

# Pyrolysis of Ethylene Vinyl Acetate Polymer by Natural Zeolite Catalyst as an Alternative Fuel

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**Abstract**—In Indonesia, ethylene vinyl acetate polymer type of sponge waste increases in number. The increase was due to the increase of the shoe factory which was the main consumer of this type of sponge. Conversion of this type of waste is done as an alternative fuel oil through pyrolysis process. The purpose of this study is to convert the sponge waste through pyrolysis process using a batch type reactor with the aid of a natural zeolite catalyst. The research used variation of the catalyst weight from 2%, 4%, 6%, 8%, 10% out of 200 grams of the weight of the feed with variations in reaction time ranging from 60 minutes, 90 minutes, 120 minutes, 150 minutes, and 180 minutes. The results showed that the optimum yield obtained was 51.22% using 4 gram weight of catalyst with 180 minutes processing time. The GC-MS analysis showed that the largest functional group of pyrolysis products for the fraction above distillation, the fraction before distillation, and the fraction under distillation, respectively, are 3-Nitro-1,2-Benzenedicarboxylic acid (88.11%), Cyclopentane, 1,1'-[3-(2-Cyclopentylethyl)-1,5-Pentanediy] Bis-(CAS)1,5-Dicyclopentyl-3-(2-Cyclopentylethyl)-Pentane(19.77%), and 1,13- Tetradecadiene (10.07%). The calorific value of the pyrolysis oil produced was 10992.6 calories/gram. This result was similar to the calorific value of gasoline fuel (10509 calories/gram). In addition, the analysis of the physical characteristics of the pyrolysis oil fraction on distillation was the same as the standard specifications for petrol and diesel fuel oils.

**Keywords**—waste slippers, EVA (ethylene vinyl acetate), pyrolysis, catalyst, natural zeolite

## I. INTRODUCTION

### A. Background

Solid waste is now very much piled up, with a weight of 1.3 billion tons per year in 2013 and is estimated to increase up to 2.7 billion tons per year by 2050 [1]. Indonesia is ranked second in the world of country producing plastic waste. Indonesian plastic production reaches 187.2 million tons per year [2]. With such a big problem, it needs big commitment to solve this. Currently, technology has been developed that can solve this problem, one of which is pyrolysis technology. Pyrolysis is defined as a process that utilizes heat to break down organic components without the use of oxygen [3]. The decomposition process of the pyrolysis on organic components can produce liquid, solid, and gas products which can be used as alternative fuels [4]. The resulting liquid product is a complex mixture of organic compounds such as styrene, ethyl-benzene, toluene, and others whereas the solid product is in the form of char/residue and inorganic material, and the gas products produced are in the form of hydrocarbon, CO and CO<sub>2</sub> [5]. The amount and quality of pyrolysis products is influenced by several parameters including the

type of reactor, temperature, and the time spent in the reactor [6]. There are several types of pyrolysis reactors in general, such as batch/semi-batch types, fixed bed reactors, fluidized bed reactors, spouted beds and screw kilns [5].

The Raw materials of pyrolysis used are very diverse, one of which is an EVA (Ethylene Vinyl Acetate) polymer type of sponge which is a waste of the slipper industry. EVA is basically a copolymer made from two different types of monomers to ethylene (ethene) and vinyl acetate [7]. EVA basically is very dangerous. This waste is classified as Crosslinked Material which is a material that if disposed of and piled up in the soil, it cannot be degraded by microbes [8].

Most footwear industries located on Surabaya, Yogyakarta and West Java used the EVA soles and the total EVA soles waste generated is around 750 tons/year [8]. From the previous research, pyrolysis using EVA was carried out with a TGA connected to the FTIR spectrometer through a heated line to determine the copolymer decomposition. The results of the research showed that there were two main decomposition events: first, the acetoxy group from the vinyl acetate (VA) comonomer and producing a 'polyene' domain in the polymer chain. Second, in high temperature there were two separate processes which were the decomposition of the 'polyene domain' and also the decomposition of the 'polyethylene (PE) domain', which corresponds to the initial ethylene unit. The result of TGA (Thermo Gravimetric Analyzer), EVA polymer has a degradation point at 423°C and when the EVA residue is 0%, the temperature recorded in TGA is 477 °C [9].

