EVALUATING THE EFFECTS OF REACTOR TYPE ON PYROLYSIS OF *NANNOCHLOROPSIS OCULATA* ON BIO-OIL AND BIO-CHAR PRODUCTS AND BIO-OIL UPGRADING USING CATALYSTS

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ABSTRACT

Evaluating the Effects of Reactor Type of *Nannochloropsis Oculata* on
Bio-oil and Bio-char Products and Bio-oil Upgrading Using Catalysts

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Pyrolysis products from microalgae using two types of reactors, a batch and an auger, will be investigated and compared at a temperature of 500^{o}C. Also, the bio-oil will be upgraded through hydrotreatment to be used as a substitution of petroleum fuels. The pyrolysis products of bio-char, bio-oil, and combustible gases will be analyzed. The ultimate analysis will also completed and it shows the HHV (Higher heating value) of the bio-oil from a batch reactor. Chemical compositions of bio-oils using Gas Chromatography-Mass Spectrometry (GC-MS) will be categorized which indicates a potential of bio-oil as a substitute for crude petroleum oil. HHV of bio-char will also evaluated and it is anticipated to contain considerable energy and to be used for additional energy sources or other applications. Then, the produced bio-oil from a batch reactor will be upgraded in a catalytic reactor. A hydrotreatment process will be applied that uses catalysts with hydrogenation and deoxygenation, which reduces the oxygen contents of bio-oil. The initial oxygen content in algae bio-oil will be reduced with catalysts while the carbon and hydrogen contents will be increased. The O/C ratio of bio-oil will be obtained and it will be compared to the O/C ratio of petroleum products (less than 0.06). The pyrolysis results using the microalgae feedstock (N.oculata) will show that the products are potentially valuable sources of fuels and chemicals.

CHAPTER I

INTRODUCTION

Objectives

The objective of this project is examination of bio-oil and bio-char as new energy sources through evaluating the effect of the batchwise and auger reactor on pyrolysis of *Nannochloropsis oculata (N.oculata)*, bio-oil and bio-char products. I also aim bio-oil upgrading using catalysts to enhance the Higher heating value (HHV) of it.

Background

N. oculata is a very promising energy source since it has a high ratio of lipid content and grows faster than lignocellulosic biomass. And N.oculata has a high productivity and a high photosynthetic efficiency. One previous study in this field showed the effect of temperature on pyrolysis of *N.oculata* based on its product yields and characteristics. In that previous study, pyrolysis of N. oculata was completed with batch reactor at different temperatures. In addition, analyzing methods such as Ultimate analysis, Fourier transform infrared spectroscopy (FRIR), Gas Chromatography-Mass Spectrometry (GC-MS) and Energy yield calculations were completed under specified temperature conditions. The result of the previous study includes the bio-oil with HHV of about 38MJ/kg and high carbon ratio (76wt%), hydrogen ratio (11wt%) and oxygen (7wt%) which are produced from *N. oculata* [1]. This previous research showed me the lists of the possible analyzing methods and expected results for this project.

Bio-oil upgrading will be conducted using catalysts and catalytic reactor under various pressure conditions. The anticipated result will be a decrease of oxygen content in bio-oil because it will lead to an increase of bio-oil heating value. The result of the bio-oil upgrading process will show the potential of bio-oil as a substitution of the petroleum fuels with comparable HHV. The HHV of bio-char will also be used to check availability for the sub-level energy source.

