The combined process of pyrolysis and catalytic cracking of rice straw using ZSM-5 and γ-Al₂O₃ catalyst prepared by physically mixing

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Abstract. Rice straw contains high lignocellulose so it can be used as a raw material for producing bio-oil through pyrolysis process. The combined with catalytic cracking, the product of bio-oil could be shifted to the certain compound toward cyclohexene selectively using catalyst. Cyclohexene is important compound as the precursor of bio-polymer adipic acid that the route lead to the manufacture of nylon 6,6. This study is to give insight the possibility to produce cyclohexene from rice straw as renewable source material with variation of catalyst composition and the temperature. The ZSM-5/γ-Al₂O₃ catalyst composition is varied to observe the effect on its product distribution mainly on the influence in producing the target products. By this way, the optimum catalyst composition to maximize the target products could be confirmed. The bio-oil product and the product of catalytic cracking were characterized by Gas Chromatography Mass Spectroscopy (GC-MS). The result showed that the using of catalyst composition with 60% ZSM-5 and 40% Al₂O₃, the yield of cyclohexene up to 61.12% has been achieved as the main product under pyrolysis condition of 425°C in the atmospheric condition with 80 ml/min nitrogen flow rate.

1. Introduction
As the main precursor for nylon 6,6 and polyurethane plastics, the adipic acid (ADA) has great importance to industry. It is commonly prepared in industrial process by oxidizing cyclohexanol or cyclohexanone using nitric acid (shown in Figure 1) [1, 2].

Some conventional methods that have been applied to produce cyclohexene are considered less effective and require a high financial cost. Agricultural waste such as straw can be used as raw material for the production of cyclohexene using pyrolysis and catalytic cracking method [3].

Figure 1. The possible reaction pathway proposed by [2]
Studies to date have shown that both furfural and furan are major intermediates products resulting from the catalytic fast pyrolysis of glucose and cellulose (shown in Figure 2). With catalytic fast pyrolysis over ZSM-5-based catalysts in a continuous fixed-bed system, furfural was converted into gasoline-type fuels. The first step in furfural conversion is the de-carbonylation of furfural to form furan, followed by furan conversion into intermediates such as cyclohexene and 3,4-dimethylbenzaldehyde, in the ZSM-5 pores. These intermediates are subsequently available for transformation into aromatics, coke, light olefins and carbon oxides [4, 5].

**Figure 2.** Reaction chemistry of the catalytic fast pyrolysis of biomass [4]

Biomass can be converted into a variety various hydrocarbon compounds or chemicals using different technologies. One type process is fast pyrolysis, which is convenient for the conversion of biomass into liquid products known as bio-oils [4]. However, the bio-oils are of poor quality if they are to be used as a replacement for diesel and gasoline fuels. They are thermally unstable, degrade with time, acidic, and are not compatible with existing petroleum-derived oils. Pyrolytic bio-oil has great potential to be utilized and these it must be upgraded [6].

The catalytic conversion of biomass is the proven ways that can be used to improve the quality of bio-oil. Basically, this process involves the biomass thermal decomposition stage as occurs in conventional pyrolysis process, but with the presence of catalyst. Catalyst addition to this process led the biomass pyrolysis vapor consisting of small oxygenate compounds enter the pores of the catalyst in which they are converted to CO₂, water, coke, and aromatic hydrocarbon compounds [7].

Rice straw is selected as the raw material manufacture of cyclohexene because the numbers are abundant in Indonesia and has not been fully utilized. Availability of rice straw increased also food needs so the costs required for production becomes cheaper. The second reason is the handling of waste rice straw that has been done so far has caused many environmental problems. Rice straw wastes are more often left to rot, piled and burned. The smoke from burning may cause pollution and negative impact on the environment, so it should be considered preventive efforts. This experiment will help to find a new way of producing cyclohexene.