### B. Research on Pyrolysis

In addition to experiments with different raw materials, the pyrolysis process was also carried out by adding catalysts. The main purpose of the use of catalysts is nothing but the need for a better process so that the oil products produced are better. The use of catalysts will reduce the oil fraction and residue and increase the gas fraction when compared to ordinary thermal degradation. This phenomenon happened because oil fraction resulting from thermal degradation has been cracked using a catalyst so that the long chain of hydrocarbons is cut into shorter chains [10]. Other studies have suggested that an increase in the production of light oil fractions occurs as the time of catalyst usage increases, thus causes a decrease in catalyst activity [11]. In addition, the use of catalysts in several studies showed a decrease in oil fraction and residue while increasing gas fraction [12]. This result occurs due to continued cracking of the product of oil fraction into gas. In addition, the catalyst surface area will also affect the results of pyrolysis. Based on previous researches, catalysts in the form of pellets produce less oil products than those in the form of

powder catalysts with a larger surface area than pellets. It has also been stated in other studies that the greater the surface area of the catalyst contributes to the degradation process of HDPE plastic to produce more short chain hydrocarbon gases [10]. According to [13], pyrolysis liquid is influenced by the character of the catalyst which will determine the mechanism of product formation, and the type of catalyst that is often used in Indonesia is zeolite. Zeolite is categorized the good catalyst because of the present of active centers channels in this type of catalyst [14]. Mechanism of catalyzation process is diffusion of molecules to empty space between crystal dan chemical reaction occurs on the surface of said zeolite catalyst. Aside from cracking process, isomerization and hydrocarbon alkylation, zeolite can also be used as absorbent because it is inexpensive and save. In Indonesia, natural zeolite deposits are quite plentiful and their purity is quite high. Natural zeolite is a hydrated porous alumina silicate crystal mineral that has a three-dimensional skeletal structure formed from tetrahedral  $[SiO_4]^{4-}$  and  $[AlO_4]^{5-}$ . The two angles are connected by oxygen atoms and produce open and hollow three-dimensional structures in which metal atoms are filled. The metals used are usually alkaline or alkaline earth and water molecules that can move freely [15].

### C. Research Objective

This study aims to determine the effect of the weight variations of the natural zeolite catalyst and the processing time to the oil volume resulting from the pyrolysis of EVA type polymer waste generated. In addition, the process of characterization of pyrolysis products is carried out so that it is known whether the product produced is in accordance with the desired oil characteristics. The product is analysed using a Bomb Calorimeter in the form of calorimeter value. The properties of the product compound are characterization using the GC-MS (Gas Chromatography-Mass Spectroscopy) instrument. The liquid product is also tested for its properties such as density and so forth. This template, modified in MS Word 2007 and saved as a "Word 97-2003 Document" for the PC, provides authors with most of the formatting specifications needed for preparing electronic versions of their papers. All standard paper components have been specified for three reasons: (1) ease of use when formatting individual papers, (2) automatic compliance to electronic requirements that facilitate the concurrent or later production of electronic products, and (3) conformity of style throughout a conference proceedings. Margins, column widths, line spacing, and type styles are built-in; examples of the type styles are provided throughout this document and are identified in italic type, within parentheses, following the example. Some components, such as multi-leveled equations, graphics, and tables are not prescribed, although the various table text styles are provided. The formatter will need to create these components, incorporating the applicable criteria that follow.

## II. RESEARCH METHODOLOGY

### A. Material

The raw material used in the research was EVA sponge from shoe factories around Yogyakarta. The natural zeolite catalyst used was ready-made ones and distilled water used were purchased from the Bratachem chemical store in Yogyakarta.

