Characterization of non-oxygenates hydrocarbon product from the catalytic pyrolysis of rice straw

Sabiq Mufarrid1, Angela Lesmono1, Jessica Mei1, Felix Subakti1, and Setiadi1,*

1 Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus Baru UI, Depok 16424, West Java, Indonesia.
* Corresponding Author: setiadi@che.ui.ac.id

Abstract. The usage of fossil fuel as petrochemical feedstock becomes problems due to the depletion of its supply coupled with the issue of global warming and air pollution, thus a new alternative is needed. Lignocellulose biomass can be converted into hydrocarbons for the petrochemical industry’s feedstock through pyrolysis process, which is a thermal decomposition of biomass in an oxygen-free condition. The materials used in this experimental study consist of rice straw as the main feedstock, ZSM-5 as the catalyst. Rice straw is lignocellulose biomass that has the potential in Indonesia because of its abundant supply in many locations. Biomass catalytic pyrolysis was carried out using a fixed bed reactor with the varied ratios of ZSM-5 and biomass mixture and the products in the form of gaseous phase come out from the bottom of the reactor by flowing it into a glass test tube with a diameter of 2.5 cm. Pyrolysis process was carried out at temperature variations of 450°C, 500°C, and 550°C in a nitrogen gas flowing condition of 10-20 ml/minute. To detect the non-oxygenate hydrocarbon products, the sampling of the gas product was done by taken it using the glass syringe in the reactor bottom. The gas analysis was performed using Gas Chromatography-Mass Spectroscopy (GC-MS) and the calibration curve was then prepared to quantify the results by GC-MS analysis for various pyrolysis vapor compounds with their respective peak areas. With the variation of pyrolysis temperature, this study shows that the olefin group produced in catalytic pyrolysis neither does the conventional pyrolysis. But the pyrolysis produced the paraffin group in any type of pyrolysis condition process. This study also found that olefin group production was decreased in the longer time of stream reaction, while the aromatic group was increased. Generally, the amount of aromatic compound formation depends on catalyst ratio.

1. Introduction

Fossil fuels, especially petroleum and natural gas, have been used as fuel and raw material for the petrochemical industry. The fuel and raw materials of the petrochemical industry are non-oxygenated hydrocarbon chemicals. However, due to the depletion of the supply of fossil fuels coupled with the issue of global warming and air pollution, new pathways and sources are needed to obtain raw materials from renewable and environmentally friendly materials. One of the alternatives is lignocellulose biomass [1]. Lignocellulose biomass can be converted into hydrocarbons for the petrochemical industry’s raw materials through the pyrolysis process. This process aims to decompose the organic matrix of biomass into bio-oil, charcoal and other uncondensed gases [2].

However, most pyrolysis products are still in the form of oxygenates (ketone, aldehyde, alcohol) compounds. This is a major problem because the compound cannot be used directly for the petrochemical industry. These compounds need to be converted into non-oxygenated hydrocarbons.
using a selective reaction with the use of a ZSM-5 type catalyst. ZSM-5 is a clay material that has acidic properties and has the shape-selective ability that makes the ZSM-5 suitable for cracking and deoxygenation processes to obtain non-oxygenated hydrocarbon compounds [3].

In this study, the fixed bed composed of the catalyst and rice straw biomass mixtures with a varied ratio of catalyst/biomass was to investigate which one produces the most non-oxygenated hydrocarbons. The temperature of the pyrolysis reaction was also varied to increase the formation of non-oxygenated hydrocarbons. Besides, the sampling at various course of reaction time was also be carried out to observe the composition of non-oxygenate products produced during course of reaction time. So, this experiment could ascertain the stability of the ZSM-5 catalyst during the reaction of catalytic pyrolysis from lignocellulose biomass to produce non-oxygenates hydrocarbon products.

2. Materials and Methods

2.1. Materials

The material used in this experimental study was rice straw that was obtained from Sumedang Regency, West Java, Indonesia and had already been dried. The ZSM-5 catalyst was obtained from Gongyi City Meiqy Industry, China via alibaba.com in the form of white pellet granule particles with a size of 5-10 mm. These granules need to be ground with mortar of up to 1-3 mm in size in order to make it easier to insert into the reactor and to increase the contact surface. The catalyst powder was appropriate size in order to overcome the excessive pressure drop inside the reactor bed when the reactor is operated with the rate of nitrogen gas flowing in and the rising temperature. The catalyst was then mixed with rice straw with various composition ratios.

