nature of bayah Banten was done to modify the skeletal structure or non-zeolite framework in order to enhance its power. Activation zeolite was carried out physical and chemical treatment. The physical activation aimed to evaporate the water captured in the pores of the zeolite crystal that was carried out at a temperature of 110°C for 24 hours so that the surface area of the crystal pores increased. The chemical activation was performed by using a KOH solution to clean the pore surface, remove the impurity compound and rearrange molecule composition of zeolite. Impregnation is carried out using a KOH solution at a temperature of 60°C, for 2 hours, inputting the oven to 60°C for 24 hours and separating it with a vacuum filter pump. Furthermore, the catalyst was calcined and dried in the oven at 110°C for 24 hours so that the obtained catalyst was relatively stable at high temperatures. The process was carried out by means of a heated zeolite temperature of 450°C, 4 hours in calcination time, chill and the catalyst is ready for use. Calcination time for 4 hours [16]

Characterization of material and catalyst

Characterization of Bayah Banten natural zeolite catalyst was conducted by using several methods, such as using XRD brand Malvern Panalytical Empyrean Diffractometer, to analyze the type and composition of crystals of zeolite. FTIR was conducted to determine the functional groups present in the zeolite. FTIR analysis was performed on Shimadzu 840°S FTIR instrument in the range of 4000-500cm brand thermo scientific seri Nicolet i5. Micrograph Electron Scanning Method (SEM-EDX) brand TESCAN was conducted to determine the composition of the potassium element of the crude zeolite, modified zeolite and zeolite used for the transesterification reaction.

Method

Research methodology is focused to the ion exchange engineering as a heterogeneous catalyst for biodiesel synthesis to obtain optimum result with various time, catalyst, and temperature by activating ion exchange used firstly, i.e. Bayah Banten natural zeolite (ZABrht). The research was done in the Bioprocess Laboratory of Chemical Engineering Department, Engineering Faculty, Universitas Indonesia Depok 16424.

RESULTS AND DISCUSSION

Characteristic of waste cooking oil

Physical and chemical properties analysis were performed on cooking oil including density (ASTM D4052), kinematic viscosity (ASTM D445), free fatty acid content. The results of analysis characteristics of cooking oil could be seen in Table 1.

Catalyst characterization

X-ray Diffraction (XRD)

Table 1: Characteristic of Waste Cooking Oil

Characteristic	Amount
Density at 25°C, kg/L	9,0268
Kinematic viscosity at 23,4°C, Cst	40,67
Fatty acid content, %	0,03

Spectroscopic analysis of X-ray diffraction(XRD) is required to identify the zeolite crystallinity characteristic before and after impregnation. All materials contain specific crystal when analyzed with XRD will produce specific peaks. XRD analysis Difactogram resulted shows crystallinity level solids. Material and crystallinity are good if they have high peak incisive intensity and a good peak separation. Natural zeolite XRD spectrum (Figure 1) shows peaks of Bragg angle (2θ) 10°, 23,5°, 26°, 31°, 33°, 37°, 47°, 59° and 62,5°. This indicates the Bayah natural zeolite is klinoptilolit. High intensity peaks show Bayah natural zeolite having high crystallinity.

From Figure 2. Treatment of zeolite and KOH decreases or also damages zeolite crystallinity because of desilicate process, it is pointed by loss of high intensity peaks at 10°, 23°, and 62,5° Bragg angle to zeolite after base treatment. However, zeolite XRD spectrum after the treatment showed the significant new peaks especially