The tools used in this study were a series of pyrolysis devices consisting of a pyrolysis reactor, condenser, reactor suspension, condenser suspension, and a glass beaker as a reservoir for the oil produced. The series of devices used can be seen in Figure 1. Other equipments used were scales to calculate the weight of raw materials for sponges waste, catalysts, and pyrolysis products, scissors, measuring cup, 100 ml beaker, 25 ml picnometer, sample bottles, lumps, pestle, oven, muffle, and a series of distillation devices which consist of three neck flasks, ball coolers, and lab scale condensers. The series of distillation devices can be seen in Figure 2.

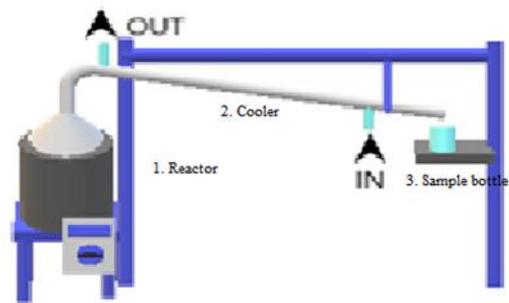


Fig. 1. Pyrolysis Reactor

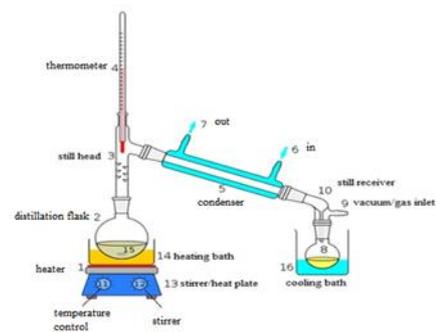


Fig. 2. Distillation Equipment

### B. Testing Instrument

The instruments used were calorimeter bomb as an instrument to test the number of calories of the product and GC-MS to determine the types of compounds found in the final product. The analysis of product characteristics was based on the desired oil characteristics. Calorific value testing was conducted at the Integrated Research and Testing Laboratory, Gadjah Mada University, Yogyakarta. Furthermore, type of compound analysis by Gas Chromatography- Mass pec spectrometry ( GC-MS) was carried out at Ahmad Dahlan University Pharmacy Laboratory, Yogyakarta, and the analysis of product characteristics was carried out at the Gas and Petroleum Technology Laboratory, Department of Chemical Engineering, Gadjah Mada University, Yogyakarta.

### C. Method

The research started with the preparation of raw materials and catalysts. The natural zeolite catalyst in the form of crystals was initially crushed by a crusher until smooth. The zeolite powder is soaked in distilled water with stirring for 1 hour at 25oC. The soaked catalyst was filtered with filter paper and then oven at 100oC for 3 hours. The natural zeolite

catalyst in the form of powder was refined by Porcelain Ware Crucible Gooch and then filtered with a 100-mesh filter before calcination with a muffle at 500oC for 4 hours. The zeolite powder was washed with distilled water to pH 7 and then dried in an oven at 110oC until dry. Preparation of raw materials was done by cleaning and choosing the sponge of slippers material so that waste other than sponge waste does not add weight. Next, the sponge slipper was cut with scissors to 1-2 cm<sup>2</sup> to accelerate the heating. Sponge was weighed up to 200 grams and mixed with natural zeolite catalyst (varies between 2, 4, 6, 8, and 10 grams) and then hydrolyzed. Pyrolysis was done by heating the reactor until it reaches a temperature of 450oC. After the temperature is reached, the processing time was varied with 60, 90, 120, 150, and 180 minutes. The liquid product was collected with a beaker and the volume was measured using a measuring cup, and the product was distilled. Distillation process carried out to purify the pyrolysis results. Distillation was done by assembling the distillation apparatus then inserting the pyrolysis product and heating it with boiling water temperature (100oC) for 180 minutes until no water drips from the condenser discharge pipe. The final product was tested for calories, the types of compounds contained, and the characteristics of the oil. Calories contained in oil were analyzed by a calorimeter bomb and the types of 2. MS.

### III. RESULTS AND DISCUSSION

The resulting pyrolysis oil with natural zeolite catalyst is dark brown with a scent like gasoline as can be seen in Figure 3.

