Potential use of waste rubber tires containing polystyrene to produce gasoline-like hydrocarbon by thermal catalytic cracking

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Abstract. Rubber tire waste from abundant amount of vehicles are naturally unbiodegradable, without proper treatment they shall accumulate uncontrollably. Polystyrene is a synthetic polymer contained in rubber tires and it is usually unrecycled, therefore it needs a further study to recycle polystyrene effectively. In this research, waste tires are used to produce gasoline-like hydrocarbon using thermal catalytic cracking method uses high temperatures and catalysts of NaOH and zeolite. The ratios of zeolite and NaOH are 0:1 ; 2:3 ; 1:1 ; 3:2 ; 1:0 with waste tire mass of 400 g, the temperature used varies, which are 300°C, 350°C, and 400°C with pyrolysis durations of 1, 2 and 3 hrs. The thermal catalytic cracking method is a simple solution to break the hydrocarbon chains of polystyrene with considerably shorter length of time aided by the catalysts. The highest volume of gasoline-like hydrocarbon produced is 255 ml with 2 hrs pyrolysis at 400°C. The addition of 25% NaOH and 75% zeolite as the catalyst in the process has given the most favorable result in research octane number (RON) that is 113. The maximum point of heating value is 10223.161 cal/g with 3 hrs pyrolysis duration at 400°C temperature.

1. Introduction

Tire production in Indonesia continues to increase from year to year. Along with that, the waste of unused tires in the environment is also increasing. A problem emerges because the waste tires are difficult to decompose naturally. Therefore, it takes some efforts to convert waste tires into something useful, one of them is by converting waste tires into liquid fuel or gasoline by catalytic cracking process. Rubber tires containing polystyrene are highly difficult to be cracked compared with other thermoplast, because of the bonding structures and the cracking pattern. Therefore, catalysts such as zeolite and NaOH are required for more effective catalytic cracking. The catalyst is capable of improving the pyrolysis process by decreasing the temperature and the decomposition time, resulting in maximum liquid fuel yield [1].

Polystyrene is a molecule that has a light molecular weight, formed from styrene-sweet smearing monomers. Excess polystyrene is light, hard, heat resistant, slightly stiff, not easily broken and non-toxic. Polystyrene is a paraffinic hydrocarbon polymer formed by polymerization reaction [2]. The polystyrene-forming reaction is:

\[
\text{many} \quad \text{styrene} \quad \rightarrow \quad \text{polystyrene}
\]
Liquid hydrocarbon production process from polystyrene is able to be conducted by cracking process. This process uses high temperatures, so some catalysts such as zeolite and NaOH are needed to lower the temperature and shorten the processing time [4]. The zeolite structure consists of a negative charge, a three-dimensional framework of tetrahedral SiO\textsubscript{4} and AlO\textsubscript{4} that are combined to form a sodalite octahedral. If 6 pieces of sodalite are connected by a hexagonal prism, those will form a tetrahedral pile. This type of pile forms a large hole (supercages) and a ∼ 13Å diameter. The holes (supercages) can be formed from 4 scattered tetrahedral crystals, each of which has 12 oxygen rings and a diameter of 7.4 Å. These holes when interconnected will form a large pore system of zeolites [5], [6]. Each of the aluminum atoms in the tetrahedral coordinates in the frame carries a negative charge. The negative charge in this framework is replaced by a cation located in a non-specific framework. Zeolite contains a cross-linked zig zag system of 10 rings to produce a three-dimensional cavity system. Pore diameters range from 5.1 - 5.5 Å. Zeolite has a unique structure which allows the reaction to run well because the residence time for each reactant will be longer. In addition, zeolite also has a high selectivity to reactants and products. The zeolite frame structures are shown in Figure 2.

Cracking used rubber tires at high temperatures is the simplest process for recycling used rubber tires. In this process, the polymer material or used rubber tires are heated at high temperatures. This heating process causes the macro molecular structure of the rubber to break into smaller molecules and shorter chains, these forms the short chains of hydrocarbon. The resulting product is a gas fraction, a solid residue and a liquid fraction, containing paraffins, olefins, naphtha, and aromatics [4], [8-11]. This process has a problem that is the use of high temperature over 900°C, but it can be solved by using catalysts [12,13].

The main purpose of this research is to study the potential use of used rubber tires containing polystyrene as the raw material of liquid fuel production (gasoline-like hydrocarbon) by using zeolite and NaOH as catalysts [14]–[16]. This research was performed in order to determine the optimum operating conditions of liquid hydrocarbon production by catalytic cracking process of used tires and
determining the model of empirical equation of used tires conversion process into some liquid hydrocarbon (gasoline-like hydrocarbon).
This catalytic cracking process was carried out by heating the mixture of the scrap used tires with the catalysts at the maximum temperature of 400°C with the atmospheric pressure inside a fixed bed reactor made of stainless steel. The resulting gas is condensed to obtain liquid fuel. To obtain optimum yield of liquid product and minimum residue, this research uses varied variable designs.

2. Material and Method
The materials used in the research were waste rubber tires containing polystyrene from motor vehicles, which were cut into small pieces with size 1cm x 1cm, and then weighed according to experimental variables 400 g. The catalysts used were natural zeolite and NaOH commercially sold in markets. The rubber tire pieces then mixed with the catalysts with the ratios of 1:0 ; 3:2 ; 1:1 ; 2:3 ; 0:1 in accordance with experimental variables, and then inserted into the reactor. Afterwards, the catalytic process began by heating the reactor using electricity until reaching the determined temperatures of 300, 350 and 400°C with process time of 1, 2 and 3 hrs. The procedure is repeated for each catalysts’ ratios of zeolite:NaOH which were 1:0 ; 3:2 ; 1:1 ; 2:3 and 0:1. The formed vapor was drained from the top of the reactor for cooling process through a heat resistant tube. While the wax that came out through the bottom of the reactor was accommodated in a beaker glass. The experiment was considered to be over if there was no more flowing vapor or dripping wax.

