Producing monoaromatic compounds from pyrolytic vapour of rice straw using H-ZSM-5/B_2O_3 catalyst

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Abstract. The catalytic conversion of rice straw was done to produce mono aromatic compounds. The mixed catalyst of ZSM-5 and B_2O_3 was obtained through calcination of ZSM-5 and H_3BO catalyst mixture. The variation of the composition of the ZSM-5 and B_2O_3 catalyst was applied in order to test the effect of catalyst composition to the production of mono aromatics compounds. The composition of catalyst used were 15% ZSM-5, 30% ZSM-5, and 100% ZSM-5. Other than the variation of catalyst composition, the variation of the operating temperature of the catalytic conversion also performed in order to study the effect of the temperature to the production of mono aromatic compounds. The catalytic conversion was done at 450, 475, and 500 ^oC. Experimental results show that the addition of the catalyst resulted in the conversion of oxygenate compounds resulted from the pyrolytic process of rice straw into mono aromatic compounds. It also shows that using 100% ZSM-5 produced the highest yield of mono aromatics compounds. The amount of mono aromatic compounds produced will decrease, as the fraction of ZSM-5 catalyst used and operation temperature also decreased. Using the 100% ZSM-5, the mono aromatics compound with the highest yield is 1, 3 Dimethyl benzene or m-xylene.

1 Introduction

Biomass as a renewable source undoubtedly plays an important role in the future because the main component is carbon and hydrogen with H/C high enough comparing to other petroleum sources. But the high content of oxygen in biomass should be paid attention because it leads to lower the quality of final product after processing. Various processes may be employed to convert biomass into useful fuels and chemicals. Among those process, the conversion of biomass through a thermochemical process seems to show a promising alternative for many energy applications [1]. Pyrolysis is one of the most promising thermochemical process of converting biomass to fulfill the needs of bio fuels and chemicals [2].

The drawbacks of bio-oil from pyrolysis are high content of oxygen atom and various kind of oxygenated compounds making the low heating value and low stability which is the quality far enough from the product petroleum processing. Besides, the monoaromatic hydrocarbon in the bio-oil product in the tiny amount. So, to pave away the usage of biomass the catalytic conversion is one of the proven process that could be used to upgrade and improve the quality of the bio-oil. In this process, the biomass decomposed in the pyrolysis process, thermally decomposed the biomass producing pyrolytic vapors. Which then, the bio-oil being in form of the gaseous product could be directly upgraded using catalyst to refine the bio-oils into hydrocarbon or other intermediates [3]. With the presence of HZSM-5 catalyst, the vapor resulted from the decomposition of biomass consisting of various compound the oxygenate compounds, could be converted into mono aromatic compounds when they came in contact with the catalyst. For this work, in order to convert the biomass into mono aromatics compounds, ZSM-5 catalyst and the mixture of ZSM-5 and B_2O_3 with different composition was used. ZSM-5 catalyst is a catalyst with zeolite properties which have already proven to have the capability to convert oxygenated compounds into aromatics [4].

2 Experimental Method

There are total of three variations of ZSM-5 and B_2O_3 catalyst mixture. Those mixtures were 15% ZSM-5, 30% ZSM-5, and 100% ZSM-5. Other than the varied composition of catalyst, the catalytic conversion was done under three different operation temperature which were 450, 475, and 500^oC. These variations were applied in order to analysed and determine the most suitable mixture of catalyst and operation temperature to produce

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mono aromatic compounds.

2.1 Material

The type of biomass used as the feed for this experiment was rice straw. Before it can be used, the particle size of the rice straw was reduced to 1-3 mm using a grinder or grinding machine. Using an oven, the rice straw was then dried at the temperature of 60^{O}C for around 5 – 6 hours to reduce the water content of the rice straw to <10% of the total mass. For this experiment, 1 gram of treated rice straw, 1 gram of mixture of catalyst, and 1 gram of quartz sand mixture was used for each experiment run.

