The Characterization of hydrocarbon compounds in bio-oil produced by pyrolysis of biomass from the essential oil distilled residue using ZSM-5 and YSZ catalysts

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Abstract. The main hydrocarbon containing in petroleum and natural gas are important feedstocks for various kinds of fuel and petrochemical products, but these non-renewable resources will diminish their supply over time and that is why the development of environmentally friendly hydrocarbon resources whose more secure should be driven. One of the origins could become the residue of the distillation process of essential oils using catalytic pyrolysis that would produce the hydrocarbon distribution products. The use of acid catalysts such as ZSM-5 can improve the hydrocarbon in bio-oil. However, the use of zeolites can mainly accelerate the cracking of long molecules to make hydrocarbon molecules simpler by forming carbonium ions from the carbon-carbon chain. Thus, requiring a modification of the catalyst with adds YSZ catalyst, which can cut off oxygen from the hydrocarbon group is needed to improve the results of catalytic pyrolysis. The results of this study showed that the maximum temperature at 550 °C was able to increase the yield of steam products and the production of non-oxygenated hydrocarbon compounds. Similarly, the optimization condition of the argon gas flow rate is 100 mL/min. In that condition, the fluidization of biomass material occurs maximally, and the occurrence of the heat transfer process is very fast. While the optimum ratio of YSZ/ZSM-5 catalyst was achieved by a 3:2 ratio. YSZ is very effective at 550 °C in assisting ZSM-5 to form non-oxygenated hydrocarbon compounds. It can be proofed by GC-MS results that non-oxygenated compounds produced such a group of non-oxygenated hydrocarbon cyclic, paraffin, and aromatic compounds are dominant.

Keywords: Fuel, YSZ Catalyst, ZSM-5, Catalytic Pyrolysis, Essential Oil Distillation Residue, Hydrocarbon Distribution Product.

1. Introduction
The petroleum and natural gas had been used as a source of fuel and raw materials for the petrochemical industry, basically using aromatics and olefin compounds as raw materials. However, it should underline that petroleum and natural gas are unrenewable resources that will deplete its supply on Earth. Therefore, new resources and newlines as an alternative solution are required. The alternative solution requires should be a guaranteed source in terms of its availability. One such alternative is the use of essential oil distillation residue or better known as lignocellulose biomass. This renewable material is the solid residue from the distillation process of essential oils, due to the oil and moisture content had been evaporated.
The biomass conversion technology of essential oil distillation residue into hydrocarbon compounds through the pyrolysis process becomes potential as a new pathway in the sustainability of the petrochemical industry. However, conversion technology by relying on the raw material of distillation residue is still not established industrially. During this time, most of the commercial activity for converting biomass still relies on the raw material of the agricultural sector [1] to produce hydrocarbon compounds using a zeolite catalyst.

Essential oil distillation residues have potential in Indonesia considering the natural results of Indonesia consist of a variety of specific spices such as Nutmeg, Pepper, Clove, Fragrant Angelica root, Lemongrass, Patchouli and Cardamom which are the source of essential oil raw materials. However, due to the raw material is only take the oil physically (< 3%), then the amount of waste produced will be the same as the raw material quantity. Therefore, if it's not well managed, the solid waste will cause the large pollutions. In reducing the pollution impacts, the technology of essential oil distillation residue material could be used as a promising future technology to produce hydrocarbon products.

In developing such conversion technology, there is an absolute need for further research and development with the support of reaction and catalysis techniques. The use of a new catalyst in the catalytic conversion of biomass is a development of catalytic technology that is useful in enhancing hydrocarbon compounds in bio-oil. The catalytic pyrolysis of lignocellulose biomass into light olefins have used a zeolite catalyst [2]. However, in research conducted by Rezai, et al, produced olefins of less than 50% of the masses due to the use of zeolite only able to bend the molecules of long hydrocarbons become simpler through the formation of carbonium ions to break the Intercarbon bond becomes simpler [3]. Therefore, a catalyst modification that can cut off oxygen from the hydrocarbon group is required. With such mechanisms, it is possible to produce hydrocarbon distribution products in the bio-oil of the catalytic pyrolysis is expected to increase.

