Effect of Acid Concentration on the Activation of Bayah Natural Zeolite for Palm Kernel Shell Pyrolysis Application

Endang Suhendi *)*, Andre Wibowo, Tia Lestari, and Teguh Kurniawan

Department of Chemical Engineering, Faculty of Engineering, Sultan Ageng Tirtayasa University
Jl. Raya Jendral Sudirman KM.3, Cilegon, Banten

*) Corresponding author: endangs.untirta@gmail.com

(Received : January 01, 2020; Accepted: August 03, 2020)

Abstract

Bio-oil is the main product in the pyrolysis process which is expected to be a liquid fuel replacement solution. But the resulting bio-oil cannot be directly used because of high oxygenated compounds, high viscosity, corrosive, and unstable. Addition of activated natural zeolite catalyst to the pyrolysis process is expected to improve the quality of bio-oil to be used as a renewable liquid fuel. The research aims to determine the influence of acid concentrations on zeolite modification to the characteristics of pyrolysis products. Result of catalyst characterization indicates that zeolite activation using acid will increase Si/Al ratio as well as open the surface of previously hindered zeolite. The yield of char produced in this study tends not to undergo significant changes between the catalytic and noncatalytic pyrolysis by 33% wt. Addition of zeolite catalyst in pyrolysis proved to be able to increase the content of phenol and decrease the content of acetic acid in bio-oil by 6%. Meanwhile, yield of CO₂ increases by 20% in the use of catalysts due to the release of oxygen in the oxygenate compounds. The results of this study showed that the resulting bio-oil still does not meet the specifications of liquid fuels but can be utilized as a renewable chemical feedstock.

Keywords: pyrolysis; biomass; natural zeolite; modified

How to Cite This Article: Suhendi, E., Wibowo, A., Lestari, T., and Kurniawan, T (2020), Effect of Acid Concentration on the Activation of Bayah Natural Zeolite for Palm Kernel Shell Pyrolysis Application, Reaktor, 20(3), 109-116, https://doi.org/10.14710/reaktor.20.3.109-116

INTRODUCTION

Primary energy consumption in Indonesia reached 998.06 BOE (Barrel Oil Equivalent) in 2016 and increased by 5.9% in 2017 (Ika, 2017; MEMR, 2017). The use of fossil energy has many negative impacts, one of them is carbon emissions which can cause global warming and climate change issue. Renewable energy is a solution to meet future national energy needs. Recently, the use of renewable energy in Indonesia is still low, which the energy mix in the renewable energy sector is only 7.7% in 2017 (Wijatmoko, 2017).

Biomass such as palm kernel shell can be used as a new renewable energy source because it has great potential in Indonesia. According to data from the Association of Indonesian Palm Oil Entrepreneurs (GAPKI), the potential for biomass production from the Indonesian palm oil industry in 2018 will reach around 9.46 million tons (GAPKI, 2018).

Pyrolysis is a technology that can be utilized to convert biomass into liquid (bio-oil), solid (char), and gas products. Pyrolysis is a process of thermal decomposition of biomass at temperatures of 350 to 650 oC without the presence of air or oxygen (Basu,
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Bio-oil that produced in pyrolysis process can be used to replace the role of petroleum in the future either as fuel or as a chemical. Bio-oil that produced from the pyrolysis process generally have a high oxygen content. This causes the bio-oil cannot be directly applied as a fuel source (Zhang et al., 2006). The addition of catalysts to the pyrolysis process is an appropriate method to improve the quality of bio-oil, the catalyst that has been used for the pyrolysis process is synthetic zeolites such as ZSM-5, HZSM-5, Zeolite A, and Zeolite Y (Foster et al., 2012; Mohammed et al., 2016). The use of activated natural zeolite catalysts as a catalyst in the pyrolysis process would increase the yield of bio-oil (Martin et al., 2017).

