

Product Yields and Chemical Compounds of Cogongrass by Pyrolysis in Twin Screw Feeder

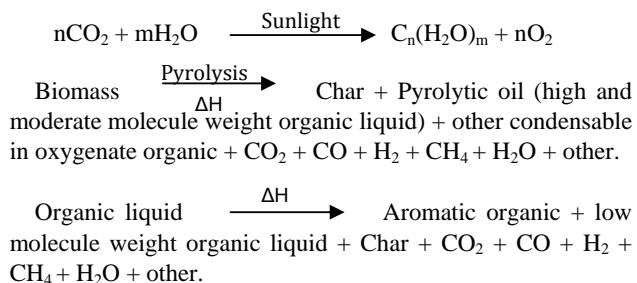
Kittiphop Promdee and Tharapong Vitidsant

Abstract—Continuous pyrolysis of Cogongrass by control temperature in the novel pyrolysis reactor were conducted at three difference temperatures 400, 450 and 500°C. Preliminary calculate of the product yields founded the liquid yield of Cogongrass was highest of 41.45 %, at 500 °C. Indicated that the liquid yield from Cogongrass had good received yields because it gave over 40 % and its produced more liquid than that solid and gas. The compounds detected in bio-oil from Cogongrass showed the functional group, especially; Phenol, Phenol, 2,5-dimethyl, Phenol, 3-methyl, 2-methyl-1,3-oxathiofane, Benzene,1-ethyl-4-methoxy, 2-Cyclopenten-1-one,2,3-dimethyl, 2- Cyclopenten-1- one, 3-Methyl.

Keywords—Pyrolysis, Cogongrass, Product Yields, Chemical Compounds, Twin Screw Feeder.

I. INTRODUCTION

PYROLYSIS process becomes one promising option for the thermo chemical conversion of cellulose, hemicelluloses and lignin of biomass into liquid fuels [1-5] because this process can increase yield of condensable liquid oil quality.



This research was conducted by using Cogongrass transformed to bio-oil (liquid) and their products (solid, gases) by continuous pyrolysis reactor on standard criteria and analyses the chemical compounds of products. In present, the fuel is being concerned in every country [6-9]. Now we are looking at the fuel which synthesized from natural matter, especially; residual plant [10-14], such as Cogongrass, by using the pyrolysis method combined with the type of screw feeder for control the temperature balance in the continuous pyrolysis reactor. The fuels from natural matter have a good

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

T. Vitidsant is with the Department of Chemical Technology, Chulalongkorn University, Bangkok, 10330, Thailand. (e-mail: tharapong.v@chula.ac.th).

solve and can reduce a waste in widespread areas of central part of Thailand [11-14].

II. PROCEDURE FOR PAPER SUBMISSION

A. Feedstock

Preparation of Cogongrass, crust and heat in oven at 90 °C for 2 hr until it is completed dry or less than 5 percent moisture. The sample sizes were separated through a sieve with approximate 0.1 – 2 millimeter.

B. Experimental Set-up

The fine Cogongrass was fed to continuous pyrolysis reactor (Fig. 1), at 400-500 °C (measuring at 400, 450 and 500 °C). The feeding rate of samples was 5 kg/hr. And then, the bio-oil product were calculated the received oil yields and analyzed the chemical compounds by Gas Chromatography with Mass Spectrometer.

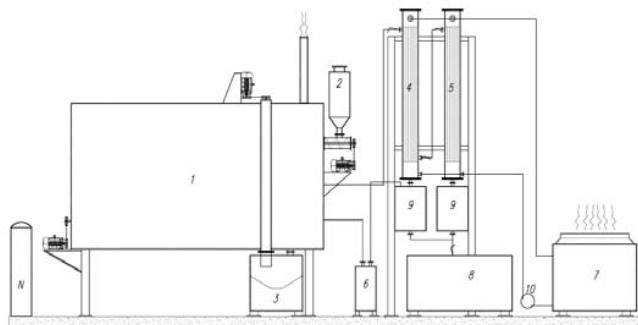


Fig. 1 Schematic diagram of novel pyrolysis reactor setup: 1) Continuous pyrolysis reactor 2) Biomass Hopper 3) Char tank 4) Condenser 1 5) Condenser 2 6) Gases storage 7) Cooling tower 8) Bio-Oil stock 9) Bio-Oil and Gasses Recovering in the system 10) Cooling pump

C. Product Yields

Product yields of solid phase implies the amount of solid left after pyrolysis and was determined gravimetrically., The gas phase was calculated as remaining after quantification of the solids and liquids phase (See in III. Math).

