

BIO-OIL FROM CATALYTIC AND NON-CATALYTIC PYROLYSIS OF GLYCEROL

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Abstract

The rapid increasing of fuel consumption cause the resource is depleting fast and threat the continuation of energy supply. That is the reason why petroleum price is rising. Therefore, the variation of alternative fuels are being exploited to sustain the energy requirements in the future.

Recently, there is no technology to utilize glycerol from transesterification process in Indonesia. However, glycerol could be utilized into fuel as bio-oil by pyrolysis. Pyrolysis is thermal decomposition occurring in the absence of oxygen and produce of brown liquid that contained oxygenated compounds, called bio-oil.

Catalytic and non-catalytic pyrolysis was run at temperatures of 400 °C, 500 °C, 600 °C and at flow rates of 300 mL/s, 400 mL/s, and 500 mL/s. Glycerol as feed was vaporized and brought by the carrier gas. For the catalytic pyrolysis, 10 g fresh Grace Davison® pellet catalyst was used for each run. The flue vapor is passed into condenser to get the liquid fraction, bio-oil.

The research obtained the liquid fraction yield, thermal stability, and also the best calorific value. The best liquid fraction yield was obtained at 600 °C and 500 mL/s for non-catalytic process. Bio-oil from catalytic pyrolysis is more stable than the other one. However, the best calorific value of bio-oil from non-catalytic process was 18645 J/g and 17149 J/g for bio oil from catalytic process.

Keywords: Pyrolysis; Glycerol; Grace Davison Catalyst; Bio-oil.

1. Introduction

Almost in one last decade, Indonesia always import petroleum oil. Directorate General of Oil and Gas said that our import volume keeps rising significantly from 106,9 million barrels in 2002 to 154,4 million barrels in 2004. Because of that, government publish the planning to reduce it with declare President's Regulation of Number 5, 2006 pertaining to National Energy Policy to develop alternative energy resources as substitution for fossil fuel. To support it, government also issuing President Instruction of No. 1, 2006 about Providing and Using Biofuel as an alternative enery. Nowadays, Indonesia has developed and produced biodiesel and bioetanol. National Energy Blue Print predicts our demand for biofuel would be 4,7 billion liters in 2025 (www.dim.esdm.go.id, 2006).

Biodiesel which produced by transesterification will convert 10 % wt of vegetable oil into glycerol as by-product. Increasing of biodiesel production for in the future will decrease glycerol price. Whereas, biodiesel production costs can be reduced by adding value to the glycerol by-product (Tyson in Valliyappan, 2004).

Since the mid 1970s, the experts have interested in thermal cracking of biomass, and now called pyrolysis. Bridgwater (2004) defined pyrolysis as a thermal decomposition process with no oxygen heating to prevent oxidation occurring which effects in decreasing product quality.

The advantages of pyrolysis process are low production cost, high thermal efficiency, short residence time, and low CO₂ emission. Pyrolysis become of promises alternative technology to give value added of glycerol, which can be chemicals such as organic acids, sugars, aldehydes, ketones, hydroxyaldehydes, and hydroxyketones, phenols and hydrocarbons for substitute fuel (Oasmaa, 2001).

Compared the conventional pyrolysis, fast pyrolysis is an advanced process, with carefully controlled parameters to give high yield of liquid. Because its process minimizes the water content in the liquid product.

Pyrolysis of glycerol was investigated with and without carrier gas in a fixed bed reactor. Chaudhari and Bakhshi (2002) ran the process at 400 °C and 500 °C, and flow rate approximately 2 g/h, reported that the operation was quite difficult without using a carrier gas because of char formation in the feed inlet.

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In the studies of Valliyappan (2004), pyrolysis and gasification focus to convert glycerol into syn-gas. He optimized the production of syn-gas quality and gas volume.

Pathak (2005), continues Valliyappan's experiment to evaluate the effects of operating conditions on glycerol conversion to liquid chemical products in the presence of acid catalysts.

Bio-oil produced from the conventional processes contains a high oxygen and water content, so become unstable under storage and heating conditions. For this reason, catalytic biomass pyrolysis could be a promising alternative for producing improved quality bio-oil.

The investigations described in this paper are fast pyrolysis of glycerol and optimization processes. And we aim to compare the decompose glycerol processes with and without catalyst.

