DEGRADATION OF NATURAL RUBBER INTO AROMATIC COMPOUNDS BY THE PYROLYSIS METHOD

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ABSTRACT

This study aims to observe the mechanism of thermal cracking of natural rubber into aromatic compounds by the pyrolysis method. Variations used in this study were cracking temperatures between 300 – 400ºC with a range of 50ºC and reaction times between 15 – 90 minutes with a range of 15 minutes. The liquid volume obtained ranged from 32.4 – 119.3 mL, with the highest liquid volume obtained at a pyrolysis temperature of 400°C with a pyrolysis time of 90 minutes. Natural rubber cracking begins with the polyisoprene chain-breaking reaction to form aromatic compounds, which are affected by temperature and processing time. The types of compounds contained in the liquid were observed by using Gas Chromatography-Mass Spectrometry (GC-MS). According to the results of the GC-MS analysis, Benzene aromatic compounds show a marked increase in yield with increasing temperature. In contrast, dipentene compounds experience a decrease in yield at high temperatures. This indicates a secondary reaction from dipentene to form the aromatic compound Benzene Toluene Xylene (BTX).

Keywords: natural rubber, polyisoprene, pyrolysis, aromatic compounds, reaction mechanism, gas chromatography-mass spectrometry

INTRODUCTION

Aromatic compounds are chemicals used as organic solvents, dyes¹, and precursors² in synthesizing food³, pharmaceuticals, and other chemical products. Most aromatic compounds are produced from petroleum derivatives into Benzene, Toluene and Xylene (BTX) compounds⁴. Compounds with cyclic molecular shapes are also classified as aromatic compounds⁵, dipentene⁶, and ethylbenzene⁷. The rubber plant (Hevea brasiliensis) is a plant that grows well in tropical climates⁸, so it grows a lot in the Southeast Asian region⁹. Indonesia is the second-largest natural rubber producer worldwide, with total production reaching 4,160,000 tons in 2020¹⁰. The problem in the Indonesian rubber industry is the emergence of a white fungus disease¹¹ which reduces the quality of the rubber produced¹². According to the Indonesian Rubber Council, this disease also causes a decline in the export value and price of rubber on the market¹³.

Pyrolysis is a method of breaking down a substance into smaller molecules by subjecting it to high temperatures without the presence of air, especially oxygen¹⁴. The process of pyrolysis will produce products in the form of solid, liquid and gas¹⁵,¹⁶. In the pyrolysis process, the hydrocarbon chains will be cut into short chain molecules¹⁷,¹⁸. The hot gas will be followed by a cooling process so that the gas condenses into a liquid¹⁹. The degradation of polyethylene at 700°C for 35 minutes resulted in an aromatic compound of 10.91%. As for the aromatic compounds produced from the degradation of polyisoprene at 430°C for 30 minutes¹⁴, they produced 50% aromatic compounds. This shows that the yield of aromatic compounds from cracking polyisoprene is quite good compared to cracking from other compounds¹⁸. In addition, the widespread use of aromatic compounds in various fields of life and the relatively high price of aromatic compounds, around US$ 134 per 1.5 mL²⁸, makes natural rubber an excellent raw material¹⁰ for conversion into aromatic compounds²⁹. This study uses a vacuum pyrolysis process to produce aromatic compounds from natural rubber raw materials³⁰. This research is focused on observing the effect of pyrolysis temperature and time on liquid volume, yield and aromatic compounds produced from the pyrolysis process.
EXPERIMENTAL

Natural rubber degradation apparatus can be seen in Fig.-1, consisting of a fixed bed type reactor, condenser, vacuum pump, and centrifugal pump to circulate cooling water and to regulate process conditions equipped with a control panel and pressure gauge in the reactor. In the series of apparatus, there are also cooling water tanks and liquid product storage tanks. The research started with raw materials preparation by reducing the size of natural rubber to ± 2 x 2 cm. Raw materials were weighed as much as 200 g for each sample. Samples were put into the fixed bed reactor (R-01). Close the reactor and turn on the vacuum pump for 10 minutes to remove any air. Set the reactor temperature through the control panel. After reaching the maximum pressure indicated on the pressure gauge, the valve at the top of the reactor is opened so gas can flow into the condenser (CD-01). Collect the condensation liquid in V-01. Sampling is done every 15 minutes. This step was repeated for each temperature variation of 300ºC, 350ºC and 400ºC. Samples were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) to determine their aromatic compounds' content.