D. Chemical Analysis

Gas Chromatography with Mass Spectrometer, GC-MS was used to analyze the light components in bio-oil and investigating the molecular compositions qualitatively [15-19]. The analyses detective and identify organic compounds

both aliphatic hydrocarbon and aromatic hydrocarbon of bio-oil from Cogongrass. The pyrolysis product was directly injected into gas chromatograph (GC) system through the pyrolysis interface line. The GC was equipped with a thermal conductivity detector and mass spectrometer (MS) detector (Agilent technologies; 7890A). The injection temperature was 300 °C and a split ratio of 50:1 was used. Pyrolysis vapors comprising condensable gases i.e. bio-oil, acetic acid and water were classified as liquid [20-22]. A total of over 100 compounds were detected.

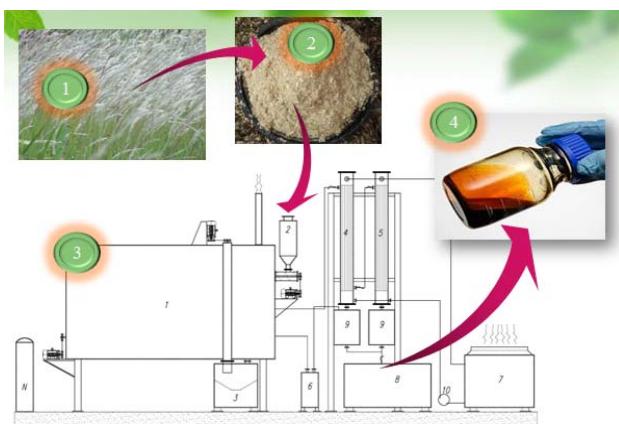


Fig. 2 Experimental process apparatus (1.Cogongrass, 2.Fine Cogongrass, 3.Pyrolysis reactor, and 4.Bio-oil stock) of renewable energy by twin screw pyrolysis reactor

III. MATH

The product yields can be calculated by following formula;

$$\% \text{ Liquid yield} = 100 \times \left[\frac{W_{Liq}}{W_{ini}} \right]$$

$$\% \text{ Solid yield} = 100 \times \left[\frac{W_R}{W_{ini}} \right]$$

$$\% \text{ Gas yield} = 100 \% \text{ Liquid yield} - \% \text{ Solid yield}$$

W_{ini} = Initial weight

W_R = Residual solid weight

W_{Liq} = Liquid product weight

IV. RESULTS AND DISCUSSION

The result of product yields [3-phase; gas, liquid (bio-oil), and solid (char coke)] of Cogongrass during pyrolysis, with temperatures between 400 - 500 °C, to compare the product yields from Cogongrass. Preliminary calculate of the product oil yield of Cogongrass, showed that the linear equation of gas yield obtained from Cogongrass were 27.38, 27.92 and 30.23 %, at 400, 450, and 500 °C., respectively (Fig. 3).

Liquid yield of bio-oil obtained from Cogongrass was highest of 41.45 %, at 500 °C. And the another of liquid yield obtained from Cogongrass were 33.55 and 36.57 %, at 400,

and 450 °C., respectively, and showed linear equation on Fig. 4.