CHAPTER II

MATERIALS AND METHODS

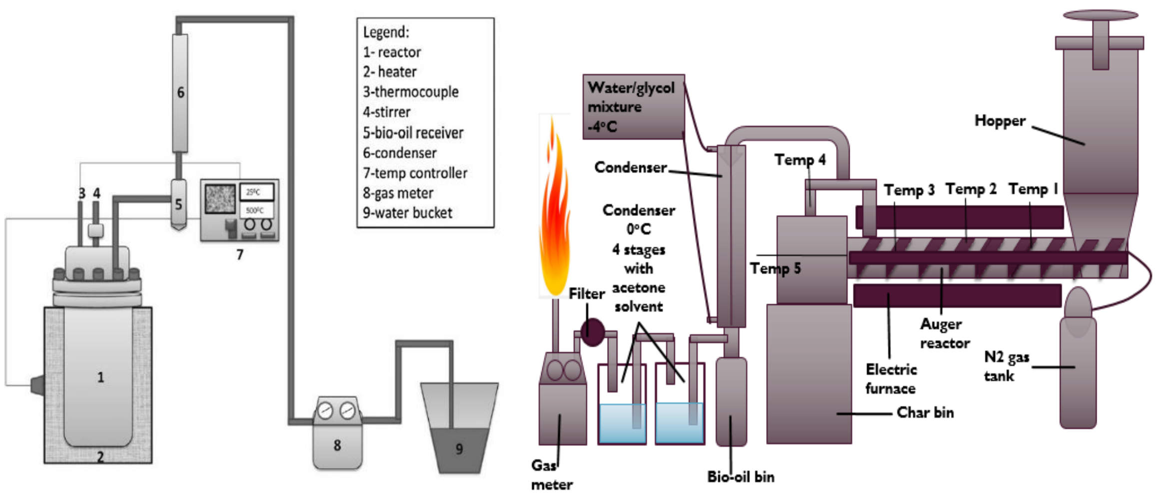
Material and equipment

N. oculata samples for this study will be obtained from the Texas Agri-Life Research Algae Pond facility in Pecos, Texas. The sample will be dried at 105℃ to make its moisture content lower than 10wt%. After that, those samples will be ground by a Wiley Laboratory Mill Model #4 (Arthur Thomas Company, Philadelphia, PA, USA). The heating value of the samples will be evaluated by ASTM D2015 using a Parr isoperibol bomb calorimeter (Model 6200, Parr Instrument Company, Moline, IL, USA). Moisture content analysis and proximate analysis will be completed by ASTM D3173, ASTM D3175 and ASTM E1755. Ultimate analysis will be completed by ASTM D3176 and ASTM D5373 using a Vario MICRO Elemental Analyzer (Elementar Analysemsysteme GmbH, Germany). Gas composition of the gas sample will be analyzed using a SRI Multiple Gas Analyzer #1 (MG#1) gas chromatography (GC) with an injector and 2 detectors (Helium Ionization Detector and Thermal Conductivity Detector).

Pyrolysis process will be completed with a fixed-bed batch-type Parr pressure reactor (Series 4580 HP/TP, Parr Instrument Company, Moline, IL, USA). The reactor is made of AISI 316 Stainless Steel and its capacity is 1.5 L. A cylindrical ceramic fiber electrical heater with a thermo-well covers the reactor. A reactor controller (Series 4840, Parr Instrument Company, Moline, IL, USA) is attached to the heater. A type J thermocouple is attached to the reactor controller and measures the temperature inside the reactor.

Pyrolysis process will also be completed with an auger-based reactor with a 3-zone cylindrical electric furnace (Linberg/Blue M from Thermoelectron Corporation/Centigrate Service Inc., NC, USA). The furnace heats the main tube reactor. The reactor is connected with an auger flight and feed hopper. A type K thermocouple attached inside the reactor measures the reaction temperature. Schematic diagrams of reactors are shown in Figure 1 below [1].

Bio-oil upgrading will be conducted with a Catalytic Packless Reactor (Autoclave Engineers, Model CRA5HC05-2H16D, PA, USA). Ru/C, HZSM and Ni catalysis will be used for hydrogenation and hydrotreatment of bio-oil under 250 ℃ and 50 psi [2]. Nitrogen gas will be used before running the reactor to ensure the absence of air.



(a) **(b)**

Figure 1. Schematic diagrams of reactors (a) batch reactor set-up [1] (b) auger reactor set-up.