2.2. Experimental Methods

Several methods are used in this experimental study. Rice straw preparation was carried out to obtain rice straw that was clean of impurities and small in the form of granules. Dried rice straw was cut into pieces with scissors and then washed using water. After that, rice straw was dried in an oven at 105°C for 6 hours. Then, rice straw was prepared into granules with a blender. Rice straw is then sieved to obtain smaller grains (less than 3 mm) and then to store in a container that is protected from sunlight and in an ambient state.

Biomass catalytic pyrolysis was carried out using a fixed bed type reactor. The reactor has a heating furnace around it as a heat source and a temperature controller to regulate the temperature of the heater. At the reactor inlet, a silicon seal is applied to prevent leakage during catalytic pyrolysis. The scheme of the catalytic pyrolysis reactor tool is shown in Figure 1.

![Figure 1. Catalytic Pyrolysis Reactor Scheme](image_url)
Quartz wool fixed at the bottom of the reactor functions as a barrier in order to catalyst powder entraining into flow gas flow and to keep residual biomass (char) that has not reacted, and/or the results of other reaction products do not fall into the reactor output stream. Quartz wool was employed because of its high-temperature resistance and does not affect the reaction process. Pyrolysis products in the form of steam will come out from the bottom of the reactor which is then condensed directly by flowing it into a glass test tube with a diameter of 2.5 cm. The reaction tube is given a gas output path to drain pyrolysis gas products and leaves a liquid product in the form of bio-oil. The output of gas products is sucked and stored in the syringe. Pyrolysis process is carried out at a temperature variation of 450°C, 500°C, and 550°C in a nitrogen gas flowing environment of 10-20 ml/minute. The flowing of nitrogen acts as an inert gas and purges the possible oxygen gas so that the condition of reactor facilitates a complete pyrolysis process. The nitrogen hose is connected to reactor tube installed above the reactor to take into nitrogen from top to bottom so that the entire pyrolysis products move down quickly to avoid reactions other than fast pyrolysis [2].

The GC-MS calibration curve was made to quantify the results of GC-MS analysis especially benzene, toluene and xylene in the form of various pyrolysis vapor compounds with their respective peak areas. For this reason, standard solutions were prepared only for aromatic compounds because it is still in the liquid phase compared to other contents such as olefins which are likely to be in the gas phase at room temperature.

3. Results and Discussion

The preparation of fixed bed composing the mixture of material catalysts and biomass is intended to facilitate the intimate contact between the pyrolytic vapor resulted from biomass and catalytic, so the once the vapor was produced subsequently the vapor undergoes the reaction catalytic in the bed system. Comparing to the configuration of the individual bed with the sequence of the catalyst bed to the biomass bed to catalyst bed, the pyrolytic product might undergo the tortuous path flowing out in its bed and then the gas entering the catalyst bed for contacting and catalytic reaction. So, the catalytic pyrolysis proceeds is considered under the two controlling steps in the individual configuration of the bed. Unlike the individual bed, the bed composed of mixture catalyst and biomass prepared is taken into account that the bed is much more simple to operate and the operation might be safer due to the pressure drop within the bed was relatively low. And the controlling step due to mass transfer of gaseous product from pyrolysis process in the bed could be diminished because the presence of ZSM-5 catalyst in the mixture leads to close contact with the gas and the occurring of catalytic reaction in the same condition with the reaction. Based on the analysis of GC-MS result for the catalytic pyrolysis, the typical chromatogram as shown in Figure 2.

![Figure 2. Chromatogram for GC-MS Peak Area from Rice Straw Catalytic Pyrolysis Vapor](image-url)
In general, this typical chromatogram showed in Figure 1 is represented by all the products analyzed by GC-MS used. It means that the position of peak at each retention time indicating a specified compound in the product resulting from the pyrolysis reaction. Due to the GC-MS used for this experiment have been completed by the software program for compound detected, so the compounds in the sample products should be assessed the quantity and quality each component. For example, at the retention time around at 2.27-min, the high possible components were aldehydes and ketones. At retention time at 3 minutes, it indicated the compound of benzene and the compound detected at 5.85 min was toluene. Particular, the peaks attributed the non-oxygenated hydrocarbons in the GC-MS chromatogram became the most dominant products i.e. paraffin, olefin, aromatic, cycloalkane, cycloalkene. The quantitative data obtained for those compounds were collected and calculated the peak area in %.

3.1. Effect of Temperature
To achieve the high formation of non-oxygenated hydrocarbons, this study examines the effect of temperature with the hope that which temperature produces the most amount of non-oxygenate hydrocarbons. The catalytic pyrolysis was conducted at 450°C, 500°C and 550°C and the 3 catalysts to feed ratios were 1:1, 1:2 and 1:3 g catalyst/g rice straw. Figure 3, Figure 4 and Figure 5 are the effect of ratios on the non-oxygenated hydrocarbon products at 450°C, 500°C and 550°C irrespectively.