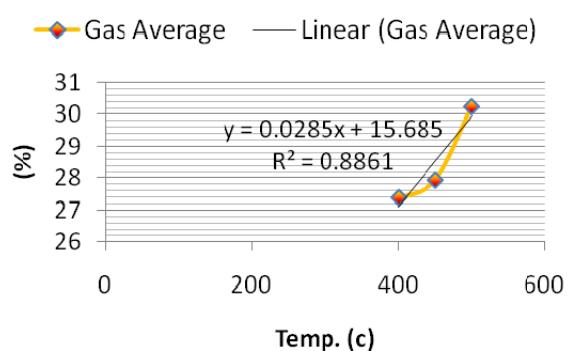


Fig. 3 Gas average of Cogongrass by pyrolysis

This result, indicated that the liquid yield of bio-oil obtained from Cogongrass was high (> 40 %) by the temperature control in twin screw pyrolysis reactor and can be improving to high efficiency of bio-oil product, causing the apparent of high functional group when detected by GC-MS analysis, can be investigating the molecular compositions qualitatively, showed some molecular in Fig. 6.

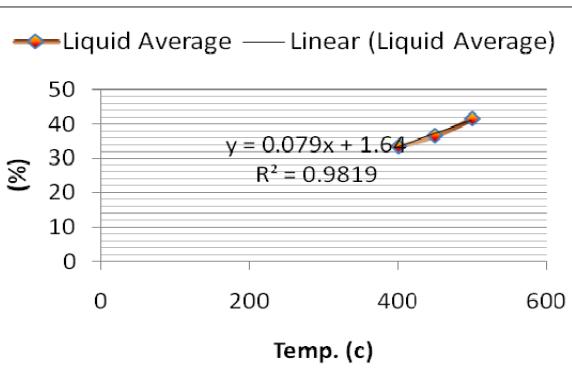


Fig. 4 Liquid yield average of Cogongrass by pyrolysis

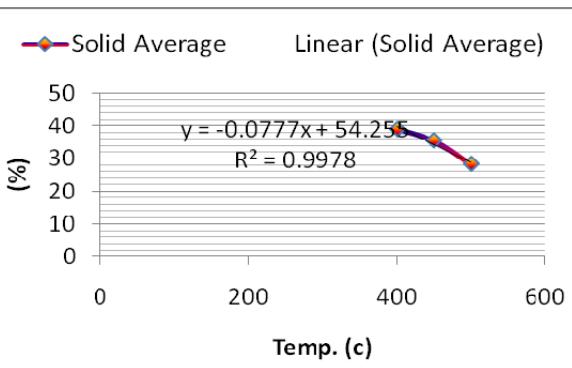


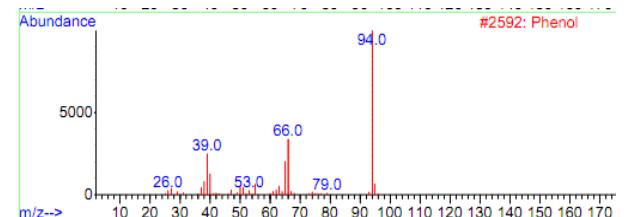
Fig. 5 Solid yield average of Cogongrass by pyrolysis

Solid yield of char coke obtained from Cogongrass was highest of 39.07 %, at 400 °C. And the another of solid yield obtained from Cogongrass were 35.51 and 28.32 %, at 450 and 500 °C., respectively (Fig. 5).

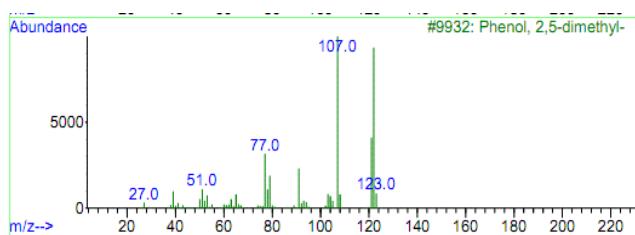
Bio-Oil obtained from Cogongrass is a complex mixture with a great amount of large-size molecules, which nearly involve all species of hydrocarbon compounds, such as phenols, esters, aldehydes, ketones, alcohols, and organic acids.

