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Hydrothermal liquefaction of *Chlorella pyrenoidosa* in sub- and supercritical ethanol with heterogeneous catalysts

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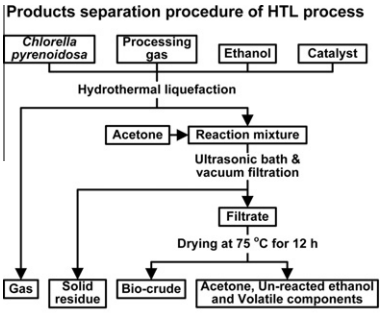
HIGHLIGHTS

- The highest mass and energy recovery ratios of bio-crude were 71.3% and 101.8%.
- Temperature was found to be the most dominant parameter on HTL process.
- H_2 as a processing gas improved the bio-crude yield and quality.
- The mass ratio of the reacted ethanol to the dry alga was about 3.26.

GRAPHICAL ABSTRACT



Mass balance of HTL process

HTL conditions	Input (g)		
	Bio-crude	Moisture	Un-reacted ethanol
240°C N_2	4.00	0.28	15.72
300°C N_2	4.00	0.28	15.72
300°C H_2	4.00	0.28	15.72
300°C H_2 Raney-Ni	4.00	0.28	15.72
300°C N_2 HZSM-5	4.00	0.28	15.72

HTL conditions	Output (g)				
	Bio-crude	Solid residue	Gas	Volatile components	Un-reacted ethanol
240°C N_2	2.90	0.69	0.09	13.27	3.05
300°C N_2	1.97	0.45	0.23	14.79	2.56
300°C H_2	2.02	0.42	0.53	14.22	2.81
300°C H_2 Raney-Ni	1.96	0.57	0.52	14.60	2.35
300°C N_2 HZSM-5	2.07	0.49	0.15	14.65	2.64

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ABSTRACT

Hydrothermal liquefaction (HTL) of low lipid content microalgae *Chlorella pyrenoidosa* with heterogeneous catalysts was processed under sub- and supercritical conditions of ethanol (200–300 °C, 2.8–9.0 MPa, 30 min). The HTL products were separated into bio-crude, gas, solid residue and volatile components, and then characterized. The highest mass and energy recovery ratios of bio-crude on the dry basis of alga were 71.3% and 101.8% respectively, obtained at 240 °C, while the highest higher heating value of bio-crude was 36.19 MJ/kg, obtained at 300 °C. Temperature was found to be the most dominant parameter. H_2 as a processing gas at an initial pressure of 1.03 MPa slightly improved the bio-crude yield and quality. Raney-Ni and HZSM-5 type zeolite catalysts had no significant effect on the presented HTL process. The results indicated that HTL with ethanol as the solvent was able to produce 50–70 wt.% of bio-crude directly from *C. pyrenoidosa*.

1. Introduction

Biofuels have drawn extensive research to address the concerns of depletion of fossil fuels, climate change and national energy security. Algae have been addressed as a next generation biofuels feedstock. Compared with biofuels from starch and lignocellulose, the use of algae enjoys the advantage of higher productivity per area per year (Demirbas and Demirbas, 2011). Additionally, algae production does not necessarily require arable land, thus has less impact on food supply. Most of the current researches are focusing on the high lipid content microalgae for biodiesel process (Mata et al., 2010). However, low lipid content microalgae typically have much higher biomass yield and can grow in harsh environments such as in wastewater, than high lipid content algae. It is worth noting that production of low lipid content microalgae offers opportunities to integrate wastewater treatment, carbon capture and biofuels production into one system. Hydrothermal liquefaction (HTL) is a thermochemical process to convert biomass feedstock into an oily liquid product, known as bio-crude or bio-oil, in and with liquid water at elevated temperature and pressure. Compared with conventional thermochemical conversion methods (e.g. fast pyrolysis, gasification), HTL does not require a drying pre-

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treatment, thus is more suitable for feedstocks with high water content, such as algae and manure. Water plays an essential role in HTL process. The dielectric constant (ε_r) of water decreases from 78.85 to 13.96 when temperature increases from 25 to 350 °C, resulting in water molecular from very polar to fairly non-polar (Archer and Wang, 1990). The dissociation constant of water (K_w) increases from 10^{-14} to 10^{-11} just below 350 °C, resulting in the increasing rate of both acid catalyzed and base catalyzed reactions in water (Bandura and Lvov, 2006). There have been some previous works on producing biofuels from macroalgae (Anastasakis and Ross, 2011; Zhou et al., 2010) and microalgae (Brown et al., 2010; Jena et al., 2011; Minowa et al., 1995; Vardon et al., 2012; Yang et al., 2004; Yu et al., 2011a; Yu et al., 2011b; Zou et al., 2010) through HTL. The bio-crude yields were in the range of 20–40% with higher heating values (HHV) of 28–40 MJ/kg. The oxygen and nitrogen contents of bio-crude were about 5–15% and 5–10%, respectively.