Experimental procedure

For each pyrolysis process, temperature level will be 500 ℃ under atmospheric pressure and from 700 g to 1500 g of dried and ground *N. oculata* samples will be used. For batch-type reactor, nitrogen gas will be used before each run to purge the reactor for 15 minutes at about 15 psi to ensure the absence of oxygen. And a stirrer is attached to a magnetic drive which will be operated at minimum level to ensure uniform temperature of inside the reactor. For the auger-type reactor, nitrogen gas will also be flowed into the reactor of 10 liters/min continuously to let the syngas flow to the exhaust pipe. For both reactors, glycol water at -4 ℃ will be used for the condenser.

When the temperature reaches 500 ℃, the reaction will be able to transpire for 30 minutes at the 500 ℃ only at the batch-type reactor. After that, the heater will be turned off to let the reactor cool down. In case of auger-type reactor, the reactor will start to be cooled down after it reaches 500 ℃. When both reactors cool down, the liquid product will be collected from the bio-oil receiver and the char product will be collected from the reactor. Both products will be weighed with analytical balance (Mettler Toledo, Model XP105DR, Switzerland). After the experiment is completed, energy yield rate of bio-oil and bio-char will be calculated using equation (1) below.

$$Energy\ recovery\ (\%) = \frac{HHV\ of\ oil\ or\ char\ \left(\frac{MJ}{kg}\right) \times Weight\ of\ produced\ oil\ or\ char\ (kg)}{HHV\ of\ N.oculata\ \left(\frac{MJ}{kg}\right) \times Weight\ of\ initial\ N.oculata\ (kg)} \times 100 \qquad (1)$$

CHAPTER III

RESULTS AND DISCUSSION

Results

Mass products were produced after pyrolysis of *N. oculata* through each batch and auger reactor. Figure 2 below shows the mass product yields of batch and auger reactor. It shows more bio-oil and aqueous substances were produced when the pyrolysis was completed with batch reactor. Inversely, with auger reactor, more bio-char, bio-gas and loss were produced and they take almost 83% among whole products.

Bio-char which was produced from pyrolysis of N. oculata was analyzed through proximate analysis. It is shown in Figure 3 on next page. It compares the raw algae and pyrolysed algae through proximate analysis. According to the Figure 3, raw algae has more volatile combustible matters (VCM), less ash and almost no fixed carbon (FC). While in pyrolysed algae, although it shows relatively less amount of VCM and more of ash than raw algae, it has much higher FC value than raw algae.

Figure 2. Mass product yields from each reactor at 500^{o}C.

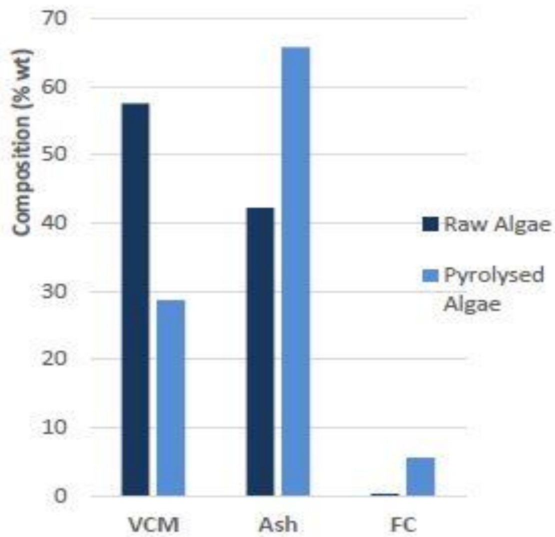


Figure 3. Proximate analysis result of bio-char.

HHV was also estimated using bomb calorimeter and its result is shown below in Figure 4. HHV of bio-oil made from batch reactor was almost 39.6 MJ/kg and 7.4 MJ/kg for its bio-char. Bio-oil made from auger reactor had HHV as high as 34.4 MJ/kg and 12.2 MJ/kg for its bio-char. Bio-oil from batch reactor has better HHV than the one from auger reactor and inverse for the bio-char.