GC-MS of class spectra showed the different profiles of the color of bio-oil from Cogongrass. The total number of compounds detected by GC-MS, These examples shown section of the chromatogram in order to show the separation of compounds, the system as a difference interaction mechanism among analyses and stationary phase is provided by the second dimension column. The mass spectra of these phenol are rather different, as shown in Fig. 6. Phenol can be find out, the obvious hi peak (base peak) at 94 Mass/Charge (m/z), and Phenol, 2,5-dimethyl, Phenol, 3-methyl, 2-methyl-1,3-oxathiofane, Benzene, 1-ethyl-4-methoxy, 2-Cyclopenten-1-one, 2,3-dimethyl, were obvious hi peak at 107, 108, 60, 121, and 67 m/z, respectively.

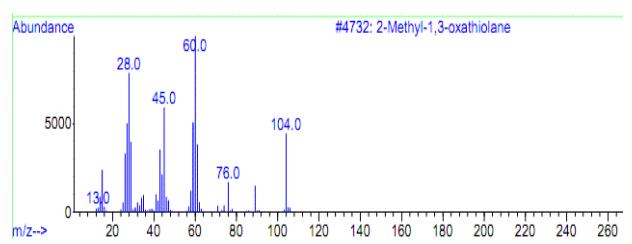
The compounds of Cogongrass bio-oil was classified in the following classes and subclasses (between parenthesis): phenols (phenols, methoxy phenols, cresols, and phenolic diols), ketones (C5- and C6-cyclic ketone, furanones, aliphatic ketones, aromatic ketone, furan ketones), acids (aliphatic acids, furan acids, benzoic acids, ketonic acids), ethers (aromatic ether, benzofuranone ethers, furan ether), aldehydes (slipahatic aldehydes, benzaldehydes, ciamaldehydes), and other. Phenols and ketones were major classes in both samples: ~ 40% (28 compounds) of phenols and ~ 15% (37 compounds) of ketones.



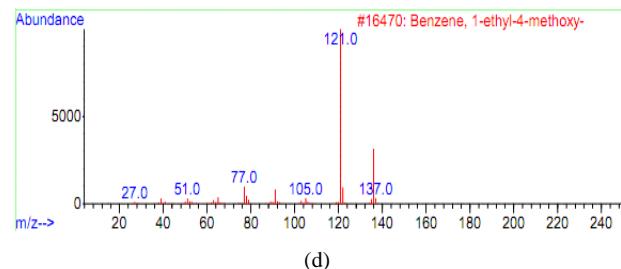
(a)



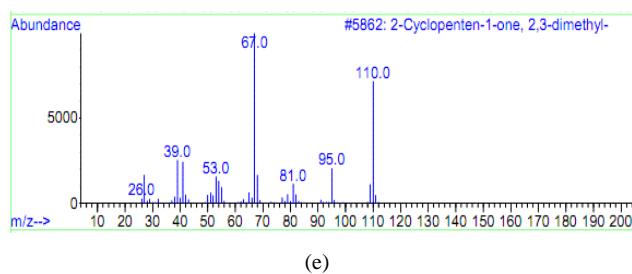
(b)



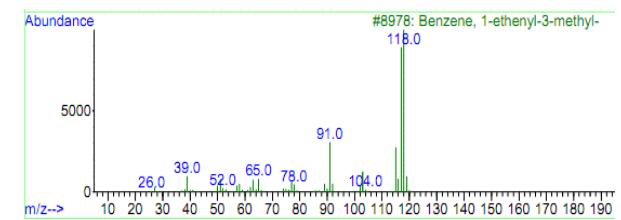
(c)



(d)



(e)



(f)

Fig. 6 GC-MS some class spectra of bio-oil obtained from Cogongrass via pyrolysis reactor; (a) Phenol, (b) Phenol, 2,5-dimethyl, (c) 2-methyl-1,3-oxathiofane, (d) Benzene, 1-ethyl-4-methoxy, (e) 2-Cyclopenten-1-one, 2,3-dimethyl, (f) Benzene, 1-ethenyl-3-methyl

All of compounds can be detected in bio-oil obtained from Cogongrass showed the main groups of hydrocarbon compounds, there are composed of hydroxyl and carboxyl groups. These compounds showed that the investigating molecular compositions. It have been detected compounds of bio-oil from several biomass [20-22], the results shown a good total of molecular compositions detected.