To improve the quality of bio-crude, two routes have been considered. One approach is via catalytic hydrothermal processing with homogeneous catalysts such as alkali catalysts or organic acids (Anastasakis and Ross, 2011; Minowa et al., 1995; Yang et al., 2004; Zhou et al., 2010; Zou et al., 2010), and heterogeneous catalysts such as zeolite or supported metal catalysts (Biller et al., 2011; Duan and Savage, 2011). The other approach is introducing organic compounds as the processing solvents in HTL (Huang et al., 2011; Matsui et al., 1997; Yang et al., 2011; Zhou et al., 2012; Zou et al., 2009), among which ethanol has attracted much of the attention. The dielectric constant of ethanol at 240 °C is 4.20 (Dannhauser and Bahe, 1964). The conventional acid/base catalyzed transesterification process has been proven to undergo a self catalyzed mechanism without the presence of catalyst in supercritical ethanol conditions. Supercritical ethanol shows comparable physical and chemical properties to those of subcritical water, thus replacing water with ethanol as the processing solvent for HTL is theoretically feasible. Some noteworthy results in literatures are summarized as followed. (1) Na_2CO_3 was reported to increase the bio-crude yield, but not necessary for feedstock that already contained significant amount of sodium (Minowa et al., 1995); (2) The gas product was mainly CO_2 when processed with alkali catalysts, while processed with organic acids produced significant amount of CO, H_2 and CH_4 (Ross et al., 2010); (3) Reducing atmosphere led to bio-crudes with a slightly increased H content and H/C ratio (Duan and Savage, 2011); (4) Supported metal catalysts resulted in bio-crudes with a lower O/C ratio. Moreover, Pt/C catalyst was active for the conversion of fatty acids into alkanes (Duan and Savage, 2011); (5) A variety of fatty acid (C_3–C_{22}) esters were detected in bio-crude obtained from HTL of high lipid content algae when processed with ethanol, indicating that ethanol acted as a reaction substrate with algae decomposition intermediates (Zhou et al., 2012); (6) Subcritical water and supercritical ethanol can serve as effective hydrogen donors (Kershaw, 1997), however, external hydrogen resource is greatly needed.

Table 1
Characteristics of *C. pyrenoidosa* (dry basis).

Chemical composition (wt.%)			
VS[a]	Crude fat	Crude protein	Non-fibrous carbonhydrate[b]
94.4	0.1	71.3	22.0
Ash	Cellulose	Hemicellulose	Lignin
5.6	0.3	0.5	0.2

Elemental composition (wt.%)			
C	H	N	O[b]
51.4	6.6	11.1	30.9

[a] Volatile solid.
[b] Calculated by difference.

Chlorella pyrenoidosa is a green unicellular alga with low lipid and high protein content that is found in both fresh and marine waters (Becker, 1994). In this study, we combined the previous two routes in one single process. The objective of this work was to investigate the HTL performance by replacing water with ethanol as the solvent, and to study the effects of temperature, processing gas and catalyst on bio-crude yield and quality. HTL of *C. pyrenoidosa* was carried out under sub- and supercritical conditions of ethanol, by adjusting temperature in the range of 200–300 °C, under N_2 or H_2 atmosphere, and with/without two catalysts, Raney-Ni and HZSM-5 type zeolite.

2. Methods

2.1. Materials

The raw material, microalgae *C. pyrenoidosa*, was obtained from a health food store as food grade material (NOW Foods, Bloomingdale, IL). It was the same batch with the raw material used in our previous works (Yu et al., 2011a,b). Characteristics of the *C. pyrenoidosa* are shown in Table 1. The elemental compositions of *C. pyrenoidosa* were determined using a CE 440 elemental analyzer (Exeter Analytical, Inc., North Chelmsford, MA). The macromolecular and chemical compositions of alga were analyzed according to the standard methods of the Association of Official Analytical Chemists (AOAC). Ammonium ZSM-5 type zeolite catalyst (Si/Al = 50) was purchased from Zeolyst International (Conshohocken, PA). HZSM-5 was prepared by calcination of ammonium ZSM-5 in air at 550 °C for 3 h. Aluminum-nickel alloy (Raney-nickel alloy, 50% Ni basis), supported platinum and palladium on alumina (5 wt.% loading Pt/Al_2O_3, Pd/Al_2O_3) were obtained from Sigma-Aldrich. Reagent grade ethanol and acetone were obtained from Fisher Scientific. High purity hydrogen and nitrogen were purchased from S.J. Smith Co. (Davenport, IA), and all chemicals were used as received.

2.2. HTL process

The HTL experiments were performed in three stainless steel cylindrical reactors of 100 ml capacity, each with a magnetic drive stirrer (model 4593, Parr Instrument Co., Moline, IL). *C. pyrenoidosa* was mixed with ethanol as the feedstock for each HTL experiment. Typically, 20 g of the mixed feedstock with 20% of dry alga and 1 g of catalyst (if added) were filled in the reactor. After the reactor was sealed, high purity hydrogen (or nitrogen) gas was charged to purge the reactor headspace five times, and to build up to a pre-set initial pressure of 1.03 MPa at room temperature. Then the reactor was heated by an electric heater up to a set-point reaction temperature, and the set-point temperature was maintained for 30 min. Stirring at 500 rpm was applied throughout the reaction. After reaction, the reactor was rapidly cooled by flowing tap water through the cooling coil located outside the reactor, and the final pressure was recorded at room temperature. Duplicate or triplicate runs were performed for every experimental condition. Average values and standard deviations were reported.

2.3. Products separation and analysis

The products separation procedure is shown in Fig. 1. Once the reactor was cooled to room temperature, the "Gas" products in the reactor were carefully released through a control valve into a Tedlar gas sampling bag (CEL Scientific CORP., Cerritos, CA). The solid/liquid products were rinsed from the reactor using twice the amount of feedstock in acetone (40 g), and the resulted suspension was treated in an ultrasonic bath for 30 min, followed by filtration