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Evaluating the effects of temperature on pressurized pyrolysis of *Nannochloropsis oculata* based on products yields and characteristics

Monet Concepcion C. Maguyon *, Sergio C. Capareda

Bio-Energy Testing and Analysis Laboratory (BETA Lab), Biological and Agricultural Engineering Department, Texas A&M University, College Station, TX 77843, USA

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ABSTRACT

Biofuels derived from pyrolysis of microalgae can be potential alternatives for petroleum-derived fuels. Pyrolysis is an easily controllable thermochemical conversion process that yields energy fuels such as bio-oil, char and combustible gases. Microalgae is a very promising feedstock for this process since it has high lipid content, grows faster than lignocellulosic biomass, has high productivity and high photosynthetic efficiency. Several reaction parameters including temperature could affect the yield and quality of biofuels from pyrolysis. This paper aimed to evaluate the effect of temperature during pyrolysis of *Nannochloropsis oculata* using a pressurized fixed-bed batch-type reactor. Based on the results, the distribution of the products significantly varied with pyrolysis temperature, and the pyrolysis process can be manipulated to favor one of its products. Bio-oil with high heating value (HHV) of about 38 MJ/kg, due to its high carbon (76wt%) and hydrogen (11wt%) contents, and low oxygen content (7wt%), can be produced from *N. oculata*. It also consists mainly of saturated (34.95%) and unsaturated aliphatics (34.43%), and aromatics (14.19%) ranging from C_8 to C_{21}, which is comparable to diesel fuel. The HHV of the char (27 MJ/kg) and gas (27 MJ/m^3) were also relatively high. Based on their heating values (HHV) and compositions, the char, bio-oil and gas produced from pyrolysis of *N. oculata* can be potentially used as alternative sources of energy. Mass and energy conversion efficiencies of the process were also estimated to be approximately equal to 76% and 68%, respectively.

1. Introduction

The economic development of an industrial society relies heavily on the availability of energy sources. Fossil fuels still serve as the main source of energy at present. However, issues arising from the unsustainable use of fossil fuels such as increasing greenhouse gas (GHG) emissions, increasing fuel prices, and depleting petroleum fuel reserves prompted researchers to look for alternative sources of energy that are less carbon-intensive and renewable [1–4].

Biofuels are fuels that are derived from renewable feedstocks which may be in solid, liquid or gaseous forms. Biomass pyrolysis is one of the technologies that are being explored nowadays for the production of biofuels. Pyrolysis is a thermochemical conversion process that produces energy fuels with high fuel-to-feed ratio, and the process can be easily adjusted to favor char, bio-oil or gas production [5]. The bio-oil from pyrolysis of agricultural biomass is comparable to crude oil, which can be easily stored and transported, and it has low nitrogen and sulfur contents [5]. It can be used for direct combustion or can be upgraded further to liquid transport fuels and bio-chemicals [6]. Char, on the other hand, could potentially be used as fuel or fertilizer due to its N, P and K content [5]. Whereas, the recoverable energy from the combustible gases produced could possibly compensate the energy requirement of the pyrolysis process [6]. Biofuels are the only sustainable source of energy nowadays [7]. The biomass-to-fuel cycle is also considered as CO_2-neutral hence it does not contribute to the greenhouse effect [7,8].

Various agricultural biomass such as rice husks [8], rice straw [9], bagasse [10], sawdust [11], wheat straw [12], rapeseed straw and stalk [13], corn residues [14] and switchgrass [15] were already tested for the production of bio-oil through pyrolysis. However, the bio-oil obtained from lignocellulosic residues needs to be upgraded to be used as fuel since it has high oxygen content, high viscosity, high corrosiveness and relative instability [16,17]. These characteristics may be attributed to the main chemical components of lignocellulosic biomass which include cellulose, hemicelluloses and lignin [13].

