# Analysis of Bio-Oil Produced by Pyrolysis of Coconut Shell

D. S. Fardhyanti, A. Damayanti

***Abstract*—**The utilization of biomass as a source of new and renewable energy is being carried out. One of the technologies to convert biomass as an energy source is pyrolysis which is converting biomass into more valuable products, such as bio-oil. Bio-oil is a liquid which is produced by steam condensation process from the pyrolysis of coconut shells. The composition of a coconut shell e.g. hemicellulose, cellulose and lignin will be oxidized to phenolic compounds as the main component of the bio-oil. The phenolic compounds in bio-oil are corrosive; they cause various difficulties in the combustion system because of a high viscosity, low calorific value, corrosiveness, and instability. Phenolic compounds are very valuable components which phenol has used as the main component for the manufacture of antiseptic, disinfectant (known as Lysol) and deodorizer. The experiments typically occurred at the atmospheric pressure in a pyrolysis reactor at temperatures ranging from 300 $^{o}$C to 350 $^{o}$C with a heating rate of 10 $^{o}$C/min and a holding time of 1 hour at the pyrolysis temperature. The Gas Chromatography-Mass Spectroscopy (GC-MS) was used to analyze the bio-oil components. The obtained bio-oil has the viscosity of 1.46 cP, the density of 1.50 g/cm$^3$, the calorific value of 16.9 MJ/kg, and the molecular weight of 1996.64. By GC-MS, the analysis of bio-oil showed that it contained phenol (40.01%), ethyl ester (37.60%), 2-methoxy-phenol (7.02%), furfural (5.45%), formic acid (4.02%), 1-hydroxy-2-butanone (3.89%), and 3-methyl-1,2-cyclopentanedione (2.01%).

***Keywords*—**Bio-oil, pyrolysis, coconut shell, phenol, gas chromatography-mass spectroscopy.

## I. INTRODUCTION

THE role of fossil fuels will be very important, but their influence will be taken by the new resources and renewable energy. One of the technologies that can be used to handle this is pyrolysis technology using the organic waste (biomass).

Pyrolysis is a thermal conversion process to convert biomass into more valuable products or liquid product, known as bio-oil. The heat energy of pyrolysis encourages the oxidation of complex carbon molecules to decompose into carbon or charcoal. Pyrolysis technology can utilize organic waste helping to create a healthier environment due to the zero waste activities and to making a final product with value-added. Biomass was converted into bio-oil and charcoal [1]. The product of pyrolysis generally contains of three types, called light gases ($H_2$, CO, $CO_2$, $H_2O$ and $CH_4$), tar and char. All the products of pyrolysis can be used as eco-friendly fuel. Pyrolysis technology also produces the other products such as biochar, petrified wood, activated carbon, charcoal briquette, bio-oil and syngas [2].

Biomass (organic material) is the product of living things, it can be obtained from agricultural waste, forests, plantations, industries and households. Hydrocarbon compounds which are contained in biomass can be used to provide heat energy, producing fuels and generating electricity. Tropical countries like Indonesia generally have an abundance of biomass resources. More than 250 billion tons per year of biomass were produced from forest biomass and agricultural waste. Agricultural waste is generally derived from palm, sugar cane, coconut, agricultural residues and other, which amounts to approximately 40 billion tons per year. The raw material of biomass are used as raw material for bio-oil producing such as durian husk [3], corn cobs [4], oak tree [5], sawdust and wheat husk [6], castor beans [7], and organic waste [8].

Bio-oil is an emulsion with a smoke-like odor which is produced by a steam condensation process from the pyrolysis of material which contains lignin, cellulose, hemicellulose and other carbon compounds. Bio-oil contains carbon, hydrogen, and oxygen with insignificant traces of nitrogen and sulfur. The organic compounds of bio-oil are acids, alcohols, aldehydes, esters, ketones, sugars, phenols, phenol derivatives, and a large proportion of lignin derived oligomers [9]. These characteristics show that bio-oil is an unpolluted fuel and has greater calorific value than the oxygen fuel (such as methanol), while its calorific value is slightly lower than that of diesel and the other light fuel oil [10]. Unfortunately, bio-oil has high viscosity, low calorific value, and is corrosive and unstable, because it contains more acids and phenolic compounds.

