

The combined process of pyrolysis and catalytic conversion from rice straw toward light olefin hydrocarbon with supported metal catalyst

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Abstract. Light olefins are one of the most common petrochemical raw materials produced using non-renewable natural resources. Nowadays, lignocellulosic biomass is a promising source of feedstock ingredients for the production of olefins by pyrolysis. This study, the process is developed by a combination of pyrolysis and catalytic cracking processes with operating temperature around 500°C and N₂ flow rate around 150 ml/min. The supported metal catalyst namely La/Al₂O₃ and Zn/Al₂O₃ made with the impregnation method are used as catalysts. The catalytic pyrolysis process was carried out in a fixed bed tubular reactor with electric furnace as the heat source. To comprehend the catalytic cracking with catalyst, the experiment was also performed in condition without catalyst so that it could be compared to pyrolysis process itself. The output of pyrolysis is condensed by using cold absorption trap with acetone. FT-IR (Fourier Transform - Infrared) and GC-TCD (Gas Chromatography-Thermal Conductivity Detector) serve as analytical instrument in order to identify the presence and the quantity of light olefins group in bio-oil and bio-gas. In this method, there are several variations to be determined, there are type of catalyst and catalyst composition (1%, 5%, and 10%).

1 Introduction

Olefins and aromatic compounds are among the main products obtained by catalytic cracking of biomass pyrolysis vapors/bio-oil. These two hydrocarbon groups are the building blocks of petrochemical industry. Considering the wide range of applications of olefins and aromatics, it seems worthwhile to determine the factors which influence their production in bio-oil upgrading. Selectively, production of high yields of green aromatics and olefins through catalytic cracking of biomass pyrolysis vapor/bio-oil can be available alternative for production of these compounds from fossil fuel. This work is the first attempt to review the researches held in catalytic cracking of biomass pyrolysis vapors/bio-oil and bio-oil model compounds with the aim of defining the effects of the catalyst properties and reaction conditions which can change reaction selectivity in favor of aromatics and olefins [1].

Light olefins (i.e., ethylene, propylene and butylenes), which are the basic feedstocks for the petrochemical industry, are primarily produced through steam cracking and fluid catalytic cracking (FCC) using naphtha, light diesel and other petroleum products [2], but the production of olefins using biomass or biomass-derived feedstocks is also possible [3].

Catalytic conversion of biomass feedstocks into olefins was studied using HZSM-5 containing 6 wt.%

lanthanum. Biomass rich in cellulose or hemicellulose achieved higher olefins yield than the high-lignin feedstocks. Moderately increasing the medium acid sites of HZSM-5 via the incorporation of lanthanum effectively improved the selectivity and yield of olefins. Catalytic pyrolysis enhanced the production of olefins as comparing to pyrolysis. The results indicate that lignocellulosic biomass is a promising source of feedstock for the production of olefins [4].

The formation of light olefin compounds is commonly minor product in biomass pyrolysis. More likely, light olefins are only an intermediate during pyrolysis and susceptible converted into other compounds during the proceed of pyrolysis reaction, thus causing only a small amount of those olefins compounds could be obtained in the end of pyrolysis products [4].

In this study, catalytic pyrolysis of biomass with La and Zn-modified Al₂O₃ catalyst for selective light olefins production was carried out in a fixed bed reactor. There are several variations to be determined, there are type of catalyst and catalyst loading composition (1%, 5%, and 10%). The study may be helpful to deeply further the understanding of different parameters on biomass to light.

2 Experimental

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2.1 Materials

The type of biomass used as feed in this research is a rice straw. The samples of rice straw were originated from Pangandaran, West Jawa Indonesia. Rice straw was grinded and sieved into particle size of 400 μm . The samples were then dried in an oven at 60° C until attained a constant weight. All the samples were stored in sealed containers. The amount of samples used for each pyrolysis experiment was 2 g. The sample of rice straw had main characteristic of the cellulose (37.8%) [5].

