

**Pyrolysis of Palm Kernel Shell to Chemicals by Using Bayah Natural Zeolites**Endang Suhendi[✉], Pipiet P.U. Naibaho, Eka R. Fauzan, Teguh KurniawanDOI: <https://doi.org/10.15294/jbat.v9i1.22250>Chemical Engineering Department, Sultan Ageng Tirtayasa University, Jl. Jendral Sudirman Km. 3
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Abstract

Palm kernel shell (PKS) is one of the biomass with high potential that can be converted into chemicals. In this study, palm kernel shell (PKS) was converted by pyrolysis method to produce condensed liquid products, gas, and solid. The purpose of this study was to determine the effect of catalyst activation time on yields and characteristics of PKS waste pyrolysis products. The pyrolysis process was carried out at a temperature of 500°C. Based on the results obtained with the addition of catalysts at 7 hr of activation can reduce the yield of solid products by 1.5% wt and 9.01% wt of liquid and increase the yield of gas products by 10.51% wt. On the characteristics of solid product there is a decrease in volatile matter by 55.04% wt and an increase fixed carbon by 40.27% wt. The gas characteristics, the H₂ and CO gas decreases by 5.43% v/v and 1.36% v/v and the increase in CH₄ and CO₂ gas by 1.07% v/v and 5.72% v/v. Characteristics of the liquid obtained an increase in the amount of acetic acid by 11.75% v/v and decrease phenol compounds by 13.08% v/v. The result liquid product can be applied as a chemical.

INTRODUCTION

Indonesia is a tropical country, where all kinds of plants can grow and develop well. From the various plantations and agriculture certainly has waste that comes from plants that are not utilized. Such as waste from palm oil plantations, tobacco, rice plants, corn, and many more that are still not utilized by the surrounding community.

Palm oil is one of the cultivation plants producing vegetable oil in the form of Crude Palm Oil (CPO), one of which is oil palm plantations in Indonesia in 2016 with an area of 8,774,226 hectares and production of 33,500,691 tons (Directorate General of Plantation, 2016). Banten province has owned palm oil plantations with an area of 10,588 hectares and production of 23,471 tons (Directorate General of Plantation, 2016).

The processing of fresh fruit bunches (FFB) into crude palm oil (CPO) produces a very

large amount of by-product biomass and will continue to increase with the increase in Indonesia's FFB production. Not only palm oil seeds can be beneficial, but palm kernel shells (PKS) can also be beneficial to be processed into liquid product by pyrolysis method.

Pyrolysis is a process of combustion biomass without involving oxygen at high temperatures (temperatures between 450°C - 600°C) with the main product is a liquid (Olifitria, 2011). Liquid products require deoxygenation to reduce the level of oxygenate content that is too high in the application of liquid product as a fuel or chemical with the use of catalysts (Kim et al., 2014; Zhang et al., 2013; Muthia, 2011; Wardana, 2016). One of the more effective methods to improve the quality of liquid product by using catalytic fast pyrolysis, which is a combination of thermal pyrolysis of biomass with catalytic reforming processes for the direct conversion of

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biomass into fuel and high quality chemicals. (Zhang et al., 2013; Garcia et al., 2014). Catalysts that have been used in various catalytic pyrolysis, such as ZSM-5 (Kim et al., 2014; Garcia et al., 2014), FCC (Zhang et al., 2013; Kim et al., 2014), and nature zeolite (Muthia, 2011; Wardana, 2016).

Previous research by Damanik & Nurdianto (2017), research with pyrolysis method using PKS material, at $T = 500^{\circ}\text{C}$ and $t = 1$ hour, obtained liquid yield of 45.80%wt/wt at $T = 500^{\circ}\text{C}$ with the results of GC-MS analysis namely Acetic Acid 60.18%v/v, Phenol 14.69%v/v, Acetaldehyde 14.78%v/v, and Acetone 7.18%v/v.

The aim of investigation is to study the effect of zeolites activation time to the yield and characteristics of pyrolysis products from palm kernel shell.