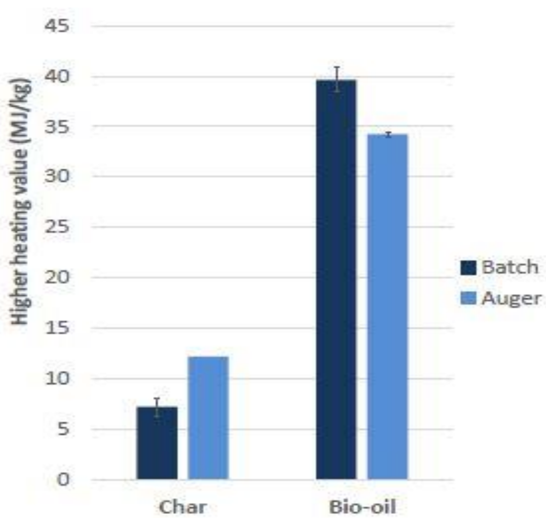


Figure 4. Higher heating value (HHV) of bio-oil and bio-char.

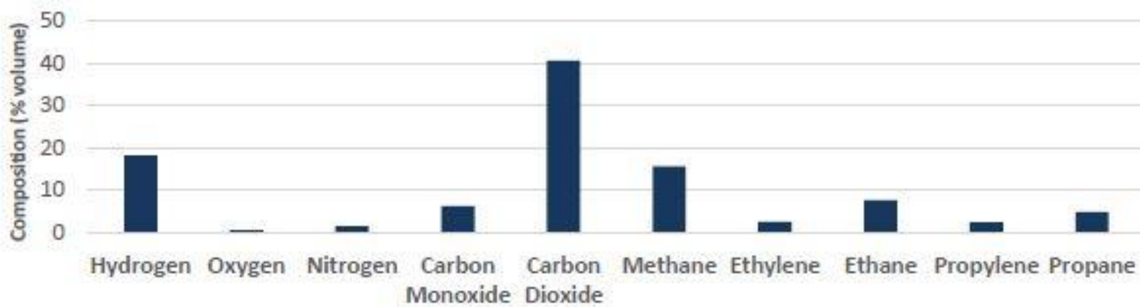


Figure 5. Chemical compositions of bio-gas.

The bio-gas was produced during the experiment and it was collected after the experiment was completed and reached its steady state. The collected gas was analyzed using gas chromatography (GC) machine. The result is shown above in Figure 5. It shows composition of carbon dioxide is the highest, as much as 40%. The second highest component is hydrogen which takes almost 19%. Some other components such as methane, ethane, carbon monoxide, propane, ethylene and propylene also take some part of the bio-gas. Existence of oxygen is normally derived from any contamination for the most case. However in this case, the amount of oxygen is negligible and so does nitrogen.

Bio-oil was analyzed and classified as their functional groups in Figure 6 below. GC-MS method was used for the bio-oil analysis. In the bio-oil, alkanes, alkenes and nitriles occupy big portion of the bio-oil. Some other functional groups, such as Alkynes, Amides, Alcohols, Esters, Benzenes and aromatics and Ketones, also exists in the bio-oil. Relative content of each component are drawn depends both on area and height.