V.CONCLUSIONS

The continuous pyrolysis reactor for produce by-products from Cogongrass founded that the content of liquid yield obtained from Cogongrass was a moderate-high weight (%). The compounds detected in bio-oil from Cogongrass showed that the hydrocarbon compounds that were composed of

hydroxyl and carboxyl groups, especially; Phenol, Phenol, 2,5-dimethyl, Phenol, 3-methyl, 2-methyl-1,3-oxathiofane, Pyridine, 2-methyl, Pyrine, Benzene, 1-ethyl-4-methoxy, 2-Cyclopenten-1-one, 2,3-dimethyl, 2- Cyclopenten-1- one, 3-Methyl, alcohols, and ketones. Thus, in this research, the process of continuous pyrolysis depended on the temperature and the mechanism of reactor and concern that the overall performance system of the continuous pyrolysis reactor to renewable storage fuel.

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

- [1] 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 , 45 (3) (2005) 195-209.
- [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, 91 (3) (2010) 296-305.
- [3] G. Duman, C. Okutucu, S. Ucar, R. Stahl, and J., Yanik, "The slow and fast pyrolysis of cherry seed," Bioresource Technology, Vol 102, Issue 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, Volume 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, Issue 10, 2010, pp.3672-3677.
- [8] K. Promdee, T. Vitidsant, and S. Vanpitch. "Comparative study of some physical and chemical properties of bio-oil from Manila grass and Water hyacinth transformed by pyrolysis process", International Journal of Chemical Engineering and Applications, Vol.3, No.1, pp.72-75. February 2012.
- [9] U. Jena, and K. C. Das. "Comparative evaluation of thermochemical liquefaction and pyrolysis for bio-oil production from microalgae. Energy fuels", 25 (2011), p. 5472-5482.
- [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. Duan, and P. E., Savage, "Upgrading of crude algal bio-oil in supercritical water," Bioresource Technology, Vol 102, pp.1899-1906, January 2011.
- [13] 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.
- [14] 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 A: General, Vol 407, Issues 1-2, pp.1-19, August 2011.
- [15] R. Razuan, Q. Chen, N.K.Finney, V.N. Russell, N.V. Sharifi, and J., Swithenbank. Combustion of oil palm stone in a pilot-scale fluidised bed reactor. Fuel Processing Technology, 92 (2011), p. 2219-2225.
- [16] L. Mei-kuei, T. Wem-tien; S. Yi-lin and L. Sheau-horng. Pyrolysis of Napier Grass in an Induction-heating Reactor. Analytical and Applied Pyrolysis, (2010),Vol 88, Issues 2, pp. 110-116, July 2010.
- [17] H. Kazemi Esfeh, B. Ghanavati, and T. GhaleGolabi. "Properties of modified bitumen obtained from natural bitumen by adding pyrolysis fuel oil", International Journal of Chemical Engineering and Applications, Vol.2, No.3, pp.168-172, June 2011.
- [18] H. Chen, B. Dou, Y. Song, Y. Xu, Y. Zhang, C. Wang and X. Zhang. Pyrolysis characteristics of sucrose biomass in a tubular reactor and a thermogravimetric analysis. Fuel 2012 (95), pp. 425-430.
- [19] S. Bilgen, S. Keles and K. Kaygusuz. Calculation of higher and lower heating values and chemical exergy values of liquid products obtained from pyrolysis of hazelnut cupulae. Energy 2012, pp. 1-6.
- [20] C. LaMarca, B.M. Moreno, and M.T. Klein. Characteristics of optimal chain transfer solvents for pyrolysis kinetics. Energy & Fuels 2012, 26, 55-57.
- [21] Y. Wang, X. Li, D. Mourant, R. Gunawan, S. Zhang, and C-Z. Li. Formation of aromatic structures during the pyrolysis of bio-oil. Energy & Fuels 2012, 26, 241-247.
- [22] Y. Huang, S Kudo, K. Norinaga, M. Amaike, and J-I Hayashi. Selective production of light oil by biomass pyrolysis with feedstock-mediated recycling of heavy oil. Energy & Fuels. 2012, 26. 256-264.

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.