The usage of carbon dioxide gas on pyrolysis process and its effect on biomass catalytic conversion

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Abstract. Several advantages of the usage of CO$_2$ gas in pyrolysis theoretically could be the role for thermal efficiency, elimination oxygenated group, deep decomposition of biomass. The aim of this study was the use carbon dioxide as carrier gas and its effect on the catalytic product distribution from the rice husk type biomass. The Nickel/Alumina catalyst was prepared by impregnation method and calcination process of the Ni(NO$_3$)$_2$ $\cdot$ 6H$_2$O and Al$_2$O$_3$ mixture. The characterization was also performed by XRD analysis and BET adsorption method. The XRD analysis confirm the high crystallinity of NiO and NiAl$_2$O$_4$ phase which is considered as the interaction result between the NiO particle and the surface of $\gamma$-Al$_2$O$_3$. But the result of BET method suggested that the blockage the pore mouth of catalyst support $\gamma$-Al$_2$O$_3$ which is more likely due to the excessive amount of NiO particles. The comparison of pyrolysis carrier gas between CO$_2$ and N$_2$ and the variation of the operating temperature were performed to determine the product distribution distinctions. The catalytic conversion was done under the temperature 450, 475, 500, and 525°C. Experimental results show that the variation of carrier gas of the pyrolysis process and the variation of operating temperatures resulted in a difference product distribution. The dominant compounds formed as the temperature increases were ketone and benzene compounds.

1 Introduction

Most commodities in agriculture waste produce nearly 80 % in the form of biomass that can be used as an alternative energy source. One of the biomass that is abundant supply in Indonesia is rice husk which has high levels of lignocellulose. The high potential of this natural resources should be explored the transformation route toward a useful hydrocarbon fuel or chemical. Commonly to achieve the route, the transformation of biomass is through the pyrolysis process with nitrogen gas as carrier gas, and it is still rarely the usage of carbon dioxide gas. Many advantages of the usage of this gas theoretically could be the role for good thermal efficiency of biomass pyrolysis, elimination oxygenated group, deep decomposition of biomass, Boudart reaction for bio-char gasification and activation. So, the aim of this study is to use carbon dioxide as the pyrolysis carrier gas and to observe the resulting product distribution. So, biomass as a renewable source, will undoubtedly play an important role in the future.

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]. Which then, the bio fuels could be upgraded using catalyst to refine the bio oils into hydrocarbon or other intermediates [3].
The catalytic conversion is one of the proven process that could be used to upgrade and improve the quality of the bio oil. For this work, in order to convert the biomass into various compounds, Ni/Al₂O₃ or Nickel-Alumina can be used as the catalyst for the pyrolysis process. The type and composition of the catalyst and operating temperature can affect the value of the conversion and selectivity of end product, making it important to know the right combination in order to produce useful hydrocarbon like aromatic, paraffin (linear or branch alkane), olefin and cyclo-paraffin with maximum selectivity. A variation of carrier gas from Nitrogen to Carbon Dioxide was also done in hopes of getting a variation of products formed by the pyrolysis of the rice husks. This was done due to the improved thermal efficiency of the pyrolysis process that carbon dioxide provides as well as the deeper decomposition of the complex compounds of the rice husks. Other than the varied carrier gas, the catalytic conversion was done under four different operating temperatures: 450, 475, 500, and 525°C. These variations were applied in order to analyse the final product distribution of each carrier gas and working temperatures.

2 Experimental method

2.1 Material
The type of biomass used as the feed for this experiment was rice husks. At the beginning of experiment, a grinder or grinding machine was used to lower the size of the rice husks down into 1-3 mm length. To reduce the water content lower than 10% of the total mass, the rice husks was placed in the electric heater is dry for 5-6 h at temperature of 60°C. For each experiment running, the fixed bed was arranged by 1 g of treated rice husks, 1 g of mixture of catalyst, and 1 g of quartz sand mixture.

Various loading composition of NiO/γ-Al₂O₃ or Nickel Alumina catalysts were used for this catalytic pyrolysis experiment. The amount of catalyst used was 1 g for all samples of different carrier gas and temperature. The bed arrangement composed of rice husk bed and catalyst bed was adjusted in the feasible amount in order the operation of the experiment in the suitable condition with the effort in the lower pressure through the bed and the product collected produced from the pyrolysis reaction runs could be allowable to detect. The Nickel-Alumina catalyst is prepared by dissolved the precursor of Ni(NO₃)₂·6H₂O crystalline into the deionized water as much as 30 ml in beaker glass. The mixture was placed on the pan of electric heater at 70-80°C equipped with magnetic stirrer and stir completely until solution Ni(NO₃)₂ prepared. This solution was then used to impregnate γ-Al₂O₃ powder by pouring it into the solution and mix completely. The mixture was then kept in drying at this heating temperature until the solvent of water evaporated and resulting the solid state. This solid was subsequently calcined in the atmospheric condition in air at temperature 300 and 600°C for 2 h irrespectively.

