

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

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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*

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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 (Wijiatmoko, 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,

2013). 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 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.

$$Y_{Biooil} = \frac{W_{Biooil}}{W_{Feed}} \times 100\% \quad (1)$$

$$Y_{Char} = \frac{W_{Char}}{W_{Feed}} \times 100\% \quad (2)$$

$$Y_{Gas} = 100\% - Y_{Biooil} - Y_{Char} \quad (3)$$

Pyrolysis Product Analysis

Pyrolysis product includes solid products (char), liquid (bio-oil), and gas were characterized. The proximate content of raw materials and pyrolysis solid products were analyzed using the Leco TGA-601 Thermogravimetric Analyzer at the Water Laboratory of PT. Indonesia Power, Cilegon. The ultimate content of raw materials and solid products was analyzed using the Leco CHN-2000 Analyzer at the Water Laboratory of PT. Indonesia Power, Cilegon. Pyrolysis liquid products were analyzed using the Gas Chromatography - Mass Spectrometry (GC-MS) 5973 Agilent Technology tool at the Police Headquarters Forensic Laboratory, Duren Sawit, East Jakarta. And pyrolysis gas products were characterized using the Shimadzu 8A TCD Detector Gas Chromatography (GC) tool at the RPKA Laboratory of the Chemical Engineering Department, University of Indonesia, Depok.

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

Acid 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 H_2SO_4 (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 $2\theta = 11.3^\circ, 13.2^\circ, 16.8^\circ, 17.2^\circ, 19^\circ, 22.3^\circ, 25.5^\circ, 25.9^\circ, 26.2^\circ, 28^\circ, 29.7^\circ, 29.9^\circ$ has an intensity which decreased of ZAB-1M sample compared to the ZAB-NA sample. The use of H_2SO_4 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.

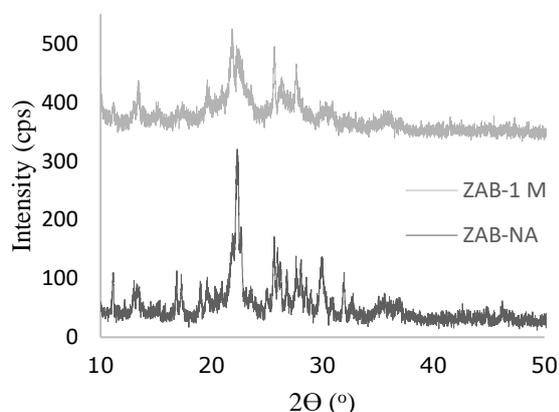


Figure 1. XRD Patterns of ZAB-NA and ZAB-1M (offset 320 cps).

Zeolite damage caused by high concentrations of H_2SO_4 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 (Sulistiyowati *et al*, 2018).

The results of XRD analysis added in figure 1 shows that some peaks at diffraction $2\theta = 11.2^\circ, 13.4^\circ, 19.4^\circ, 19.6^\circ, 19.9^\circ, 21.9^\circ, 22.8^\circ, 23^\circ, 25.6^\circ, 26^\circ, 27.5^\circ$ 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, SiO_2 -amorf, $Na_2O, K_2O, CaO, Fe_2O_3$) 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 diffracted 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) (Ismetulloh *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 $2\theta = 11.1^\circ, 17.2^\circ, 19.6^\circ, 20.9^\circ, 22.2^\circ, 23.9^\circ, 25.6^\circ, 29.9^\circ$ and the ZAB-1M sample shows that a peak at diffraction $2\theta = 9.9^\circ, 16.9^\circ, 13.4^\circ, 19.6^\circ, 22.8^\circ, 25.6^\circ, 26.2^\circ, 27.6^\circ$ that there is a similarity of the major peaks at the 2θ angle. The similarity of the peak XRD patterns at the 2θ 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 H_2SO_4 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).

