Comparative Study of Some Physical and Chemical Properties of Bio-Oil from Manila Grass and Water Hyacinth Transformed by Pyrolysis Process

Kittiphop Promdee, Tharapong Vitidsant, and Supot Vanpetch

Abstract-The analyses of the physical and chemical properties of bio-oil by pyrolysis, which takes place at temperatures in the range of 450-600°C, were to compare the quality of bio-oil extracted from different weeds that is, 1) Manila grass [Zoysia Matrella (L.) Merr] (MG) and 2) Water hyacinth [Eichhornia crassipes (Mart.) Solms] (WH). The preliminary analyses of biomass by proximate analysis. The results showed that biomass extracted from both weeds had good qualities because of low moisture content and high fixed carbon. MG found carbon content of 30.77%. While WH was 29.70%. The analysis of bio-oil can found the heating values of bio-oil from MG were difference from bio-oil obtained from WH, both held that there was in the Heating Value of high-level or better standards, especially bio-oil obtained from the MG have a heating value of about 32 MJ/Kg (at 500 °C). The content of sulfur quantity are found that bio-oil from the MG have lowest a sulfur quantity 0.26 wt.% at 400 oC; similarly; bio-oil from the WH have lowest a sulfur quantity 0.27 wt.% at 400 oC. The amount of carbon in the bio-oil obtained from MG and bio-oil obtained from WH was 55.57 wt.% and 55.03 wt.%, respectively., carbon was relatively high in both weeds. Hence; In this research are concerns the feeding rate, the control gas flow, the temperatures in reactor and reactor operate. MG and WH can produce hi quality of bio-oil and two weeds of resist in Thailand can be also used to generate the other fuel energy in the future.

Index Terms—Bio-oil, pyrolysis, manila grass [zoysia matrella (l.) merr], water hyacinth [eichhornia crassipes (mart.) solms].

I. INTRODUCTION

Energy plays an important role affecting the economy and lifestyles and makes the country move forward. The demand for energy in industry and business services to meet basic requirements is very high every year.

However, it is difficult to supply enough energy to be used in these businesses. Thus, the country somewhat depends upon the import of fuels form other countries. In addition, the costly oil price and political situation worsen the need of energy.

Thailand is one of the most important agricultural country

Manuscript received December 25, 2011; revised February19, 2012. This work was supported in part by the Department of Chemical Technology, Chulalongkorn University, Bangkok, Thailand.

Kittiphop Promdee is with the Inter-Department of Environmental Science, Chulalongkorn University, Bangkok, 10330, Thailand. (e-mail: nuumensci@hotmail.com).

Tharapong Vitidsant and Supot Vanpeth are with the Department of Chemical Technology, Chulalongkorn University, Bangkok, 10330, Thailand. (e-mail: tharapong.v@chula.ac.th: e-mail: penut9@hotmail.com).

in the world. The wastes produced by agriculture become problem i.e. rice hays and cut grass. Farmers usually get rid of them by burning which emits the toxic pollutants[1]-[4]. These wastes can become useful if they can be reformed into the petroleum products which ultimately help reduce the agriculture wastes and also cut down the cost of fuel for the farmers, etc.

The using of biomass transformed to bio-oil by pyrolysis gives good qualities similarly to fuel oil [2]-[5]. Therefore, the study was conducted by using MG and WH biomass to produce the bio-oil. The purpose of this experiment was to study the physical and chemical properties of oil derived from the local weeds which would lead to the feasibility to utilize and improve the quality of the by product as an alternative to such collaboration.

II. PROCEDURE

A. Sample Preparation

1) Preparation of MG and WH, crust and bring to oven at 85 oC for 2 hr until it is completed dry or less than 5 percent moisture. The samples were separated through a sieve to the approximate 450-1,000 microns.

2) Control the N₂ flow rate around 0, 50, 100, 150, 200, 400 ml/hr and feed samples approximately 1.66 - 1.8 kg/hr.