Natural zeolite contained in nature needs to be activated to be applied to the pyrolysis process. Dealumination process is a method that can be used to open zeolite pores by releasing aluminum in the zeolite skeletal structure using acids (Nasser et al., 2016). The removal of aluminum causes an increase in Si / Al ratio which affects the acidity and surface properties of pores as well as the pore size distribution (Wang and Peng, 2010). The acidification method not only releases aluminum in the zeolite framework structure but also removes impurities that block the zeolite pores. This shows that dealumination with acidification is a method that can be used to increase the catalytic activity of natural zeolite so that it can be used for biomass pyrolysis applications.

The purpose of this study was to determine the effect of acid concentration used on zeolite activation on the characteristics of pyrolysis products. Materials

MATERIALS AND METHOD

Materials

Palm kernel shell sample that used in this study were collected from PTPN VIII Malingping, Lebak. The natural zeolite sample were obtained from Bayah, Lebak, Banten. And sulfuric acid (Merck) with 98% purity was purchased from.

Modification of Zeolites

Rocks of natural zeolites were crushed into small sizes and then sieved to obtain a size of -10 + 14 mesh. Furthermore the sample was refluxed in a solution of H₂SO₄ (Merck) of 20 grams of natural zeolite at 400 ml of H₂SO₄ with varying concentrations of 0.5 M (ZAB-0.5M), 1 M (ZAB-1M), 1.5 M (ZAB-1.5M), and ZAB (2 M) at 90 °C for 30 minutes. Then zeolite was rinsed using distilled water until the pH was neutral then drained and allowed to stand for 24 hours at room temperature. Then drying it in oven at 110 °C for 2 hours, then calcined for 6 hours at 500 °C.

Zeolite Characterization

The zeolite characterization was performed analysis of the crystallinity and morphology of the zeolite before activated and after activated. The zeolite crystallinity analysis was performed using the Rigaku 3-kW type Smartlab X-Ray Diffractometer (XRD) at the LIPI Physics Laboratory, Serpong, Tangerang. And morphological analysis was performed using JSM-6510LA’s Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX) at Batan PSTBM Laboratory, Serpong, Tangerang.

Pyrolysis

Pyrolysis process was performed by inserting 200 grams of palm kernel shell and 20 grams of activated natural zeolite catalyst into the pyrolysis reactor. Furthermore, cooling water is flowed into the double pipe condenser using a pump and then start the heater. Cooling water is maintained at temperature of 18-20 °C. The reactor was heated to a temperature of 500 °C and kept it constant. The pyrolysis process was carried out at atmospheric pressure. After the desired pyrolysis condition was reached, it was considered as the beginning of the reaction (initial time). The process of pyrolysis was performed for 1 hour with sampling every 3 minutes. Measurement of solid products was done by weighing the char left in the reactor after the pyrolysis process. The measurement of liquid products was done by weighing the bio-oil that is accommodated in the sample bottle. And gas measurement was done by the water displacement method where the gas formed will compress the water contained in the gas reservoir.

These following Eq. 1, 2, and 3 were used to calculate the yield of bio-oil, char and also gas, which is produced by each variable.

\[ Y_{Biooil} = \frac{W_{Biooil}}{W_{Feed}} \times 100\% \]  
\[ Y_{Char} = \frac{W_{Char}}{W_{Feed}} \times 100\% \]  
\[ Y_{Gas} = 100\% - Y_{Biooil} - Y_{Char} \]
RESULTS AND DISCUSSION

Zeolite Characterization

Table 1 shows the change of natural zeolite mass after modification. The results shown that mass reduction of natural zeolite tends to increase in line with concentration of acid used in activation in which the amount of aluminum extracted in zeolite was increase at high concentration of acid variation. The reduced aluminum composition will increase Si / Al ratio of zeolite, acidity, pore-volume, and pore surface area (Morina, 2009). The zeolite activation process using acid reduces the zeolite mass due to the extraction of aluminum framework and metal oxides on zeolites.

