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# Effect of temperature and $Na_2CO_3$ catalyst on hydrothermal liquefaction of algae

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ABSTRACT

Hydrothermal liquefaction (HTL) has been identified as an innovative technique to convert aquatic or wet biomass such as algae into biofuels. In this study, HTL was performed on three algae strains viz. *Nannochloropsis*, *Pavlova* and *Isochrysis* at three temperatures of 250, 300 and 350 °C, with and without using $Na_2CO_3$ as a catalyst and a holding time of 60 min. The effect of temperature on the HTL product yields and their properties were studied for both catalytic and non-catalytic HTL. Maximum bio-oil yield for non-catalytic (48.67 wt.%) and catalytic (47.05 wt.%) HTL was obtained at 350 °C from *Nannochloropsis* and *Pavlova*, respectively. Compared to non-catalytic HTL, $Na_2CO_3$ increased the bio-oil yield for high carbohydrate containing algae (*Pavlova* and *Isochrysis*) at higher temperatures (300 and 350 °C) whereas for high protein containing algae (*Nannochloropsis*) the yield was higher only at lower temperature (250 °C). Total acid number, pH, density, higher heating value (HHV), ash, moisture and elemental composition were measured for bio-oils produced. The bio-oil obtained had the HHV in the range of 32 to 37 MJ/kg, which was comparable to heavy crude oil. Proximate and ultimate analyses were performed to characterize solid residue, and aqueous fraction was analyzed for acidity, total organic carbon and total nitrogen.



## 1. Introduction

Hydrothermal liquefaction (HTL) is a promising route for producing renewable fuels and chemicals from wet biomass [1]. It uses water at sub- or super-critical temperatures and pressures as a reactant and reaction medium [2]. It is mostly suited to wet biomass such as algae because it obviates the need to dry biomass as required in other processes such as gasification, pyrolysis, and transesterification, and reduces the energy requirements while increasing the overall energy efficiency of the system [3]. The advantages of algae over terrestrial biomass feedstock are high biomass productivity (40–60 dry ton/ha-yr) [4] and high carbon sequestration rate (1.8 kg of $CO_2$/kg of dry algae) [5], and they can be grown under conditions which are unsuitable for conventional crop production, thus relieving the food-versus-fuel pressure on agricultural land [6]. HTL of algae produces a black viscous liquid fraction also known as bio-oil or bio-crude, a solid residue fraction, a gaseous fraction and a water fraction containing some polar organic compounds also known as aqueous phase. In the case of HTL, the total oil yield is higher than the original lipid content in the algal biomass, which suggests that not only lipids but also whole algae (protein, lipids, and carbohydrates) gets converted to bio-oil [7,8].

Over the last decade, extensive research on algae HTL has been conducted in subcritical water conditions. Various process variables such as temperature [9–13], residence time [9,11–13] and heating rate [14] have been studied, using different types of algae strains as feedstock for HTL process. The primary focus of these studies has largely been on improving the bio-oil yield. Till date, the highest bio-oil yield reported is 79 wt.% [14]. Most of the HTL studies are performed at temperature range of 250 °C to 350 °C with 5 to 60 min residence time and majority in a batch reactor. In addition, most of the studies [10,12,13] have reported increase in bio-oil yield with increase in temperature till 350 °C and subsequently decrease in the yield thereafter. However, some studies have reported maximum yield at 320 °C [9] and 375 °C [11]. These variations in the reaction temperature observed for maximum bio-oil yield is mainly due to the differences in biochemical composition (proteins, lipids and carbohydrates) of the algae strains used. In addition, very few studies [15] have studied the effect of different biochemical composition on bio-oil yield. Moreover, there is a lack of understanding how the temperature would impact bio-oil yield of algae that have different biochemical compositions and many studies have not reported the effect of temperatures on the properties (e.g., acidity, density) of the bio-oil obtained.

Apart from non-catalytic HTL, introduction of different types of catalysts in the HTL process have also been reported [16–26]. Although the bio-oil obtained from non-catalytic HTL has high heating value (32–39 MJ/kg), it has several negative attributes such as high oxygen

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(typically 10–20%) and nitrogen (4–6%), and high viscosity which makes it undesirable for use as a fuel. Therefore, together with maximizing bio-oil yield, improvement in the quality of bio-oil has been the interest of most of the catalytic work performed. A number of homogenous [12,15,19,20,24–26] and heterogeneous catalysts [22,23] have been used in HTL to improve the bio-oil yield and its properties. Most of the studies have used $Na_2CO_3$ as a homogenous catalyst due to its previous usage in the HTL of lignocellulosic biomass for increasing bio-oil yield. However, some studies [18,21] found the bio-oil yield to decrease while others [17,19,25] observed its yield to increase with the addition of $Na_2CO_3$ in different algal strains [27]. This conflict of results could be due to the varied liquefaction behavior of lipids, proteins and carbohydrates in the presence of $Na_2CO_3$. The HTL study of different model compounds and microalgae was performed by Biller et al. [15]. From the study performed with model compounds, it was reported that the non-catalytic conversion of lipids and proteins to bio-oil was more efficient when compared to the lower yield with carbohydrates. In comparison, the use of $Na_2CO_3$ improved the conversion of carbohydrates and reduced the conversion of lipids and proteins. However, this study was limited to 350 °C. In addition, there is a lack of understanding of $Na_2CO_3$ and temperature effect on the bio-oil yield and its quality obtained from algae strains with different bio-chemical composition.