One of the materials that have the potential is YSZ (Yttria-Stabilized Zirconia). YSZ is known to be able to draw oxygen molecules and convert them into active oxygen (O²) due to YSZ has an oxygen lattice structure that causes an oxygen vacuum on its surface. Thus, YSZ not only attracts oxygen from the environment (O₂) but can also attract oxygen from other oxide molecules such as oxygenate groups. In this study, YSZ will be combined with ZSM-5 for the catalytic pyrolysis from the essential oil distillation residue into hydrocarbon distribution products in bio-oil.

2. Methods

The first phase of the research is by the preparation of biomass from the essential oil distillation residue carried out so that the biomass is obtained clean from impurities and granular size. The resulting residue is a residue derived from lemongrass oil distillation then it will be dried with an oven for 6 h with a temperature of 105 ℃ to lower the moisture content contained in it to less than 10% to increase energy efficiency occurring during the process [4]. The essential oil distillation residue that has been dried, then crushed with a blender to be 0.5-3 mm. The size is selected because it refers to previous research to optimize the mechanisms of mass and heat transfer during the pyrolysis process [5]. Afterward, the essential oil distillation residues which have become granules, then stored in containers that are spared from sunlight and in an ambient state.

In this study, the pyrolysis process carried out with and without catalyst with a variation of temperature from 425-550 ℃ to determine the optimum temperature conditions in Argon's gas-streamed of 100 mL/min for 60 min. The argon gas flow used to prevent the presence of oxygen in pyrolysis reactors during the process. Argon gas that flows to the reactor will cause the product of pyrolysis to move quickly through the gooseneck and the flow into the steam catcher bottle that has filled with 10 ml of ethanol. After reaching the pyrolysis time, the steam product will be contained in the catcher bottle while the remaining char is still in the reactor. The attached pyrolysis steam products cooled at −4 ℃ to ensure the perfectly dissolved. Then, the steam product would be inserted into the sample bottle to tested using GC-MS. The same method also applies to the pyrolysis of the argon flow.
rate that varies by 25-125 mL while the catalyst combination would vary with the YSZ/ZSM-5 ratio of 0:1, 1:1, 1:2, 2:3, 2:1, and 3:2.

3. Results and Discussion

Results from the pyrolysis of lemongrass essential oil distillation residue produce steam that can be condensed, and the remaining char. Steam product obtained through dissolved sampling techniques carried out in 10 mL of ethanol. The steam pyrolysis products are shown in Figure 1.

![Figure 1. Steam Pyrolysis Products in 10 mL of Ethanol](image)

Visually, Figure 1 shows the acquisition of steam pyrolysis products dissolved in ethanol has a similar color standard that is from brown to dark red close to black. The resulting steam pyrolysis products are composed of various volatile chemical compounds such as formaldehyde, acetic acid, phenols, Cyclopentane, and furfural. The color standard produced from the steam pyrolysis products can identify that a steam solution that has an increasingly thick tanned color will cause more volatile compounds produced. The example of volatile compounds that have blackish-brown color when exposed to oxygen from the air is furfural [6]. So, when the steam solution has a dark brown color, it shows more furfurals and similar compounds that formed.

3.1. Effect of Temperature

From the pyrolysis reaction, most of the lemongrass essential oil distillation residues converted into steam products and the remaining char of pyrolysis. As it is known, the higher the reaction temperature, the greater the devolatilization rate which causes lignocellulose compounds in lemongrass essential oil distillation residue to be crack and would leave less char products in the form of ash and carbon substance Figure 2 shows that the final mass of char from the pyrolysis of lemongrass oil distillation residue decreases followed by the high-temperature reaction. Meanwhile, the increasing number of volatile substances then the yield of pyrolysis products will also be increased as shown in Figure 3.

