ISBN: 978-602-71398-0-0

NON-CATALYTIC THERMAL CRACKING OF BIO-OIL TO ORGANIC LIQUID PRODUCT (OLP)

[1]Sunarno, [2]Arief Budiman

[1]Chemical Engineering Department, Riau University, Pekanbaru
[2]Chemical Engineering Department, Gadjah Mada University, Yogyakarta
Email: [1]narnounri@yahoo.com, [2]abudiman@chemeng.ugm.ac.id

Abstract. One of the ways is by using thermo chemical conversion process such as pyrolysis to convert the solid empty fruit bunch (EFB) into liquid form pyrolysis oil (bio-oil). The potential for direct substitution of bio-oil for petroleum and chemical feedstock may be limited due to the high viscosity, high oxygen content and especially the themal instability of bio-oil. Consequently, upgrading of the bio-oil before use is desirable to give liquid product that can be used in a wider variety of applications. Furthermore, upgrading process, which is neccessary to improve the quality of bio-oil through reduction of oxygenates normally involves process such as catalytic cracking. One of the main challenges in catalytic cracking of bio-oil is undesired formation and retention of carbonaceous deposits, called coke. Coke causes catalyst deactivation through poisoning catalyst acid site and pore blockage. In order to minimize catalytic coke formation, then prior to catalytic cracking, bio-oil is processed through thermal cracking. The objective of this research is to study the effect of cracking temperature (450, 500, 550, dan 600^{0}C) to yield of oil liqiud product and to determine physical and chemical properties. Bio-oil derived from EFB was upgraded through thermal cracking using series tubular reactor under atmospheric pressure. Result showed with increasing temperature from 450 to 600^{0}C, yield of OLP decrease, while calorimetric value of OLP increase. The thermal cracking at 600^{0}C produces acetone 21.84 %, acetic acid 1.53 %, gasoline 22.47 %, kerosine 13.64 %, phenol 25.52 % and oxygenated organic compounds 15 % .

Key Words: *Bio-oil ; non-catalytic ; thermal cracking ; gasoline; oil liquid*

1. INTRODUCTION

Global warning, energy crisis and depletion of world crude oil resources are some of the many reasons more environmentally friendly solutions be considered to satisfy the current energy consumption. One of the most promising and potentially least expensive fuels is bio-fuel produced from biomass. One of the ways is by using thermo chemical conversion process such as pyrolysis to convert the solid empty fruit bunch (EFB) into liquid form pyrolysis oil (bio-oil) [1].

The bio-oils chemicals properties are significantly different from that of petroleum feedstocks. In fact, bio-oils are complex mixture of water (15 – 30%) and different O- containing structures (35 – 40%), such as hydroxyaldehydes, hydroxyketones, sugar, carboxylic acid and phenols. Due to their oxygen – rich composition, they present low heating value, immicibility with hydrocarbon fuels, chemical instability, high viscosity and corrosiveness. Consequently, upgrading of the bio-oil before use is desirable to give liquid product that can be used in a wider variety of applications [2]. Furthermore, upgrading process, which is neccessary to improve the quality of bio-oil through reduction of oxygenates normally involves process such as catalytic cracking.

ISBN: 978-602-71398-0-0

One of the main challenges in catalytic cracking of bio-oil is undesired formation and retention of carbonaceous deposits, called coke. Coke can be produced through homogeneous reaction in gas phase and heterogeneous reaction over catalyst. Catalytic coke is formed in the internal channels of catalyst due to transformation of oxygenate compounds over catalyst acid sites through reaction of oligomerization, cyclization, aromatization and condensation. Coke causes catalyst deactivation through poisoning catalyst acid site and pore blockage [3].

In order to minimize catalytic coke formation, then prior to catalytic cracking, bio-oil is processed through thermal cracking. In this work, we investigate the thermal cracking of the bio-oil to oil liquid product. The objective of this research is to study the effect of cracking temperature (450, 500, 550, dan 600^0C) to yield of oil liqiud product and to determine physical and chemical properties.

2. METHODOLOGY

A. Feedstocks

Bio-oil was produced by pyrolysis of empty fruit bunch in fixed bed with capacity 1 kg/batch at 500^0C. The density of bio-oil is 0.979 gr/ml and heating value is 27.575 MJ/kg. Composition of bio-oil contains acetone 3.25%, acetic acid 1.16%, gasoline 5.43%, kerosine 9.26%, phenol 9.74% and oxygenated organic compounds 71.16% .