Handling the waste of coconut shells is quite complicated since it is flammable and has a strong odor. Coconut shell can be converted into high economic value products by applied technology.

Phenolic compounds (the main component of bio-oil) were obtained from the oxidizing process of hemicellulose, cellulose and lignin as the composition of coconut shell. Phenolic compounds are an aromatic compound. They also can bind the other groups such as acids, esters, aldehydes and ketones. Phenol is an absorption material that can be used as [11]:

1. Preservation process of raw leather.
2. Anti-bacterial.
3. Decreasing the environmental pollution which is caused by the using of unfriendly environment chemical agents

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D. S. Fardhyanti and A. Damayanti are with the Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Semarang 50229, Indonesia (phone: +62-24-8508101 Ext.114; fax: +62-24-8508101 Ext.109; e-mail: dewiselvia@yahoo.com, dewiselvia@mail.unnes.ac.id).

for the preservation process of raw leather.

The aim of this research is to convert waste of biomass into new raw materials or products that have an economic value such as bio-oil (as an alternative energy resource).

This next research needs to be done to extract phenolic compounds as the main component of bio-oil which is corrosive, unstable and also difficult to be upgraded into ideal fuels [1]. Phenolic compounds are useful for disinfectants or floor cleaner. For the rubber industry, phenol is used to increase the quality of rubber.

## II. Materials and Method

### A. Material

The coconut shell was obtained from local market at Semarang, Central Java, Indonesia. Other supporting materials are such as glass wool and $N_2$ gas.

### B. Experimental

Sample Preparation

Coconut shell was washed using distilled water and then cut into small pieces and dried in an oven at 105$^o$C for 24 hours. Dried coconut shells were crushed using a hammer mill and separated by size using a sieve shaker.

TABLE I
Conditions of Analysis Using GC-MS

| GC-MS: GCMS-QP2010S Shimadzu | | |
|---|---|---|
| Column: Rastek RXi-5MS | | |
| Column: | | |
| Inner diameter | [m] | 2.5 x $10^{-4}$ |
| Length | [m] | 30 |
| Carrier gas | - | He |
| Split ratio | [-] | 153 |
| Flow rate | [cm/sec] | 26.6 |
| Sample volume | $m^3$ | $1.10^{-9}$ |
| Injection temp. | [K] | 583 |
| Column temp. | [K] | 313 – 578 |
| Pressure column | kPa | 10.0 |
| Column flow | mL/min | 0.54 |
| Detector (FID) temperature | [K] | 583 |

Pyrolysis Process

Pyrolysis process is conducted by following the procedures that have been used by Suyati [12]. The dried coconut shell is weighed, as much as 5,000 g, and is used as feed. The dried coconut shells are heated in a pyrolysis reactor gradually; temperature increase of 30 $^o$C per minute. Nitrogen gas (flow rate of 100 mL/minute) was used to carry the gaseous pyrolysis products and to obtain the inert condition. Then gas was condensed by a condenser to produce the liquid that contain bio-oil and water. The pyrolysis temperature was raised from 100 $^o$C to 300 $^o$C for 15 minutes. The heating process is stopped at 350 $^o$C and the bio-oil is obtained. The pyrolysis reactor temperature decrease with $N_2$ carrier gas is still turned on, so there is still a residual gas which can come out. Bio-oil is collected in a container with ice cooling system. The results are stored in the refrigerator and used for the next step. Bio-oil is analyzed for its components and concentration by using GC-MS. From the analysis by GC-MS on bio-oil, the concentration of each component will be obtained. The principal conditions of this analysis are shown in Table I.

A schematic of the experimental coconut shell reactor pyrolysis is shown in Fig. 1.