![Figure 2. Effect of the reaction temperature on the results of char products (g)](image)
Figure 3. Effect of the reaction temperature on the results of steam products (%)

Effect of the reaction temperature on the results of pyrolysis products sown as in Figure 2 and 3, where the yield of the steam pyrolysis product in the form of mass other than the remaining pyrolysis char increased with the temperature of pyrolysis. Figure 3 shows the maximum reaction temperature in achieving the most yield is at a temperature of 550 °C. While in Figure 2 shows the change of final mass of char from the pyrolysis process that has a downward tendency as the temperature increases which the smallest mass of char obtained at a temperature of 550 °C. This phenomenon occurs due to the rise of pyrolysis temperature resulting in persistent devolatilization reactions which at higher temperatures, then the available energy becomes higher so that the more numerous lignocellulose biomass compounds are decomposed [7]. The decomposition of the biomass compounds leaves less char and increases the amount of volatile substances. Therefore, in this research, the maximum temperature in reaching the most yield of the steam products by leaving a slight mass of char occurs at a temperature of 550 °C.

3.1.1. GC-MS Results. The sample tests were conducted using GC-MS analysis aims to find out the compounds contained in the steam produced from the pyrolysis of lemongrass essential oils distillation residue. The samples used in GC-MS analysis will be taken only the best two based on the visual appearance of the color produced by the steam product and the final mass of the remaining char of each variable. Figures 4 and 5 show the results of GC-MS analysis at 450 °C and 550 °C.

Figure 4. Chromatogram for GC-MS Peak Area at 450 °C
The effect of the reaction temperature of the steam content of pyrolysis products expressed in Figure 4 and Figure 5, which both of chromatogram results can represent the overall results of GC-MS. Figure 6 shows a comparison of the results of oxygenated compounds with non-oxygenated compounds from the GC-MS analysis.

In Figure 6, the change of the steam content increases when the temperature is 550 °C. Oxygenated compounds produced both at 450 °C and 550 °C are much greater than those of the resulting non-oxygenated compounds. Nevertheless, at a temperature of 550 °C non-oxygenated compounds are much higher than at a temperature of 450 °C. It indicates that the increasing temperature could be increased the production of the desired hydrocarbon compounds in bio-oil. At 550 °C, the composition of non-oxygenated compounds with the largest peak area achieved by the presence of Cyclopropane, cyclobutane, and propane content, while aromatic compounds such as benzene and toluene are detected with a small peak area at a retention time of 4.53 min. Additionally, compounds such as furfural also detected at the 2.63 min. with a small peak area. However, when the temperature is 450 °C, the non-oxygenated compounds achieved is not as much as at the temperature of 550 °C. It evidenced that the condition that produced the most abundant of paraffin compounds, olefins, aromatic, and non-oxygenated cyclic hydrocarbon is at a temperature of 550 °C. Meanwhile, at 450 °C, compounds such as paraffin and cyclic hydrocarbon are only slightly formed with small peak areas. Furfural and aromatic compounds such as benzene and toluene are also not detected at a temperature of 450 °C. Nevertheless, the largest peak area at both temperatures achieved by the presence of the content of dimethyl ether as an oxygenate compound. Thus, from the GC-MS test
results can be concluded that the increase in reaction temperature in the pyrolysis process is very influential against the content of oxygenate and non-oxygenated compounds in the vapor of pyrolysis products. So, it proves that the selection of the reaction temperature of 550 °C as the maximum temperature in this pyrolysis is valid.

3.2. Effect of Argon Gas Flow Rate

In this study, the inert gas flow (Argon) used so that there was no oxygen present in the pyrolysis reactor during the process. The Argon gas flows varied from 25-125 mL/min. The pyrolysis process carried out using a reaction temperature that has previously been select as the optimum temperature based on the final mass of char and the yield steam product from the pyrolysis of lemongrass essential oil residue. At a variation in the flow rate of argon, the pyrolysis process carried out at a temperature of 550 °C. In this condition, the resulting char has reduced mass as the rate of argon flow in the pyrolysis process as shown in Figure 4.