The objective of this study was to understand how algae strains that have different biochemical composition perform, in terms of products yield, at different HTL reaction temperatures and how the bio-oil quality changes when it is produced at different temperatures. In addition, the study examined the role of alkaline catalyst ($Na_2CO_3$) at different temperatures on the products yield and its effect on their properties for algae strains that are rich in carbohydrates and proteins. The study hopes to fill the knowledge gap on how proteins or carbohydrates rich samples perform with or without the use of $Na_2CO_3$ catalyst during HTL process.

## 2. Materials and methodology

### 2.1. Materials

Algae samples of *Nannochloropsis*, *Pavlova* and *Isochrysis* were obtained in the form of slurry from Reed Mariculture Inc. (Campbell, CA) and stored in a freezer until they were used. Table 1 provides biochemical composition of the algae species which was provided by the supplier. Sodium carbonate ($Na_2CO_3$) was purchased from a chemical supplier (VWR, Atlanta, GA) and was used as received. Moisture content was determined by calculating the weight loss of a sample by heating it in an oven at 105 °C for 24 h. Ash content was determined according to ASTM E 1755 standard. Volatile matter was measured by using ASTM E 872. Higher heating value (HHV) was measured using an oxygen bomb calorimeter (IKA, model C2000). Elemental composition of the algae samples was determined using an elemental analyzer (Perkin-Elmer, model CHNS/O 2400). Ultrapure (Type 1) water (Synergy Ultrapure Water Systems, EMD Millipore) was used for HTL experiments. High-purity (>99.99%) helium was purchased from Airgas Inc. (Charlotte, NC).

**Table 1**
Biochemical composition analyses of algae species.[a]

| Strains | Biochemical composition (wt.%) | | |
|---|---|---|---|
| | Carbohydrate | Protein | Lipids |
| *Nannochloropsis* | 8.92 | 62.79 | 18.12 |
| *Pavlova* | 28.00 | 46.94 | 13.88 |
| *Isochrysis* | 25.46 | 44.36 | 18.98 |

[a] Values reported by Reed Mariculture Inc. on dry basis.

### 2.2. Experimental setup and procedure

HTL experiments were performed in a high pressure experimental unit as shown in Fig. 1. The experimental unit consisted of a batch reactor of 1 in. internal diameter (i.d.) and 100 mL internal volume (High Pressure Equipment Company, Erie, PA) and equipped with an electrical heating unit. The temperature inside the reactor was continuously monitored using a 1/16th in. K-type thermocouple (Omega, Stamford, CT) attached to one end of the reactor. An in-line filter (pore size of 0.5 μm) was placed at the outlet of the reactor to prevent the entrainment of solids in the existing downstream system. The pressure in the reactor was measured using a pressure gauge, and the gas outlet line was connected to the moisture absorber cylinder installed prior to the gas collection chamber.

The reactor was loaded with approximately 10 g of algae (on a dry weight basis) at an algae:water ratio of 1:6 (14 wt.% solids) for all three algal feedstocks. With regard to catalytic HTL process, the reactor was additionally loaded with a $Na_2CO_3$ catalyst (5 wt.% of the dry solid for all samples). From here on, HTL process without using $Na_2CO_3$ is termed as non-catalytic HTL and processes using $Na_2CO_3$ is termed as catalytic HTL. In-line filter and valve assembly were connected to the reactor and securely tightened to seal the reactor. After the reactor was sealed, the headspace in the reactor was purged with helium gas by opening valve 3 to remove residual air and to create an inert environment for the reaction to occur. After purging with helium, valve 2 was closed, and the reactor was pressurized to an initial pressure of 35 psig after which valve 3 was closed.

The reactor was then heated to a desired temperature at the heating rate of 30 °C $min^{-1}$, and Fig. 2 shows a typical temperature and pressure profiles during an HTL experiment. After holding the reactor at a desired temperature for an hour, the reactor was cooled down to room temperature using cold water and the residual pressure created by gas formation during the reaction was then released to a gas chamber by opening valve 2. Both the catalytic and non-catalytic experiments were performed in triplicates and statistical analysis of the data (ANOVA, Tukey's HSD) was performed to understand whether or not the obtained results were statistically different. All the statistical analyses were performed at 95% confidence interval.

### 2.3. Product separation

After the gas fraction was released to the gas chamber, the reactor was opened by removing the valve assembly to recover the liquid and solid fractions. The composition of the gas fraction was not analyzed in this study. The content in the reactor was poured in to a flask (F1) and in most of the cases, the products separated naturally in the flask in a bio-oil and an aqueous phases. The bio-oil phase appeared to float in the aqueous phase. The solid phase remained mixed with both the bio-oil phase and aqueous phase. The aqueous phase along with some solid fractions was then decanted to another flask (F2) but not all the aqueous phase decanted as some remained in the flask, F1, along with bio-oil and some solids. The procedure to separate different product fractions after the reaction is illustrated in Fig. 3.

Equal amount of ultrapure water and acetone were used to rinse the reactor. Other solvents could be used to extract organic portion of the bio-oil such as dichloromethane (DCM). First, acetone was used to rinse, followed by the water; the rinsed acetone with bio-oil was collected in flask F1 while the rinsed water was collected in flask F2 along with decanted aqueous phase. The content in both of the flasks (F1 & F2) were vacuum filtered. Vacuum filtration was carried out using Whatman No. 5 filter paper (particle retention size of 2.5 μm) to recover the solid product. Content of flask (F2) was vacuum filtered to obtain solid residue and aqueous phase filtrate. The aqueous phase obtained was collected in a vial. Similarly, the content of the other flask (F1) was also vacuum filtered to recover solid products as residue and organic phase/acetone soluble phase as filtrate. The organic phase consisted of