2.2 Methods
The catalytic pyrolysis was performed at the atmospheric pressure with the gas rate of N₂ or CO₂ at around 40 ml/minute, and the operating temperature of 450, 475, 500, and 525°C. The reactor tube was 300 mm in length, and 12 mm in diameter, and fabricated from materials that are inert properties at high temperatures experimental running. The arrangement of bed inside the reactor was carried out carefully. Quartz wool was used at the lower part of the reactor tube to plug the catalyst, preventing the bed from slip down from the tube. The amount of the rice straw, catalyst, and quartz sand is 1 gram each. The amount of bed should be adjusted so bed of the rice straw, catalyst, and quartz sand inside the reactor tube were avoid the reactor tube being clogged. After reactor tube has been perfectly filled by the catalyst and rice bed inside, the reactor was then placed into an electric cylindrical shape furnace with an effort to put the rice husks and catalyst at the position where the heat is at the highest.

As shown in figure 1, the arrangement of bed in such way the pyrolysis of rice husks was firstly to take place, by placing the bed of rice husks over the bed catalyst with mixture with quartz sand as function of a reducing the pressure drop through the bed and to homogenously temperature. By this way, the pyrolytic vapour resulted from the thermal decompose of biomass bed was be directly contacted with catalyst in the lower part position. This way, the vapour from the rice husks should be upgraded when it flowed down through the layer of catalyst. The carrier gas rate was 40 ml/minute N₂ or CO₂,
besides was able to carry out the vapour product form the rice husks decomposition for contacting to the layer bed of catalyst, its function also could purge the possible air existence inside the reactor tube.

![Diagram of experimental apparatus for biomass catalytic conversion](image)

**Figure 1.** Schematic diagram of experimental apparatus for biomass catalytic conversion.

The product of the catalytic conversion between the rice husks and catalyst was visually indicated by the occurrence of gaseous formation at the bottom of the reactor. The gas produced from the catalytic conversion was then dissolved by a method of cold acetone absorption filled in glass bottle submerged in the ice-water bath. The bath temperature was kept near 0°C by holding it inside the Dewar flask. Therefore, the gas undergone a condensation and dissolution process perfectly and finally this catalytic conversion product mixture as liquid sample for chemical analysis by GC-MS. The GC-MS was high performance instrument analysis performed by courtesy of the Forensic Laboratory of Polri institution with using capillary column Agilent 19091S-433 HP-5MS.

### 3 Result and Discussion

#### 3.1 Product distribution

The carrier gas used for the pyrolysis process was either Nitrogen or Carbon Dioxide. Beside carrier gas variation, the catalytic conversion was conducted under different temperatures. This experiment was conducted under the Temperature variation of 450°C, 475°C, 500°C, and 525°C. Figures 2 and 3 show the product distribution resulted from catalytic conversion of rice husks using different carrier gas and at different operating temperatures. For the catalytic conversion at 450°C, Both the Nitrogen sample and the CO₂ sample yield large amounts of Ketone Compounds and Benzene compounds with Ketone compounds dominating the sample analysis results with more than 50% detected on both samples.

When the temperature was bumped to 475°C, it’s observed that the trend is going to be decrease in the most detected compounds, Ketone and Benzene, and the increase of the more complex compounds as well as other compounds such as Furan Compounds and Aldehyde compounds. Ketone production dropped significantly in both the nitrogen and carbon dioxide samples while Benzene increased in the...
nitrogen sample but decreased in the carbon dioxide sample. This is due to Carbon Dioxide preventing the formation of VOCs, thus suppressing the benzene production.

The trend of increasingly diverse compound production continues as temperatures rise to both 500 and 525°C. The trend of decreasing ketone production on both the nitrogen and carbon dioxide samples also continues with the nitrogen sample detecting as small as 15% on the 525°C sample. The decreasing benzene formation trend on the carbon dioxide samples also seems to continue as the temperature increases, incrementally decreasing from 25% on the 450°C sample to around 15% on the 525°C sample. Meanwhile production of other compounds, particularly Acetic Acid and other complex compounds incrementally increases as the temperature increases.

Figure 2. Product distribution from catalytic conversion of biomass over four different temperatures using nitrogen carrier gas.