The catalysts used for this experiment were ZSM-5 and boron oxide (B_2O_3) catalyst with various compositions. The amount of catalyst used for catalytic conversion was 1 gram with different composition of ZSM-5 and B_2O_3 catalyst. If the amount of the catalyst was excessive weight, the bed of catalyst might block the pathway of the flowing products out of the tube, so there was no products could be collected. On the contrary, the experimental running with small amount of the catalyst, the catalytic conversion process resulted the bio-oil containing product in the difficulties to analytical detection.

The mixture of ZSM-5 and boron oxide (B_2O_3) catalyst was prepared by physically mixing of boric acid (H_3BO_3) as boron oxide precursor and ZSM-5 commercial catalyst. Then, the calcination process will be applied on the mixture at the atmospheric condition with the temperature of 300 and 600^{o}C respectively for 2 hours each to get the supported boron oxide catalyst onto H-ZSM-5. H_3BO_3 was as the oxide precursor to decompose into water vapour and metabolic acid (HBO_2) at around 170 ^{O}C, and further heating above 300^{0}C will decomposed (HBO_2) to produce more steam and boron oxide (B_2O_3) solids.

2.2 Methods

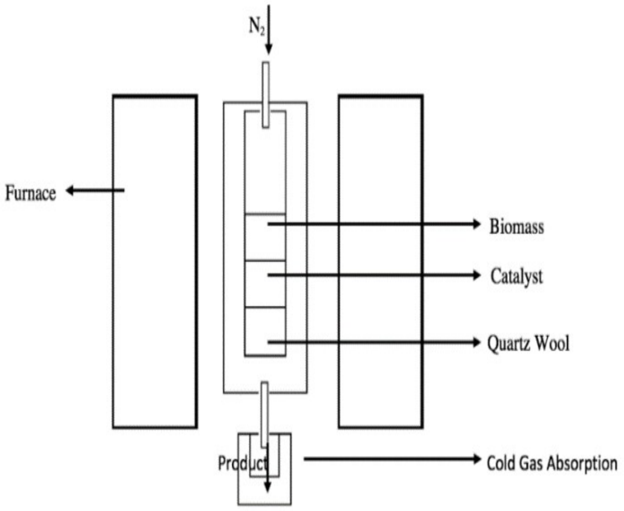

Fig. 1. Schematic diagram of experimental set-up apparatus for biomass catalytic pyrolysis

The conversion was done under atmospheric pressure, with the flow rate of N_2 at around 40 ml/minute, while the operation temperature was 450, 475, and 500 ^{o}C. The reactor tube is 300 mm long, and 12 mm in diameter, which made from SS 316 which was the inert materials and was suitable for working in a high temperature environment. The tube was placed into an electric cylindrical shape furnace with an effort to put the rice straw and catalyst at the heating area where the heat is at the highest. Quartz wool was used at the lower end of the reactor tube to plugged the catalyst, preventing it to drop. The amount of the rice straw, catalyst, and quartz sand was one gram each. The high amount of the rice straw, catalyst, and quartz sand inside the reactor tube could lead to the reactor tube being clogged.

The schematic diagram of experimental equipment is shown in figure 1. The pyrolysis pyrolysis of the rice straw, firstly the nitrogen gas was surely introduced into reactor for purging the possible air presence inside the reactor and as carrier gas function in flowing out the vapor product resulted from the pyrolytic decomposition process. And the vapor could be upgraded by employing the catalyst, the rice straw was placed over the mixture of catalyst and quartz sand as a fixed bed. This way, the vapor product of the decomposition of the rice straw should be upgraded when it flowed down through the layer of catalyst. The usage the stream of 40 ml/mine N_2, beside to push the downwards flow of the vapour product of the decomposition of rice straw to the layer of catalyst for the upgrading process, the function was also used to remove the air inside the reactor tube.