Rice straw contains lignocellulose high enough so that it can be used as an alternative energy source. Lignocellulosic biomass contains the main constituent components, namely cellulose (30-50 wt%), hemicellulose (15-35% by weight), lignin (13-30 wt%), and other organic compounds. In regard to the conversion of biomass such as rice straw, the most important part is the polysaccharide because the part that will be hydrolyzed into monosaccharides such as glucose, sucrose, xylose, arabinose and other compounds before they are converted into products [8].
Therefore, in this work to convert biomass into bio-oil contains cyclohexene compounds mixed catalyst of ZSM-5/Al$_2$O$_3$ are used. The composition of the catalytic conversion product of biomass will be analyzed to determine the effect of temperature and ZSM-5 percentage in the mixed catalyst in forming the target product (cyclohexene).

2. Experimental

2.1. Materials

The type of biomass used as a feed in this experiment is a rice straw. Rice straw must be grounded to a particle size of 1 mm by a grinding machine, it then dried by oven at 60°C for 5 hours to reduce its water content to <10% of total mass. In this case alumina and ZSM-5 can be combined directly without having to do any further process. The total mass of catalyst is 1 gram, the catalyst used in each catalytic conversion process with different composition variations is as much as 1 gram. The catalyst used cannot be excessive so as not to cover the flow of N$_2$ gas which will cause the blockage of flow in the tube. However, if the amount of catalyst used is too small it will cause the catalytic conversion process to be less than optimal.

2.2. Methods

The biomass catalytic conversion was performed in a stainless-steel reactor tube. The reactor tube has a length of 40 cm, 4.2 cm in diameter and it has the capacity up to 60 grams. The material used for the reactor tube was stainless SA-304 type because it is resistant to high temperature until 800°C. To prevent the rice straw from falling through the bottom of the tube, it was added with a steel filter with the size of 60 mesh. The scheme of the flow can be seen in Figure 3.

![Figure 3. Schematic diagram of experimental apparatus for biomass pyrolysis](image)

Biomass pyrolysis was performed at 550°C and 1.2 atm pressure. N$_2$ gas with a flow rate of 80 ml/min was used as an inert pyrolysis gas. The N$_2$ gas will remove the air present in the reactor tube before the catalytic conversion reaction takes place. N$_2$ gas will also force the pyrolysis gas vapor to move downward and enter the pores of the catalyst in which they are upgraded.

Catalytic cracking is the last process, at this stage the product from pyrolysis is injected to the catalytic cracking, which than reacted with the catalyst. This process will produce a final sample in gas phase. Schematic diagram of experimental apparatus for catalytic conversion was shown in Figure 4. Then make variation type and composition of catalyst, the catalyst composition of ZSM-5 in the mixed catalyst used was 100%, 90%, 80%, 70%, and 60% wt. by weighting the alumina and ZSM-5 with certain mass, based on the composition that is tested. After having the result from the previous catalytic
cracking. Than we maximize the result by making variation of temperature to maximize the yield of cyclohexene, varies from 325-425°C with the difference of 25°C.

Figure 4. Schematic diagram of experimental apparatus for bio-oil catalytic conversion

3. Results and Discussion

3.1 Pyrolytic Bio-Oil

This experiment is required to produce bio-oil from the pyrolysis process without using a catalyst. These pyrolytic bio-oil is what will be used for the process of catalytic cracking in the next stage. The operating conditions used are temperature of 550 °C, 1.2 atm pressure, and N₂ gas with a flow rate of 80 ml/min. Throughout the pyrolysis process that has been repeated 7 times under a constant condition and the same process, have produce pyrolytic bio-oil with an average of 35.90%. (shown in Figure 5).

Figure 5. Product yield from rice straw pyrolysis at temperature of 550°C
These results indicate that the use of 50 grams of rice straw biomass feed has been good enough to produce bio-oil for feeds in the next process in this experiment. The nitrogen gas spreads perfectly in the tube as it flows from the top of the reactor and passes through the whole bed of rice straw. The gas product is quenched in a spiral tube submerged in a tub of cooled water in order to form a product in liquid form (bio-oil).