3) The samples were fed to continuous reactor for pyrolysis process at 450-600 oC. Controlling a feeding rate with 1.30 kilograms per hour and reaction time of 0.5 to 2 seconds.

4) The bio-oil product were analyzed by Ultimate analyzer, Proximate analyzer and Heating value analyzer. Which could be evaluated by the standard criteria.



Fig. 1. Schematic diagram of experiment setup: 1. hopper 1 2. hopper 2 3. screw feeder 1 4. Screw feeder 2 5. tube furnace 6. separator 7. condenser 8. vacumn pump

B. Proximate Analysis

Proximate analysis is the most often used analysis for characterizing coals in connection with their utilization, this experiment was analysis by ASTM D 3173-3175. The process are determined the distribution of products obtained when the sample is heated under specified conditions. Proximate analysis separates the products into four groups: (1) moisture, (2) volatile matter, consisting of gases and vapors driven off during pyrolysis, (3) fixed carbon, the nonvolatile fraction of char, and (4) ash.

C. Ultimate Analysis

In the experiment was analysis form of element components of bio-oil concerned with determination of only Carbon (C), Hydrogen (H) and Nitrogen (N) in a sample, these analyzed by Ultimate analyzer [3]-[9].

D. Gross Calorific Value (GCV) or Heating Value

The GCV are defined as the quantity of heat generated by the combustion and subsequent cooling of the exhaust gases to 25 °C. Both the energy required to heat the combustion air and the exhaust gases, and the heat generated by the evaporation or condensation of liquid, particularly water are taken into account in this parameter., this experiment was analysis by ASTM D1826.

III. RESULTS AND DISCUSSION

The analysis of the physical and chemical properties of bio-oil by During pyrolysis, which takes place at temperatures in the range 450-600°C, using a particle size of 450-1,000 microns, and feed rate of 1.66 - 1.8 kg/hr., for compare the two types of plants, MG and WH. Preliminary analysis of the biomass used in the two species was found that the proximate analysis of MG and WH showed in the figure 2. that composed of a fixed carbon, volatile matter, ash, and moisture.

The proximate analysis showed that the fixed carbon of MG was higher than the WH were 21.55, and 20.30 wt.%., respectively., which will have a major effect on the quality of bio-oil as well. The other three left of the WH were higher than the following; The volatiles of the MG And WH were 59.25 and 60.10 wt.%, respectively., the ashes of MG and WH were 18.68 and 19.00 wt.%, respectively., the moisture content of the MG And WH With 0.52 and 0.60 wt.%, respectively. The results of the analysis found that the low moisture content and high fixed carbon of MG, which was likely to have a good quality bio-oil. According to the analysis of safflower seed [10] founded that the volatile matter was 83.0 wt.%, and fixed carbon was 14.0 wt.%, indicated that the difference natural material have received the difference value contents by proximate analysis.





Fig. 2. The proximate analysis of MG and WH.

However, the results showed that a stability for the range of material compound in MG and WH, can be synthesized bio-oil in high efficiency on next step, because consist of the high fixed carbon and volatile matter, and low ash and moisture.

The element contents of MG and WH composed of carbon, hydrogen, oxygen, nitrogen and sulfur, MG was found that the carbon content was 30.77 % over the WH which was 29.70 %. The other elements can be found the hydrogen, oxygen, nitrogen and sulfur in MG were 4.72, 63.3, 0.96, 0.25 %, respectively., in WH were 4.52, 64.60, 0.97, 0.21 %, respectively (Figure.3)., difference from the analysis of safflower seed results showed [10] the carbon, hydrogen, nitrogen, and oxygen of 49.5, 6.9, 3.0, and 40.6, respectively.