The product of the catalytic conversion resulted from the pyrolysis of rice straw and catalytic reaction was obtained by capturing the gaseous product in the bottom of the reactor. The gas produced from the catalytic conversion was trapped using cold absorption trap method with using acetone as the solvent. The gas that came out at the bottom of the reactor was maintained a direct contact with the solvent inside of a cold glass tube submerged in the ice-water bath kept near 1 ^{o}C. Therefore, the gaseous products underwent the process of condensation and directly dissolved in the bulk of acetone solvent. The sample products dissolved were characterized for identifying and measuring the composition using GC-MS (Gas Chromatography Spectroscopy) instrument analysis.

3 Experimental Results

The catalysts used for this experiment was physically mixture of ZSM-5 and B_2O_3 catalyst. The catalyst composition used for this experiment were 15% ZSM-5 + 85% B_2O_3, 30% ZSM-5 + 70% B_2O_3, and 100% ZSM-5, and without catalyst. Beside catalyst, the catalytic conversion was conducted under different temperature. This experiment was conducted under the Temperature variation of 450^{o}C, 475^{o}C, 500^{o}C. Figure 2 through figure 4 show the product distribution resulted from catalytic conversion of rice straw for different composition of the ZSM-5 and B_2O_3 catalyst and different operation temperature.

Fig. 2 is result of the catalytic conversion under the temperature of 450 ^{O}C, with the addition of mixture of 15% ZSM-5 and 85% B_2O_3 catalyst, the yield of mono aromatics compound produce increased from 0% to 15.95%. After that, when the 30% ZSM-5 and 70% B_2O_3 catalyst was used, the yield of mono aromatics compound increased up to 23.11%. When the 100% ZSM-5 catalyst was used, the yield of mono aromatics compound went up again to 53.88%.

The same pattern can be seen in the result of sample of catalytic conversion under the temperature of 475 ^{o}C (Fig. 3). When the 15% ZSM-5 and 85% B_2O_3 was added, it increased the production of mono aromatics compound by 19.85% from when there was no catalyst used which it produced 0% mono aromatics compound. The yield of monoaromatics compound increased again to 25.1% when the 30% ZSM-5 and 70% B_2O_3 was applied. After that, it went up again to 64.22% when the 100% ZSM-5 was used.

The catalytic conversion under the temperature of 500^{o}C (Fig. 4) shows that with the addition of 15% ZSM-5 and 85% B_2O_3 there are an increase of 26.66% of mono aromatics compound from 0% in which the catalyst was not present during the catalytic conversion process. Then, the usage of 30% ZSM-5 and 70% B_2O_3 catalyst pushed the yield of mono aromatics compound to 48.26%. After that it went drastically to 79.09% when the 100% ZSM-5 catalyst was applied. It shows that with the addition of ZSM-5 + B_2O_3, it helps the process to produce mono aromatics. With the increasing fraction of ZSM-5, it will also increase the yield of mono aromatics produced from the result of catalytic conversion.

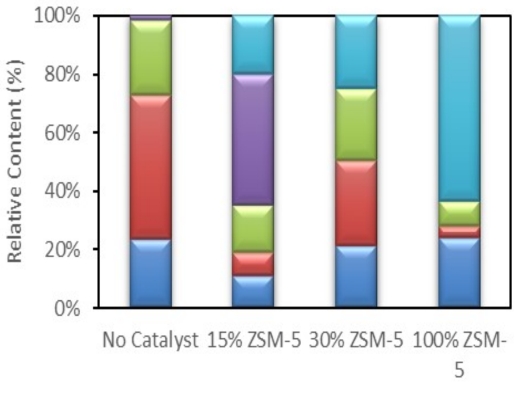

Fig. 2. Product distribution from catalytic conversion of biomass over three different composition of ZSM-5/B_2O_3 catalysts: 15% ZSM-5, 30% ZSM-5, 100% ZSM-5 at 450 ^{O}C. Key—others: blue, phenol: red, ketone: green, acid: purple, mono aromatics: light blue.