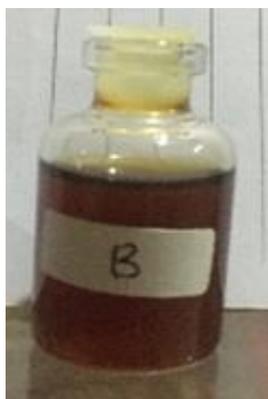


Fig. 3. Oil Product of Pyrolysis Process

#### A. Result of catalyst weight variable

The catalyst weight variable in the pyrolysis process was carried out at a fixed temperature of 450oC with a processing time of 180 minutes. The weight of the catalyst used varied between 0, 2, 4, 6, 8, and 10 grams. The result of pyrolysis with catalyst weight as variable produced the highest product yield at 4 gram catalyst weight, with a yield of 51.220%. Whereas with the weight of catalysts 0, 2, 6, 8, and 10 grams the yields were 37.770%, 46.386%, 49.250%, 43.450%, and 37.224% respectively. From these results it can be seen that the product yield increases with the addition of catalysts, from 0 to 4 grams by weight of zeolite catalyst. But after an increase in the amount of catalyst, a decrease in product yield happened, this is likely because of saturation of the catalyst because the active side of the catalyst were used up and that causes a decrease in performance of the catalyst. Another possibility is that the natural zeolite catalyst has not been fully

activated causing the catalyst to reach its optimum point quickly and at the same time the decomposition process became ineffective [16][17]. Another possible cause is the presence of bulk in the reactor so that the catalyst's role is less than optimal. The results of pyrolysis catalyst weight variation can be seen in Table 1.

TABLE I. THE RESULT OF CATALYST WEIGHT VARIATION TO PRODUCT YIELD

Weight of catalyst (gram)	Yield (%)
0	37.770
2	46.368
4	51.220
6	49.250
8	43.450
10	37.224

#### B. Result of the reaction time variable

The temperature of pyrolysis process using reaction time as variable was regulated at 450oC, the weight of catalyst was 4 grams, and the time variations used were 60, 90, 120, 150, 180, and 210 minutes. The results of pyrolysis process using reaction time variable produced the highest yield at 180 minutes (37.77%) and decreased when the time began to reach 210 minutes. This is likely to occur because the catalyst used has a saturation phase at 180 minutes, so the active side of the catalyst is used at the maximum reaction time of 180 minutes. The results of pyrolysis on time variations can be seen in Table 2.

TABLE II. THE RESULT OF VARIATION TIME TO % YIELD OF PRODUCT

Time Process (Minutes)	Yield (%)
60	27.202
90	28.500
120	29.84
150	32.65
180	37.77
210	35.12

#### C. Characteristic of pyrolysis product

##### 1. Characteristic of pyrolysis product: purification product

The resulting pyrolysis product consists of top yields and bottom yields. In this study, the main results of testing the product for pyrolysis results without catalysts are smaller than using catalysts. The yield without catalyst was 14.549% while the yield with catalysts was 15.203%. This result is caused by the catalyst reaction that can accelerate the distillation reaction; this phenomenon happened because the gases dissipated [18]. The lower yield consisting of pyrolysis components that have not been degraded completely with and without the catalyst is known in which the results without catalyst is 49.662% while the results with the present of catalyst is 50.625%. These results indicate that the bottom yield in the form of residue is greater when catalyst is used.

##### 2. GC-MS analysis result of pyrolysis product before distillation process

The pyrolysis product tested was the product which was found from the optimum condition (catalyst weight of 4 gram with a processing time for 180 minutes). GC-MS results from the fraction before distillation showed that the component which had a fairly large percentage composition was Cyclopentane, 1,1'-[3-(2-Cyclopentylethyl)-1,5-Pentanediy] Bis-(CAS)1,5-Dicyclopentyl-3-(Cyclopentylethyl)-Pentane (19.77%). A visual image of the chromatogram showing the results is shown in Figure 4 and the percentage graph of pyrolysis product composition before distillation can be seen in Figure 5.