RESULTS AND DISCUSSION

The Effect of Pyrolysis Temperature and Pyrolysis Time on Liquid Volume

Figure-2 shows that the liquid product produced in each sample produces a different color, from clear to blackish brown. This indicates differences in the composition of the aromatic compounds produced and the polyaromatic compounds as side reactions. Temperature variations also result in color differences in the samples. This explains that the higher the temperature, the darker the color of the resulting sample due to the reformation of monomers into dimers and trimers.

In Figure-3 it can be observed the effect of pyrolysis temperature and time on the volume of natural rubber degradation products. The volume gain affected by temperature and pyrolysis time produces the same trend for each variation; with increasing temperature and residence time, more volume is produced. This is because the energy in the reactor will increase with increasing temperature and cause the breaking of the polymer chains in natural rubber to be faster. Termination of the polyisoprene chain starts from the
homolytic termination of the β bond, which will form two free radical chains\textsuperscript{23,26}. At 400°C and a residence time of 90 minutes produced the most volume 119.3 mL. It is shown that the selection of temperature and pyrolysis time makes the product produce a lot. It is better if the temperature and pyrolysis time increased by paying attention to the by-products produced.

![Fig.-3: The Effect of Pyrolysis Temperature and Time on Pyrolysis Liquid Volume](image)

**The Effect of Temperature and Time of Pyrolysis on the Content of Aromatic Compounds using Gas Chromatography-Mass Spectrometry (GC-MS)**

This study used variations in cracking temperature and pyrolysis time. The content of aromatic compounds from the analysis of Gas Chromatography-Mass Spectrometry (GC-MS) at each temperature and time variation is shown in the following Figure:

![Fig.-4: The Effect of Time on the Content of Aromatic Compounds Resulting from Pyrolysis at 300 °C](image)

At a temperature of 300°C with a time variation of 15-90 minutes and a range of 15 minutes. Pyrolysis results showed that the dominant compound formed was dipentene. The most dipentene compounds were obtained in the 45\textsuperscript{th} minute. Then it decreased with long residence time. The formation of other aromatic compounds tends to fluctuate from 15 minutes to 90 minutes. However, the tendency of benzene formation is inversely proportional to that of dipentene. At a long residence time, the percentage of benzene produced increases. The detection of the naphthalene compound indicated a side reaction since, at the time of sampling for the first time, namely when the maximum pressure was reached, this condition resulted in the formation of polyaromatic compounds\textsuperscript{24}. The presence of naphthalene affects the color of the pyrolysis liquid, which is darker than the other samples. The benzene and xylene compounds formation indicate that some dipentenes have undergone dehydrogenation and dealkylation reactions\textsuperscript{1}. Figure-5 shows the effect of a temperature of 300°C on the content of aromatic compounds produced through the pyrolysis process. The highest yield of aromatic compounds was dipentene, formed from free radical cyclization reactions resulting from breaking the polyisoprene β bonds. This shows that the β bonds of polyisoprene have been broken under these conditions, and many have been converted to dipentene compounds. Dipentene undergoes a carbon chain termination reaction to form an alkatriene compound.
which then undergoes a cyclization reaction to become a cycloalkene compound. This compound will undergo a dehydrogenation reaction to form other aromatic compounds.

![Graph showing the effect of temperature on aromatic compounds](image1)

**Fig.-5: The Effect of Temperature 300°C Against Aromatic Compounds Resulting from Pyrolysis**

![Graph showing the effect of time on aromatic compounds](image2)

**Fig.-6: The Effect of Time on The Content of Aromatic Compounds Resulting from Pyrolysis at 350 °C**

In Figure-6 it can be seen the effect of temperature of 350°C and the variations in residence time. In Figure 6, the content of benzene compounds is produced more than other aromatic compounds. The large number of benzene compounds at a cracking temperature of 350°C indicates that the cracking of polyisoprene produces many dipentenes. However, dipentenes undergo secondary reactions to form other aromatic compounds. At this temperature, many naphthalene products indicate a side reaction to produce a group of polyaromatic compounds.