RESEARCH METHODOLOGY

Material

The raw material used in this study is PKS from PTPN VI Malingping, Pandeglang Regency, Indonesia. The catalyst used in this research was natural zeolite tuff from Bayah, Banten. The acid solution used is HCl 32% obtained from the chemical store. The aquadest used was obtained from the Chemical Engineering Operation Lab, Engineering Faculty, Sultan Ageng Tirtayasa University.

Preparation of PKS

The Palm Kernel Shells was separated from its fiber sand sun drying for several days to reduce water content. The dried PKS were crushed and filtered to get a size of 5-10 mm, then weighed as much as 200 grams each.

Natural Zeolite Preparation and Activation

Zeolite tuff were crushed and then screened to obtain a size of -10+14 mesh. Zeolite were treated with 1M HCl solution at 60°C for 1, 5, and 7 hr. The acid treated zeolites were washed using aquadest for 3 times. The zeolites was dried at room temperature for 24 hr, after that it is dried in an oven for 6 hr at 110°C , followed by calcination at 550°C for 6 hr. The calcined zeolites were stored in a desiccator to avoid excessive water absorption.

Pyrolysis Process

A number of 200 gr of PKS and 20 gr of zeolite were loaded into the reactor and pyrolysis process is carried out. Cooling water was circulated using a double pipe condenser and start to turn on the heater. The reactor was heated until a temperature of 500°C was reached and kept constant for 1hr. Figure 1 shows the scheme of the pyrolysis process carried out in this study.

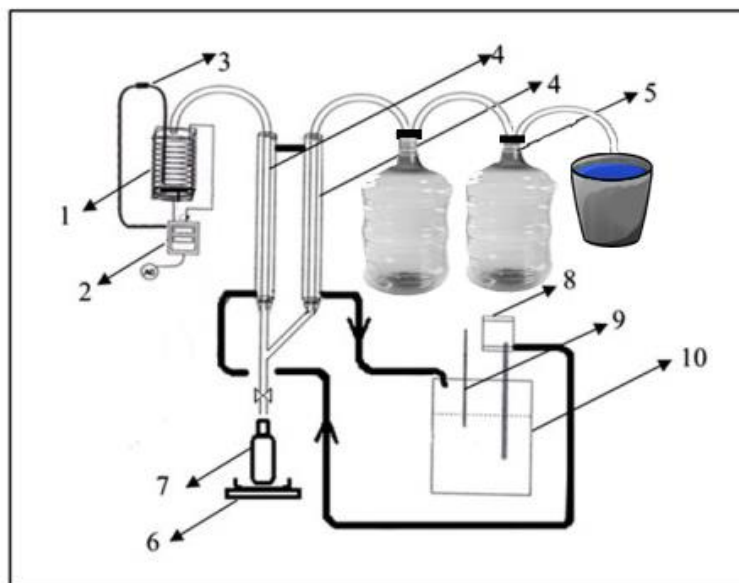


Figure 1. Scheme of The Pyrolysis Process (1) Reactor (2) Temperature Control (3) Thermocouple (4) Double Pipe Condenser (5) Gas Collector (6) analytical balance (7) Liquid Collector (8) Cooler Pump (9) Thermometer (10) Cold water reservoir

RESULTS AND DISCUSSION

Effect of Activation Time of Catalyst on Yield of Pyrolysis Products

Figure 2 shows the profile of yield with respect to the time of pyrolysis process for each variable.

It can be seen in Figure 2 that the higher pyrolysis time, solid mass decreased, this is caused by the breaking of the long chain contained in the biomass by heat generated in pyrolysis reactor then produces liquid and gas products. The decline of the solids results an increase in liquid and gas products. In this process, the hemi-cellulose thermal degradation process occurs at

temperatures of 200-260°C, cellulose at temperatures of 240-350°C, and lignin at temperatures of 280-500°C (Wijaya, 2011). Liquid and gas products increase significantly at initial temperatures because the content in biomass still has a high volatile matter which produced compounds such as liquid hydrocarbons, and gas i.e. CO₂, CH₄, CO, and H₂. After the temperature is reached the gas and liquid masses continue to increase but not significantly and slowly begin to constant until the end of reaction time. The yield change profile in Figure 2 obtained is in accordance with the results of research conducted by Damanik & Nurdianto (2017) and Wijaya (2011).

