

Pyrolysis of *Spirulina* sp. Microalgae: Effect of Temperature on Chemical Compositions of Bio-Oil and Aqueous Phase

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Abstract

Pyrolysis of *Spirulina* sp. Microalgae was carried out in a semi-batch glass reactor system. Effect of temperature on the yields of pyrolytic products (gaseous, liquid and solid residue) and chemical composition of the liquid products were investigated. All experiments were performed in 25 mL/min nitrogen atmosphere with 15 g feedstock which was dry and powder form of *Spirulina*. Temperature was varied from 470 to 620 °C with 50 °C break by utilizing PID controller which was setted 10 °C/min heating rate. The aqueous phase and bio-oil (organic phase) of the liquid products were characterized by GC-MS. Maximum yields of bio-oil and aqueous phase were obtained approximately as 30 wt. % at 520 °C and as 20 wt. % at 470 °C. When temperature was increased, oxygenated compounds and aromatic hydrocarbons decreased. However, nitrogenous compounds and alkanes increased in the microalgal pyrolytic bio-oil.

Keywords: Microalgae, pyrolysis, biomass, bio-oil

1. Introduction

Due to run out of fossil fuels, researchers have studied on renewable and sustainable energy sources that are wind, solar, tide, waste and biomass. Plants, algae, animal wastes are in biomass class. Biofuel (bioethanol, biodiesel, biogas) are obtained from biomass. Besides that, biomass can be used for produce green chemicals, adsorbent and catalyst by pyrolysis.

Microalgae as a biomass source of pyrolysis can be cultivated in wastewater and barren fields in a short span of time. Additionally microalgae are carbon-neutral, i.e., carbon dioxide was taken by them from the atmosphere during photosynthesis is equal to released carbon dioxide when they are used for whatever purpose.

Liquid product of microalgae pyrolysis includes two phases that are called aqueous phase and bio-oil. These two phases can be seperated from each other easily.

Chaiwong et al. were studied on microalgae pyrolysis in 2013. The researchers fulfilled pyrolysis of *Spirulina* as a microalgae in fixed bed reactor at 450-600 °C. They obtained maximum bio-oil yield at 550 °C and determined the main components of bio-oil are

heptadecane, toluene, ethylbenzene and indole as a result of GC-MS analysis.

In this research, we aimed to observe temperature (470, 520, 570, 620 °C) effect on the product (bio-char, liquid, gaseous) yields and the liquid composition by carrying out pyrolysis of *Spirulina* sp. microalgae. Bio-oil and aqueous phase were analyzed by GC-MS comprehensively.

2. Material and Methods

2.1 Characterization of Sample

Spirulina in powder form was bought from a local herbalist. Particle size measurement of the *Spirulina* was made by using Malvern Mastersizer 2000 Particle Size Analyzer. According to the analysis results, average particle size of the sample was detected 37 µm by volume. Elemental analysis of *Spirulina* was performed by utilizing Leco brand and CHN628 model with Sulfur add-on module equipment. Result of the analysis was shown in Table 1.

Table 1. Elemental composition of microalgae (wt. %, ash free and dry basis)

C	H	N	S	O*
46.69	6.22	10.76	1.55	34.78

* by difference

2.2 Pyrolysis of Microalgae

Feedstock was put in the reactor before the experiments, and product was taken continuously. The setup was shown in Fig. 1.

3. Results and Discussion

3.1 Yields of microalgae pyrolysis products

Maximum liquid product yield was obtained between 520 and 570 °C for *Spirulina*' conventional pyrolysis. Besides that, maximum organic and aqueous phase yield were arrived at 520 and 470 °C respectively. These findings are

also compatible with literature. Pan et al. (2010) were observed maximum bio-oil and aqueous phase yield are approximately 30 wt. % and 20 wt. % respectively as a result of their slow pyrolysis research for *Nannochloropsis sp. microalgae*. Effect of temperature on the product yield and total conversion (gaseous + liquid product yield) can be seen in Fig. 2.

3.2 Chemical Compositions of phases in liquid product

It was observed that the pyrolytic bio-oil of *Spirulina* composed of hydrocarbons such as alkanes and aromatic compounds such as toluene, o-xylene, oxygenated compounds such as phenol, oleic acid, nitrogenous compounds such as pyrrole. However, the pyrolytic aqueous phase of *Spirulina* formed oxygenated compounds such as phenol, oleic acid, nitrogenous compounds such as pyrrole and some compounds can be entered this two class such as 2-Phenyl-3-nitropyrrole mainly. In Fig 3, retention time in GC column and peak size of some components in bio-oil were shown.