Figure 3. Product distribution from catalytic conversion of biomass over four different temperatures using Carbon Dioxide Carrier Gas.
3.2 Rice husks Conversion

The results of performing pyrolysis of rice husks with NiO/γ-Al2O3 catalyst with either N2 (nitrogen) or CO2 (Carbon dioxide) as the carrier gas. The reasons of CO2 was used as an experimental carrier gas because in the case of integrated valorization of biomass by pyrolysis or gasification, CO2 can play a vital role in each stage, mainly including biomass pyrolysis, biomass/ biochar gasification, biochar activation, and tar cracking/reforming. CO2 as a reaction medium can significantly improve the thermal efficiency of biomass pyrolysis. Pyrolysis in CO2 results in deep decomposition of biomass compared to pyrolysis in N2. Also, CO2 has an affinity to react with hydrogenated and oxygenated groups, leading to biochar with a higher specific surface area (SBET). Thus, exploiting CO2 as a reaction medium in biomass pyrolysis provides an attractive option for enhanced generation of syngas and tuned adsorption capability of bio-char. In addition, the CO2 pyrolysis of biomass can enhance the thermal cracking of harmful organic compounds, thus suppressing of the formation of benzene derivatives (e.g., volatile organic compounds) and polycyclic aromatic hydrocarbons. In general, CO2 gasification of biomass serves a dual purpose of reducing pollution and generating syngas. In addition, introducing CO2 with steam as a gasifying agent can enhance CO production.

Besides having varied carrier gas, the catalytic conversion was also performed under varied temperature values (450, 475, 500, and 525°C). This range of temperatures was selected because the temperature less than 450°C, the activity of catalyst under low performances. The result was showed in table 1.

Table 1. The conversion risk husk under N2 and CO2 carrier gas at various pyrolysis temperatures

| No. | Sample Code | Carrier Gas | Temperature (°C) | Conversion |
|-----|-------------|-------------|-----------------|------------|
| 1   | 450. N2     | Nitrogen    | 450             | 84.5 %     |
| 2   | 475. N2     | Nitrogen    | 475             | 84.6 %     |
| 3   | 500. N2     | Nitrogen    | 500             | 84.7 %     |
| 4   | 525. N2     | Nitrogen    | 525             | 85.0 %     |
| 5   | 450. CO2    | Carbon Dioxide | 450       | 89.3 %     |
| 6   | 475. CO2    | Carbon Dioxide | 475       | 89.5 %     |
| 7   | 500. CO2    | Carbon Dioxide | 500       | 89.7 %     |
| 8   | 525. CO2    | Carbon Dioxide | 525       | 89.8 %     |

As shown in the table, the rice hulk conversion was little bit increased along with the increasing in pyrolysis temperature range using for both N2 and CO2 carrier gas. But the conversion difference was ca. 5 % with the higher conversion using CO2 as carrier gas for each temperature pyrolysis. This result is consistent to the considerations previously that CO2 as carrier gas could enhance the thermal efficiency and it makes the deep decomposition of rice hulk comparing those to usage N2 as carrier gas.

3.3 XRD and FTIR characterizations

Figure 4 showed the XRD (X-Ray Diffraction) of the sample Nickel-Alumina catalyst prepared impregnation and after undergoing calcination. Based on the JCPDS Cards-Metallic nickel-PDF65-0243--NiO-PDF22-1189, the XRD peaks appeared at 2θ are 37° and 63° indicating the NiO and diffraction peak with 2θ at 45° indicating the metallic Ni.
Figure 4. XRD (X-Ray Diffraction) Graph of the Nickel-Alumina Catalyst.

And the standard XRD peaks for $45^\circ$, $52^\circ$, and $77^\circ$ belong to the phase of NiAl$_2$O$_4$. The Figure 4 is clearly shown that the intensities of peaks indicated the high crystallinities for NiO at position $37^\circ$ and $63^\circ$ and for NiAl$_2$O$_4$ at those peaks suitable to the standard peak positions. It could be understood that the formation of NiO is obviously originated from the precursor of Ni(NO$_3$)$_2$ which undergone the decomposition and oxidation during the calcination stage. This transformation of Ni nitrate to be oxide phase (NiO) by oxidation is absolutely to occur because the such condition of calcination in the electric furnace operated at temperature $600^\circ$ C and the precursor directly contacted to atmospheric air.

As the figure shown, the peak attributing metallic Ni was nothing, this is logically suggested that a such condition of the calcination condition was impossible for the formation metallic phase catalyst. And the formation of NiAl$_2$O$_4$ phase in the catalyst prepared is considered to take place for the reaction of Ni and Al$_2$O$_4$ on the contacted surface between those particles. The formation of this phase could be function for a high stability of NiO particle dispersed on the surface Al$_2$O$_4$. It could be concluded the model catalyst system of NiO/ Al$_2$O$_4$ is perfectly prepared by impregnation method and could be a high activity catalyst in the pyrolysis.