B. Experimental setup and product analysis

The thermal cracking of bio-oil was carried out in series tubular reactor under atmospheric pressure.This system consist of tube reactor (inner diameter : 70 mm, length : 300 mm), a liquid feed system, a liquid feed pump, furnace, stove, a gas of LPG system, a condenser and a cooler water pump. Reactor was heated with LPG fuel until setted temperature of operation. Futhermore, bio-oil was flowed with with volumetric rate 8 ml/minute and stopped to volume of 30 ml. The vapor produced was condensed in water cooled condenser and collected in the erlenmeyer. After there was no oil liquid produced, the OLP was weighed to determine OLP yield. The density of bio-oil and OLP were measured using picnometer and weighing with digital analytical balance. Calorimetric value of OLP was measured using bomb calorimetric. Compound composition of bio-oil and OLP were measured using gas chromatography-mass spectroscopy (GC-MS).

3. RESULTS AND DISCUSSION

A. Influence of Temperature on Yield of Product

Figure 1 shows the effect of temperature on non-catalytic transformation of the bio-oil. The yields of liquid organic products (OLP) decreased with increasing the reaction temperature. With the increase of temperature from 450^0C to 600^0C, the yield of OLP decreased from 47.8% to 25.6%. Contrary to yield of OLP, with

ISBN: 978-602-71398-0-0

increasing temperature, the total gas shows an increase (Fig.2), indicating that high temperature is more more favorable to cracking of oxygenated compounds in the bio-oil [6]. A higher temperature will lead to second cracking of liquid organics and the formation of gas hydrocarbons such as gaseous alkanes olefin, CO, CO_2, and CH_4[7]. Temperature also had an effect on quality of oil product. With the increase of temperature from 400^0C to 600^0C, the heating value of OLP increased from 34.4 to 37.2 MJ/Kg as seen in figure 3.