Table 1. Change of Zeolite Mass After Activation

| Concentration | Mass Before Activation (g) | Mass After Activation (g) |
|---------------|-----------------------------|---------------------------|
| 0.5 M         | 100                         | 77.7                      |
| 1 M           | 100                         | 72.3                      |
| 1.5 M         | 100                         | 71.6                      |
| 2 M           | 100                         | 70.6                      |

XRD (X-Ray Diffraction) analysis was performed on natural zeolite samples without activation (ZAB-NA) and natural zeolite activated with 1 M H₂SO₄ (ZAB-1M). XRD testing was carried out to determine the effect of acid concentration used in the zeolite activation process toward the crystallinity of zeolites. Figure 1 shows that there was a significant change in the ZAB-1M sample with the ZAB-NA sample in the form of decrease in diffractogram intensity. The peak at diffraction 2θ = 11.3°, 13.2°, 16.8°, 17.2°, 19°, 22.3°, 25.5°, 25.9°, 26.2°, 28°, 29.7°, 29.9° has an intensity which decreased of ZAB-1M sample compared to the ZAB-NA sample. The use of H₂SO₄ in the zeolite activation process causes dealumination, in which this is the cause of decrease intensity of ZAB-1M sample (Nasser et al, 2016). Dealumination causes damage to the structure of the alumina silica framework by breaking aluminum within the zeolite framework into aluminum outside the framework.

Zeolite damage caused by high concentrations of H₂SO₄ used in the activation process (Lestari, 2010). Termination of aluminum in the zeolite framework causes decrystallization which results in an increase of the amorphous phase of the zeolite (Sulistyowati et al, 2018).

The results of XRD analysis added in figure 1 shows that some peaks at diffraction 2θ = 11.2°, 13.4°, 19.4°, 19.6°, 19.9°, 21.9°, 22.8°, 23°, 25.6°, 26°, 3°, 27.5° had a higher intensity in the ZAB-1M sample compared to the ZAB-NA sample. The increase of intensity at some peaks occurs due to the presence of impurity metal oxides (MgO, SiO₂-amorf, Na₂O, K₂O, CaO, Fe₂O₃) which exchange with the H⁺ cation on the zeolite surface so that the zeolite surface is not blocked by impurities (Yasin, et al., 2016). The zeolite surface becomes more open, thus the X-ray imposed on the zeolite surface is completely diffraction and not blocked by impurities, this is the cause of the increased intensity and crystallinity of the zeolite.

Bayah Natural Zeolite are known as zeolite Mordenite (MOR) and Clinoptilolite (HEU) (Ismetullloh et al., 2019). The XRD patterns (Figure 1) will be compared with the JCPDS (Joint Committee on Powder Diffraction Standards) data according to the International Zeolite Association (IZA) to prove the similarity in zeolite types (Treacy et al., 2001). The ZAB-NA sample shows that a peak at diffraction 2θ = 11.1°, 17.2°, 19.6°, 20.9°, 22.2°, 23°, 25.6°, 29.9° and the ZAB-1M sample shows that a peak at diffraction 2θ = 9.9°, 16.9°, 13.4°, 19.6°, 22.8°, 25.6°, 26.2°, 27.6° that there is a similarity of the major peaks at the 20 angle. The similarity of the peak XRD patterns at the 20 angle shows that the materials have the same structure (Sumari, et al., 2018). It can be concluded that Bayah Natural Zeolite is a type of zeolite Mordenite (MOR) and Clinoptilolite (HEU).

In this study SEM-EDX testing was also carried out to determine the effect of the acid concentration used in the zeolite activation process toward the morphology and elemental composition of the zeolite. SEM test results can be seen in figure 2 which shows that no significant morphological differences were seen on the zeolite surface. However, the EDX results showed that the change in the composition of aluminum in zeolites after activation.