![Figure 7. Effect of argon gas flow rate on the results of char products (g)](image)

Figure 7 shows the influence of argon's gas flow rate as an inert pyrolysis of the solid residue of lemongrass oil. Argon flow acts as an inert gas and oxygen cleanser to prevent the perfect combustion of the pyrolysis in progress. In the graph above, the change of the final mass of char in the pyrolysis has continued to decrease, to the rate of a certain flow, the final mass of biomass char reaches its consistency. It can be concluded that the argon gas that flowed into the reactor helps the pyrolysis process occur perfectly by pressing the oxygen gas in the reactor out, so the perfect combustion can be minimized, and the yield of the desired pyrolysis products will increase.

![Figure 8. Effect of argon gas flow rate on the results of steam products (%)](image)
The Yield of steam products increased along with the argon gas flow into the reactor. It is shown in Figure 8, where the yield of steam products increased to achieve the optimum flow rate. The graph shows that the maximum steam product yield reached at the argon gas flow rate of 100 mL/min. It means that the effect of the inert gas rate (argon) is very helpful in the occurrence of fluidization of biomass material so the heat transfer process occurs very quickly and forms more steam products that can be condensed rapidly. When the argon flow rate reaches of 125 mL/min, the yield of steam products tends to decrease even though it is insignificant. It caused by the magnitude of the inert gas flow rate (argon) that added to the reactor is not comparable to the mass of its biomass, resulting in a decline in the resulting steam yield of the product. This decline caused due to the increasing number of inert gas that will result in the formation of compounds such as CO₂ is greater than the desire volatile compounds so that the yield of steam products decreased. Therefore, in this study, the optimal argon gas flow rate achieved at the flow rate of 100 mL/min with the temperature of 550 °C.

3.2.1. GC-MS Results. The GC-MS was also performed during a variation of the inert gas flow rate to determine the influence of the inert gas flow rate (Argon) on the pyrolysis product content. GC-MS results in Figure 9 and Figure 10 demonstrate chromatogram pyrolysis products on the variation of the inert gas flow rate.

![Figure 9. Chromatogram for GC-MS Peak Area at 25 mL/min](image1)

![Figure 10. Chromatogram for GC-MS Peak Area at 100 mL/min](image2)

From Figure 9 and Figure 10 show the results of chromatogram samples of flow rate variations at 25 and 100 mL/min at a maximum temperature of 550 °C. The comparison of the oxygenate and non-
oxygenated in steam products with the change of peak area of the two compositions of the steam product to the argon gas flow rate shown in Figure 11.

![Figure 11](image)

**Figure 11.** Effect of argon gas flow rate to oxygenated and non-oxygenated content

The results shown in Figure 11 indicate a change of oxygenate and non-oxygenated compounds at two different flow rates. The compound content produced at argon gas flow rate of 25 mL/min indicates that almost most of the reaction and deoxygenation occurs in a selective direction against the oxygenate compounds while the oxygenate compounds detected by GC-MS are only a small fraction with a very small peak area. Meanwhile, the argon gas flow rate of 100 ml/min Indicates that more oxygenated compounds with a relatively greater peak area compared to the flow rate of argon 25 mL/min, which is the % area of oxygenated compounds are barely noticeable.

In Figure 4.30 shows similarities to the compound content at a temperature of 550 °C. It occurs because of the variation of pyrolysis temperature performed with the argon gas flow rate of 100 mL/min. Thus, when a variation of the argon flow rate is performed at a temperature of 550 °C, the chromatogram produced when the variation at 100 mL/min does not show significant results differently. The content of the volatile compounds produced at the argon gas flow rate of 100 mL/min is much more than when the argon gas flow rate is 25 ml/min. Due to the magnitude of the argon gas flow rate is not comparable to the mass of its biomass. Besides, the presence of oxygen detected at some peak in the variation of argon 25 ml/min can decrease the desired product. The emergence of oxygen detected at 25 mL/min obtained from the sampling technique of the researcher’s bottle when it poured into a GC-MS vial bottle that allowed the air to enter the vial. Therefore, the optimum flow rate of argon achieved at the gas flow rate of 100 mL/min.