The catalyst mass was 200 g and the cooling water temperature used was between 12-15°C, ice and salt additions were necessary to maintain the cooling water temperature. The natural zeolite as one of the catalysts needed to be activated before use. This experiment used 20 mesh of 1000 g zeolite, dried in the oven until water and impurities were estimated to be vaporized thoroughly.

Figure 3. The device scheme for catalytic cracking process [17]
3. Results and Discussions

The parameters used are flash point, calorific value, heating time and volume of the gasoline-like hydrocarbon produced. The resulting liquid product was analyzed using IROX 2000, Viscometer Bath SETA KV-6 and Bomb calorimeter Parr 6400.

3.1. Flash Point

Flash Point is the temperature at which fuel will produce a spontaneous fire (burning) at the time it is subjected to a fire source. Flash point is the lowest temperature where the oil (oil vapor) and its product lights up when it is exposed to sparks and then turned-off quickly afterwards. Petroleum that has the lowest flash point will be hazardous, because it is highly flammable. If the oil has a high flash point, it is also unrecommended, because it will be difficult to experience combustion. But in terms of safety, the oil which has a high flash point is considered safe because it will not be easily burned. The standard flash point of gasoline is 37.8-38°C, based on that, it is expected that the pyrolysis results are capable of representing qualifications of gasoline [9], [16], [18]. The following is the analysis results of flash points on various catalysts compositions.

![Figure 4. The effect of catalysts composition ratios (NaOH:zeolite) on flash point at various temperatures](image)

From the results shown on figure 4, the composition of 25% NaOH gives the highest flash point that is 33°C to the gasoline-like hydrocarbon produced at 300°C, because the 25% NaOH raises iso-octane content that gives a positive impact to the flash point. However, the composition of 50% up to 100% NaOH resulting declining to the flash point, the excessive concentration of NaOH will lead to obstruction to zeolite's structure. Therefore, the lowest flash point given by 100% NaOH at temperature of 300°C that is 30°C.

3.2. RON (Research Octane Number)

The research octane number (RON) indicates the durability of the fuel in handling pressure before it burns spontaneously. The RON on the resulting liquid volumes are expected greater than 88 which is the standard RON for gasoline [19]. The following figure shows RON values in the volume of liquid.
Figure 5. The effect of catalysts composition ratios (NaOH:zeolite) on RON at various temperatures

Figure 4 shows that the highest RON is 113 at 300°C with 25% NaOH composition, the addition of 25% NaOH forms mesopores in zeolites that increases the silica diffusion process. However, the addition of 50% to 100% NaOH causes a decrease of RON. Thus the lowest RON is 94.5 at 400°C with 100% of NaOH. This is due to the reduced porosity of zeolite as the result of too high temperature (above 350°C) gives a destructive impact to zeolite frames causing smaller amount of aromatic compounds resulting on RON decrease. RON is directly proportional to the aromatic content, the aromatic compound is capable of increasing the RON value due to its ability in giving the branch to the aromatic chain [20].

3.3. Pyrolysis Duration
The time varied by 1, 2, and 3 hours which aims to see the effect of pyrolysis duration on the volume of gasoline-like hydrocarbon produced. The results are at 400°C temperature shown in figure 5.

Figure 6. The effect of pyrolysis duration on the volume of gasoline-like hydrocarbon produced

Pyrolysis duration affects the gasoline-like hydrocarbon production because the longer the process of pyrolysis then the product formed will be increased. In figure 5, it can be seen that the volume of liquid fuel product has increased at 2 hours that is 255 ml and decreased at 3 hours to 247 ml. Increased time limits on optimum points will improve gas and coke formations. This is due to secondary gas decomposition formed from the primary vapor produced from pyrolysis of the materials at the maximum time [21].
3.4. Calorific Value

The calorific value is a number which denotes the amount of heat/calories produced from the combustion process.

![Graph showing the effect of pyrolysis duration on calorific value of gasoline-like hydrocarbon produced.](image)

**Figure 7.** The effect of pyrolysis duration on calorific value of gasoline-like hydrocarbon produced

Based on figure 5 above, it shows that longer pyrolysis duration will increase the caloric value, that occurs because the longer the heating time causing the temperature inside the reactor gets higher so that the amount of fuel volume will be greater and it increases the calorific value [22]. The maximum calorific value obtained at 3 hours process that is 10223.161 cal/gr.

4. Conclusions

- The highest flash point is 33oC with the composition of 25% NaOH and 75% zeolite at 300oC. The lowest flash point is 30oC given by 100% NaOH without zeolite addition at temperature of 300°C.
- The highest RON is 113 at 300°C with 25% NaOH and 75% zeolite composition, the lowest RON is 94.5 at 400°C with 100% of NaOH without zeolite addition.
- The best pyrolysis duration to produce gasoline is 2 hrs which produces 255 ml at 400°C temperature.
- The maximum calorific value is 10223.161 cal/g with 3 hrs pyrolysis at 400°C temperature.
- This research requires further investigations in order to produce qualified and purified fuel in terms of qualitative and quantitative regarding the compositions of zeolite and NaOH as catalyst.

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