2.2 Catalyst Impregnation Procedure

Catalysts used for this experiment was consisted of two parts; the supporting catalyst and active side. Alumina (Al_2O_3) was used as supporting catalyst meanwhile Lanthanum and Zinc metals were used as active site catalyst. The method for preparing the catalyst is called impregnation method. The supporting catalyst and the aqueous nitrate solution of active site precursors were mixed in beaker glass with each catalyst composition was 1%, 5%, and 10% w/w.

The mixture was dried by placing in a magnetic stirrer with equipped with heating pan at 80°C for two hours until the powder form formation. The calcination was carried out in electric furnace furnace at 300°C in 2 hours to remove the water content perfectly and subsequently calcined at 600°C for 2 hours to the formation of metal oxides form and to produce the strong interaction of dispersed metal oxides on the surface of Al_2O_3 catalyst support. The resulted catalyst preparations were denoted by $\text{La}/\text{Al}_2\text{O}_3$ and $\text{Zn}/\text{Al}_2\text{O}_3$. The amount of catalyst sample used for each pyrolysis experiment was 1 gram for each experiment.

2.3. Pyrolysis procedure

The combined process of pyrolysis and catalytic conversion was conducted in the operation of fixed bed reactor. The reactor was made from stainless-steel 316 tube with a diameter of 20 mm. The configuration of fixed bed was composed of 2 g rice straw biomass in the upper part of bed and 1 g of catalyst in the lower one. Detail arrangement of reactor bed system is shown in fig.1.

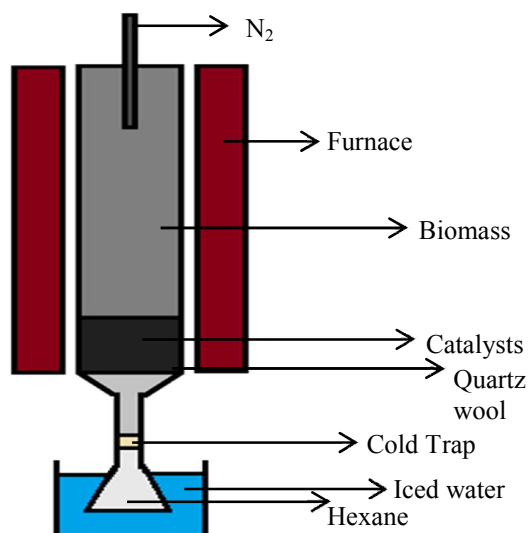


Fig. 1. Schematic diagram of experimental apparatus for biomass pyrolysis

The reactor was inserted into the electric furnace equipped with temperature control box with thermocouple injected in the middle position of furnace. The tip point of thermocouple was confirmed to contact to the wall of stainless steel reactor in order to fix the temperature set. The Nitrogen gas was introduced into the reactor through the top side and the operation of reactor pyrolysis was started by flowing the N_2 gas flow rate fixed at 150 ml/min in atmospheric pressure. The gas flow was controlled by flow controlling valve and then measured the N_2 flow in the effluent of reactor by bubble soap flowmeter. The function of N_2 gas was an inert pyrolysis gas and to remove the possible air presence inside the reactor tube and to lead the reactor in the homogeneous temperature condition.

The operation of combined pyrolysis was previously to set up the furnace with the temperature control box at 500°C. After the temperature reached, the fixed bed reactor was carefully fixed into the furnace and the N_2 gas flowed into the reactor to carry out the gaseous product of pyrolysis at the bottom of reactor tube. Carries N_2 and the products moved out and enter the absorption tube submerged in the cold ice-water bath kept in Dewar flask. The Liquid product could be perfectly condensed in this cold trap and the uncondensed gas was then flowing out from the cold absorption trap entering gas bag for collected samples. The condensation trapping condensation and gas absorption were shown in the figure 2.