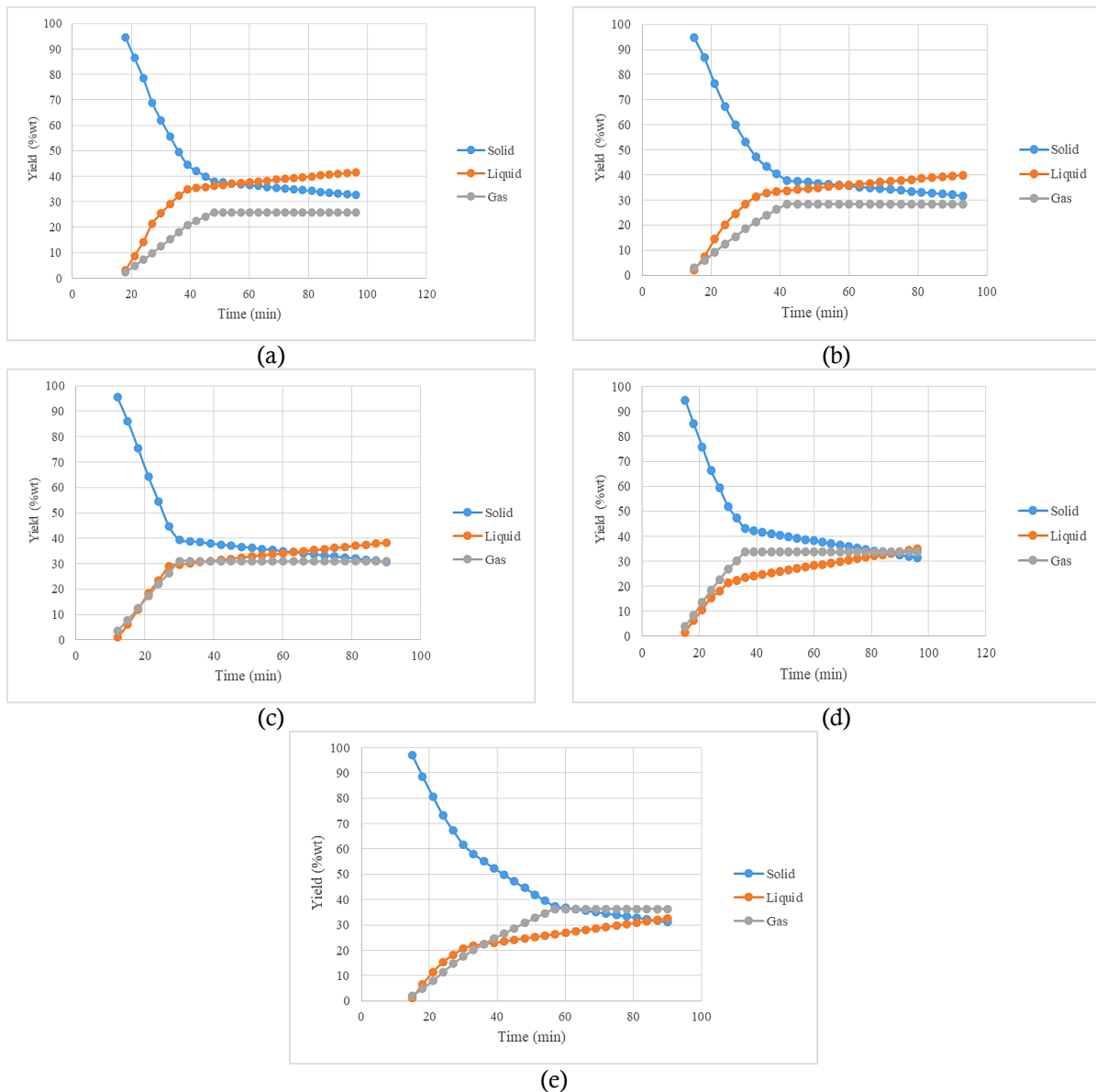


Figure 2. Yield Change Profile of Solid, Liquid, and Gas to the Time in each variable. (a) Without Catalyst, Activation Time (b) 0 hr (c) 1 hr, (d) 5 hr, and (e) 7 hr.