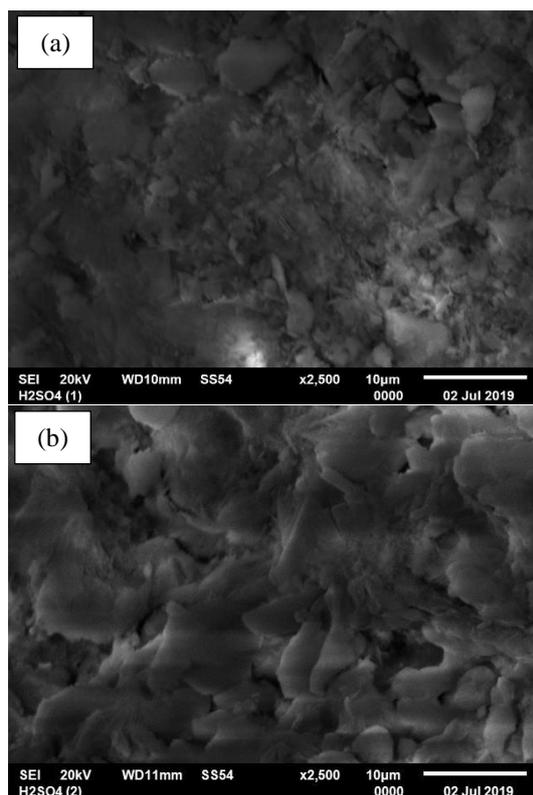


Figure 2. SEM Images (a) ZAB-NA, (b) ZAB-1 M

Table 2. Elemental Composition by EDX analysis

Composition	ZAB-NA (wt %)	ZAB-1M (wt%)
O	49.81	47.15
Na	0.53	0.00
Mg	0.65	0.08
Al	6.70	3.08
Si	38.30	48.01
K	1.61	0.29
Ca	2.26	0.48
Fe	0.14	0.91

Increased of Si/Al ratio affects the characteristics of zeolite as a catalyst such acid strength, pore volume and surface area. Catalysts with high acidity have high activity at the zeolite acid site, thus it is very effective in the catalytic process of breaking and forming bonds (Morina, 2009). Table 2 shows that impurity content of ZAB-NA samples such as Ca, Mg, K, Na were decrease due to exchange with the H⁺ cation found in acids (H₂SO₄) which increases the zeolite pore volume.

Characterization of Raw Materials

Properties of palm kernel shells including proximate analysis, ultimate analysis, and calorific value were determined. Proximate analysis showed 16.95 wt% fixed carbon, 9.51 wt% water content, 64.95 wt% flying matter, and 4.08 ash content. Ultimate analysis shows 48.78 wt% carbon, 6.94 wt% hydrogen, 0.67 wt% nitrogen, 43.61 wt% oxygen, and

undetectable sulfur content. The palm kernel shell HHV value obtained was 22.61 MJ / kg.

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%.

Table 3. Yield of Product Pyrolysis

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

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

Table 4. Physical Properties of Bio-oil

Sample	Density (kg/m ³)	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, hydroxyaldehyde, 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.

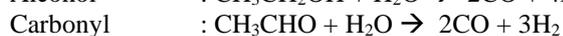
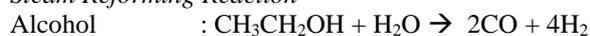
According to Yu *et al*, 2012 and Jae *et al*, 2011 the critical diameter owned by phenol compounds was 6.73 Å while the acetic acid compound was 3.35 Å, where the smaller the critical diameter of a compound the easier it would be to diffuse into the zeolite pore. The phenol compound can diffuse into 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.

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

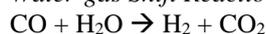
Compound	Area (%)					
	Without Catalyst	ZAB-NA	ZAB-0.5M	ZAB-1M	ZAB-1.5M	ZAB-2M
Acetaldehyde	0.91	1.05	1.29	0.78	1.21	1.00
1,2 – Propadiene	-	-	3.58	-	2.90	3.82
2 Propynol	-	-	-	3.26	-	-
2-Methoxy Isobutane	-	-	2.84	-	-	1.56
Acetone (2-Propanon)	5.94	5.04	-	-	-	-
Acetic Acid	48.00	49.02	42.59	48.59	48.86	43.92
Propanoic Acid	2.69	2.26	1.07	1.89	1.58	1.91
2-Furancarboxaldehyde	2.14	1.81	1.47	1.47	-	2.21
Phenol	40.31	40.83	47.47	43.90	45.94	45.57

The results of gas formed in the pyrolysis process of palm shell are dominated by CO and CO₂ with a range of 34 - 55 wt% and 26 - 53 wt%. CO and CO₂ 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). CO₂ 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.

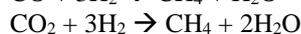
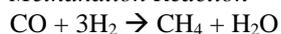
Steam Reforming Reaction



Water-gas Shift Reaction



Methanation Reaction



Based on Figure 3, CO₂ 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 CO₂ yield increased to ~ 41 - 53 wt%. It occurs the release of oxygen compounds in the secondary cracking of bio-oil by forming CO₂ gas and carboxylation compounds or

commonly called the decarboxylation process. Increased CO₂ 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 CO₂ 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, CO₂ gas can also be formed from a water shift gas reaction mechanism, this route will increase CO₂ gas yield by reducing CO gas yield. Meanwhile, the use of ZAB-NA catalysts produces a minimum CO₂ 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 H₂ 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 decarbonilation 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 CH₄ and H₂ gas.