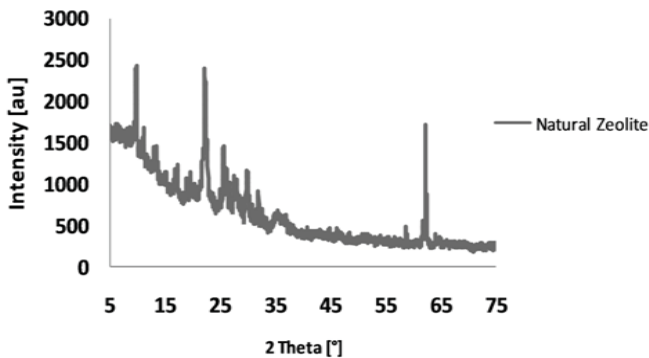


Figure 1: XRD Pattern Bayah Banten Natural Zeolite

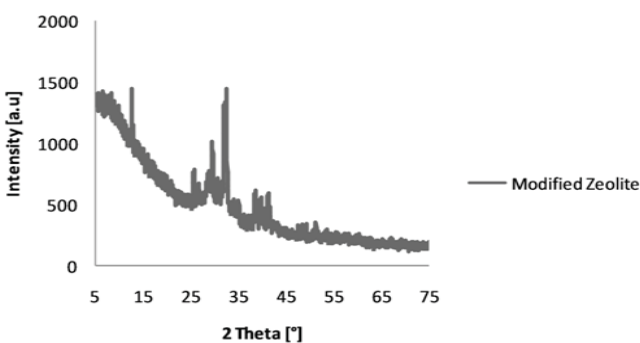


Figure 2: XRD Pattern Modified Bayah Banten Natural Zeolite

at 12.5°, 26°, 29°, 31°, 33°, 35°, 38°, 40°, 41°, 49°, and 51.5° the Bragg angle providing from K₂O oxide. K₂O formation indicates KOH which is in the surface and zeolite matrix changing to K₂O during the impregnation and calcination process. The impregnated K₂O in zeolite can put up a high catalytic activity.

FTIR

Band in 3613,179cm⁻¹ and 1635,06 cm⁻¹ wavenumbers indicates the O-H cluster stretching vibration to silanol (Si(OH)Al) and also water (H-O-H). The most powerful band which appeared in 1016,116cm⁻¹ wave number indicating the asymmetric stretching vibration of T₀₄ (T=Si, Al) tetrahedral, typical of zeolite (Intrapong Pisitpong et al, 2003). Absorption band in 788,15cm⁻¹ shows the symmetrical stretching vibration of Si-O-Al. Whereas band in 593,66cm⁻¹ is bending vibration of O-Si(Al)-O.

Treatment of zeolite and KOH occurs a new absorption band significantly on 1300-1400cm⁻¹ wavenumber which is Al-O stretching vibration absorption. Linearity of band intensity and KOH concentration indicates high desilication level (zeolite silica increasing).

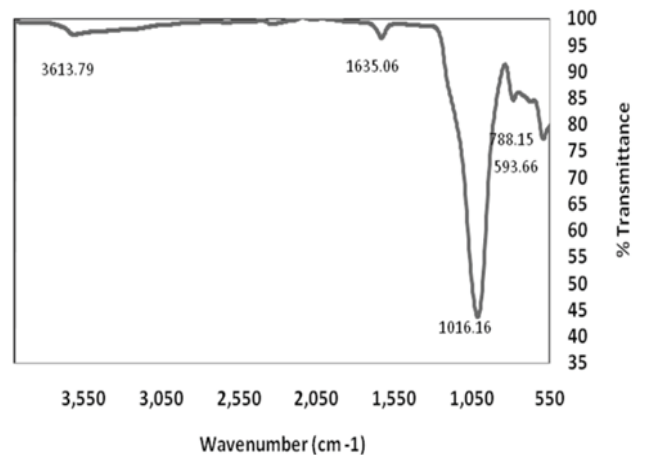


Figure 3: FTIR Spectrum of Bayah Banten Natural Zeolite

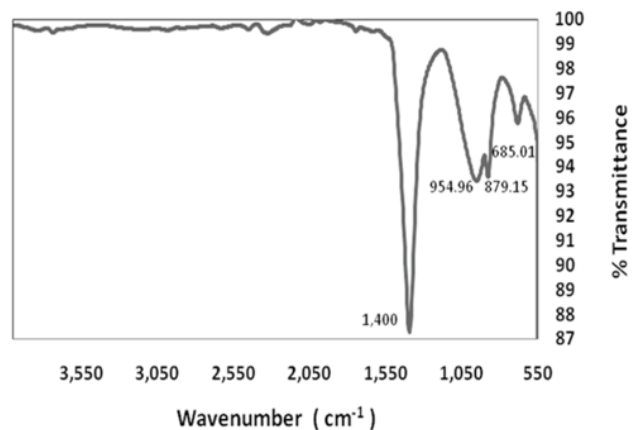


Figure 4: FTIR Spectrum of Modified Bayah Banten Natural Zeolite

SEM-EDX

SEM-EDX analysis was conducted to find out the surface morphology of raw zeolite, modified zeolite and zeolite used for transesterification. Acl SEM-EDX analysis was shown in Figure 5. The result showed that the macro structure of bayah banten natural zeolite did not change after calcination and could be concluded that zeolite has good thermal stability.