![Figure 3](image3.png)

**Figure 3.** The effect of g catalyst/ g rice straw on the formation of non-oxygenated hydrocarbons from rice straw at 450°C

Fig. 3 is clearly showed that the effect of using the ZSM-5 catalyst on pyrolysis, the formation of non-oxygenated hydrocarbon was trace amount of non-oxygenated hydrocarbon with the total peak area as much as 0.12 x 10^9 when the pyrolysis was done in absence of ZSM-5 catalyst. But, the use of ZSM-5 catalyst enhances the formation of non-oxygenated hydrocarbon with total peak area 0.96 x 10^9 for ratio 1:1, 0.46 x 10^9 for ratio 1:2 and 1.02 x 10^9 for ratio 1:3. This result indicated the role of ZSM-5 to catalyze the gaseous product resulted from rice straw pyrolysis. The hydrocarbon product for paraffin group was found in three ratios of pyrolysis condition, while olefins were found only after the catalyst was presence in the bed. The formation of aromatics could be found in tiny amount in pyrolysis without catalyst, but the formation was drastically increased in a significant amount after the pyrolysis used ZSM-5 catalyst. This result indicated that the role of ZSM-5 in the shape-selective catalyst for the formation this benzene ring structure because the pore dimension is close to size of mono-aromatic molecules. The formation of non-oxygenated hydrocarbons like cycloalkanes and cycloalkenens could be detected in small amount after the catalyst was introduced in bed. This figure and observation prove that catalysts do indeed increase the production of non-oxygenated hydrocarbons.
Fig. 4 shows the result of the effect of catalyst/ g rice straw on non-oxygenated hydrocarbons at 500°C. This result shows that even the pyrolysis employed without catalysts, the reaction is sufficient to produce a considerable amount of non-oxygenated hydrocarbon with a total area of 0.36 x 10^9 especially for the product of paraffin and aromatics. The only pyrolysis with the ratio 1:1 was found to give higher formation of non-oxygenated hydrocarbon with total peak area was 0.63 x 10^9. The pyrolysis with both ratio 1:2 and 1:3 used, the formation of non-oxygenated hydrocarbons was the same and even lower than that of no catalyst one. Apparently, the condition of pyrolysis temperature at 500°C is having energy enough to exceed the activation energy of pyrolysis. Upon treatment of catalyst, olefin could be found and yet paraffin became absent after the thermal cracking reaction. Cyclic chains (cycloalkanes group) were also found more abundant compared to other temperature treatments in 1:2 catalyst/feed ratio. Aromatics could be present more prominently under 1:3 catalyst/feed ratio. Therefore, the catalyst/feed ratio is affected by the product distribution of the catalytic pyrolysis process.

Fig. 5 shows the result of the effect of catalyst/ g rice straw on non-oxygenated hydrocarbons at 550°C. More likely that the phenomena for the formation of catalytic pyrolysis at 550°C are similar to that at 500°C namely the total peak area of non-oxygenated hydrocarbon for pyrolysis without catalyst at this temperature was quite similar to that of pyrolysis using ZSM-5 with the ratio of 1:3. The total area of non-oxygenated hydrocarbon was 0.98x10^9 and 1.05x10^9 for no catalyst and ratio 1:3 respectively. Maybe, the pyrolysis temperature more than 500°C should achieve the activation energy, so the pyrolysis process could proceed under absence catalyst especially for the formation of aromatic compounds and olefin compounds. In general, the acid strength of zeolite is commonly at the
temperature above 500°C, so the bronsted acid site was not under favorable condition to catalyze the reaction. As shown in Fig. 5, the total area for non-oxygenated hydrocarbons were only 50 % increase from the non catalytic pyrolysis i.e 1.50 x 10^9 (ratio 1:1) and 1.52 x10^9 (ratio 1:2). But, those ratio conditions and temperature for pyrolysis achieved consistently the formation aromatic with high dominant product and ZSM-5 was shown to be capable of increasing non-oxygenated hydrocarbons from pyrolysis; it was due to ZSM-5’s acidic site which assisted in breaking the oxygenated bonds.

3.1.1. Olefins Production. As shown in Fig. 6 under the condition of temperature at 450°C, the result shows that the most prominent olefin found within the reaction of 1:1 catalyst/feed ratio is 2,4-dimethyl-1,3-pentadiene and 4-methyl-3-heptene as shown by its much higher peak area. These results show that the ZSM-5 catalyst could catalyze the reaction toward the formation olefin compounds from oxygenated product compounds from rice straw biomass pyrolysis through the cracking of functional groups.