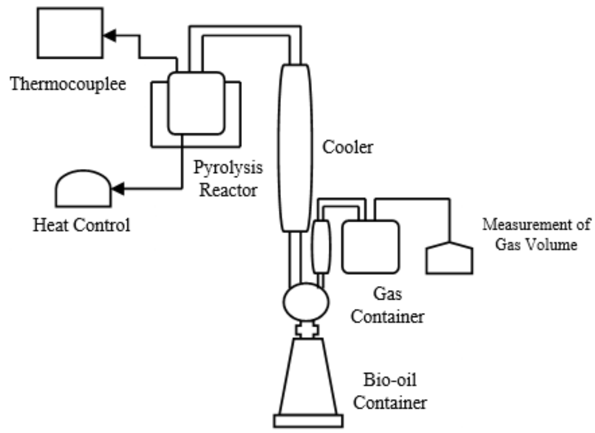


Fig. 1 Equipment of Coconut Shell Reactor Pyrolysis and Products Separation

## III. Results and Discussion

Proximate analysis for the coconut shell is shown in Table II.

TABLE II
Proximate Analysis of Coconut Shell

| Properties | Dried Base (%) |
|---|---|
| Water content | 13.2 |
| Ash | 0.6 |
| Volatile matter | 58.4 |
| Fixed carbon | 23.6 |
| Higher Heating Value (HHV) (MJ/Kg) | 16.9 |

The pyrolysis process of 5,000 g coconut shell produced 1,200 mL bio-oil and the product conversion was 24%. The process took three hours and produced a liquid compound called bio-oil. The bio-oil has so many various components and it depends on the time and temperature of the process. The components of the bio-oil were also very complex, containing various types of hydrocarbon compounds with a lot of molecular weight range.

The pyrolysis process is not a simple destructive reaction; the result of thermal degradation products depends on of the process conditions. By degasification or decomposition process, pyrolysis reaction of coconut shell for producing bio-oil was occurred in several stages. The first stage was the breaking of the aliphatic carbon bonds (at low temperature), then followed by elimination of the complex hetero ring and the breaking of C-H bonds. The maximum product of the decomposition process occurred at temperatures between 300-350$^o$C. If the pyrolysis process temperature was 350-700°C, it is a process called low temperature carbonization; but above 900$^o$C, it is called high temperature carbonization. The low temperature carbonization produced more liquid substance and less gas, but the high temperature carbonization produced less liquid substances and more gas. Even though it used the same biomass, low temperature carbonization produced liquid substances that were very different to the liquid substances produced by the high temperature carbonization. Liquid substances produced by low temperature carbonization contained more acids and bases than liquid substances produced by the high temperature carbonization.

The pyrolysis reaction needed a specific time, the decomposition would not be complete in a short time reaction However, the long time reaction affected the amount of gas released. The pyrolysis time increased the possibility of the products colliding with each other on the reactor wall, which was caused by the formation of molecules with higher hydrocarbon chains (secondary reaction of destructive distillation, where it produced a larger compound). Thus, the conversion product of bio-oil will decrease [1].

The time of pyrolysis also resulted in the release of many volatile substances in the bio-oil and produced a lot of heavy fraction compounds. This reduces the process efficiency as the processing was much more difficult and the product contained many impurities, such as inorganic compounds, sulfur and other substances. The pyrolysis process converted organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) which contain fixed amount of carbon and ash. The composition of the gas that was produced from the pyrolysis process is carbon monoxide, hydrogen, methane, and other hydrocarbon compounds.

Pyrolysis is the processing (at low temperature, 300-350$^{o}$C) to obtain bio-oil and to determine the components of bio-oil. The characterization of bio-oil has the density of 1.50 g/cm3, the viscosity of 1.46 cP, a molecular weight of 1996.64, and a calorific value of 16.9 MJ/kg. The chromatograms of the GC-MS analysis are shown in Fig. 2.