Figure 2 through figure 4 also shows as the fraction of ZSM-5 gradually increase, it will also increase the yield of mono aromatic chemical compound in the sample. It is shown by the increasing yield of mono aromatics chemical compound as the fraction of ZSM-5 catalyst increased starting from 15%, 30%, and finally 100%. At the point of where the fraction of ZSM-5 is 100%, it produced the highest yield of mono aromatics. It means, ZSM-5 catalyst, a zeolite-based catalyst, has the advantages of shape-selective reaction, which it can maximize the production of mono aromatics compound.

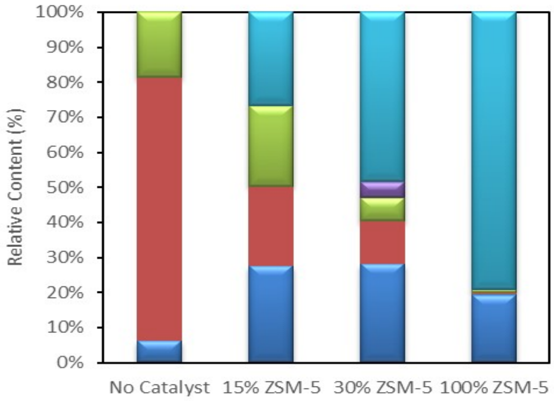

Fig. 3. Product distribution from catalytic conversion of biomass over three different composition of ZSM-5/B_2O_3 catalysts: 15% ZSM-5, 30% ZSM-5, 100% ZSM-5 at 475 ^{O}C. Key—others: blue, phenol: red, ketone: green, acid: purple, mono aromatics: light blue

It is found that H-ZSM-5 catalyst have a high performance in the formation monoaromatic compounds. Therefore, the use of H-ZSM-5 without addition of boron oxides is observed more detailed to obtain the distribution of the monoaromatics compounds produced.

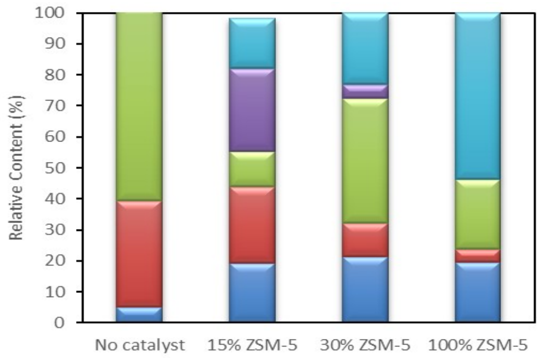

Fig. 4 Product distribution from catalytic conversion of biomass over three different composition of ZSM-5/B_2O_3 catalysts: 15% ZSM-5, 30% ZSM-5, 100% ZSM-5 at 500^{O}C. Key—others: blue, phenol: red, ketone: green, acid: purple, mono aromatics: light blue.

The results can be seen from the Fig. 5 for reaction at 450 ºC, Fig. 6 for reaction at 475 ºC and the reaction at 500 ºC shown in Fig. 7. It can been concluded that the monoaromatics compound with the highest yield for all samples is 1,3 dimethylbenzene or m-xyelene.

1,3-dimethylbenzene is consistencely presence in the three samples with the highest yield. The yield of 1,3 Dimethyl benzene produced from the result of catalytic conversion process of rice straw using 100% HZSM-5 catalyst under the temperature 450 OC is 23.95% peak area. Then, when the operation temperature was raised from 450 ^{o}C to 475 C, while using the same composition of 100% HZSM-5 it yielded 18.71% of 1,3 Dimethyl benzene. The yield of 1,3 Dimethyl benzene produced from the result of catalytic conversion process of rice straw under the temperature 500 C is 25.75%.