Microalga is another feedstock for biofuel production that is of interest to researchers nowadays. The potential of microalgae as feedstock has already been studied by several researchers [18–21]. The interest in algae as biofuel feedstock was mainly based on its high lipid (or oil) content [18,19,22]. Moreover, compared to lignocellulosic materials, microalgae grows faster [5,6], has high

* Corresponding author. Tel.: +1 (979) 997 0607.
E-mail address: monet.maguyon@yahoo.com (M.C.C. Maguyon).

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photosynthetic efficiency [5], and high productivity [5,18]. It can be cultivated on salty water [18] and does not require arable soils [6,23]. The bio-oil produced from microalgae is more stable due to lower O/C ratio and has higher HHV compared to wood oil [5]. Also, microalgae, which has protein, lipid and carbohydrate as its main components, devolatilizes at lower temperatures than lignocellulosic materials [6,24].

Several factors including reactor design, reaction parameters (temperature, heating rate, residence time, pressure and catalyst), and biomass type and characteristics (particle size, shape and structure) largely affects the yield and quality of the products formed during pyrolysis [12]. Different species of algae also contain varying amounts of oil that contains different compounds. Grierson et al. studied the thermo-chemical properties of *Tetraselmis chui*, *Chlorella like*, *Chlorella vulgaris*, *Chaetocerous muelleri*, *Dunaliella tertiolecta* and *Synechococcus* using slow pyrolysis process (100C/min up to 710 °C) and Computer Aided Thermal Analysis (CATA) under unsteady state heating conditions [6]. The highest bio-oil yield (43%) was attained at 500 °C using *T. chui* as feedstock while the lowest was obtained from *D. tertiolecta* (24%). Fast pyrolysis (heating rate of 600 °C/s at 500 °C), on the other hand, was studied by Miao et al. using *Chlorella protothecoides* and *Microcystis aeruginosa*. Bio-oil yields of 17.5% and 23.7% were obtained from *C. protothecoides* and *M. aeruginosa*, respectively [5]. TGA/FTIR analysis was used by Marcilla et al. to examine the decomposition during pyrolysis of dry *Nannochloropsis sp*, its lipid extract and extract residue [25]. In this study, it was found out that the decomposition process has three stages, namely: (1) dehydration (<180 °C), (2) devolatilization (180–540 °C) and slow decomposition of the solid residue (>540 °C). Also, the decomposition of the lipid (or hexane-soluble) extract at around 450 °C resulted to 82.7% weight loss during pyrolysis. The main pyrolysis reactions for *Spirulina platensis* and *C. protothecoides*, which include depolymerization, decarboxylation and cracking, was observed at 150–560 °C by Peng et al. using TGA at different heating rates (15, 40, 50, 80 °C/min up to 800 °C) [24]. Direct and catalytic pyrolysis of *Nannochloropsis sp* residue were compared by Pan et al. using a fixed-bed reactor (outer tube: 35 mm diameter × 600 mm height; inner vessel: 25 mm diameter × 120 mm height) at different pyrolysis temperatures (300, 350, 400, 450 and 500 °C) and catalyst-to-material ratios (0/1, 0.2/1, 0.4/1, 0.6/1, 0.8/1, 1/1) [26]. The highest bio-oil yield obtained in this study was 31.1wt% at 400 °C and 0/1 catalyst loading. This value decreased to 20.7wt% with an increase in catalyst (1/1); however, the bio-oil obtained has more carbon and hydrogen, less oxygen and has higher HHV.

Previous studies showed that the yields and qualities of pyrolysis products vary depending on microalgae species and reactor configuration. In this paper, a pressurized fixed-bed reactor was used to evaluate the effects of temperature on the yields and qualities of pyrolysis products using *Nannochloropsis oculata* as feedstock. The characteristics of *N. oculata* were also assessed to determine its suitability as feedstock for production of biofuels through pyrolysis. The heating values and composition of the char, bio-oil and gas produced at each temperature were analyzed to determine its potential as alternative energy sources. Mass and energy yields based on initial biomass input were also estimated in an attempt to establish mass and energy conversion efficiencies of the pyrolysis process.