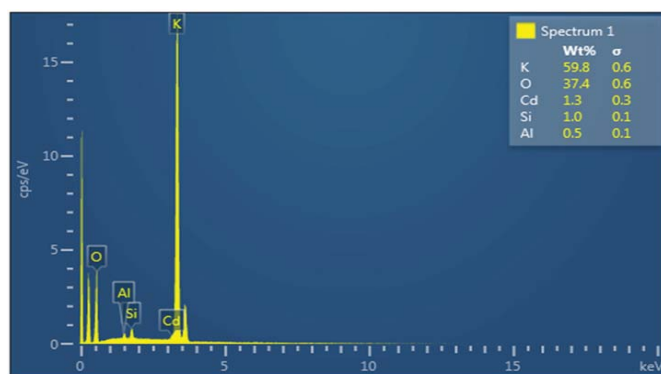
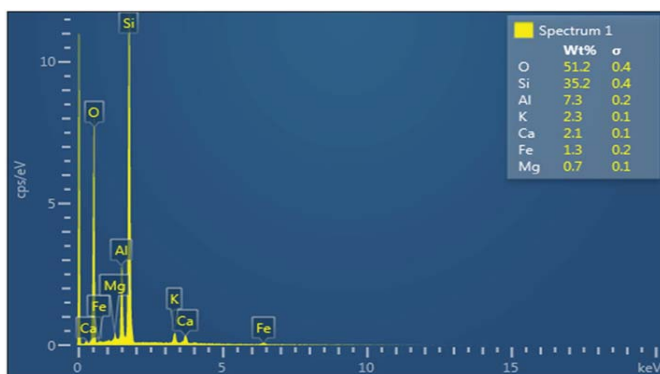
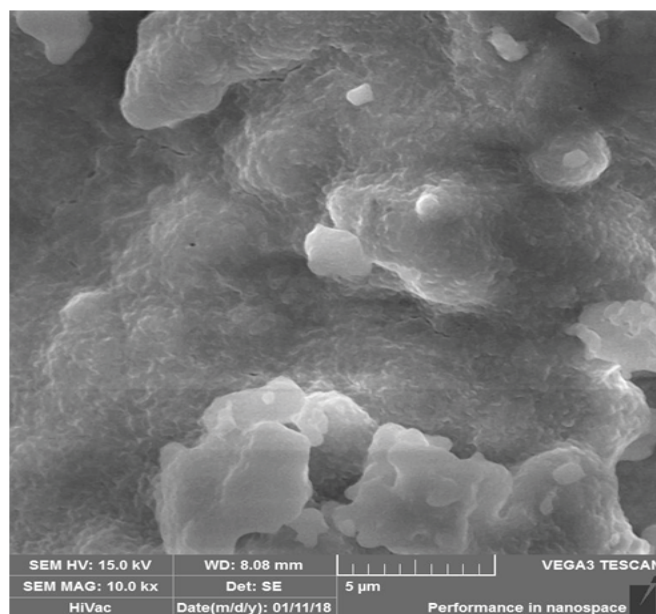
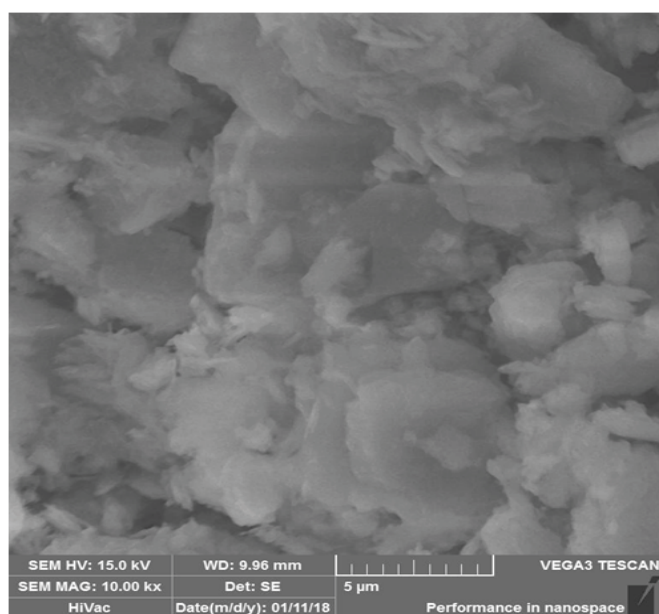
SEM-EDX analysis was performed to determine the amount of potassium in the zeolite before it was modified and after modification. The results showed an increase in the element of potassium in the zeolite after the modification process. It showed that the impregnation process of KOH into the surface of the zeolite occurred perfectly.