From EDX result that shown in table 2 Si / Al ratio in the ZAB-1M (Si/Al = 14.98) sample increase compared with the ZAB-NA (Si/Al = 5.49) sample. It can occur due to the process of dealumination by H₂SO₄ which cause the disconnection of aluminum due to H⁺ ions, thus affecting free electrons in O atoms to form coordination bonds. Al-O bonds will lack electrons so they will be more polar and not as strong as before so that Al will break from the bonds (Norvia et al, 2016). Increasing the Si / Al ratio will cause zeolites to have hydrophobic (lipophilic) properties and absorb non-polar molecules, so they can be used as acid catalysts for hydrocarbons (Sa'diyah and Juliastuti, 2015).
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Characterization of Pyrolysis Products

Table 3 shows the product distribution from the catalytic and non-catalytic pyrolysis process. Bio-oil yield tends to increase in the catalytic pyrolysis process compared to non-catalytic processes from 31 wt% to 36-38 wt%. The concentration of acid used in the activation process tends to affect bio-oil yields insignificantly, increasing the concentration of acid used relatively increases the bio-oil yield. Meanwhile, gas yield decreased in the catalytic process in various variations of acid concentration (24 - 31 wt%) compared to non-catalytic processes by 31 wt%.

| Sample                      | Solid (wt %) | Liquid (wt %) | Gas (wt %) |
|-----------------------------|--------------|---------------|------------|
| Without Catalyst           | 31.68        | 31.93         | 31.98      |
| ZAB-NA                      | 33.84        | 29.60         | 31.35      |
| ZAB-0.5M                    | 32.09        | 36.28         | 26.83      |
| ZAB-1M                      | 32.16        | 38.44         | 25.20      |
| ZAB-1.5M                    | 32.41        | 37.04         | 26.32      |
| ZAB-2M                      | 32.72        | 38.34         | 24.83      |

External acidity level of zeolite was increase at higher concentration of acid used in the activation process. The level of zeolite acidity will affect the catalytic reaction by increasing the cracking activity of the lignocellulose component in the biomass, thus the bio-oil yield was increase in pyrolysis using a catalyst (Mihalcik et al., 2017; Martin et al., 2017). The maximum bio-oil yield was obtained in the ZAB-1M zeolite variation with 38.44 wt% and then decreased in the ZAB-1.5M and ZAB-2M variations to 37.04 wt% and 38.34 wt%. Increased the concentration of acid used allows zeolite damage that causes lignocellulosic cracking activity to be reduced. Zeolite damage occurs due to the amount of aluminum that separated from the zeolite structure (Basabe, 2010).

The use of zeolite catalysts in the pyrolysis process generally increase excess gas production as a result of secondary cracking of lignocellulose (Kim et al., 2014). But in this research the gas yield has decreased in the use of catalysts from ~ 32 wt% to ~ 26 wt%. The reduced gas yield on catalyst use occurs because there is no secondary cracking due to the closure of the catalyst pores by the coke formed on the surface of the catalyst, so that condensable steam cannot diffuse to the active site of the catalyst. In the same study by (Kim et al., 2014) gas yields have decreased in the use of E-cat type catalysts by increasing solid and bio-oil yields.

Char yield does not given significant change between catalytic and non-catalytic pyrolysis, which was in the range 31 - 33 wt%. Char yield is strongly influenced by chemical composition of biomass (lignin, cellulose) and the operating conditions of the process generally increase excess gas production as a result of secondary cracking of lignocellulose (Kim et al., 2014). But in this research the gas yield has decreased in the use of catalysts from ~ 32 wt% to ~ 26 wt%. The reduced gas yield on catalyst use occurs because there is no secondary cracking due to the closure of the catalyst pores by the coke formed on the surface of the catalyst, so that condensable steam cannot diffuse to the active site of the catalyst. In the same study by (Kim et al., 2014) gas yields have decreased in the use of E-cat type catalysts by increasing solid and bio-oil yields.

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pyrolysis process, including temperature and reaction time (Kim et al., 2013).