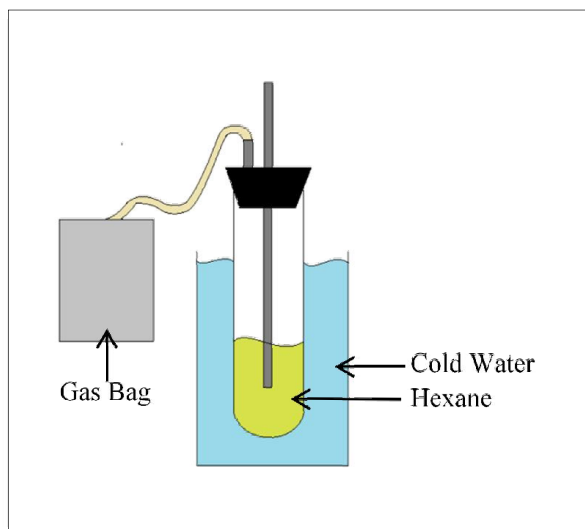


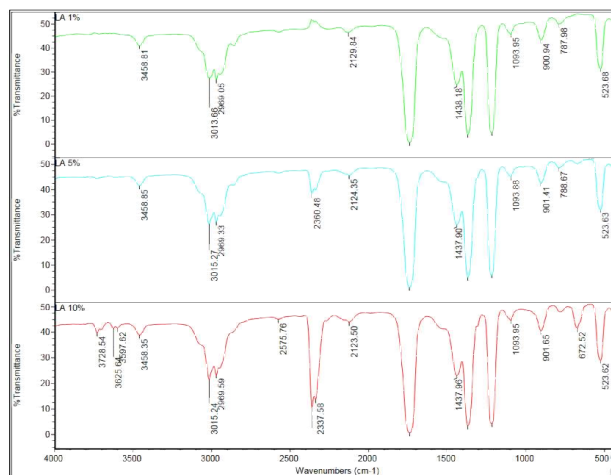
Fig. 2. Schematic diagram of experimental apparatus for condensation and gas absorption

The ice-water bath and hexane solvent for cold absorption trap was considered at same temperature measured 1°C because those liquids were kept in the dewar flask. Non-condensable gas such as light olefin was stored in gas bags. Non-condensable gas was further analyzed with FT-IR (Fourier Transform Infrared) and GC-TCD (Gas-Chromatography Thermal Conductivity Detector) to identify the presence and of light olefin in gas.

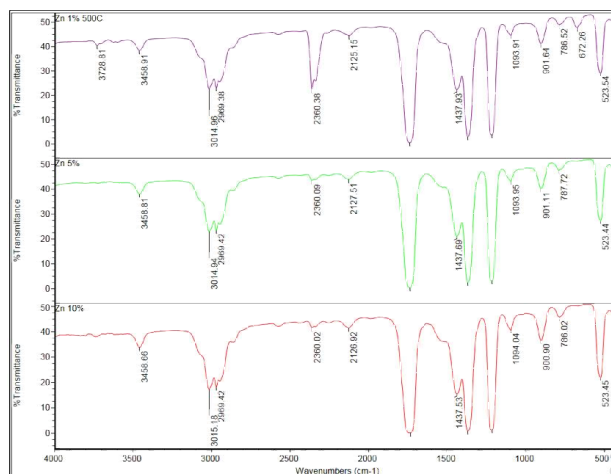
3 Result and discussion

3.1 Characterization of light olefin

The objective of this study is primarily to obtain the light olefin compounds in non-condensable gas product. Light olefins should be in the form of gaseous product due to the condition of atmospheric pressure and the tiny amount comparing the N₂ carrier gas. So, the olefins could be collected in the non-condensable gas after flowing the cold trap absorption. By using FT-IR, the presence of light olefin in the sample of gas could be detected and was shown in fig. 3. Light olefin is mainly consisted of light alkene, the presence could be attributed by the infrared spectrum in the range of wave number is 3010-3095 cm⁻¹, 1610-1680 cm⁻¹, and 675-995 cm⁻¹ with the intensity for each wavelength is moderate, changeable, and strong [6], which is shown in two figures a and b below.