Table 2: Potassium Content of Zeolite Based on SEM-EDX Analysis

Catalyst	K (% wt.)
Bayah Banten Natural Zeolite	23
Modified Bayah Banten Natural Zeolite	59.8

The Effect of various temperature, time, and catalyst concentration toward % yield biodiesel

Figure 6. shows the optimum condition was obtained at the temperature variation toward produced biodiesel was at temperature of 60°C with 2-hour reaction time. At catalyst concentrations of 50 gram KOH/100ml, 75 gram KOH /100ml, 100 gram KOH/100ml), resulted biodiesel of 94%, 87,8%, 86% respectively. After passing optimum temperature, the yield of biodiesel was reduced for each particular optimum condition, figure (a), (b) and (c). Temperature has an important role to produce quality of biodiesel products. The reaction temperature did not exceed the boiling point of methanol, because when the methanol evaporates at the time of the resulting biodiesel yield reduced, if methanol gets less volume in the reaction due to evaporation, the transesterification rate reaction between the cooking oil and methanol was slow. However the length of reaction time as could be seen above, there was an optimum point, and after passing through the optimum point that causes the reaction, it will return to the beginning so that the product obtained could be reformed into reactants.



(a)

(b)

Figure 5: (a) SEM-EDX of Bayah Banten Natural Zeolite Catalyst, (b) Modified Zeolite