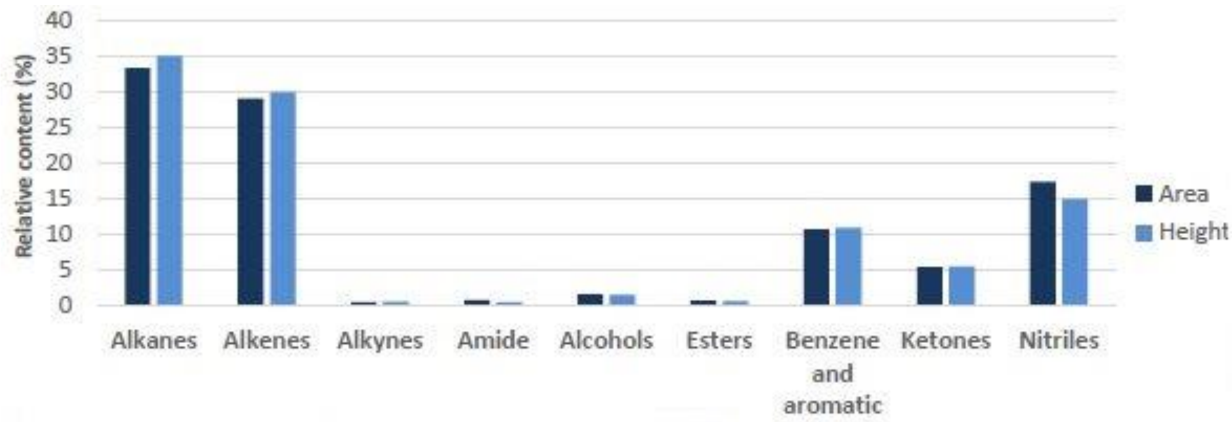


Figure 6. Chemical compositions of bio-oil using GC-MS.

Ultimate analysis was applied to check relative atomic composition of bio-oil and bio-char. Figure was drawn using the criterion of some atoms, such as Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S), and Oxygen (O). Results are shown below in figure 7 and 8. Atomic composition of bio-oil and bio-char was slightly different depending on the reactor type. For the bio-oil produced from batch reactor has relatively higher carbon value and lower oxygen value than the bio-oil produced from auger reactor. On the other hand, for the bio-char produced from batch reactor, has relatively lower carbon and oxygen value but higher ash value than the bio-char produced from auger reactor.

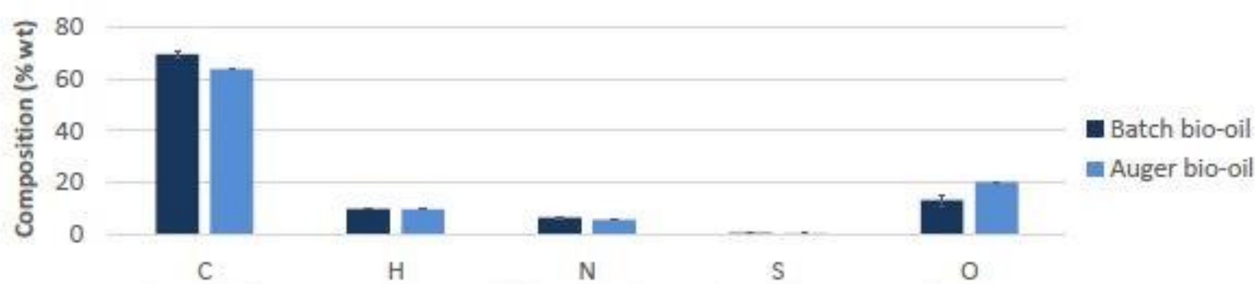


Figure 7. Chemical compositions of bio-oil using Ultimate analysis.

Figure 8. Chemical compositions of bio-char using Ultimate analysis.

Energy yield rate was calculated using the equation (1). It is shown below in Figure 9. The results are compared between batch reactor and auger reactor. About 30% of the original energy was recovered as bio-oil through the batch reactor but only about 15% of the original energy was recovered as bio-oil through the auger reactor. Reversely, about 15% of the original energy was recovered as bio-char using the batch reactor but 30% with auger reactor. Under 500℃ and atmospheric pressure, original energy was recovered more as bio-oil than bio-char with the batch reactor, and the results were reverse when these were done by the auger reactor.