2. Experimental

Pyrolyzer was a horizontally tubular reactor constructed by stainless steel, which is shown schematically in Figure 1. It was operated at 400 °C, 500 °C, 600 °C as pyrolysis temperature, and measured by K-type thermocouple to monitor the reactor temperature.

The carrier gas was nitrogen of 99.995% purity. It is inert gas used to clean oxygen from reactor. Its flow rate (300 mL/s, 400 mL/s, and 500 mL/s) make the residence time of the feed is below 2 s.

A hundred grams glycerol 98 % wt vaporized as a feed into pyrolyzer in each set of experiments. Its flow rate was 157,625 g/h.

Vapor flew from pyrolyzer passed the catalytic reactor which was fulfilled with fresh Grace Davison® pellet. There was 10 g catalyst inside the reactor. The uncatalytic pyrolysis product passed the catalytic reactor as blank pipe.

The liquid and gaseous products flew through a water-cooler and chilled-water condenser where most of the liquid product condensed and uncondensable gases were collected in a collector glass.

Fresh bio-oil was analyzed viscosity and density to compare with bio-oil that had been heated 80 °C for 24 hours.

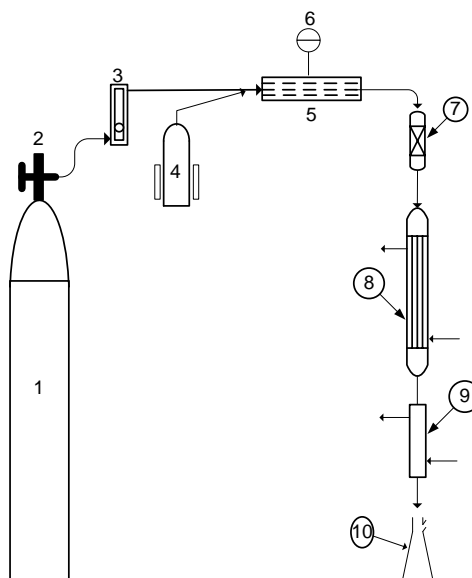


Fig. 1. Schematic diagram of the pyrolysis system: (1) Nitrogen gas cylinder; (2) Regulator; (3) Flowmeter; (4) Glycerol vaporizer; (5) Pyrolyzer; (6) K-type thermocouple; (7) Catalytic Reactor; (8) Cooler; (9) Condensor; (10) Bio-oil Collector

3. Results and discussion

3.1 Bio-oil yields

The yield of resulting liquid products from the fast pyrolysis of glycerol were studied under the effect of pyrolysis temperature and carrier gas flow rate.

The effect of temperature on product yield during pyrolysis of glycerol with a carrier gas flow of 500 mL/s is shown in Figure 2. It is observed from Figure 2 that the amount of liquid product increased as the temperature

increased from 400^oC to 600^oC. For pyrolysis of glycerol in the absence of catalyst, the liquid product was increase in yield from 49 wt.% to 58 wt.% as the increasing temperature of pyrolysis.

Figure 2 also shows the liquid product yield from the catalytic pyrolysis of glycerol, and the yield of oil 45 wt% at 400^oC and was increased to 52 wt% as the increasing temperature to 600^oC.

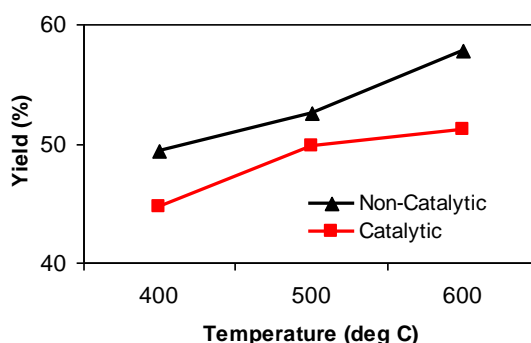


Fig.2. Temperature dependence of the liquid products yield at carrier gas flow rate of 500 mL/s.

Since the cracking reaction is an endothermic, the reaction would be effective in high temperature. So, increasing temperature makes the reaction rate faster and decompose more glycerol (Nasikin, M. 2006).

The best yield from catalytic pyrolysis was lower than from non-catalytic pyrolysis. Comparison of the liquid yield after catalysis with those for biomass pyrolysis in the literature shows similar results. For example, Williams and Horne (1994) pyrolysed biomass in the form of wood in a fluidized bed with catalytic upgrading. They also showed that there was a marked reduction in oil yield from 43.3 wt% for uncatalyzed pyrolysis reducing to 8.8 wt% at a catalyst temperature of 400^oC. Antonakou et al (2006) also reported that was liquid product yield decreased when he ran experiment with catalyst. The catalyst strongly favors the secondary reactions that lead to the tar decomposition.