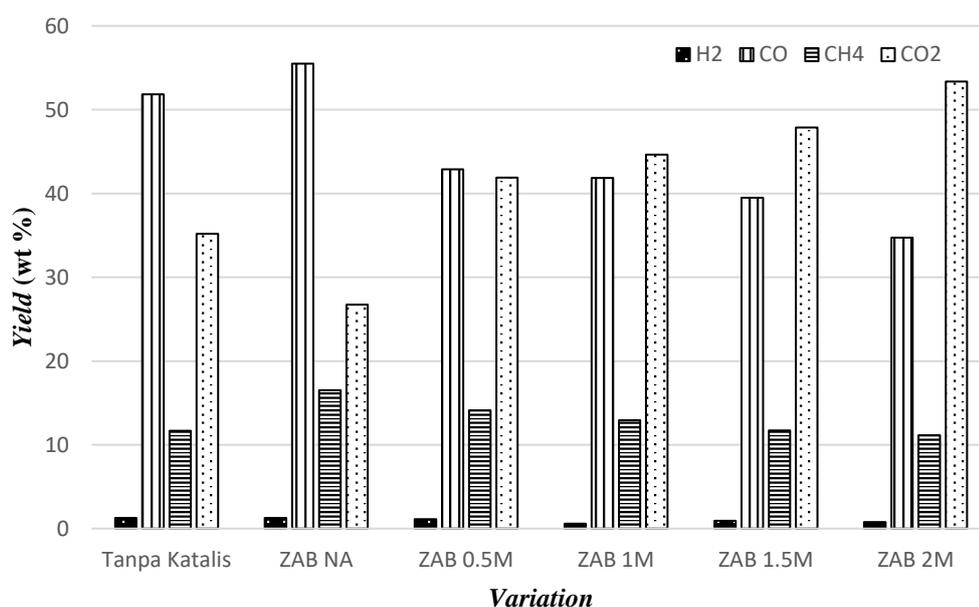


Figure 3. Compositions of Gases Product from Pyrolysis by GC Analysis

Table 6. Pyrolysis Gas Energy Value

Sample	HHV (MJ/Nm ³)
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

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.

REFERENCES

- Asadullah, M., Rasid, N.S., Kadir S.A., and Azdarpour, A., (2013,) Production and detailed characterization of bio-oil from fast pyrolysis of palm kernel shell, *Biomass & Bioenergy*, 59, pp. 316-324.
- Basabe, Y.G., Iznaga, I.R., Menorval, L.C., and Liewellyn, P., (2010), Step wise dealumination of natural clinoptilolite: structural and physicochemical characterization, *Microporous and Mesoporous Materials*, 135, 187-196.
- Basu, P., (2013), *Biomass Gasification, Pyrolysis, and Torrefaction: Practical Design and Theory*, Elsevier Inc, London.
- Cefic, (2015), Guidelines for The Safe Handling of Phenol, European Chemical Industry Council, Belgium, pp. 7.
- Diebold, J.P., and Bridgewater, A.V., (1997), *Developments In Thermochemical Biomass Conversion*, Springer Science and Business Media Doedrecht, Kanada.
- Dimian, A. C., Bildea, C. S., and Kiss, A. A., (2019), Acetic Acid. Applications in Design and Simulation of Sustainable Chemical Processes, pp. 483–519.
- GAPKI, (2018), Energi Biomassa Berbasis Cangkang Kelapa Sawit Butuh Intensif, <https://gapki.id/news/4864/energi-biomassa-berbasis-cangkang-sawit-butuh-intensif>. [Accessed : 5th May 2018]
- Ika, (2017), Konsumsi Energi Meningkat 5,9 % Pada Tahun 2017, <https://ugm.ac.id/id/berita/14723konsumsi.energi.indonesia.meningkat.59.persen>. [Accessed : 15th April 2018]
- Ismetulloh, M., Gumelar, F., Nuryoto, and Kurniawan, Teguh., (2019), Modifikasi Zeolit Alam Bayah Menggunakan Asam dan Pengaplikasiannya dalam Pengurangan Amonium pada Kolam Ikan Bandeng, *Jurnal Integrasi Proses*, 8 (12), pp. 07-13.
- KESDM, (2017), Handbook of Energy & Economy Statistic of Indonesia 2017, KESDM, Jakarta.
- Kim, S.W., Koo, B.S., Jaw, W.R., Ryu, J.W., Lee, J.S., Kim, C.J., Lee, D.H., Kim, G.R., and Choi, S., (2013), Bio-oil from pyrolysis of palm and Jathropa waste in a fluidized bed, *Fuel Processing Technology*, 108, pp. 18 – 24.
- Kim, S.W., Koo, B.S., and Lee, D.H., (2014), Catalytic Pyrolysis of Palm Kernel Shell in a Fluidized Bed. *Bioresour Technology*, 167, pp. 425 – 432.
- Lestari, Y. D., (2010), Kajian Modifikasi dan Karakterisasi Zeolit Alam dari Berbagai Negara, Prosiding Seminar Nasional Kimia dan Pendidikan Kimia, Yogyakarta.