![Figure 6. Olefins under 450°C treatment](image)

Fig. 7 shows the formation of olefin compound at 500°C. The results show that the peaks were found to be much lower compared to that at 450°C. Although 2,4-dimethyl-1,3-pentadiene still dominates the product alongside 3,3-dimethyl-1,4-pentadiene; also olefins that had octenes as their main functional chain was produced in small amounts replacing heptenes.

![Figure 7. Olefins under 500°C treatment](image)
It shows with the figure above that the peak showed a slight increase, with 2,4-dimethyl-1,3-pentadiene still firmly dominating the product. That makes 2,4-dimethyl-1,3-pentadiene the most consistent olefin to be produced across all treatments. In this scenario, 2,4-dimethyl-1,3-pentadiene showed the most amount produced, this proves that within 500-600°C range, production of 2,4-dimethyl-1,3-pentadiene increased in proportion with temperature (Fig. 8).

![Figure 8. Olefins under 550°C treatment](image)

3.1.2. Aromatics Production. Figure 9 shows that benzene is much more dominant than Toluene. the 1:1 ratio to be the most effective composition for the reaction. Benzene being much smaller than Toluene was benzene much more selective towards ZSM-5. It was owed to ZSM-5’s pore rendering it as a Shape selective catalyst. That meant only molecules smaller than the pores could end up as the main product.

![Figure 9. Aromatics Production under 450°C](image)
Figure 10. Aromatics Production under 500°C

Figure 10 shows that the reaction under 500°C produces aromatics with fewer amounts compared to aromatics that are produced under 450°C. Catalyst usage is not affecting the production of aromatics that much with the highest concentration is produced by the feed ratio of catalyst/rice straw 1:1.

Figure 11. Aromatics Production under 550°C

Benzene is the most dominant aromatic found under such treatment. With the 1:1 ratio suitable for the production. While the 1:3 ratio became the most suitable for Toluene.

3.2. Effect of Sampling Time

Figure 12. Effect of time towards the production of non-oxygenates under 1:1 feed ration

As the figure implies, olefin production dwindles as time goes on. It was concluded that olefin was the most abundant at the start of the process. Afterward, the olefins underwent an aromatization process...
that transformed them into aromatic substances. Aromatic production also showed a tendency to dwindle over time. Cycloalkanes could be replaced with cycloalkenes during the process.

![Figure 13. Effect of time towards the production of non-oxygenates under 1:3 feed ration](image1)

Similarly, under 1:3 feed ratio, Olefin and cyclic hydrocarbons decrease over time. Aromatics also experience a similar decrease despite being much more abundant. These were caused by catalyst deactivating by the formation of charcoal on its surface.

3.2.1. Effect of Time towards Olefins Production. The decreasing of peaks indicates that olefin production decreases over time. But (E)-4-methyl-2-heptene can be found after 30 minutes. It shows that although scarce, olefins are still being produced.

![Figure 14. Effect of time towards olefins production under 1:3 feed ration](image2)

![Figure 15. Effect of time towards olefins production under 1:3 feed ration](image3)
A similar result is shown in figure 12 where a decrease in olefin production happens in respect of time. This confirms that olefins are formed at the first minutes of pyrolysis and being aromatized that it shifts towards aromatics.

3.2.2. Effects of Time on Aromatics Production. According to the figure, the concentration of benzene is superior against toluene, except at the 30 minutes mark, this indicates a deactivation process overtime. A similar finding was indicated by the figure (Fig. 16 and Fig 17), but the overall amount was way less compared to the 1:1 feed ratio. It could be inferred that the catalyst loading ratio directly affected the aromatics produced.

![Figure 16. Effect of time towards aromatics production under 1:1 feed ration](image1)

![Figure 17. Effect of time towards aromatics production under 1:3 feed ration](image2)

4. Conclusion
Rice straw could be used as the feedstock to produce non-oxygenates hydrocarbon products through catalytic pyrolysis especially olefin and aromatic compounds in the range of 450-550°C and the three catalysts/biomass weight ratio (1:1, 1:2 and 1:3). Among the olefin compounds, 2,4-dimethyl-1,3-pentadiene was the dominant product and its formation is supposed from the result of de-oxygenation reaction of pentanedione. The formation of aromatic products with the benzene as the high selectivity was obtained and these product formations were considered to be closely related to the shape-selective catalyst performance of ZSM-5 for the aromatic compounds. The synthesis of those hydrocarbons fully depends on the sampling time and catalyst ratio.
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