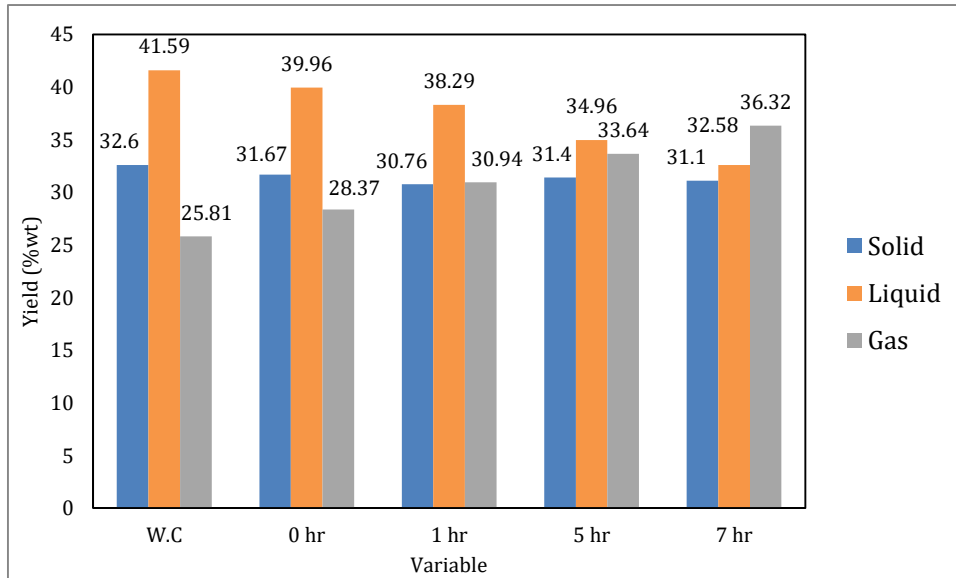


Figure 3. The Effect of Activation Time on The Yield of Pyrolysis Product.

The effect of addition and catalyst activation time on yield on each product can be seen in Figure 3.

Based on Figure 3, it can be seen that all yield profiles of liquid product have the highest compared to other products, except for the 7hr activation time where the gas yield is more than other products. In Solid products, the yield value of each variable experiences irregular increase and decrease and the range of values is not too far away at each variable and the pyrolysis temperature is fixed at each variable of 500°C, it can be concluded that the variable of catalyst activation time does not affect the amount of solid product result. The decrease in the amount of liquid yield and the increase amount of gas yield signify the success of the zeolite catalyst in cracking the biomass hydrocarbons. The presence of zeolite causes the long chain of hydrocarbons to break into short chain hydrocarbons, where these short chain hydrocarbons tend to remain a gas phase when going through a condensation process. The yield graph obtained in this study is comparable to the research conducted by Muthia (2011), who has conducted catalytic pyrolysis research from palm oil empty fruit bunches, and Wardana (2016) who has conducted catalytic pyrolysis research from a mixture of palm shells and plastics.

The addition of catalysts at 7 hours of activation resulted in a gas product yield of 36.32% at a temperature of 500°C, more effective than research by Damanik & Nurdianto (2017) with pyrolysis temperatures of 600°C without the

addition of catalysts, the gas product yield was only 30.01%.

Characteristics of Solid Products

Figure 4 shows a picture of a solid product produced from this study. The Solid produced has the following characteristics as in Tables 1 and 2. These characteristics are obtained based on the results of proximate and ultimate analysis tests.



Figure 4. Solid Products

Tables 1 and 2 show proximate and ultimate analysis results to determine the content of solid products.