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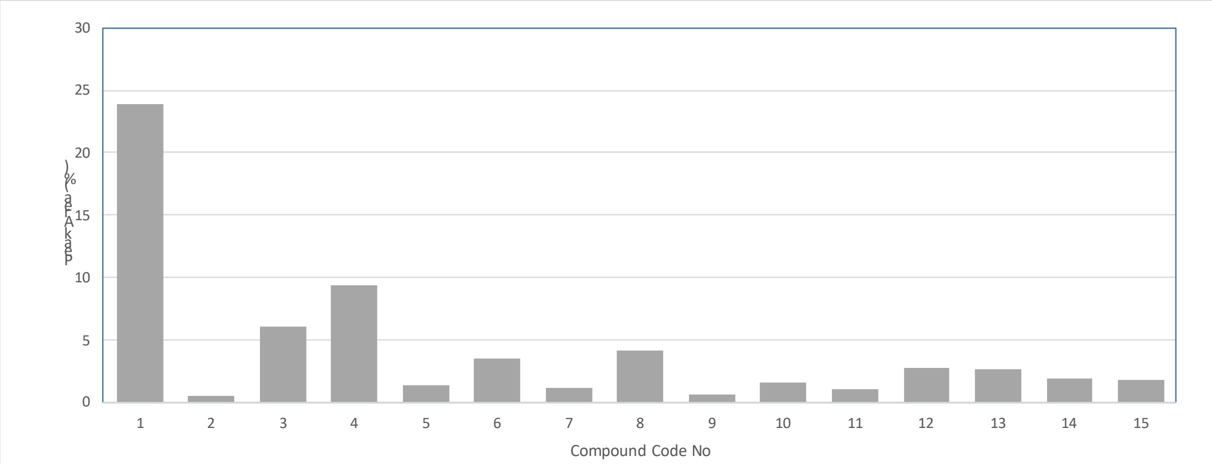

Fig. 5. Monoaromatics product distribution resulted from the catalytic conversion of rice straw using 100% H-ZSM-5 at 450 °C, Code No :

1	1,3-dimethylbenzene/m-xylene	6	1-propynylbenzene	11	1-methyl-2-(1-methyl-2-propenyl-indene
2	*n*-propylbenzene	7	diethylbenzene	12	2,3-dihydro-1H-indene
3	1-ethyl-2-methylbenzene	8	2-methyl-1-propenylbenzene	13	2,3-dihydro-5-methyl-1H-indene
4	1,2,3-trimethylbenzene	9	1,2,4,5-tetramethylbenzene	14	2-methylindene
5	*o*-diethylbenzene	10	1-methyl-2cyclopropen-1yl-benzene	15	4,7-dimethyl-1H-indene