(a)



(b)

Fig. 3. FTIR spectrum of gas olefin product resulted from catalytic pyrolysis of rice straw (cellulose-rich biomass) using catalyst : (a) La/Al₂O₃ (a) and (b) Zn/Al₂O₃

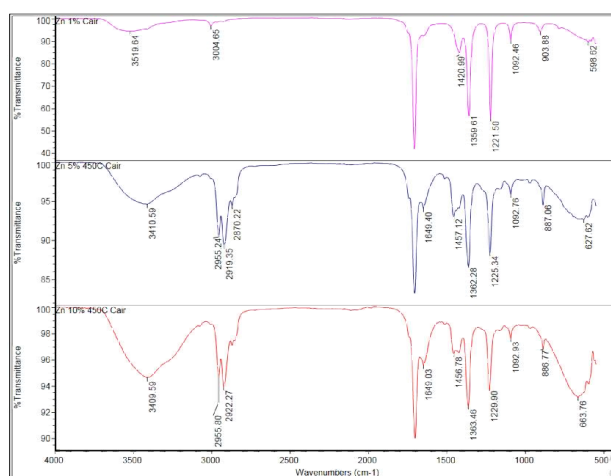


Fig. 4. FTIR spectrum of gas olefin product sample resulted from catalytic pyrolysis of lignin-rich biomass using catalyst Zn/Al₂O₃

Figure 4 is clearly shown that FTIR spectrum of the sample gas with the using of lignin-rich biomass is enough different comparing to figure 3. This result suggested that the amount of olefins produced from catalytic pyrolysis of cellulose-rich biomass is much higher than the olefins from that of lignin-rich one. So, the reaction mechanism for the formation of olefin compounds should be employed the feed stock from cellulose-rich biomass. To compare the result of olefin produced with using La/Al₂O₃ and Zn/Al₂O₃ catalyst, the following table (table 2) presents the results of the transmittance FT-IR spectrum data for light olefins peaks.

Table 2. Composition of light olefins from rice straw (cellulose-rich) pyrolysis

Catalysts	Composition	Light Olefins Transmittance (%)		
		3010-3095 cm ⁻¹	1610-1680 cm ⁻¹	675-995 cm ⁻¹
La/Al ₂ O ₃	1%	27	44	42
	5%	25	42	42
	10%	22	40	41
Zn/Al ₂ O ₃	1%	22	42	38
	5%	22	41	38
	10%	18	40	34

In general, the table 2 showed that the increasing of catalyst composition for La/Al₂O₃ and Zn/Al₂O₃ is lead to the decreasing of % transmittance for all ranges of wavenumber. But, it seems that the % transmittance of La/Al₂O₃ catalyst with the wavenumber range 3010-3095 cm⁻¹ is lead to significantly decreasing with the increasing of the composition than that of Zn/Al₂O₃ catalyst. And also the % transmittance of this range showed the significantly decrease as the increasing of La/Al₂O₃ catalyst composition than that of other ranges. Indeed, the trend of % transmittance should be inverse to the amount of light olefin containing in the samples.

To find how much yield of light olefin produced from pyrolysis process, the analytical instrument used was GC-TCD. The following table 2 presents the results of the GC-TCD analysis indicating light olefins content.

Table 2. Composition analysis of light olefins from rice straw (cellulose-rich) pyrolysis

Catalysts	Composition (%)	Yield Light Olefins (%)
La/Al ₂ O ₃	1	0.1
	5	0.26
	10	0.48
Zn/Al ₂ O ₃	1	0.36
	5	0.1
	10	0.08

The largest presence of light olefin content in the test results using FT-IR is in the sample Zn/Al₂O₃ with Zn content of 10% in wavelength 3010-3095 cm⁻¹, but the largest yield of light olefins content in the results using the GC-TCD is in the sample La/Al₂O₃ with La content of 10%. On FT-IR, that wavelength 3010-3095 cm⁻¹ is for alkene, which means the presence of 10% Zn sample does not all contain light olefins, but is still in the alkene category. In addition, the difference in transmittance in the 10% Zn sample percent and La 10% did not differ significantly, 18% and 22%, respectively.