### 3.3. Effect of Catalyst

Catalysts in the pyrolysis of lemongrass essential oil distillation residue using a combination of YSZ and ZSM-5 catalysts. The Variation of the ratio of the two catalysts can be seen in Figure 12 and Figure 13 that shows the change a final mass of char and steam pyrolysis products with the temperature and the optimum argon gas flow rate that has previously been determined at 550 °C and 100 mL/min.
Figure 12. Effect of YSZ/ZSM-5 catalysts on the results of char products (g)

Figure 13. Effect of YSZ/ZSM-5 catalysts on the results of steam products (%)

Figure 12 and Figure 13 indicate the mass change of char and yield of steam pyrolysis products to YSZ/ZSM-5 ratio. The final mass of char decreases following the ratio of YSZ/ZSM-5 catalysts, which causes the yield of steam products to become higher as the variation catalyst ratio changed. The final mass of char decreases following the ratio of YSZ/ZSM-5 catalysts, which causes the yield of steam products to become higher as the variation catalyst ratio changed. While, if it compared to the pyrolysis without catalysts with the same operating conditions, the catalytic pyrolysis reaches the yield of steam products greater than pyrolysis without catalyst. Figure 3 shows that the pyrolysis without catalyst at a temperature of 550 °C only obtained a yield of 74%. Meanwhile, when the Pyrolysis is done by a catalytic process with the ratio of YSZ/ZSM-5, the yield of steam product generates a trend that rises as the variation of a ratio is done with a maximum yield of 78% at the ratio of 3:2. It because the existence of a catalytic effect can result in fewer of char so that the pyrolysis steam product consisting of volatile compounds obtained are in maximum condition. Besides, the acid catalyst used in this research can also prevent the occurrence of the formation of a coke that can cover the pores of biomass in the reactor, so that the pyrolysis process can last more maximally [8]. Meanwhile, YSZ catalysts on pyrolysis greatly help the performance of the ZSM-5 catalyst at high temperatures. Thus, when the temperature at 550 °C, YSZ catalysts works more effectively than the ZSM-5 catalyst which at a temperature greater than 500 °C will be over crack.
3.3.1. GC-MS Results. The GC-MS conducted on YSZ/ZSM-5 catalysts were carried out at the ratio of 2:3 and 3:2 catalysts with the argon gas flow rate of 100 ml/min and a temperature of 550 °C. Figure 14 and Figure 15 shows the GC-MS chromatogram results on catalyst ratio variations.

![Figure 14](Figure 14. Chromatogram for GC-MS Peak Area of 2:3 YSZ/ZSM-5 Catalyst)

![Figure 15](Figure 15. Chromatogram for GC-MS Peak Area of 2:3 YSZ/ZSM-5 Catalyst)

The chromatogram results in Figure 14 and Figure 15 have similarities when viewed from the emergence of the peak. The content of oxygenated and non-oxygenated compounds at both catalysts ratio is more varied compared to the results of pyrolysis without catalysts. However, to compare the compounds contained in both ratios of the catalyst can be seen in Figure 16. Meanwhile, the comparison of non-oxygenated compounds contained in pyrolysis with and without catalysts can be seen in Figure 17.
In Figure 16 and Figure 17 indicate that the presence of the catalyst added to the pyrolysis process plays a good role in forming the desired compounds in steam pyrolysis products. In pyrolysis without catalysts, it is known that most of the reaction and deoxygenation occurs in a selective direction against non-oxygenated cyclic hydrocarbon compounds, whereby cyclopropane compounds detected in the pyrolysis without a catalyst strongly dominate by area of 30.60%. However, non-oxygenated compounds detected in this condition are only limited to the cyclic hydrocarbon compounds, while the oxygenated compounds such as acetic acid and dimethyl ether are dominant. It is different when pyrolysis conditions are present in the role of catalysts therein. There is not much noticeable difference from the compound components contained in the steam products in both ratios of the catalyst. The results of both chromatograms also have the same peak layout. However, large areas of peak in each component, both oxygenated and non-oxygenated compounds are different.