Fixed carbon

Based on the results carried out by the addition of zeolite catalyst activation time to the content of solid products seen that the results of fixed carbon in proximate analysis decreased in proportion to the results of the analysis of C (carbon) content in the ultimate analysis it can be concluded that the addition of zeolite catalyst activation time to the solid product yield decreased because conditions in the reactor become reactive

Table 1. Result of Solid Product Proximate Analysis Tests

| Analysis | Unit | Raw Material | W.C | Activation Time (hr) | | | |
|-----------------|------------|--------------|-------|----------------------|-------|-------|-------|
| | | | | 0 | 1 | 5 | 7 |
| Moisture | (%wt, adb) | 9.51 | 6.94 | 6.94 | 7.01 | 6.94 | 6.6 |
| Ash | (%wt, adb) | 4.08 | 4.78 | 4.37 | 4.46 | 9.91 | 21.77 |
| Volatile Matter | (%wt, adb) | 69.45 | 16.76 | 15.77 | 16.82 | 18.01 | 14.41 |
| Fixed Carbon | (%wt, adb) | 16.95 | 71.52 | 72.91 | 71.71 | 65.15 | 57.22 |

Table 2. Results of Solid Product Ultimate Analysis Tests

| Analysis | Unit | Raw Material | W.C | Activation Time (hr) | | | |
|----------|------------|--------------|-------|----------------------|-------|-------|-------|
| | | | | 0 | 1 | 5 | 7 |
| C | (%wt, adb) | 48.78 | 78.46 | 79.26 | 78.55 | 71.01 | 62.58 |
| H | (%wt, adb) | 6.94 | 3.43 | 3.37 | 3.43 | 3.42 | 2.78 |
| N | (%wt, adb) | 0.67 | 0.65 | 0.64 | 0.6 | 0.6 | 0.54 |
| O | (%wt, adb) | 43.61 | 17.46 | 16.73 | 17.42 | 24.97 | 34.1 |

with the presence of a catalyst that causes the gas condensed from the solid to react with the H⁺ content found in the activated zeolite catalyst. The decrease in fixed carbon content and C (carbon) content is comparable to research conducted by Polii (2017).

Moisture

Based on the results carried out by the addition of zeolite catalyst when the activation of solid product content is seen in the results of moisture on the addition of catalyst when activated on the results obtained decreased moisture content in solid product but in the variable of activation 1hr increase, this increase is due to the storage of PKS samples not stored in a desiccator that causes moisture to enter the sample. This increase in moisture content as carried out by researchers by Putra et al. (2018).

Ash

Based on the results carried out by the addition of zeolite catalyst when the activation of the solid product content is seen that the ash results in the proximate analysis have increased it can be concluded that the increase in ash content in the solidproduct is caused by the formation of mineral salts in the carbonation process and in the further process will form fine particles of mineral salts that cause an increase in ash content and when compared with the result of fixed carbon analysis witch decreases in 7 hr activation time variable due to conditions in reactor to be reactive, so that the ash content produced increases sufficiently significant on these variable. This

increase in ash levels as carried out by researchers by Putra et al. (2018).

Volatile matter

Based on the results carried out by the addition of zeolite catalyst the activation time of the solid product content seen in the results of the volatile matter in the proximate analysis has decreased, it can be concluded that the addition of the catalyst can reduce this volatile matter because it evaporates volatile compounds and then reacts with the catalyst, so that it can convert the product liquid and gas are better than variables without catalysts. These results are in accordance with research conducted by Polii (2017).

Characteristics of Liquid Products

The liquid product is obtained from the reactor output gas condensation process. Not all gases produced change phase into liquid, condensed gases are called condensable gases while uncondensed gases are called non-condensable gases which are then declared as gas products produced from the pyrolysis process.

Liquid products obtained have the characteristics of yellowish brown, thick and pungent odor. Liquid products from pyrolysis can be seen in Figure 5. The picture shows a comparison of the physical appearance of 5 liquid products produced with different independent variable treatments.