3.2 The effect of Lanthanum and Zinc metals as active site

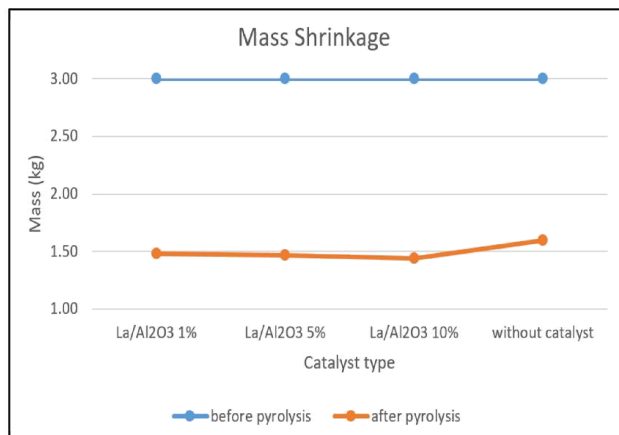
The effect of active side catalysts on the pyrolysis product (light olefins) content is shown in Table 2. There is a slight difference in the transmittance percentage of the peak that indicating the presence of light olefins. The catalyst with zinc as an active site produces a smaller transmittance percentage.

In terms of active site composition against Al₂O₃ support, both active metals exhibit the same pattern. The greater the content of the active metal composition of the catalyst, the smaller the percent transmittance produced. Thus, the more detected light olefins content.

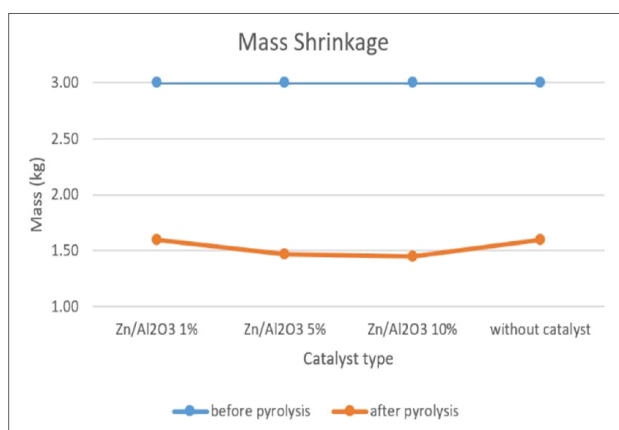
3.2 The effect of catalyst on mass changes during pyrolysis of rice straw

To investigate the effect of catalyst on changes in mass during pyrolysis of rice straw and coconut fibre, the mass of biomass and catalyst prior to pyrolysis are weighed, and byproducts after pyrolysis are also weighed so that the mass loss occurs during pyrolysis can be determined.

Non-catalyzed biomass pyrolysis is also carried out in order to know effect of the catalyst in the mass shrinkage of biomass during pyrolysis process. The following graphic presents the results of the weighed biomass and catalyst before and after pyrolysis.



(a)



(b)

Fig. 5. Results of the weighed sample before and after pyrolysis for La/Al₂O₃ (a) and Zn/Al₂O₃ (b) catalysts type

Based on the above graph it can be seen that the composition of the catalyst metal active at the time after pyrolysis is very small or can be considered does not affect the shrinkage of mass that occurs during pyrolysis. The difference of mass after pyrolysis of each sample is very little due to the mass measurement done manually. The non-catalytic pyrolysis sample is also tested and the presence or absence of catalyst also does not affect the shrinkage of mass that occurs during pyrolysis. The interval mass after pyrolysis of each sample is around 1.53 kg – 1.6 kg.

4 Conclusions

Catalytic pyrolysis of raw rice straw were conducted in a fixed bed reactor with the absence and presence condition of impregnated catalysts La/Al₂O₃ and Zn/Al₂O₃. Pyrolysis experiments of rice straw were

carried out in a fixed bed reactor with lanthanum and nickel metals as active catalyst to identify the presence and the yield of the light olefin.

The correlation tendency of % transmittance of light olefin in the FT-IR analysis is significantly decreased along with the increasing the catalyst composition of La/Al₂O₃ in wavelength 3010-3095 cm⁻¹. But for the sample Zn/Al₂O₃ with Zn content of 10% with the FTIR of wavelength 3010-3095 cm⁻¹ have lowest % transmittance.

The yield of olefins tends to increase with the increasing of the catalyst composition of La component. The largest yield of light olefins content using the GC-TCD analysis is achieved by the sample La/Al₂O₃ with La content of 10%

The performance of catalyst did not affect the mass decreasing during biomass thermal pyrolysis of rice straw by demonstrating the mass interval after pyrolysis at small intervals (1.53 kg - 1.6 kg).

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