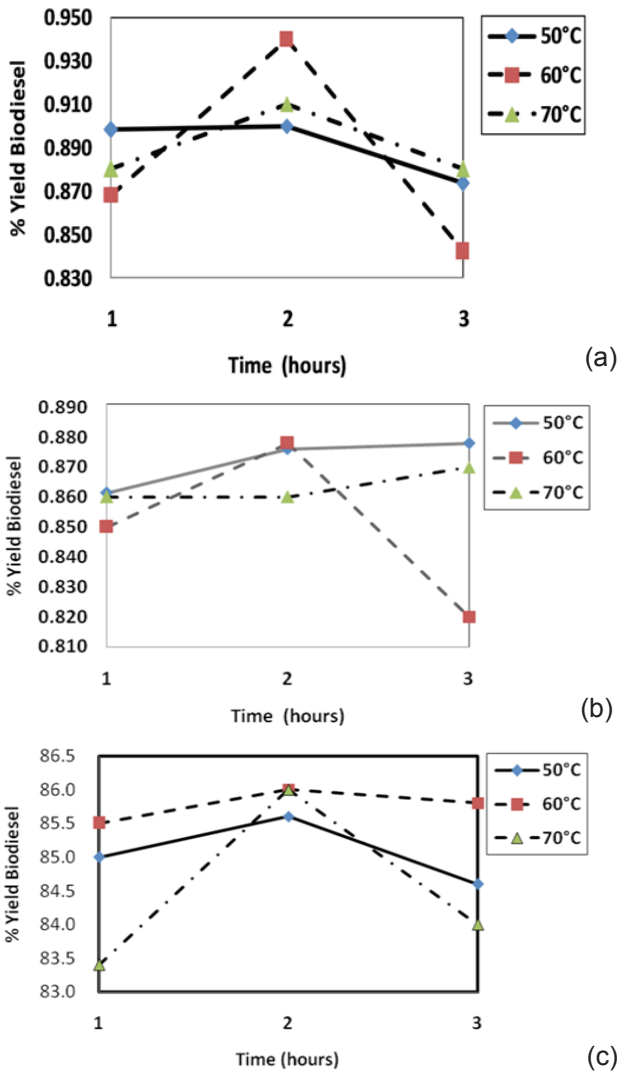


Figure 6: The Effect of Use (a) 50 g KOH/100ml, (b) 75 g KOH/100ml and (c) 100 g KOH/100ml toward Biodiesel Yield

The effect of KOH/100 ml gram concentration (50.75 and 100) on optimum conditions

The effect of KOH/100ml gram concentration on optimum condition to % yield biodiesel produced is shown in figure 7.

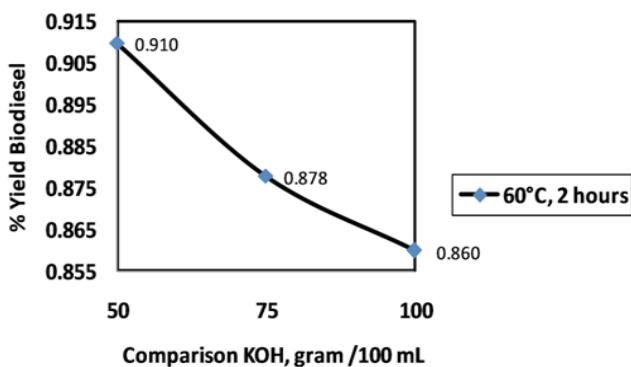


Figure 7: Optimum Condition of Biodiesel Produced

A number of modified zeolite with KOH concentration variations, i.e. 50 gram KOH/100ml, 75 gram KOH/100ml, and 100 gram KOH/100 ml. From figure 7, obtained results that the greater KOH concentration used in zeolite modification process, then the result of yield biodiesel will be declined. The more the catalyst concentration (KOH) used will not accelerate biodiesel formation reactions and will form lathering or side reactions on experiments conducted. Content of % Yield biodiesel on optimum conditions can be seen in Table3.

Table 3: %Yield Biodiesel on Optimum Conditions Produced in Various Concentration (50 gram KOH/100 ml, 75 gram KOH/100ml and 100 gram KOH/100ml)

Concentration	% Yield
50 gram KOH/100 ml	91,0
75 gram KOH/100 ml	87,8
100 gram KOH/100 ml	86,0

Metil ester content

The content of methyl ester produced from biodiesel using a heterogeneous catalyst of Bayah Banten zeolite natural (ZAABrht) was analyzed by using GC Ester content at various concentrations shown in Figure 8.