![Graph showing the effect of temperature on aromatic compounds](image3)

**Fig.-7: Effect of Temperature 350°C Against Aromatic Compounds Resulting from Pyrolysis**

Figure-7 shows the content of aromatic compounds produced at 350°C. The most significant component of the aromatic compound obtained was 40% benzene. This shows that dipentenes undergo further reactions to become alkatrienes, and then cyclization reactions occur to become cycloalkenes. Cycloalkenes are dehydrogenated and dealkylated to give other aromatic compounds. At this temperature, there is also a content of xylene, ethylbenzene, naphthalene, toluene and dipentene. The presence of dipentene indicates that the conversion to other aromatic compounds still occurs at this temperature and can continue if the temperature is raised. The presence of naphthalene products in this sample indicates a side reaction and affects the colour of the pyrolysis results, becoming darker.
Figure-8 shows the effect of a temperature variation of 400°C, which produces a dominant group of benzene compounds. Many benzene compounds indicate that most of the dipentenes undergo secondary reactions to produce other aromatic compounds. At this temperature, there are also many naphthalene products at the end of the process, indicating side reactions caused by high temperatures and long residence times to produce polyaromatic compounds.

Figure-9 shows that at 400°C, the most component of aromatic compounds is benzene at 43.92%. At a temperature of 400°C, the β bonds of polyisoprene are broken, and many are converted to dipentenes, but dipentenes experience cracking to produce other aromatic compounds through secondary reactions. At this temperature, there is also a content of xylene, ethylbenzene, dipentene, toluene and naphthalene. The presence of dipentene indicates that the conversion to other aromatic compounds is still occurring at this temperature and will continue if the temperature is raised. When compared with the previous temperature, there is a reduction in the percentage of dipentene remaining, which indicates that the higher the temperature, the more dipentene will be converted into other forms of aromatic compounds. And this also indicates that the higher the temperature chosen will produce more aromatic compounds.

**Formation Mechanism of Aromatic Compounds from cis 1,4 polyisoprene**

Degradation of natural rubber begins with the homolytic cleavage of the β bond, which will form two free radical chains that occur at temperatures less than 380°C\(^\text{20}\). This free radical chain will undergo an intermolecular cyclization reaction\(^\text{21}\), forming dipentene and 1,5-dimethyl-5-ethenyl-cyclohexene\(^\text{22}\).

![Degradation Process of cis 1,4 Polyisoprene and Cyclization of Free Radicals](image-url)
Dipentene compounds will undergo isomerization reactions to become terpinolene and α-terpinene and γ-terpinene. Terpene compounds will undergo hydrogenation reactions to become p-cymene. Dipentenes can undergo carbon chain termination at 400°C to form alkatriene compounds which will undergo cyclization reactions to become cycloalkene compounds.

Furthermore, there will also be p-cymene dealkylation reactions and cycloalkene dehydrogenation which will form other aromatic compounds such as benzene and xylene.

Another aromatic compound, namely toluene, is formed from the cracking of natural rubber, which also experiences breaking the β homolytic bond, forming two free radical chains that occur at temperatures less than 380°C. The free radical chain will also undergo a cyclization reaction between its molecules forming cyclohexane, 4-ethyl-. Then cyclohexane, 4-ethyl- will undergo a dehydrogenation reaction to become ethylbenzene and a dealkylation reaction to become toluene, as shown in Fig.-13 below.

Naphthalene is formed from a deuteration reaction between o-benzyne and benzene which produces biphenyl, benzbicyclo [2,2,2] octatriene and benzcycloocta-tetraene. The most abundant naphthalene is produced from the thermal fragmentation of benzbicyclo [2,2,2] octariene compounds.

**CONCLUSION**

Variations of pyrolysis temperature and time significantly affect the volume of liquid and the content of the aromatic compounds produced. The higher the temperature and the longer the pyrolysis time, the liquid volume will increase. Under conditions of low temperature and short residence time, the predominant compound produced is dipentene. However, the percentage of dipentenes continues to decrease at high temperatures and long residence times; this indicates that dipentenes undergo a secondary reaction to form...
other aromatic compounds. The percentage of benzene recovery increases with increasing temperature and
residence time. At a temperature of 300ºC, the dipentene compound still dominates; namely, the fault is
76.02%, decreasing to 53.91% at a temperature of 400ºC.

![Diagram of chemical reactions]

Fig.-14: Formation of Naphthalene Compound

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved
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REFERENCES

2. J.I. Osayi, S. Iyuke, M.O. Daramola, P. Osifo, I.J.V.D. Walt and S.E. Ogbeide, Chemical Engineering
https://doi.org/10.1016/S0165-2370(00)00136-4
5. A. Valiev and D. Zemskii, Web of Conferences, 157, 1(2020),
https://doi.org/10.1051/epjconf/202015702027
http://dx.doi.org/10.31788/RJC.2018.1134035
https://doi.org/10.3390/ijerph15010016

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