The pyrolysis product (bio-oil) is characterized using Gas Chromatography Mass Spectrometry (GC-MS). The purpose of this characterization is to determine the component containing the bio-oil. The instrument of GC-MS is “Agilent Technologies 7890A Gas Chromatograph with Auto Sample and 5795C Mass Selective Detector with data system from Chemstation, also the column use was HP 5 MS Capillary Column. The characterization result is shown chromatogram that is based on the retention time and the peak area of the component. The characterization for bio-oil can be seen in Figure 6.

![Chromatogram of GC-MS for sample resulting from the pyrolysis of rice straw at 550°C.](image)

**Figure 6.** Chromatogram of GC-MS for sample resulting from the pyrolysis of rice straw at 550°C.

Based on Table 1, it can be seen that bio-oil derived from rice straw biomass contains phenol compounds (23.73%), ketones (24.35%), furans (15.48%) as main products. There is no cyclohexene content in the bio-oil of this process. This result will be compared with the bio-oil composition of the catalytic conversion, especially for the study of cyclohexene product yield.

**Table 1.** The main product from rice straw pyrolysis at 500°C and 1.2 atm

| Groups   | Compounds                                    | Area (%) | Total (%) |
|----------|----------------------------------------------|----------|-----------|
| Phenols  | Phenol                                       | 4.86     |           |
|          | Phenol, 4-Methyl                             | 3.86     |           |
|          | Phenol, 2-Methoxy                            | 2.45     |           |
|          | Phenol, 2,6-Dimethoxy                        | 1.62     |           |
|          | 1,2-Benzenediol                              | 3.91     |           |
|          | 1,4-Benzenediol                              | 3.66     |           |
|          | 1,2-Benzenediol, 4-Methyl                    | 2.06     |           |
|          | 1,4-Benzenediol, 2-Methyl                    | 1.31     |           |
| Ketones  | 2-Cyclopenten-1-One, 2-Hydroxy-3-Methyl       | 4.83     | 24.35     |
|          | 2-Cyclopenten-1-One                          | 4.28     |           |
| Groups | Compounds | Area (%) | Total (%) |
|--------|-----------|----------|-----------|
|        | 2-Cyclopenten-1-One, 3-Methyl | 2.22 |         |
|        | 2-Cyclopenten-1-One, 2-Methyl | 1.72 |         |
|        | 2-Cyclopenten-1-One, 3-Ethyl-2-Hidroxy | 1.29 |         |
|        | 2-Propanone, 1-Acetyloxy | 4.09 |         |
|        | 1-Hydroxy-2-Butanone | 4.08 |         |
|        | 2-Butanone, 3-Hydroxy | 1.84 |         |
| Furans | 2-Furanmethanol | 6.10 |         |
|        | 2-Furanone, Dihydro | 6.09 |         |
|        | 5-Hydroxymethylhydrofuran | 1.68 | 15.48 |
|        | Tetrahydro-2-Furanylmethanol | 1.61 |         |

### 3.2 The Effect of Catalyst Composition

The catalyst composition used in this experiment were 100, 90, 80, 70 and 60% with a constant temperature at 425°C. The variation of catalyst compositions is to determine mainly on the formation cyclohexene compound product.

**Table 2.** The effect of catalyst composition to pyrolysis product

| Temperature | Sample name | 1 | 2 | 3 | 4 | 5 |
|-------------|-------------|---|---|---|---|---|
| 425°C       | ZSM-5       | 100% | 90% | 80% | 70% | 60% |
|             | Al₂O₃       | 0% | 10% | 20% | 30% | 40% |
| Main Product| Pentadecyne | 7- | 9,17-Octadecadienal | 3,13-Octadecadienol | 7-Pentadecyne | Cyclohexene |
| Yield (%)   |             | 60.55 | 48.74 | 60.21 | 51.64 | 61.12 |

The Table 1 shows sample 1 to 5, the product of catalytic cracking with catalyst composition 100%, 90%, 80%, 70%, and 60% of ZSM-5/Al₂O₃ at the temperature of 425°C. The GC-MS chromatogram from sample 1 to 5 inform that each sample has different result as the main product of pyrolysis. The highest concentration was from sample 1 (60.55% area) is with retention time of 52.788 s. Based on the Chemstation data base this compound is 7-Pentadecyne with quality 90. In sample 2, the retention time is 52.726 with highest concentration of 48.74%, this compound is 9,17-Octadecadienial (quality of 89). Chromatogram of product from sample 3 has 52.840 retention time with highest concentration of 60.21%. Based on Chemstation data base this compound is 3,13-Octadecadienial with quality 53. In sample 4, 7-Pentadecyne is the highest concentration (51.64%) with quality 90 at 52.840 retention time. And sample 5, cyclohexene at 52.989 retention time is the highest concentration (61.12%) with quality 91.