Table 4. Physical Properties of Bio-oil

| Sample          | Density (kg/m³) | pH  |
|-----------------|-----------------|-----|
| Without Catalyst| 1014.8          | 2.93|
| ZAB-NA          | 1015.2          | 3.00|
| ZAB-0.5M        | 1012.8          | 3.10|
| ZAB-1M          | 1020.0          | 3.04|
| ZAB-1.5M        | 1014.4          | 3.00|
| ZAB-2M          | 1014.0          | 2.98|

Table 4 shows the physical properties of bio-oil in each variation. It can be seen that bio-oil density measured at room temperature is in the range of 1014 - 1015.2 kg/m³. The resulting bio-oil density is greater than the density of liquid fuel (diesel fuel) i.e. 815 - 860 kg/m³ (Pertamina, 2020). The effect of the addition of catalysts activated by acid did not significantly influence the value of bio-oil density. Bio-oil from the pyrolysis of the coconut shell contains a lot of heavy fraction hydrocarbon compounds such as phenol and acetic acid which have a density value of ~ 1050 kg/m³ (Dimian et al., 2019; Cefic, 2015). The pH value of the bio-oil produced in each variation of pyrolysis is at an average value of ~ 3, which means the bio-oil produced has acidic properties. Acidity in bio-oil is caused by the presence of organic acids such as acetic acid and its derivatives as well as phenols and their derivatives in bio-oil (Asadullah et al., 2013).

The component that contained in the bio-oil was identified using a Gas Chromatography - Mass Spectrometry (GC-MS) tool. The component of bio-oil in each variation of pyrolysis is shown in Table 5. The dominant compounds found in bio-oil are carboxylic acid (acetic acid) and phenolic (phenol) compounds which have a large % area ratio. Another short chain compounds such alkene group, hydroxyldehyde, hydroxyketones, and furan were found in bio-oil. The addition of zeolite as a catalyst in the pyrolysis process will produce new compounds that are not produced in the non-catalytic pyrolysis process and catalytic pyrolysis without activation such as 1,2-Propadiene, 2-Propynol, and 2-Methoxy Isobutane. It caused by zeolites which have selective properties that can control compounds entering or leaving zeolite active sites, so that only certain compounds smaller than the zeolite pore size can enter and break bonds from long chain hydrocarbon compounds into short chain hydrocarbon compounds.

Natural activated zeolite in this study has Si / Al ratio of 14.98 similar to the characteristics of zeolites conducted by (Yu et al., 2012) which show that the zeolite has a Si / Al ratio of 16.1 with a pore size of 7 x 5.6 Å, thus it can be seen from the similarity of the Si / Al ratio in this study has the same pore size as the pore size in the study (Yu et al., 2012). In the study (Yu et al., 2012) also explained that the zeolite pore size can be enlarged during heating 275-400 °C in the pyrolysis process to 9-10 Å. The enlarged zeolite pore size will affect compounds that can enter the zeolite and having reactions on the active site.

According to Yu et al., 2012 and Jae et al., 2011 the critical diameter owned by phenol compounds was 6.73 Å while the acetic acid compound was 3.35 Å, where the smaller the critical diameter of a compound the easier it would be to diffuse into the zeolite pore. The phenol compound can diffuse into the zeolite pore which has a pore size of 7 Å due to the critical diameter of the phenol molecule of 6.73 Å thus increasing the phenol compound. Meanwhile, the acetic acid compound is a carboxylic acid group which has a critical diameter of 3.35 Å, where the compound can diffuse into zeolite pores which have a large enough pore size that is 7 Å. The acetic acid compound which enters the zeolite pores will undergo a decarboxylation process on the active side of the catalyst so that the bonding of the acetic acid compound will form a CO₂ gas. Gas is one of the products formed during the pyrolysis process. The formed gases is a gas with low molecular weight (lower molecular weight gases) that cannot be condensed such as carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄) and hydrogen (H₂) (Basu, 2010). The composition of pyrolysis gas produced in this study can be seen in Figure 3.