Based on Figure 5, it can be seen the difference in color of the liquid product in plain view. Liquid products obtained without the addition of catalysts tend to have a yellowish-

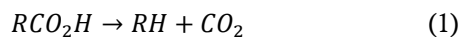
brown color, liquid products obtained by using catalysts with activation time variable are reddish brown and get darker with the longer zeolite activation time.



Figure 5. Liquid Product Pyrolysis, from left to right variable activation time 0hr, without catalysts (W.C), activation time 1, 5, and 7 hr.

The characteristics of the liquid product analysis test results using GC-MS can be seen in Table 3.

Based on Table 3 it can be seen that the most components contained in liquid products are acetic acid compounds, and phenols. The presence of acetic acid comes from the degradation of biopolymers such as cellulose and hemi cellulose while the degradation of lignin compounds is identified by the presence of phenol compounds (Olifitria, 2011).



The decrease of phenol compounds in liquid products can occur due to a secondary reaction by the catalyst that is a decarbonylation reaction such as the reaction above which causes a

decrease in phenol compounds to reach 26.43% v/v and increase CO₂ gas in the gas product.

According to Muthia (2011), the effect of the presence of zeolite catalysts should reduce the content of oxygenate compounds in the form of carbonyl and carboxyl group compounds, while increasing the phenol content. The results obtained by Muthia are reducing oxygenate content from 42.48% to 33%v/v and increasing phenol content from 10.74% to 26.5%v/v. In this study, there were no results close to the results obtained by Muthia. However, seeing that the amount of acetic acid produced is quite high at 57.11%v/v, the resulting liquid product can be applied as a chemical.

Previous research by Damanik & Nurdianto (2017) found that the results of pyrolysis liquid with acetic acid content of 60.18%v/v and phenol of 14.69%v/v at pyrolysis temperature of 500°C without the addition of catalysts, while the results obtained in this study with the same variable, the amount of acetic acid was 45.36 % and phenol 39.51%, the difference can be due to differences in treatment during preparation as well as different raw material content.

Characteristics of Gas Products

The gas produced from the pyrolysis of PKS has the characteristics as shown in Figure 5. The chart was made based on the results of analysis using GC Shimadzu.

From Figure 6, it can be seen that the most gas produced is CO₂, followed by CO, and methane and the least is H₂. Hydrogen is a component that can be used as a manufacture of methanol and can also be used as fuel, and methane is also a component that can be used as fuel.

Table 3. Analysis results of Liquid Products with GC-MS

| No | Component | Chemical Formula | W.C | 0 hr | 1 hr | 5 hr | 7 hr |
|----|-----------------------------|--|-------|-------|-------|-------|-------|
| 1 | Acetaldehyde (CAS) | C ₂ H ₄ O | 0.91 | 1.05 | 0.92 | 0.83 | 0.97 |
| 2 | Acetone | C ₃ H ₆ O | 5.94 | 5.04 | 3.57 | 3.97 | 3.59 |
| 3 | Acetic Acid, methyl ester | C ₃ H ₆ O ₂ | 5.33 | 4.76 | 5.55 | 7.45 | 6.70 |
| 4 | Acetic Acid (CAS) | C ₂ H ₄ O ₂ | 45.36 | 46.52 | 51.84 | 55.14 | 57.11 |
| 5 | 2-Furancarboxaldehyde (CAS) | C ₁₀ H ₈ N ₂ O ₂ | 2.14 | 1.81 | 2.17 | 3.61 | 3.89 |
| 6 | Phenol (CAS) | C ₆ H ₆ O | 39.51 | 40.51 | 35.47 | 27.46 | 26.43 |
| 7 | Phenol, 2-methyl-(CAS) | C ₇ H ₈ O | 0.80 | 0.32 | 0.47 | 0.54 | - |
| 8 | Phenol, 2-methoxy | C ₇ H ₈ O ₂ | - | - | - | 1.01 | 1.32 |