The heating value of bio-oil (Figure.4) from MG were difference from bio-oil obtained from WH. The results showed that at 450 °C, bio-oil obtained from MG showed a heating value of about 27 MJ/Kg, and the heating value of bio-oil from the WH was about 31 MJ/Kg, indicating the heating rate of bio-oil obtained from WH at 450 °C release the heat as much as possible. On the other hand, the temperature of 500 °C, bio-oil obtained from the MG showed a heating value about 32 MJ/Kg whereas bio-oil obtained from the WH showed heating value about 29 MJ/Kg, indicating that the rate of heat, the bio-oil obtained from the MG was higher at temperatures 500 °C to release the heat as much as possible. Studies on the Heating value of biomass as well as two examples of this weed. Determination of the optimal conditions for the heat of the bio-oil has a specific temperature [3]- [12].



This is one factor that was used in determining the quality of bio-oil obtained from this research in conjunction with other factors in physical and chemical of the compound to be analyzed [7]. According to a result analyzed safflower seed [11] founded that the heating value was about 61 MJ/Kg at 500 °C. Same as the result of MG in this experiment.



Fig. 5. The quantities of sulfur in bio-oil from MG and bio-oil from WH.

The content of sulfur quantity showed on the figure 5, Bio-oil from the MG showed the highest sulfur quantity 0.45 wt.% at 450 °C, and the lowest 0.26 wt.% at 400 °C; Bio-oil from the WH have highest a sulfur quantity 0.34 wt.% at 500 °C, and lowest 0.27 wt.% at 400 °C. The sulfur can cause corrosive material or substrate and reduce the efficiency of fuel [8]-[12]., thus, in the experiment treat the sulfur by clearing off from bio-oil, the quantities of sulfur will be reduced performance of bio-oil.



From the analysis of data obtained from the experiments of the element of bio-oil showed that the amount of carbon in the bio-oil obtained from the MG rather than bio-oil obtained from the WH about 0.54 wt.% and the amount of carbon in the bio-oil obtained from MG and bio-oil obtained from the WH was 55.57 wt.% and 55.03 wt.%., respectively., similar a result analyzed safflower seed [11] founded that the value of bio-oil components were averaged 63.56 and 23.32 wt.%, of carbon and oxygen, respectively, that moderate to high value. Conversely, the result of catalytic reforming in the aqueous phase derived from fast-pyrolysis of biomass [6] founded that carbon was 43.17 wt.%, and oxygen was 48.89 wt.%. Indicating that the bio-oil in this study presented high efficiency for produce the fuel on next step by fractional distillation, because the bio-oil showed the highest carbon and consist of oxygen and hydrogen values on the appropriate standard range.

IV. CONCLUSION

In the experiment by pyrolysis of biomass for two samples

of weeds found that the element contents of MG and WH were composed of carbon, hydrogen, oxygen, nitrogen and sulfur, MG was found the carbon content with 30.77 % over the WH at about 29.70 %. The element contents of MG and WH presented a high carbon content. The heating value of bio-oil from MG was different from bio-oil obtained from WH, both held that there was in the heating value of high-class or better standards. Sulfur was not an element that exceeds the standard. There are also few amounts. Of course, the amount of the elemental composition of the oils derived from weeds, the concentration of carbon was relatively high in both weeds. oxygen was also higher, but the amount which may be a minor problem in the management of the trial in order to obtain products from biomass, both of which are higher quality. So that, the bio-oil in two weeds of resist in Thailand can be used to generate the fuel energy, however; we would like to concern and consider the properties of proximately analysis, reactor temperatures, sulfur content and elemental compounds for improving a high quality of bio-oil in the next research.

ACKNOWLEDGMENT

"This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (Project Code : EN272A)", and thank you for Department of Chemical Technology, Faculty of Science, Chulalongkorn University, were advised and supported the laboratory for experiment and analysis in this research.