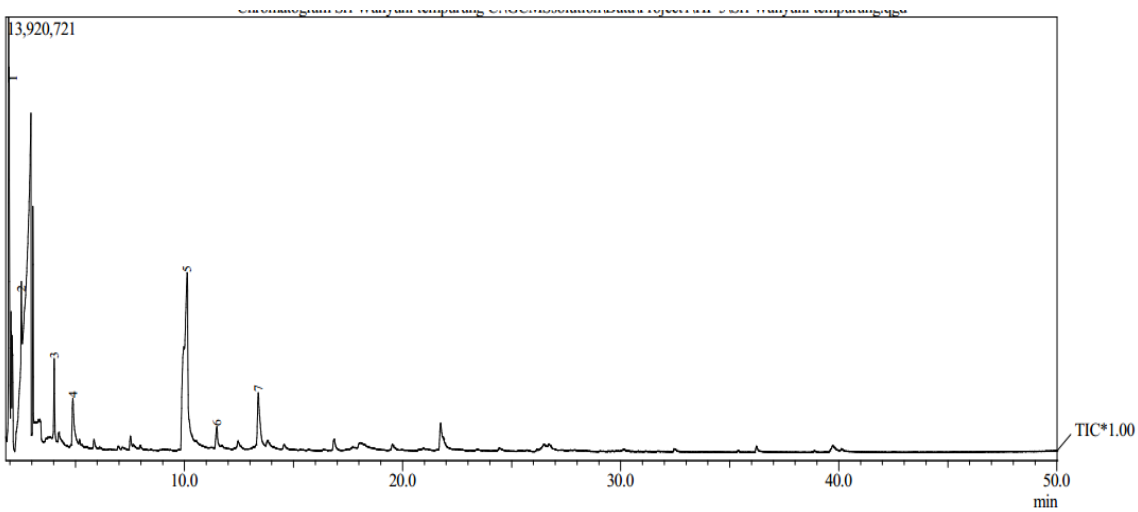


Fig. 2 GC-MS of Components Produced from the Pyrolysis of Coconut Shell

The results of the GC-MS analysis of the bio-oil showed that it contained more than seven chemical compounds such as ethyl ester, phenol, furfural and others. The main components of bio-oil from coconut shell are presented in Table III.

TABLE III
THE COMPOSITIONS OF BIO-OIL FROM PYROLYSIS OF COCONUT SHELL

| Peak Number | Compounds | Percentage (%) |
|---|---|---|
| 1 | Ethyl ester | 37.60 |
| 2 | Formic acid | 4.02 |
| 3 | 1-Hydroxy-2-butanone | 3.89 |
| 4 | Furfural | 5.45 |
| 5 | Phenol | 40.01 |
| 6 | 3-Methyl-1,2-cyclopentanedione | 2.01 |
| 7 | 2-Methoxy-phenol | 7.02 |

The percentage (%) of the compositions of the bio-oil analysis by GC-MS was obtained from the percentage area of the peak or the height of the peak in the chromatograms. Using a method of GC-MS, this work presents a composition of the bio-oil generated in the experiment. The total phenolic compounds contained in bio-oil are 47.03%. It was caused by the pyrolysis processing at 300-350°C (low temperature carbonization), which produce more substances that contain ester and phenolic compounds. The composition of biomass such as hemicellulose, cellulose and lignin will be oxidized to phenol as the main component of the bio-oil.

## IV. CONCLUSION

Pyrolysis is the processing (at low temperature, 300-350$^{o}$C) to obtain bio-oil.

The bio-oil from the pyrolysis of coconut shell has the calorific value of 16.9 MJ/kg, viscosity of 1.46 cP, density of 1.50 g/cm$^{3}$, and a molecular weight of 1996.64.

The total phenolic compounds contained in bio-oil are 47.03%. It was caused by the pyrolysis processing at 300-350°C (low temperature carbonization) that produce more substances contain ester and phenolic compounds.

The analysis of the GC-MS result showed that the bio-oil contained some seven chemical compounds such as ethyl ester (37.60%), formic acid (4.02%), 1-hydroxy-2-butanone (3.89%), furfural (5.45%), phenol (40.01%), 3-methyl-1,2-cyclopentanedione (2.01%), and 2-methoxy-phenol (7.02%).

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