Figure 4 shows that the peaks of GC-MS results tend to be parallel, thus indicating that the constituent components have similar amount to each other. The predominant functional group is the alkane. Alkanes are known to be compounds containing petroleum that are used as compilers of polymer goods such as used sponge sandals such as EVA. Figure 5 shows the amounts of alkanes was 66% while alkenes is in the second place with a total amount of 14%. Alcohol is ranked third with a total amount of 11%. Carbon, phenyl, and carboxylic acids have the lowest composition of all.

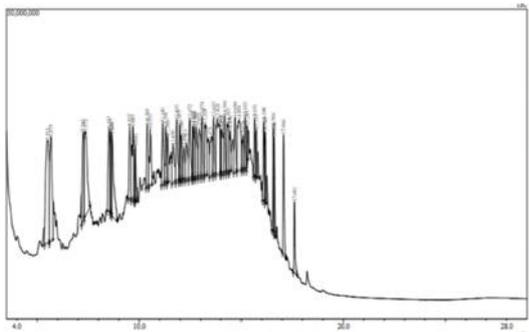


Fig. 4. Chromatogram of the Lower Distillation Fraction

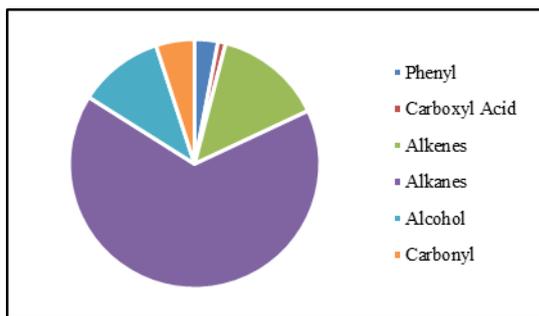


Fig. 5. The result of component product before distillation process

3. GC-MS analysis result of pyrolysis product after distillation process

The results of GC-MS analysis of pyrolysis products after distillation showed that the distilled component with the highest content of 3-Nitro-1,2-Benzenedicarboxylic acid (88.11%) which can be seen on the chromatogram resulting from GC-MS analysis in Figure 6. Figure 6 shows the highest peak result on the pyrolysis process after distillation. The functional groups in the result are dominated by the

type of carboxylic acid (unsaturated), this is probably due to the raw material of EVA type of sponge slippers. The graph of compositions of pyrolysis products after distillation can be seen in Figure 7. Figure 7 showed that carboxylic acid dominates the amount of compound content in the sample followed by the significant amounts of ketones and alkenes. This happens because the alkane fraction experiences gas or short chain integration. In addition, the distillation reaction also undergoes polymer breakdown from ethylene vinyl acetate compounds.