2. Materials and methods

2.1. Feedstock preparation and characterization

N. oculata samples used in this study was obtained from the Texas Agri-Life Research Algae Pond facility in Pecos, Texas. The samples were oven-dried at 105 °C until less than 10wt% moisture was obtained. Then, the dried algae samples were ground using Wiley Laboratory Mill Model #4 distributed by Arthur Thomas Company, Philadelphia, PA, USA. The average particle size diameter (PSD) of the ground algae samples was determined using USA Standard Sieve Nos. 20, 30, 40, 60 and 80 (ASTM E-11 specification, Fisher Scientific Company, USA). The HHV of the sample was determined subsequent to ASTM D 2015 using PARR isoperibol bomb calorimeter (Model 6200, Parr Instrument Company, Moline, IL). Moisture content and proximate analysis were determined in reference to ASTM standards (D 3173, D 3175 and E1755). The ultimate analysis was determined using Vario MICRO Elemental Analyzer (Elementar Analysemsysteme GmbH, Germany) in accordance with ASTM D 3176. Compositional analysis of *N. oculata* was done using NREL procedures: (1) Determination of Acid Soluble Lignin Concentration Curve by UV–Vis Spectroscopy (NREL/TP-510-42617), (2) Determination of Structural Carbohydrates and Lignin in Biomass (NREL/TP-510-42618), and (3) Determination of Extractives in Biomass (NREL/TP-510-42619). Lipid content (wt%), on the other hand, was analyzed by soxhlet extraction for 24 h using hexane as solvent. 10 g of dry microalgae sample was used in the analysis. After the extraction process, the solvent was removed from the extracted solution by rotary evaporation (rotavap) at 40 °C and 23 mmHg vacuum pressure. Then the amount of lipid (wt%) extracted was calculated by dividing the amount of dry oil in the flask by the initial amount of dry microalgae.

2.2. Pyrolysis experiment

Pyrolysis experiments were performed using a fixed-bed batch-type Parr pressure reactor (Series 4580 HP/HT, Parr Instrument Company, Moline, IL) illustrated in Fig. 1. The reactor is made of AISI 316 Stainless Steel with the capacity of 1.5 L. The reactor is inserted into a cylindrical ceramic fiber electrical heater with thermowell attached to a reactor controller (Series 4840, Parr Instrument Company, Moline, IL). A Type J (iron-constantan) thermocouple, also attached to the reactor controller, measures the temperature inside the reactor. Pressure gage (0–5000 psi capacity) with T316 Stainless Steel Bourdon tube measures the pressure build-up inside the reactor.

Pyrolysis runs were carried out subsequent to a three-level, one-factorial completely randomized experimental design. The reactor temperature served as the main factor in the experiment.

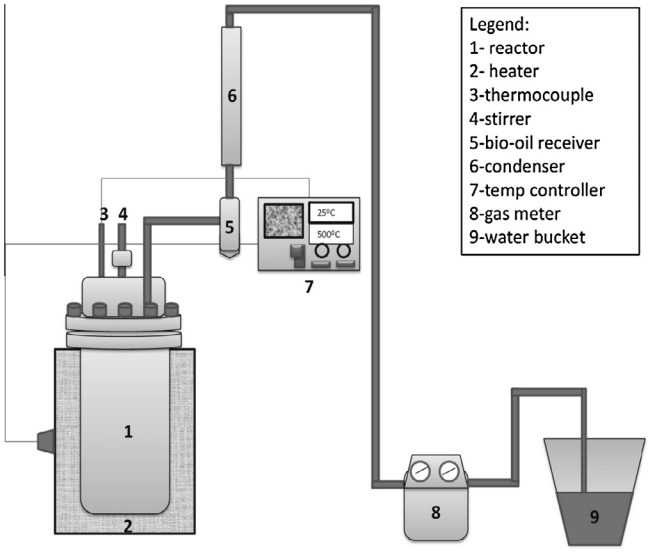

Fig. 1. Pyrolysis experimental set-up.