REFERENCES

- M. Patel, M. Neelis, D. Gielen, J. Olivier, T. Simmons, and J. Theunis, "Carbon dioxide emissions from non-energy use of fossil fuels: Summary of key issues and conclusions from the country analyses," *Resources, Conservation and Recycling*, Vol. 45, pp.195-209, July 2005.
- [2] M. Garcia-Perez, J. Shen, X. S, Wang, and C-Z Li, "Production and fuel properties of fast pyrolysis oil/bio-diesel blends," *Fuel Processing Technology*, Vol. 91, no.3 pp.296-305, March 2010.
- [3] G. Duman, C. Okutucu, S. Ucar, R. Stahl, and J. Yanik, "The slow and fast pyrolysis of cherry seed," *Bioresource Technology*, Vol. 102, no. 2, pp.1869-1878, January 2011.
- [4] D. Wu, S. Zhang, J. Xu, and T, Zhu, "The CO₂ Reduction Effects and Climate Benefit of Beijing 2008 Summer Olympics Green Practice," *Energy Procedia*, Vol. 5, pp. 280-296, April 2011.
- [5] Q. Lu, W-Z. Li, and X-F, Zhu, "Overview of fuel properties of biomass fast pyrolysis oils," *Energy Conversion and Management*, 50, pp.1376–1383, May 2009.
- [6] H. Li, Q. Xu, H. Xue, and Y, Yan. 2009, "Catalytic reforming of the aqueous phase derived from fast-pyrolysis of biomass," *Renewable Energy*, pp.1-6, April 2009.
- [7] H.S. Heo, H. J. Park, J. H. Yim, J.M. Sohn, J. H. Park, S-S. Kim, C.K. Ryu, J-K. Jeon, and Y-K., Park. "Influence of operation variables on fast pyrolysis of Miscanthus sinensis var. purpurascens," *Bioresource Technology*, Vol. 101, no. 10, 2010, pp.3672-3677.
- [8] P. Duan and P. E, Savage, "Upgrading of crude algal bio-oil in supercritical water," *Bioresource Technology*, Vol. 102, pp.1899-1906, January 2011.
- [9] C.A. Mullen, A. Charles, and A., Akwasi, "Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops," *Energy & Fuels*, pp.2104-2109, April 2008.
- [10] S. Sevgi and D. Angin, "Pyrolysis of safflower (*Charthamus tintorius L.*) Seed press cake: Part 1. The effect of pyrolysis parameters on the product yields," *Bioresource Technology*, 99, pp.5492-5497. September 2008.
- [11] S. Sevgi and D. Angin, "Pyrolysis of safflower (*Charthamus tintorius L.*) Seed press cake in a fixed-bed reactor: Part 2. Structural

characterization of pyrolysis bio-oils," *Bioresource Technology*, 99, pp.5498-5504, September 2008.

[12] P. M. Mortensen, J-D. Grunwaldt, P. A. Jensen, K. G. Knudsen, and A.D, Jensen," A review of catalytic upgrading of bio-oil to engine fuels," *Applied Catalysis*, Vol. 407, no. 1-2, pp.1-19, August 2011.



Kittiphop Promdee was born in Ubonrachathani Province, Thailand, in 1975. He received the M.S. degree in environmental science from the school of environmental science, Kasetsart University, Bangkok, Thailand, in 2004. His research interests include agricultural residuals, renewable energy, environmental energy, green and biomass technology and catalytic pyrolysis processes. He is

currently pursuing the Ph.D. degree with Inter-Department of Environmental Science, Chulalongkorn University, Bangkok, Thailand



Tharapong Vitidsant received the B.S. degree and the M.S. degree in chemical engineering from Chulalongkorn University, Bangkok, Thailand. He received the Ph.D. degree from . Institut National Polytechnique de Toulouse (INPT), France, in 1999. He is currently an associate professor with Department of Chemical Technology, Chulalongkorn University. His research interests

include renewable energy, fuel energy, catalytic pyrolysis processes and reaction engineering.



Supot Vanpeth was born in Nakorn Sri Thammarat Province, Thailand, in 1982. He received the B.S. degree in industrial chemistry from King Mongkut's University of Technology North Bangkok, in 2005 and the M.S. degree in chemical technology from Chulalongkorn University, in 2007. His research interests include renewable energy, fuel energy, slow and fast pyrolysis processes and industrial chemistry.