To determine the effect of carrier gas flow rate on the liquid product yield, the experiments were conducted at a flow rate of 300, 400, or 500 mL/s. Figure 3 showed that variations of yields in the oil were observed. It could be seen that the maximum yield (58 wt%) of non-catalytic pyrolysis liquid product were obtained at the flow rate of 500 mL/s. Even though, 52wt% was the maximum yield of catalytic pyrolysis liquid product. Both of them were taken at temperature of 600^oC.

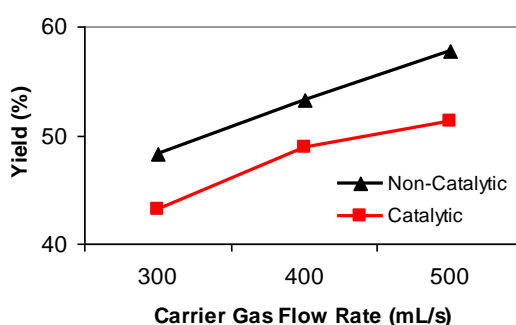


Fig.3. Carrier gas flow rate dependence of the liquid products yield at temperature of 600^oC .

Figure 3 observed that the amount of liquid product increased as the carrier gas flow rate increased. It caused decreasing of residence time (< 2 s) of glycerol vapor in pyrolyzer. This short residence time reduced factors for occurring the secondary reaction in pyrolysis product, like repolymerization or char recondensation. So, it could minimize gas product formed.

Calorific value of the liquid product was determined by using a bomb calorimeter (Model: C2000 basic, IKA Co., Germany). The best calorific value (high heating value) was 18.645 J/g for non-catalytic process at temperature of 400^oC and flow rate of 500 mL/s. And for catalytic process, 17.149 J/g was the best calorific value at same condition.

Catalysts, however, radically affect the bio-oil characteristics apart of its yield. This is because of the presence of increased amounts of water and lighter organic compounds in the catalytic bio-oil due to cracking.

It can be seen that the calorific value of the pyrolysis liquid were not as high as those of commercial heating oils (43.000 J/g for gasoline; Ullmann, 2007). It showed that they might be contain lots of non-hydrocarbons and water.

Table 1. Liquid product yield from catalytic and non-catalytic pyrolysis of glycerol (wt%)

Pyrolysis Temperature ($^{\circ}$ C)	Liquid Product Yield (wt%)					
	Non-Catalytic			Catalytic		
	300 mL/s	400 mL/s	500 mL/s	300 mL/s	400 mL/s	500 mL/s
400	39	47	49	33	40	44
500	46	48	52	43	45	50
600	48	53	58	44	48	52

3.2 Thermal stability of bio-oil

The thermal stability of liquid product is described in figure 4, and appears that the catalytically produced bio-oil was more stable than the non-catalytic one. It can be explained that catalyst presence produced lighter organic compounds and inhibited a thermal polymerization on the bio-oil component.

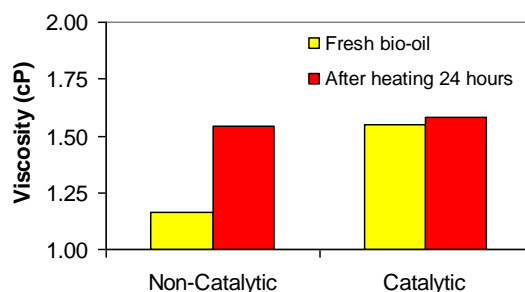


Fig.4. Catalyst in pyrolysis dependence of the bio-oil thermal stability at temperature of 600 $^{\circ}$ C, flow rate of 500 mL/s, heating temperature of 80 $^{\circ}$ C, and viscosity measurement at ambient temperature.

4. Conclusions

Both catalytic and non-catalytic experiments were performed. The liquid products were increase in yield as the increasing temperature of pyrolysis. High liquid yield (58 wt%) has been achieved from non-catalytic process at temperature of 600 $^{\circ}$ C and flow rate of 500 mL/s. While catalytic process gave a lower yield (52 wt%) at the same conditions.

Grace Davison catalyst reduced the thermal unstable characterization of bio-oil but it reduced its calorific value.

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