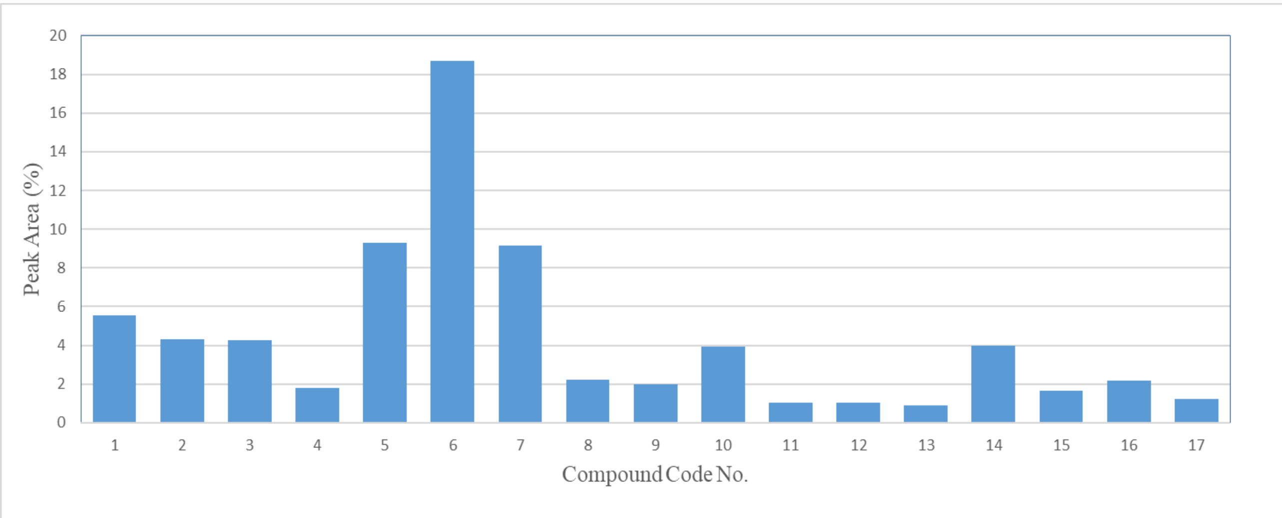

Fig. 6. Monoaromatics product distribution of catalytic conversion process of Rice straw using 100% H-ZSM-5 at 475 °C, Code No :

1	ethylbenzene	7	1-ethyl-2-methylbenzene	13	1-methyl-1-butenylbenzene
2	1,4-dimethylbenzene	8	cyclopropylbenzene	14	Indene
3	Ethenylbenzene/Styrene	9	diethylbenzene	15	2,3 Dihydro-5-methyl-H-indene
4	n-propylbenzene	10	methy (1-methylethyl) benzene	16	2-methylindene
5	1,2,3-trimethylbenzene	11	1,2,3,5-tetramethylbenzene	17	1,3-dimethyl-1H-Indene
6	1,3-dimethylbenzene/m-xylene	12	2-Methyl-2 cyclopropen-1-yl benzene		

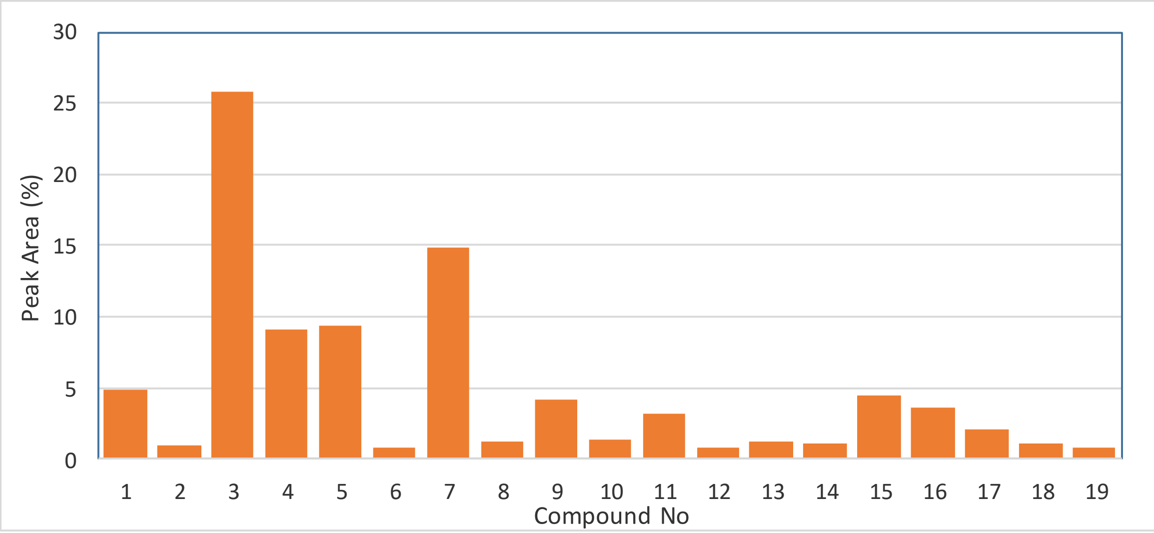

Fig. 7. Monoaromatics product distribution for catalytic conversion process of rice straw using 100% ZSM-5 at 500°C, Code No :