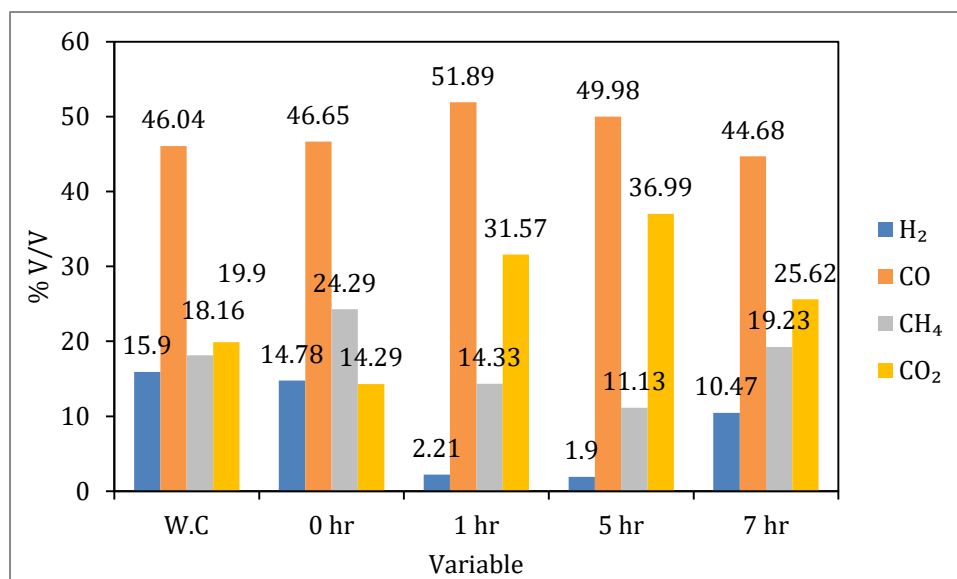
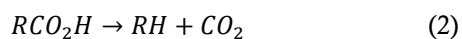


Figure 6. Chart of Gas Product Analysis Results

The most gas content is owned by CO & CO₂ gas as a result of the combustion process of biomass, as well as the result of the decarbonilation reaction of liquid products because it uses a catalyst. The decarbonylation reaction is characterized by a decrease in the carbonyl compound in the liquid product, which results in an increase in the CO & CO₂ gas content in the gas product. The reaction that occurs is shown in Eq. (2).



Based on the Diebold & Bridgwater (1999), in the pyrolysis process the value of CO produced is the most dominant compound in gas products, and in this study the values obtained on the chart are in accordance with the chart obtained by bridgwater. Seen from the amount of carbon monoxide (CO) gas compound of 46.06% v/v in the variable without catalyst (W.C) which then increased to 51.89%v/v at a variable of 1hour activation time, which then decreased to 44.68%v/v at 7 hours activation time variable. Overall on all variables of the analysis of gas products the value of CO gas tends to be greater. Then the value of methane gas (CH₄) as much as 18.16%v/v on the variable without catalyst (W.C) then increased to 19.23%v/v on 0 hr activation time, then decreased to 11.13%v/v at the variable of activation time 5 hr, and at the 7 hr activation time it increased to 25.62%v/v. The value of hydrogen gas (H₂) as much as 15.90%v/v in the

variable without catalyst (W.C) then decreased to 10.47%v/v at 7 hours of activation time variable.

Figure 7 shows the results of trials on gas products produced by the pyrolysis process. The figure shows that the product of combustible gas and fire produced is quite large.



Figure 7. Combustion Test on Gas Products

CONCLUSION

The addition of zeolite catalyst resulted in a decrease in the amount of yield of liquid products, and increased the amount of yield of gas products, on solid products the amount of yield did not change significantly. The volatile matter and fixed carbon of solid product produced in the presence of catalysts were decreased. In liquid products the most dominant content is acetic acid and phenol, with the presence of a catalyst increases the amount of acetic acid and decreases

the amount of phenol. The resulting liquid product has the potential to be used as a chemical. Gas products, with the addition of catalysts, increase the amount of CO and CO₂ gases, and reduce the amount of CH₄ and H₂ gases.

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