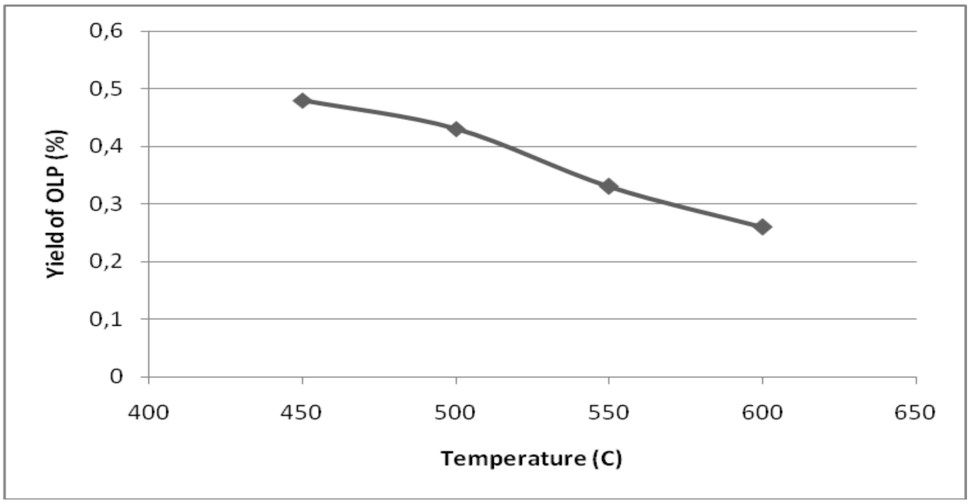

Figure 1 Effect of temperature to yield of OLP

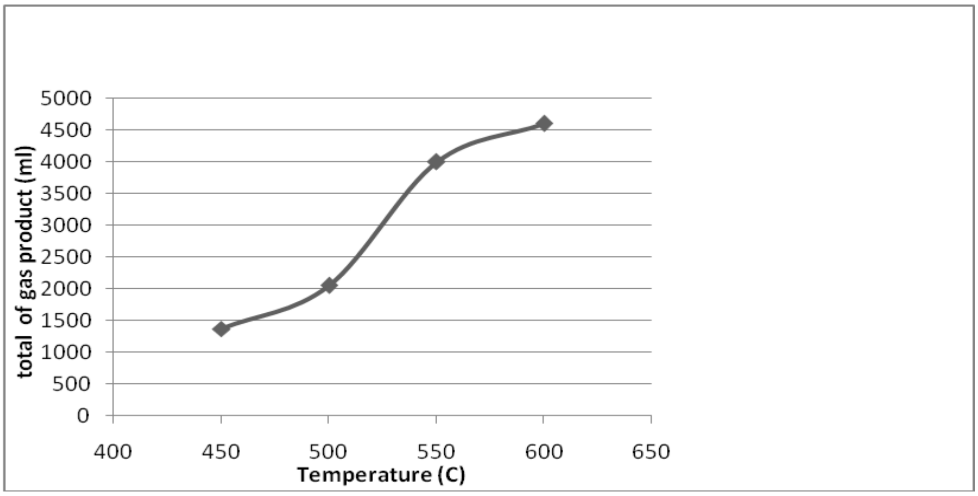

Figure 2 Effect of temperature to total of gas product

ISBN: 978-602-71398-0-0

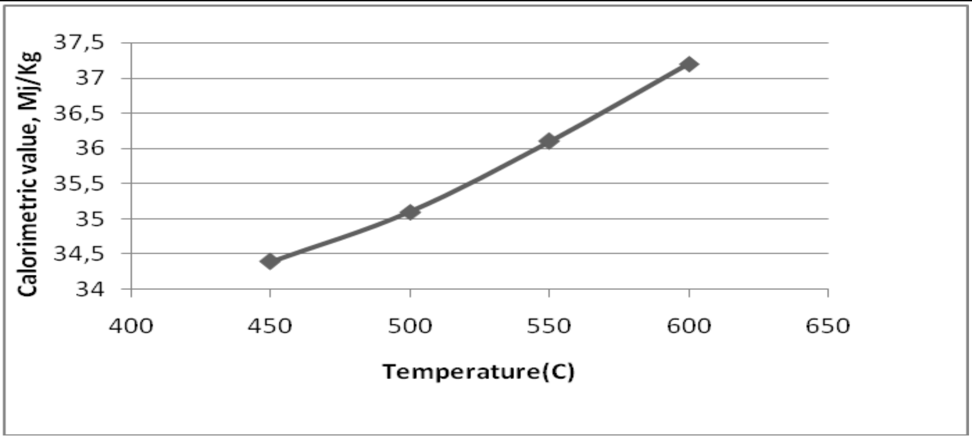

Figure 3 Effect of temperature to heating value of OLP

B. Production Gasoline from Thermal Cracking of Bio-oil

As shown in table 1 the raw material of bio-oil had different composition from oil product of thermal cracking at 600^0C. The percentage of gasoline from the raw material bio-oil is much lower than oil product of thermal cracking. Content of gasoline increased from 5.43% to 22.47% The results indicated that the process of thermal cracking has occured deoxygenation of bio-oil(oxygenated organic compounds) to gasoline.

Table 1 Comparison between composition of bio-oil with OLP

No	Kinds	Bio-oil (%)	OLP(%)
1	Acetone	3.25	21.84
2	Acetic acid	1.16	1.53
3	Gasoline	5.43	22.47
4	Kerosine	9.26	13.64
5	Phenol	9.74	25.52
6	oxygenated organic compounds	71.16	15

4. CONCLUSIONS

Thermal cracking of bio-oil for production OLP was performed at 450-600^0C. With the increase of temperature , the yield of OLP decreased while the heating value of OLP increased, with highest heating value was 37.2 MJ/Kg. OLP contains 22.47% gasoline and 13.64% kerosine.

ISBN: 978-602-71398-0-0

REFERENCES

[1] Hew, K.L.,Tarmidi,A.M., Yusup,S.,Lee,K.T. and Ahmad,M.M, 2010, Catalytic Cracking of Bio-oil to Organic Liquid Product, Bioresource Technology, 101, 8855-8858.

[2] Graca, I., Ribeiro, F.R., Cerqueira, H.S, Lam, P.L. and Almeida, M.B.B., 2009, Catalytic Cracking of Mixture of Model Bio-oil Compounds and Gasoil, Applied Catalysis B : Environmental, 90, 556 – 563.

[3] Mortensen, P.M., Grunwaldt, J.D. Jensen, P.A, Knudsen,K.G. and Jensen,A.D.,2011, A Review of Catalytic Upgrading of Bio-oil to Engine Fuels, Applied Catalysis A : General, 407, 1-19.

[4] Payormhorm, J., Kangvansaichol, K., Reubroycharoen,P., Kuchonthara,P. And Hinchiranan, N., 2013, Pt/Al_2O_3-Catalytic Deoxygenation for Upgrading of Leucaena Leuchocephola-pyrolysis oil, Bioresource Technology, 139, 128-135.

[5] Rezaei, P.S., Shafaghat,H. And Daud, W., 2014, Production of green aromatic and olefin by catalytic cracking oxygenate compounds derived from biomass pyrolysis, Applied Catalysis A : General, 469, 490-511

[6] Yuan, Y., Wang, T. And Li,Q., 2013, Production of Low-carbon Light Olefin from Catalytic Cracking of Crude Bio-oil, Chinese Journal of Chemical Physics, 26 (2), 237 – 244.

[7] Zhu,J., Wang, J. And Li,Q,. 2013, Transformation of Bio-oil into BTX by Bio-oil Catalytic Cracking, Chinese Journal of Chemical Physics, 26 (4), 477 – 483.