1	ethylbenzene	8	1-propenylbenzene	15	Indene
2	Propylbenzene	9	cyclopropylbenzene	16	2,3-Dihydro-5-methyl-1H-indene
3	*m*-xylene	10	Diethylbenzene	17	2-MethylIndene
4	*o*-Xylene	11	2-methylpropenyl benzene	18	2,3-dihydro-4,7-dimethyl-1H-Indene
5	1-ethyl-2-methylbenzene	12	2-Methyl-2-propenylbenzene	19	1,1-dimethyl-1H-Indene
6	1-ethyl 3-methylbenzene	13	1,2,4,5-tetramethylbenzene		

The data also implies that the presence of B_2O_3 in the mixture of the catalyst have no significant effect on the product distribution of the monoaromatics. The reason why that the presence of B_2O_3 in the mixture of the catalyst have no significant effect on the product distribution of the mono-aromatic compounds is due to the mixing process of HZSM-5 catalyst and B_2O_3 wasn't done using the proper method. There are several methods for catalyst mixing, which one of the best way is by impregnation [5]. Impregnation is a process where the porous support is impregnated with a solution of a compound of the desired catalytic constituent.

According to a research done by Asaftei, et al.[6] which was the conversion of Butane-Butylene mixtures into more valuable aromatic rich hydrocarbons over HZSM-5 and boric acid prepared by impregnation technique, suggested that the boric acid (oxide precursor of B_2O_3) impregnation of HZSM-5 zeolite may narrow the pore openings, so the specific active area is decreased. The dispersion of B_2O_3 that takes place inside the pores and outside on the surface of HZSM-5 leads to the formation of monolayer of B_2O_3. The presence of B_2O_3 particles changed the diffusivity of hydrocarbons by reducing the number of accessible active sites. The changes of both diffusivity and acidity enhance the shape selectivity. The mono layer of B_2O_3 inside the pores of HZSM-5 blocked most of the bronsted acid sites. Then, the HZSM-5 catalyst with the addition of boron species proves to be useful in conversion process to produce aromatics such as benzene, toluene, and xylene compounds. While in this research, the mixing process of the HZSM-5 and B_2O_3 catalyst was only done by physical mixing using mortar and pestle.

The preparation of catalyst by physical mixing, it suggested that the B_2O_3 catalyst was low homogeneous mixed and the particle in low dispersion throughout the surface pores of HZSM-5 catalyst. Due to this low dispersion, B_2O_3 catalyst led to the accumulation of B_2O_3 catalyst in the mouth of the pores of HZSM-5 catalyst instead of reducing some of the active sites of the HZSM-5 catalyst to enhance the shape selectivity of the HZSM-5catalyst. Shafagat [7] reported that the toluene was produced from the direct hydrodeoxygenation of cresol (methyl-phenol). Toluene then with the help of zeolites properties of the ZSM-5 catalyst, will be converted to 1,3 Dimethyl benzene or m-xylene through the reaction of trans alkylation. Meshram [8] also reported that ZSM-5 zeolites possess high selectivity and stability in the transalkylation reaction. So, it explains how the high yield of 1,3 Dimethyl benzene was produced.

4 Conclusions

The catalytic conversion of rice straw with ZSM-5 catalyst and its mixture with B_2O_3 with different fraction of ZSM-5 and B_2O_3 resulted in the production of mono aromatics compound. Monoaromatics compound can be produced through catalytic conversion process of rice straw using the mixture of HZM-5 and B_2O_3 catalyst under 450, 475, and 500 ^{O}C in the atmospheric operating condition. The products resulted from the catalytic conversion of the rice straw can be distributed in to 4 major chemicals compound groups which are phenol compounds, ketone compounds, mono aromatic compounds, acid compounds, and other chemical compounds. The catalytic conversion of the rice straw using 100% HZM-5 catalyst under the temperature of 450 ^{O}C yielded 63.11% mono aromatic compounds. With the operating temperature of 475 ^{O}C, it yielded 73.21 %. And the operating temperature of 500 ^{O}C yielded 91.33% of aromatic compounds. The yield of mono aromatic compounds will increase as the amount of fraction of HZM-5 in the mixture of HZM-5 and B_2O_3 catalyst, and the operating temperature also increased.

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