Product distribution of pyrolysis of polystyrene foam waste using catalyst of natural zeolite and nickel/silica

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Abstract. Polystyrene, especially polystyrene foam product, has been widely utilized in daily life that lead to generate polystyrene foam waste in the environment. The waste is very hard to degrade in the nature. The aims of this study are to investigate pyrolysis for polystyrene foam waste that can produce liquid products for fuel. The study comprises characterization of polystyrene foam and pyrolysis process with and without catalyst (zeolite and nickel/silica). The decomposition of polystyrene foam occurred at a temperature of 360–460 °C. Pyrolysis was carried out at the range of 360–460 °C based on the decomposition temperature. The yield of the liquid product increases with increasing temperature. Catalyst has boosted the increase of yield. The nickel/silica shows better performance than zeolite on boosting the yield of liquid product. The liquid product contains many aromatic compounds such as benzene, toluene, styrene and others

Keywords : Pyrolysis, Polystyrene, zeolite and silica.

1. Introduction

The plastic waste problem has promoted the utilization of pyrolysis. In the pyrolysis process, the polymer or plastic material is heated at high temperatures, so that its macromolecular structure will split into smaller molecules and hydrocarbons of a wide range [1]. The pyrolysis process involves heating at a temperature of 400-700°C. The organic components will decompose to produce liquids (oils) and gases useful for fuels or chemicals [2]. Thermo gravimetric analysis (TGA) is widely selected as a useful technique for studying the solid matter decomposition process. Information from this technique can be useful for designing reactors, where thermal decomposition occurs [3,4,5] .

Wang et al. [6] studied the morphology of polypropylene and polyethylene waste during the pyrolysis process. Plastic pyrolysis involves four stages: melting, two stages of decomposition which are indicated by bubble formation caused by volatile material evaporation, and ash buildup. Each stage is characterized by phase and morphological changes. After melting, the phase change behavior is very similar to the behavior of boiling and evaporating water. The deposits or ash consist of impurities and additives incorporated in plastics.

The pyrolysis process generally produces liquid products, gases and residues. The residue is produced from inorganic materials contained in plastic (additives). The amount of each product depends on the type of material being processed. Williams and Williams [7] stated that the results of pyrolysis of plastic materials vary widely, some of which produce gas between 9.79-88.76% and liquid (oil) in the range of 18.44-57.11%. The higher the pyrolysis temperature, the greater the amount of aromatic product in the liquid product.

Some studies of plastic waste pyrolysis have been done with various combinations of raw material and processes [8, 9, 10, 11, 12]. However, the results are still not satisfying, both in terms of yield and product distribution. The use of catalysts should be considered to increase yields and get expected products.
In this research, the catalysts i.e. zeolite and nickel/silica are applied for pyrolysis of polystyrene foam. The goal is to produce a flammable liquid product (fuel).

2. Experimental

2.1. Materials

Polystyrene foam waste was collected and crushed into small size. Natural zeolite with size of 100 mesh and Ni/Si-Al catalyst are prepared for pyrolysis.

2.2. Method

2.2.1. Preparation of materials

Polystyrene foam waste materials cleaned and cut into small pieces. The material was then dried in an oven for 2 hours at a temperature of 80 °C. The natural zeolite was used with drying treatment only, without activation.

2.2.2. Decomposition test

Decomposition temperature was investigated using a thermo gravimetric analyzer (TGA), which can also be used to determine the residual amount. The heating rate of the test was 20°C/min from ambient temperature up to 1000°C with nitrogen gas injection.

2.2.3. Pyrolysis

The pyrolysis was carried out in the reactor that operate at maximum temperature of 700 °C and utilized with water condenser and product tank. The pyrolysis product condensed along the condenser and collected in the container. The temperature rise and final temperature were controlled using an electronic control device. The temperature range of pyrolysis was determined by decomposition temperature from TGA test. The pyrolysis process was carried out in three different steps. First step, the polystyrene foam material (130 gr) were processed without catalyst. The pyrolysis process was repeated at least three times to gain the reliable data. The operating conditions of the reactor was optimized to produce maximum liquid yield, at 380, 420 and 460 °C.

Second step, polystyrene foam were mixed with a zeolite catalyst content of 10% wt/wt at temperature of 460°C. Third step, polystyrene foam were mixed with a nickel/ silica (Ni/Si) catalyst content of 10% wt./wt. at temperature of 460°C. The liquid product of every step was collected for checking the yield and then analyzed using GC-MS spectrometer.

3. Result and discussion

3.1. Thermal decomposition

Thermal decomposition test has been carried out with TGA. The test results are shown in Fig. 1. Fig. 1 shows a thermogravimetry (TG) curve and a derivative thermogravimetry (DTG) curve. The TG curve shows that the thermal decomposition of polystyrene foam takes place from 360 °C and ends at 460 °C. The highest decomposition rate was reached at 410 °C as shown in the DTG curve.

Polystyrene foam decomposition temperature occurs in a relatively narrow range, compares to packaging plastic waste in the range 300-500 °C or PVC that decomposes from 200-800 °C [13].
Figure 1. TG and DTG curve of polystyrene foam

The temperature of pyrolysis process is to be based on the temperature of the thermal decomposition. The pyrolysis process of polystyrene foam should be carried out at the temperature of the thermal decomposition at the range of 360-460 °C.