- Martin, S.A., Barrera, C.C., and Montecinos, A., (2017), Catalytic Pyrolysis of Chilean Oak : Influence of Bronsted Acid Sites of Chilean Natural Zeolite, *Catalyst*, 7, pp. 356 - 369.
- McKendry, P., (2002), Energy Production From Biomass (Part 1) : Overview of Biomass. *Bioresource Technology*, 83, pp. 37-46.
- Mihalcik, D.J., Mullen, C.A., and Boateng, A.A., (2011), Screening acidic zeolites for catalytic fast pyrolysis of biomass and its components, *Journal of Analytical and Applied Pyrolysis*, 92, pp. 224 – 232.
- Mohammed, I. Y., Kazi, F. K., Yusup, S., Alaba, P. A., Sani, Y. M., Abakr, Y. A., (2016,) Catalytic intermediate pyrolysis of napier grass in a fixed bed reactor with ZSM-5, HZSM-5 and zinc-exchanged zeolite-A as the catalyst, *Energies*, 9, pp. 246.
- Morina, Sidjabat O. (2009) Pengaruh Logam Kalsium (Ca) dan Kromium (Cr) dalam Pembuatan Biogasoline Setara Bensin Dengan Bahan Baku Metil Ester. *Pusat Penelitian dan Pengembangan Teknologi Minyak dan Gas Bumi "LEMIGAS"*, Jakarta.
- Nasser, G.A., Kurniawan, T., Tago, T., Bakare, I.A., Taniguchi, T., Nakasaka, Y., Masuda, T., and Muraza, O., (2016), Cracking of N-Hexane Over Hierarchical MOR Zeolites Derived From Natural Minerals, *Journal of The Taiwan Institute of Chemical Engineers*, 61, pp. 20 – 25.
- Norvia, S., Suhartana, and Pardoyo, (2016), Dealuminasi Zeolit Alam Menggunakan Asam (HCl dan H₂SO₄) untuk katalis pada Sintetis Biodiesel, *Jurnal Kimia Sains dan Aplikasi*, 19 (2), pp. 72 – 76.
- Nunes, L.J.R., Matias, J.C.D.O., and Catalao, P.D.S., (2018), *Torrefaction of Biomass for Energy Applications*, Elsevier Inc, London.
- Pertamina, (2019), Properties of Solar or Biosolar. <https://www.pertamina.com/industrialfuel/media/6796/biosolar.pdf> . [Accessed : 18th July 2019]
- Ringer, M., Putsche, V., and Scahill, J., (2006), Large-Scale Pyrolysis Oil Production : A Technology Assesment and Economic Analysis, National Renewable Energy Laboratory, U.S.A.
- Sa'diyah, K., and Juliastuti, S. R., (2015), Pengaruh Jumlah Katalis Zeolit Alam Pada Produk Proses Pirolisis Limbah Plastik Polipropilen (PP), *Jurnal Bahan Alam Terbarukan*, 4(2), pp. 40-45.
- Sulistyowati, N., Sriyanti, and Darmawan, A., (2018), Effect of Acid on Natural Zeolite Dealumination on Indigo Carmine Adsorption Capability, *Jurnal Kimia Sains dan Aplikasi*, 21(2), pp. 102-106.
- Sumari, Fajaroh, Fuziatul., Santoso, Aman., and Wardani, Riski W., (2018), Performace of Activated Natural Zeolite/Cu as a Catalyst on Degradation of Glycerol into Ethanol Assisted by Ultrasonic. *Journal of Physics*, Conference Series 1093, 012036.
- Teacy, M. M. J., Higgins, J. B., (2001), Collection of Simulated XRD Powder Patterns for Zeolites, Elsevier Inc, London.
- Wang, S., and Peng, Y., (2010), Natural zeolites as effective adsorbents in water and waste water treatment, *Chemical Engineering Journal*, 156, pp. 11–24.
- Yasin, Sahl I. B., Elmugdad, A. A., and Ahmed, Adil E., (2016), Treatment of Drilling Mud Waste Water of Block Six Oilfield Plant Sudan using Zeolites. *International Journal of Multidisciplinary Research and Development*, 3, pp. 70-74.
- Zhang, Q., Chang, J., Wang, T., and Xu, Y., (2006), Upgrading Bio-oil Over Different Solid Catalysts, *Energy and Fuels*, 20, pp. 2717-2720.
- Wijiatmoko, B., (2017), Pemerintah Terus Maksimalkan Potensi EBT. <http://ebtke.esdm.go.id/post/2017/11/24/1827/pemerintah.terus.maksimalkan.potensi.ebt>. [Accessed : 15th April 2018]