The characterization with GC-MS instrument shows the result with various composition of catalyst. It could be concluded among the 5 product samples with various catalyst compositions, the sample 5 with 60% ZSM-5 and Al₂O₃ gives the result of product catalytic cracking with high concentration of cyclohexene. As seen in the chromatogram (shown in Figure 7), the sample 5 has cyclohexene compound with the quality 91. Cyclohexene in the chromatograph is shown in the retention time at 53 minutes.
Figure 7. Chromatogram of GC-MS for sample resulting from the pyrolysis of rice straw with 60% ZSM-5 and Al2O3 at temperature of 450°C.

3.3 The Effect of Temperature of Catalytic Cracking Bio-Oil Product

After obtaining the cyclohexene, the experiment of catalytic cracking was done with variation of temperatures: 325, 350, 375, 400, and 425°C. This experiment of variation temperature could maximize the selectivity of cyclohexene product formation.

Figure 7 shows catalytic cracking product with catalyst composition 60% ZSM-5 and 40% Al2O3, at temperature of 425°C. This sample is the best example condition we will discuss further. The result of GCMS chromatogram the retention time is 52.989 with Cyclohexene concentration of 61.12 %.

The characterization from this catalytic cracking shows various temperatures with the lowest temperature 325°C and the highest temperature at 425°C. Since below 325°C the product from the catalytic cracking is still in liquid phase and above 425°C the tube inside the furnace will not stand the heat and crack. All compounds are measured based on the retention time. As seen from the chromatograph above, cyclohexene is at the retention time of 52.989.

Phenolic compounds were proceeded through catalytic cracking reaction. Hydrogenolysis removes the oxygen benzene ring, then subsequent hydrogenation cyclohexene. However, it is possible for the reaction to proceed primarily through hydrogenation of the aromatic ring to cyclohexanol with subsequent hydrogenolysis to rapidly dehydrate the alcohol to cyclohexene. Product of phenol are commonly benzene, cyclohexane and cyclohexene.

From the Figure 8 we can conclude that the most optimal for cyclohexene production is at temperature of 425°C. It has catalyst composition of 60% ZSM-5 and 40% Al2O3, also the temperature is at 425°C.

Based on the experiment that is done, with 100% ZSM-5 will not produce cyclohexene. The amount of catalyst composition will give effect on the production of cyclohexene. If the ZSM-5 composition is too much it will not produce cyclohexene as shown in the result. However, with the right amount of composition which is 60% ZSM-5 and 40% Al2O3 it will produce cyclohexene. Temperature plays a big role in the concentration of cyclohexene produce. As seen on Figure 8 the higher the temperature the greater the concentration of cyclohexene.
Figure 8. The effect of Temperature of catalytic cracking to cyclohexene product.

4. Conclusions
The combined process of pyrolysis and catalytic cracking of biomass rice straw to find toward the special target compound can be performed adequately. The catalyst used in this reaction was high significantly selective due to the composition product of bio-oil produced from pyrolysis is quite different with the composition of products resulted the catalytic cracking especially for the formation cyclohexene compound. The product distribution of catalytic cracking reaction of bio-oil is very sensitive with the catalyst composition mainly to produce cyclohexene compound and the reaction temperature was favorable for production of cyclohexene in the higher temperature is needed. Based on the temperature observed, at temperature 425℃ of catalytic cracking using 60% ZSM-5 and 40% Al₂O₃ produced the highest cyclohexene concentration which is attained up to 61.12%.

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