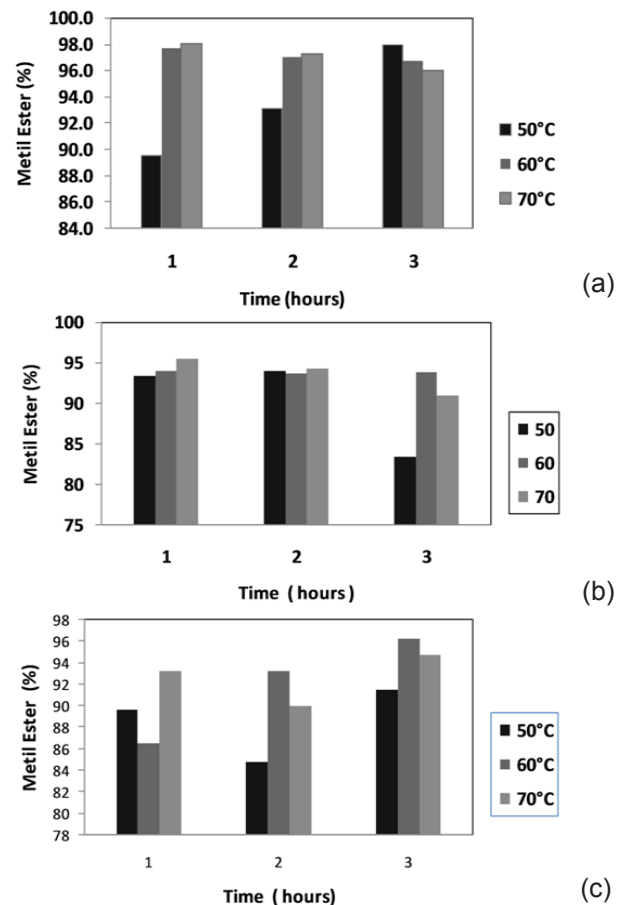


Figure 8: Methyl Ester Content in Various Concentration (a) 50 Gram KOH/100ml, (b) 75 Gram KOH/100ml, (c) 100 Gram KOH/100ml

As shown in Figure 8 result, increasing of methyl ester number produced in KOH concentration that is added to temperature and time varied. In using of 50 gram KOH/100 ml concentration indicates the amount of methyl ester produced greater than 75 gram KOH/100 ml and 100 gram KOH/100 ml, as described in the discussion viscosity which states the number of metoksida kalium (K+CH₃O) that reacts with waste cooking oil (triglycerida) so that the process of fat cluster chain cracking process higher.

Content of methyl ester greater from various concentration and time done is on the condition of 50 Gram KOH/100 ml at 60°C and 2 hours operating time. Methyl ester content produced can be seen in Table 4.

Table 4: Methyl Ester Produced in Various Concentration (50 gram KOH/100ml, 75 gram KOH/100ml and 100 gram KOH/100ml)

Concentration	Methyl Ester
50 gram KOH/100ml	97
75 gram KOH/100ml	93
100 gram KOH/100ml	93,2

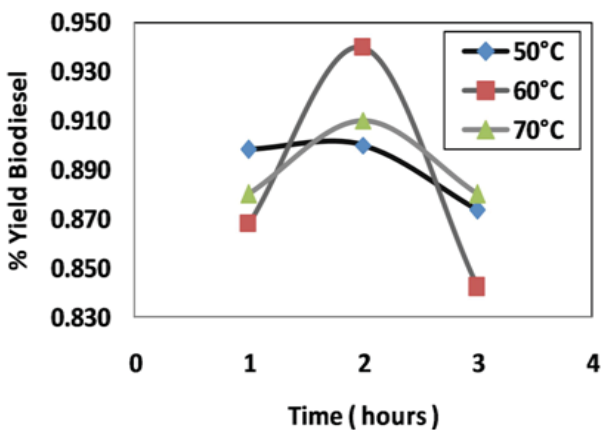


Figure 9: Transesterification Kinetics at various temperatures: 50°C, 60°C and 70°C. 50 Gram KOH/100ml

Transesterification Kinetic

The Transesterification kinetic process in this experiment was measured as a function of temperature. Temperature was varied to be range 50°, 60° and 70°C (Figure 9) on the use of 50 grams KOH/100ml. For kinetic analysis it was used equations (1) first - order reactions and equations (2) second-order reactions to represent all reaction behavior during reaction time.

$$kt = \ln (C_{A0}/C_A) \tag{1}$$

$$kt = (1/C_A - 1/C_{A0}) \tag{2}$$

(18) stated that transesterification occurred based on first-order reaction equation, while [19] stated that Transesterification of catalysed alkali occurred in second-order

der reaction, while [20] stated that acid Transesterification occurred in first-order reactions.

To prove first or second order the calculation of reaction rate constant was carried based on FFA concentration during reaction, the determination of transesterification reaction order must be conducted based on chemical evaluation if the reaction was 1st order, $\ln (C_{A0}/C_A)$ would be linearly dependent toward $100/T$ (reaction temperature in Kelvin) and if the process was second order C_A would be inversely propositional dependent on the value of $1000 / T$. As shown in Fig. 4, the results showed that Transesterification catalyzed by the Bayah Banten natural zeolite (ZABBrht) occurred in first-order reactions, since all kinetic data curves made up the equation with high correlation ($R^2 = 0.810$). The second-order reaction equation was also attempted to satisfy the data, but the regression results did not correlate well ($R^2 = 0.761$). It could be concluded that the Transesterification process catalyzed with Bayah Banten natural zeolite (ZABBrht) in this research found to first order reaction and reaction constant rate (k) based on temperature could be seen in Table 5.