Table 5. Compounds Identified in The Bio-oil by GC-MS Analysis

| Compound                      | Area (%) |
|-------------------------------|----------|
|                               | Without Catalyst | ZAB-NA | ZAB-0.5M | ZAB-1M | ZAB-1.5M | ZAB-2M |
| Acetalddehyde                 | 0.91     | 1.05   | 1.29   | 0.78   | 1.21   | 1.00   |
| 1,2 – Propadiene              | -        | -      | 3.58   | -      | 2.90   | 3.82   |
| 2 Propynol                    | -        | -      | -      | 3.26   | -      | -      |
| 2-Methoxy Isobutane           | -        | -      | 2.84   | -      | -      | 1.56   |
| Acetone (2-Propanon)          | 5.94     | 5.04   | -      | -      | -      | -      |
| Acetic Acid                   | 48.00    | 49.02  | 42.59  | 48.59  | 48.86  | 43.92  |
| Propanoic Acid                | 2.69     | 2.26   | 1.07   | 1.89   | 1.58   | 1.91   |
| 2-Furancaboxaldehyde          | 2.14     | 1.81   | 1.47   | 1.47   | -      | 2.21   |
| Phenol                        | 40.31    | 40.83  | 47.47  | 43.90  | 45.94  | 45.57  |
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The results of gas formed in the pyrolysis process of palm shell are dominated by CO and CO$_2$ with a range of 34 - 55 wt% and 26 - 53 wt%. CO and CO$_2$ gases are formed from the thermal decomposition of oxygen groups in biomass, which this process remove large amounts of oxygen from the biomass molecular structure (Nunes, 2018). CO$_2$ is the main gas which formed during thermal cracking processes such as decarboxylation. In addition, other gases formed during the pyrolysis process are methane and few hydrogen. Methane gas and carbon monoxide are generally produced in the secondary cracking process of biomass. Meanwhile hydrogen gas in the pyrolysis process is formed through several reaction mechanisms including the steam reforming process, and water-gas shift reaction. The reaction mechanism for the formation of gases in the pyrolysis process is as follows.

Steam Reforming Reaction
Alcohol : CH$_3$CH$_2$OH + H$_2$O $\rightarrow$ 2CO + 4H$_2$
Carbonyl : CH$_6$CHO + H$_2$O $\rightarrow$ 2CO + 3H$_2$
Carboxylate : CH$_3$COOH + H$_2$O $\rightarrow$ 3CO + 5H$_2$

Water-gas Shift Reaction
CO + H$_2$O $\rightarrow$ H$_2$ + CO$_2$

Methanation Reaction
CO + 3H$_2$ $\rightarrow$ CH$_4$ + H$_2$O
CO$_2$ + 3H$_2$ $\rightarrow$ CH$_4$ + 2H$_2$O

Based on Figure 3, CO$_2$ yields was increased in catalytic pyrolysis by ~ 18 wt% at maximum values which yields of noncatalytic pyrolysis was 35.20 wt%. During the catalytic pyrolysis the CO$_2$ yield increased to ~ 41 - 53 wt%. It occurs the release of oxygen compounds in the secondary cracking of bio-oil by forming CO$_2$ gas and carboxylation compounds or commonly called the decarboxylation process. Increased CO$_2$ yields will result in decreased concentrations of carboxylic compounds found in bio-oil.

The concentration of carboxylic compounds (acetic acid) in bio-oil has decreased in catalytic pyrolysis (ZAB-0.5 M) compared to non-catalytic pyrolysis. It can be seen in Figure 3 that the increased concentration of acid used in the zeolite activation process will increase the CO$_2$ gas yield obtained. This increase occurs because the higher the concentration of acid used, the active site of the catalyst will increase and accelerate the decarboxylation reaction. Apart from the decarboxylation route, CO$_2$ gas can also be formed from a water shift gas reaction mechanism, this route will increase CO$_2$ gas yield by reducing CO gas yield. Meanwhile, the use of ZAB-NA catalysts produces a minimum CO$_2$ gas yield of 26.70 wt%, it because the use of the ZAB-NA catalyst not allows water shift gas reaction mechanism to occur, thus many CO gas produced are not converted to H$_2$ gas.