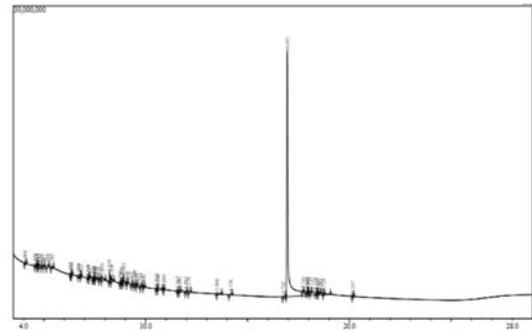


Fig. 6. The Chromatogram of the up distillation result

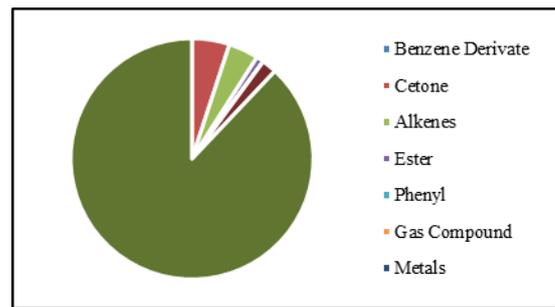


Fig. 7. The Component of up fraction of Pyrolysis result

4. GC-MS analysis result of pyrolysis product on yield fraction

GC-MS results on yield products indicate that there are constituent compounds in the form of 1,13-Tetradecadiene with high composition of 10.07%. Visualization of chromatograms can be seen in Figure 8. Figure 8 showed the existence of parallel peaks which indicates that the components of the yield product have similar compound content. Component or functional group that dominates is alkane (unsaturated) hydrocarbon compounds. Graphs of percentage composition of yield products can be seen in Figure 9 which also showed that alkanes dominate the amount of compounds contained in the yield phase of pyrolysis product. After alkanes, alcohol and alkenes were also contained in a large amount.

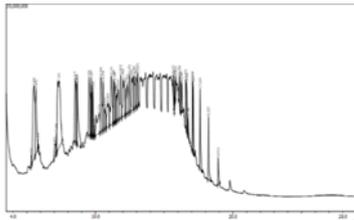


Fig. 8. The Chromatogram result of pyrolysis product on rendement fraction

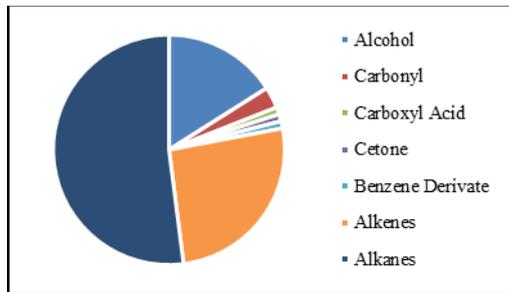


Fig. 9. Components result of Pyrolysis product on rendement fraction

### 5. Calorific value of pyrolysis product (Liquid phase)

The calorific value testing of liquid product of pyrolysis before the distillation process is carried out on a catalyst weight of 4 grams and pyrolysis time of 180 minutes. The results obtained were the calorific value of 10,992.6 calories/gram which was approaching the calorific value of gasoline of 10.509 calories/gram [19].

### 6. Physical characteristic of liquid product of pyrolysis

The characteristics of pyrolysis oil prior to distillation have approached the standard specification of gasoline fuel type (standard 0.744) for the specific gravity, this is based on the specific gravity value of pyrolysis oil which is 0.7930. Viscosity kinematic of pyrolysis oil before distillation was 2,065 mm<sup>2</sup>/s and it meets the minimum standard of gasoline type oil (0.550 mm<sup>2</sup>/s). Another indication of pyrolysis oil before distillation is the viscosity kinematic value that meets the specifications of fuel oil types (minimum standard 2.0 mm<sup>2</sup>/s). Flash point of pyrolysis oil before distillation was <20°C, this result also meets the minimum standard of gasoline oil of 7.2°C. The pyrolysis oil pour point before distillation was 21°C.

## IV. CONCLUSIONS

The optimum yield of EVA pyrolysis process was 51.22% which was obtained at a catalyst weight of 4 grams and a processing time of 180 minutes. In process time variable, the process without the use of catalyst with a processing time of 180 minutes produces a yield of 37.77%. The product after purification produced top yield and bottom yield. The optimum yield produced after the purification process was 15.202%. The bottom yield produced using a catalyst was 50.625%.

GC-MS analysis showed distilled compounds dominated by alkanes with the components being Cyclopentane, 1,1'-[3-(2-cyclopentylethyl)-1,5-

pentanediyl] bis- (CAS) 1,5- Dicyclopentyl-3-(2-Cyclopentylethyl)-Pentane (19.77%). When the distillation was completed, the highest compound obtained was carboxylic acid with an amount of 66.11% while the GC-MS results for the yield of distillation were dominated by 1,13-Tetradecadiene compounds (10.07%). The calorific value of the pyrolysis before distillation with a catalyst weight of 4 grams and the reaction time of 180 minutes was 10992.6 calories/gram and this value approaches the calorific value of gasoline which is 10509 calories/gram. The analysis of the physical characteristics of pyrolysis oil showed that the pyrolysis oil produced is in accordance with the specifications of the type of gasoline and diesel fuel oils.

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