3.2. Yield of pyrolysis of polystyrene foam

Pyrolysis without catalyst is carried out at a temperature of 380, 420 and 460 °C. Yields of liquid at various temperatures of pyrolysis without catalyst are shown in Fig. 2. The pyrolysis process is highly influenced by the process temperature. The yield of the liquid increases with increasing process temperature.

Figure 2. Volume of liquid and mass of residue at various temperature
Based on temperature of highest yield in Fig. 2, catalytic pyrolysis using zeolite or Ni/Si has carried out at 460 °C. The yield of liquid are presented in Table 1.

| No | Catalyst               | Yield (%) |
|----|------------------------|-----------|
| 1  | Without catalyst       | 71.53     |
| 2  | Zeolite                | 86.69     |
| 3  | nickel/silica (Ni/Si)  | 91.65     |

The use of zeolite in pyrolysis of polystyrene foam waste, has increased yield of liquid product. For example at a temperature of 460 °C, every 130 g of polystyrene foam, with pyrolysis without catalyst produces 93 ml of liquid product or yield of 71.53%. While with zeolite catalyst results in a yield of 86.69% or 112.70 ml, and with nickel/silica catalyst results in a yield of 91.65% or 119.15 ml.

Pyrolysis with a natural zeolite catalyst and also with a Ni/Si catalyst shows an increase of yield. This is due to the utilization of natural zeolite catalysts has affected the decomposition process. The selectivity of natural zeolite as a catalyst on hydrocarbon decomposition process is very good at high Si / Al ratio, since it tends to absorb non-polar molecules. In addition, natural zeolite also has a basic framework consisting of tetrahedral units of AlO$_4$$^{2-}$ and SiO$_4$. Both are interconnected through the O atoms, and the structure of Si$_4^+$ can be replaced with Al$_3^+$, or vice versa. The role of zeolite as a catalyst in pyrolysis is in line with the use of Y-zeolite since 1962 as a catalyst in the Petroleum Industry. The data show that the use of Y-zeolite can produce 25% more products and produce less coke than the use of γ-Alumina previously used in the industry [14]. Zeolite-Y has a high selectivity in petroleum cracking [15]. With Ni/Si catalyst, the yield of liquid increases to 91.64%. This is probably due to Ni being embedded in silica having an acidic surface that allows the carbocation mechanism, since the metals will provide an active site on the surface of the carrier.

3.3. Product distribution of pyrolysis of polystyrene foam

Chromatograms of the liquid products at various process, i.e. without catalyst, with zeolite catalyst and with Ni/Si catalyst, respectively are shown in Fig. 3-5. Figure 6 shows the product distribution of the liquid product of pyrolysis.

![Chromatogram](image-url)
Figure 4. Chromatogram of liquid product of pyrolysis with zeolite catalyst

Figure 5. Chromatogram of liquid product of pyrolysis with Ni/Si catalyst

Figure 6. Product distribution of liquid product of pyrolysis
Pyrolysis without catalyst, the dominant compounds are styrene (50%) and ethyl benzene (34.5%). The use of a catalyst in polystyrene foam pyrolysis aims to decompose polystyrene to become a smaller compound. The double bond in the styrene monomer compound can be broken into long chain hydrocarbon compounds in the presence of a catalyst. The results show that the liquid product mostly still contains styrene.

On the other hand, pyrolysis with natural zeolite catalysts results in the decrease of toluene content to 16.53%, but new compounds i.e. ketones and di-phenyl compounds, are formed until 47.69% of total contents. Probably some elements in the zeolite react with decomposed polystyrenes. Zeolite is a crystalline alumina silicate with a three-dimensional polymeric form. The structure of the skeleton is built by tetrahedral (SiO$_4$)$^4^-$ and (AlO$_4$)$^5^-$ which is bound by the use of one oxygen atom by 2 tetrahedral so that each tetrahedral will bind to the other 4 tetrahedral. The oxygen element reacts to form a ketone compound. Pyrolysis with alumina silica catalyst produces styrene (59.22%), isopropyl benzene (4.06%) and di-phenyl compounds (11.49%). The other compounds: i.e. benzene (0.65%), ketone (0.28%) and carboxylic acid (17.92%) are also formed. The formation of new compounds shows that the activity of the catalyst are not optimal yet.

The mechanism of the catalytic pyrolysis using Ni/Si is an ion-carbon intermediate mechanism. Ni is attached to silica has an acidic surface that allows the mechanism to occur. Breaking of C-H bonds from polystyrene molecules can form both carbonium and carbocation ions. The carbonium ion is also the intermediate of the C-C bond forming and breaking reaction, which causes the volume of liquid product to increase as well as the formation of new compounds [15].

The formation of benzene compounds and isopropyl benzene shows that the C = C bond in the styrene monomer has broken. However, the presence of aromatic compounds shows that the catalyst is still not able to break all the closed-chain aromatic compounds into a shorter chain-linked compound. There is still a few amount of the C = C bond left behind.

4. Conclusion

The thermal decomposition test of polystyrene foam waste has been conducted to determine the temperature of pyrolysis. Polystyrene foam waste has a decomposition temperature of 360-460 °C. The yield of liquid increases with the increase of temperature of pyrolysis. The use of catalysts both zeolite and Ni/Si results in the increase of yield. The catalysts are able to decompose polystyrene foam with higher yields than without catalyst.

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