Table 5: Transesterification Reaction Rate Constant

Reaction Temperature (°C)	Reaction rate constant (s ⁻¹)
50	0.003
60	0.004
70	0.005

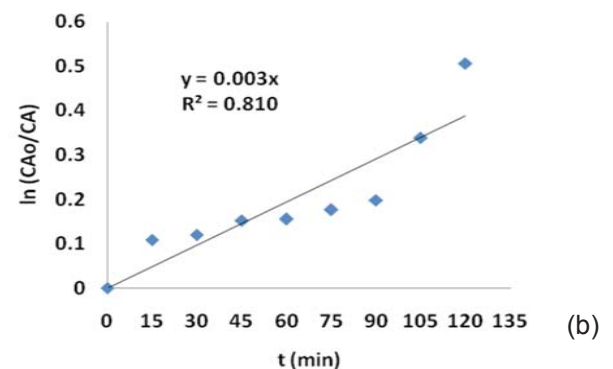
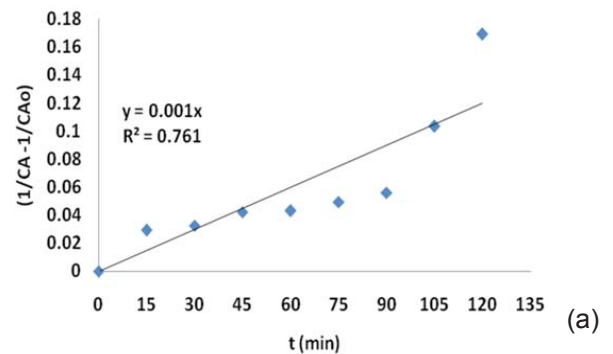


Figure 10: Kinetically Curve of the Bayah Banten (ZABBrht) 1st Order Reaction; (B) 2nd Order Reaction Transesterification Process of Natural Zeolite Catalyst

The high temperature effects to the high reaction temperature on the rate constant of the reaction, in this study, the correlation used the Arrhenius equation (3) which was logarithmically correlated at the reaction rate constant [ln (k)] with the inverse temperature (1/T). The activation energy (Ea) of the Transesterification reaction could be calculated.

$$k = A \exp (-E_a/RT) \quad (3)$$

$$\ln (k) = \ln(A) - E_a/RT \quad (4)$$

In which R is the ideal gas constant, 8.314 J/mol, A Conversion factor, seconds⁻¹, and T The absolute temperature (K)

Table 6: Data for Calculating Activation Energy (Ea) and Conversion Factor

Reaction temperature	T(K)	1/T	k(s ⁻¹)	ln k
50	323.16	0.003094	0.003	-5.80914
60	333.16	0.003002	0.004	-5.52146
70	343.16	0.002914	0.005	-5.29832

The correlation of ln (k) and (1/T) changed linearly with temperature of 50°, 60° and 70°C and obtained Activation energy (Ea = 23570, 19 J/molK), Conversion Factor (A = 19.53094/s) and the following equation was obtained.

$$k = 19, 53094 \exp (-23570.19/8,314 (T))$$

From explanation above that the overall process has been controlled by chemical reaction.

Biodiesel characteristic

Biodiesel produced with heterogeneous KOH / zeolite catalyst meets ASTM as an International Standard (Table 7).

Table 7: Comparison of Biodiesel Characteristic, Research Result, and ASTM as an International Standard

Characteristic	Research result	ASTM
Density at 25°C, kg/L	0.8629	D 4052 (0.82 – 0.86)
Kinematic viscosity at 23,4°C, Cst	4.51	D 445 (2.0 – 4.5)

CONCLUSION

The Bayah Banten natural zeolite that was impregnated with KOH could be used as a heterogeneous base catalyst to produce biodiesel by Transesterification process from waste cooking oil by Transesterification process. The optimum conditions were 60°C at 2 hours, reaction time with 50g KOH in 100ml of distilled water.

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