The emergence of non-oxygenated compounds in the ratio of 3:2 catalysts more appears almost in every peak even though with a relatively small area. At the result of the chromatogram ratio of the 3:2 catalyst is known at the time of 2.09 is detected for compounds such as hexene, pentene, cyclopropane, and cylobutane even tough with a relatively small peak area. Aromatic compounds such as benzene and toluene are detected at some peak with a relatively small area. It suggests that a small fraction of the catalytic deoxygenation and repercussions have resulted in paraffin, olefins, cyclic hydrocarbons compounds, and continued to the aromatization process. Meanwhile, at a ratio of 2:3 catalysts, the emergence of paraffin compounds, olefins, and cyclic hydrocarbons is not as frequent as the ratio of
3:2 catalysts. The emergence is only on some peak with a relatively small area. However, the aromatic compounds of benzene at 2:3 catalyst ratios are more detected. At a retention time of 7.93 to 7.99 min. shows only Benzene detected with a relatively small peak area. Meanwhile, non-oxygenate compounds paraffin, olefin, and cyclic hydrocarbon are less than the ratio of the 3:2 catalyst.

A large number of paraffin compounds, olefins, and cyclic hydrocarbons detected in the catalytic pyrolysis compared with the non-catalytic pyrolysis caused due to the presence of the YSZ and ZSM-5 catalysts active in achieving optimum conditions. The ZSM-5 catalyst plays a role in breaking down the long hydrocarbon molecules to be simpler. Besides, the role of YSZ on pyrolysis allows hydrocarbon products in bio-oil to increase as it can attract oxide molecules from the oxygenate group, so it will produce more the non-oxygenated products [9].

4. Conclusion
Based on the discussion that has been made, the conclusions that can be withdrawn from this study is the operating conditions that produce the highest yield of steam product from the pyrolysis of lemongrass essential oil distillation residue at 550 °C with the argon gas flow rate of 100 ml/min while the optimum ratio of YSZ/ZSM-5 achieved at 3:2. Meanwhile, the GC-MS results detect that the compounds produced from pyrolysis with the largest peak area are of the acidic group (oxygenated), then continued with a group of paraffin compounds, olefins, aromatic, and non-oxygenated hydrocarbon cyclic.

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References

[1] Anca-Couce, A. 2016. Reaction Mechanism and Multi-Scale Modelling of Lignocellulosic Biomass Pyrolysis. Progress in Energy and Combustion Science, Volume 53, pp. 41-79.
[2] Rezai, P. S., Shafragh, H. & Wan Daud, W. M. A., 2014. Production of Green Aromatics and Olefins by Catalytic Cracking of Oxygenate Compounds Derived from Biomass Pyrolysis: A Review. Applied Catalyst: General, Volume 469, pp. 490-511.
[3] Nasikin, M. & Heru, Bambang. 2010. Katalisis Heterogen. 1st ed. Depok: Universitas Indonesia.
[4] Supramono, D. J. 2016. Improving Bio-oil Quality through Co-Pyrolysis of Corn Cobs and Polypropylene in a Stirred Tank Reactor. International Journal of TechnologY, 7, 1381.
[5] Setiadi, &. H. 2018. Product distribution from catalytic conversion of biomass over B2O3/γ-Al2O3 catalyst. IOP Conference Series: Earth and Environmental Science, 105, 012007.
[6] Kan, T., Strezov, V. & Evans, T. J., 2016. Lignocellulosic Biomass Pyrolysis: A Review of Product Properties and Effects of Pyrolysis Parameters. Renewable and Sustainable Energy Reviews, Volume 57, pp. 1126-1140
[7] Collard, F.X., & Blin J. 2014. A Review on Pyrolysis of Biomass Constituents: Mechanism and Composition of the Products obtained from the Conversion of Cellulose, Hemicellulose, and Lignin. Renewable and Sustainable Energy Reviews, Volume 38, pp. 594-608.
[8] Naqvi, S. R., Uemura, Y. & Yusup, S. B., 2014. Catalytic Pyrolysis of Paddy Husk in a Drop Type Pyrolyzer for Bio-Oil Production: The Role of Temperature and Catalyst. Journal of Analytical and Applied Pyrolysis, Volume 106, pp. 57-62.
[9] Tsampas, M. N. 2015. Application of Yttria Stabilizide Zirconia (YSZ) in Catalyst. Catalysis Science & Technology, Volume 00, pp. 13.