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References

Chaiwong, K., Kiatsiriroat, T., Vorayos, N., and Thararax, C. (2013), Study of bio-oil and bio-char production from algae by slow pyrolysis, *Biomass and bioenergy*, **56**, 600-606.

Chen, W., Li, K., Xia, M., Yang, H., Chen, Y., Chen, X., ... and Chen, H. (2018), Catalytic deoxygenation co-pyrolysis of bamboo wastes and microalgae with biochar catalyst, *Energy*, **157**, 472-482.

Demirbas, A. (2008), Biofuels sources, biofuel policy, biofuel economy and global biofuel projections, *Energy conversion and management*, **49**(8), 2106-2116.

Jin, H., Hanif, M. U., Capareda, S., Chang, Z., Huang, H., and Ai, Y. (2016), Copper (II) removal potential from aqueous solution by pyrolysis biochar derived from anaerobically digested algae-dairy-manure and effect of KOH activation, *Journal of Environmental Chemical Engineering*, **4**(1), 365-372.

Kothari, R., Tyagi, V. V., and Pathak, A. (2010), Waste-to-energy: A way from renewable energy sources to sustainable development, *Renewable and Sustainable Energy Reviews*, **14**(9), 3164-3170.

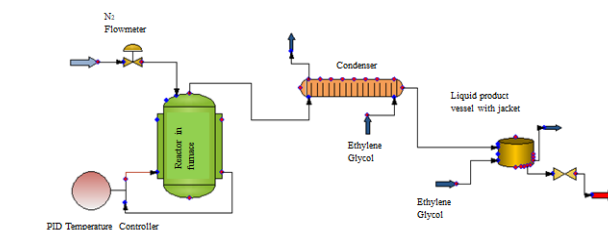


Figure 1. Chemcad drawing of the experimental setup

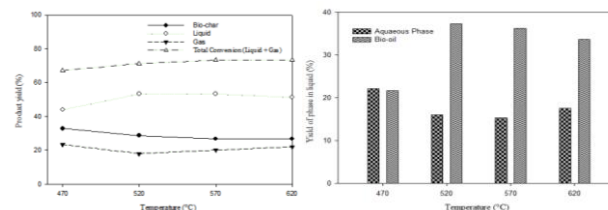


Figure 2. Change in product yields with temperature

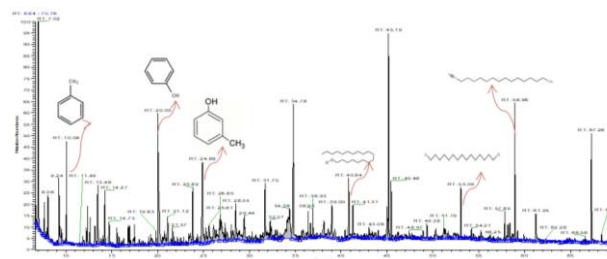


Figure 3. GC-MS chromatogram of *Spirulina* bio-oil at 520 °C

Li, Y., Horsman, M., Wu, N., Lan, C. Q., and Dubois-Calero, N. (2008), Biofuels from microalgae, *Biotechnology progress*, **24**(4), 815-820.

Maguyon-Detras, M. C., and Capareda, S. C. (2017), Upgrading of bio-oil and aqueous liquid product from pyrolysis of microalgae (*Nannochloropsis oculata*) by fractional distillation, *International Journal of Biosciences*, **10**(1), 218-231.

Pan, P., Hu, C., Yang, W., Li, Y., Dong, L., Zhu, L., ... and Fan, Y. (2010), The direct pyrolysis and catalytic pyrolysis of *Nannochloropsis sp.* residue for renewable bio-oils, *Bioresource technology*, **101**(12), 4593-4599.

Panwar, N. L., Kothari, R., and Tyagi, V. V. (2012), Thermo chemical conversion of biomass—Eco friendly energy routes, *Renewable and Sustainable Energy Reviews*, **16**(4), 1801-1816.

Thangalazhy-Gopakumar, S., Adhikari, S., Chattanathan, S. A., and Gupta, R. B. (2012), Catalytic pyrolysis of green algae for hydrocarbon production using H+ ZSM-5 catalyst, *Bioresource Technology*, **118**, 150-157.

Wu, X., Wu, Y., Wu, K., Chen, Y., Hu, H., and Yang, M. (2015), Study on pyrolytic kinetics and behavior: the co-pyrolysis of microalgae and polypropylene, *Bioresource technology*, **192**, 522-528.