As shown Table 2, characterization of NiO/ Al$_2$O$_4$ catalyst have been accomplished for the sample catalyst prepared by impregnation method and calcination to convert the precursor to be the oxide form of catalyst. The measurement by BET was commonly conducted by the nitrogen adsorption technique at temperature cryogenic which was submerged in the nitrogen liquid in the liquid form kept in the dewar flask. The data from the measurement was the amount nitrogen adsorbed with relative pressure. The results from the calculation of physorsorption data have been analyzed using the Langmuir model, the Brunauer-Emmett-Teller (BET) method, the Barret-Joyner-Halenda (BJH) method, and the de Boer and Halsey t-method.

Table 2. The Characterization of Nickel-Alumina Catalyst to quantify the impregnation effect.
### Method

| Method | Surface area |
|--------|--------------|
| Single Point Surface Area at P/P₀ = 0.267906954 | 3.1774 m²/g |
| BET Surface Area | 3.1481 m²/g |
| Langmuir Surface Area | 10.3295 m²/g |
| t-plot Micropore Area | 1.4912 m²/g |
| t-plot External Surface Area | 1.6569 m²/g |
| BJH Adsorption Cumulative Surface Area of Pores between 1.7 nm and 300.0 nm diameter | 1.484 m²/g |

### Method

| Method | Pore volume |
|--------|-------------|
| Single Point Adsorption Total Pore Volume of Pores less than 135.8492 nm diameter at P/P₀ = 0.985688417 | 0.008214 cm³/g |
| t-plot micropore volume | 0.000748 cm³/g |
| BJH Adsorption Cumulative Surface Area of Pores between 1.70nm and 300.0 nm diameter | 0.007441 cm³/g |

### Method

| Method | Pore size |
|--------|-----------|
| Adsorption Average Pore Width (4V/A by BET) | 10.4371 nm |
| BJH Adsorption Average Pore Diamater | 20.0611 nm |

The surface areas of catalyst calculated were 3.1774 m²/g by single point method, 3.1481 m²/g by BET method and 10.3295 m²/g by Langmuir method. Moreover, information such as pore size distribution, pore shape, monolayer volume, micropore volume and thickness of adsorption layer were also obtained. The calculation result of the surface area by single point was close to the that of BET method, indicates that this result should be referenced than the the that of Langmuir method. The Langmuir calculation method is assumed that the surface of the catalyst is uniform, that is, all the adsorption sites are equivalent. But, the real condition of such assumption is impossible, so surface area by Langmuir is three times more than the that by other methods. However, the such value of the surface area is so tiny comparing to the surface area of γ-Al₂O₃ (ca. 250 m²/g).

The phenomena of NiO pore blocking is also apparently showed by the calculation data of t-plot micropore and t-plot external surface area. Ideally, the micropore aperture has a diameter maximum 2 Angstrom (0.2 nm) and the 90% area catalyst should be dominated by micropore or internal surface than the external area. The total area of both area is the total area which is supposed to similar result with the BET or single point method. In this case, the data found is that the nearly similar result of the micropore (1.4912 m²/g) and the external area 1.6569 m²/g was lead to more strongly confirmation about the blockage of pore mouth of micropore of γ-Al₂O₃ catalyst support. The low micropore volume (0.000748 cm³/g) calculated by t-method was one tenth of surface area for pores of 1.70-300.0 nm 0.007441 cm³/g by BJH method is shown the insignificant amount of micropore than that of this kind of macropore with the aperture diameter more than 0.5 nm. In this case, the impregnation method with excessive amount of catalyst active site could transform the pore structure from the micropore dominant structure to be macropore dominant one in this case of catalyst indicating the measurement and calculation by BET and BJH Adsorption with resulting of average pore diameter 20.0611 nm It might be concluded that the impregnation method for the NiO/γ-Al₂O₃ catalyst preparation in excessive amount of NiO could decrease the change the physical properties of catalyst with the decreasing surface area and the blockage the pore of mouth of catalyst support.

### 4 Conclusions
The catalytic conversion of rice husks with Ni/Al₂O₃ Catalyst using either nitrogen or carbon dioxide carrier gas will yield different product distributions. The compounds that was produced the most out of all the samples were ketone compounds and benzene compounds. The samples that used carbon dioxide as the carrier gas yielded a larger number of compounds in general compared to the samples that used nitrogen as the carrier gas. Ketone and benzene production is shown to have a set trend (increasing or decreasing) across the board while other compound groups would fluctuate in their production. The presence of NiO particles dispersed on the surface has been blockaged onto the pore mouth of γ-Al₂O₃. So, the area was drastically decreased over than 90% from the origin surface area of γ-Al₂O₃. It might be concluded that the impregnation method for the NiO/γ-Al₂O₃ catalyst preparation in excessive amount of NiO could decrease the change the physical properties of catalyst with the decreasing surface area and the blockage the pore of mouth of catalyst support.

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