Meanwhile, CO gas yield decreased in catalytic pyrolysis compared to non-catalyzed pyrolysis. In noncatalytic pyrolysis CO gas yield was 51.84 wt% and decreased to reach the maximum value in catalytic pyrolysis on the use of ZAB-2M catalyst by 34.74 wt%, and in the use of ZAB-NA catalyst CO yield increased to reach a maximum point of 55.51 wt%. CO gas in the pyrolysis process can be formed through several routes including decarbonation and steam reforming reaction. The use of catalysts in pyrolysis will reduce CO gas yield compared to non-catalytic pyrolysis, this happens because the use of catalysts will increase methanation reaction and water shift gas reaction where CO gas formed will be converted to CH$_4$ and H$_2$ gas.

![Figure 3. Compositions of Gases Product from Pyrolysis by GC Analysis](image-url)
Pyrolysis gas products have potential energy content because there are CO, H₂, and CH₄ gases that have large calorific value. The calorific value of gas produced by biomass pyrolysis is generally in the range of 11-20 MJ/Nm³ (Diebold and Bridgewater, 1997). The calorific value of the gas produced in this study can be seen in table 6 i.e. the pyrolysis gas calorific value was in the range of values ~ 13-17 MJ/Nm³. The highest heating value generated in pyrolysis using ZAB-NA catalyst is 17.41 MJ/Nm³, this occurs because the composition of CO, CH₄, and H₂ gas produced is quite high and the CO₂ gas produced is relatively low. Meanwhile, the lowest heating value is generated on pyrolysis using ZAB-2M catalyst of 13.64 MJ/Nm³, because the use of catalyst CO₂ gas was formed relatively much compared to the use of other catalysts.

Pyrolysis gases contain components from synthetic gases (syngas) i.e carbon monoxide, carbon dioxide and hydrogen which can be used as new renewable energy sources (Mc Kendry, 2002). Pyrolysis gas can also be utilized in the pyrolysis fluidized bed system, where the pyrolysis gas will be mixed with fluidized gas. The use of pyrolysis gas in a fluidized bed pyrolysis system will increase the H/C ratio in the pyrolysis reactor system which will increase the hydrocarbon content in the bio-oil (Ringer et al, 2006).

CONCLUSION

Activation of natural Bayah zeolites with sulfuric acid changed the characteristics of zeolites, namely an increase in Si/Al molar ratio from 5.49 to 14.98 on variations of 1 M H₂SO₄ concentration and decreased crystallinity of zeolites. The addition of natural zeolite catalysts activated in the pyrolysis process increased the bio-oil yield by 6.51 wt% on variations of 1 M H₂SO₄ concentration and reduced gas yield by 7.15 wt% in the variation of 2 M H₂SO₄ concentration and did not significantly affect char yield. The addition of natural zeolite catalysts activated in the pyrolysis process increased the phenol content in the bio-oil by 7.16 area% and reduced the acetic acid content by 5.41 area% at a variation of 0.5 M concentration. While for gas characteristics, the addition of the catalyst caused an increase in CO₂ content by 20.77 wt% as a result of the reaction releasing the oxygenate component in the bio-oil.

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| Table 6. Pyrolysis Gas Energy Value |
|-----------------------------------|
| Sample   | HHV (MJ/Nm³) |
|----------|--------------|
| Without Catalyst          | 15.03        |
| ZAB-NA               | 17.41        |
| ZAB-0.5M             | 15.56        |
| ZAB-1M              | 15.15        |
| ZAB-1.5M            | 14.27        |
| ZAB-2M             | 13.64        |
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