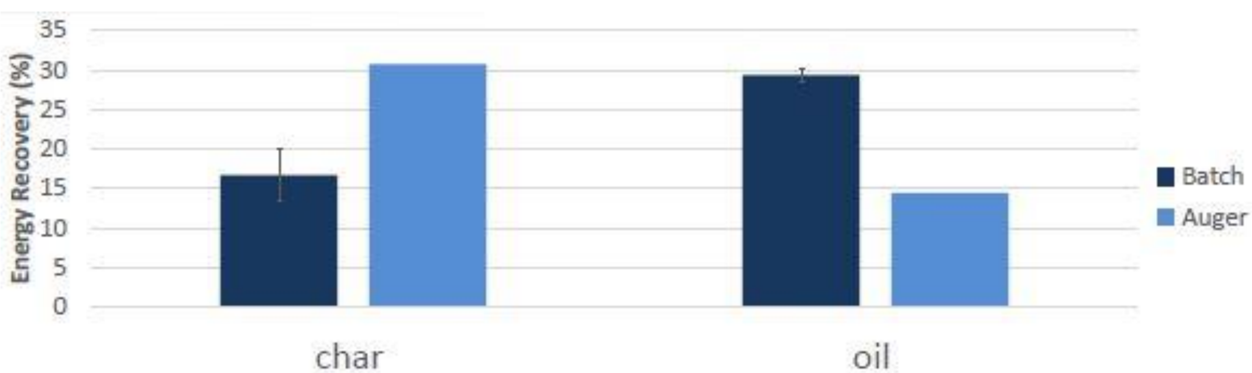


Figure 9. Energy yield rate of bio-char and bio-oil.

	Algae oil	Ru/C	HZSM	Ni 500
H/C	1.65	1.61	1.62	1.59
O/C	0.09	0.08	0.07	0.07

Figure 10. H/C and O/C ratio of upgraded bio-oil

Bio-oil was upgraded using catalysts. The experiment was completed under 250℃ and 50 psi. Ru/C, HZSM and Ni 500 catalysts were used to decrease H/C and O/C ratio to achieve better HHV because low oxygen content occur higher HHV. The results are shown above in Figure 10. Oxygen content in bio-oil was reduced up to 7.2% with HZSM catalyst. And, original H/C ratio was decreased to 1.59 with Ni 500 catalyst. The original O/C ratio was 0.09, and it was also decreased up to 0.07 using HZSM and Ni 500 catalysts. These results are meaningful because the O/C ratio of petroleum products are usually about or less than 0.06, and my O/C ratio gets closer to that value. So it could be said that the upgraded bio-oil could be used as one of alternative energy source.

Discussion

Effect of reactor type on pyrolysis of Nannochloropsis oculata on bio-oil and bio-char was evaluated through analyzing achieved bio-oil and bio-char. Maximum heating value of bio-oil and bio-char were 39.6 MJ/kg and 12.2 MJ/kg respectively, and energy recovery ratio was 29.4%

and 30.7% respectively. Oxygen content in bio-oil was reduced up to 7.2% when it was upgraded with HZSM catalyst. O/C ratio was reduced up to 0.07 with HZSM and Ni 500 catalysts.

CHAPTER IV

CONCLUSION

The experiments to figure out the effect of reactor type on pyrolysis of Nannochloropsis oculata on bio-oil and bio-char products, and bio-oil upgrading using catalyst were successfully completed. Between two types of reactors, batch and auger, batch reactor produced more amount of bio-oil than auger reactor. Reversely, more bio-char was produced from auger reactor. And the bio-oil made from the batch reactor had better HHV than the one made from auger. This is because batch pyrolysis is slow process, so it produces better quality bio-oil instead of taking a long time. This principle also works for the bio-char as the one produced from the batch reactor had better HHV. Some catalysts, such as Ru/C, HZSM and Ni 500, decreased an oxygen content in the bio-oil through upgrading process. Relatively lower oxygen content, H/C and O/C ratio were achieved through the bio-oil upgrading process, and the better HHV of bio-oil is anticipated for the future experiment. Future experiments will be performed under high pressure and higher temperature to achieve high yield ratio [3]. Upgraded bio-oil will have better HHV, which could be a substitute for crude petroleum oil. Indeed, bio-char also has a potential to be used for a secondary-level energy source. These pyrolysis results using the microalgae feedstock prove that the products are potentially valuable sources of fuels and chemicals.

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