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Co-liquefaction of micro- and macroalgae in subcritical water

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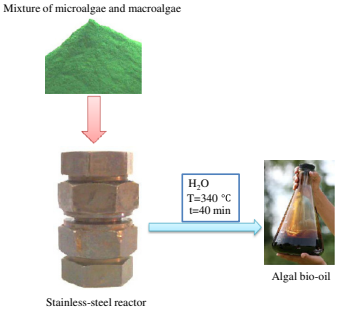
HIGHLIGHTS

- Co-liquefaction of SP and EP alleviated the severe reaction conditions.
- Positive synergetic effect existed during the co-liquefaction of SP and EP.
- Co-liquefaction improved energy recovery and promoted in situ deoxygenation of oil.
- The HHV of bio-oil was 35.3 MJ/kg from the co-liquefaction of SP and EP.

GRAPHICAL ABSTRACT



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ABSTRACT

Co-liquefaction of microalgae (*Spirulina platensis*, SP) and macroalgae (*Entermorpha prolifera*, EP) was studied in subcritical water by using a stainless-steel batch reactor at different temperature (250 to 370 °C), time (5 to 120 min), SP/EP mass ratio (0 to 100%), and water/algae mass ratio (1:1 to 6:1). The results suggested that a positive synergetic effect existed during the co-liquefaction of SP and EP, and this synergetic effect was dependent on reaction conditions. Co-liquefaction alleviated the severe reaction conditions compared to the separate liquefaction of SP and EP and also promoted the in situ deoxygenation of the bio-oil. The higher-heating-value of bio-oil produced from the co-liquefaction of SP and EP (w_{SP}:w_{EP} = 1) is 35.3 MJ/kg. The energy recovery from the co-liquefaction is larger than the average value from the separate liquefaction of SP and EP. Co-liquefaction did not affect the molecular composition but affect the relative amount of each component in the bio-oil.

1. Introduction

Recently, increasing attentions are being paid to the utilization of biofuels due to their renewability, sustainability, and carbon neutrality (Ragauskas et al., 2006; Sims et al., 2010; John et al., 2011). To date, many different kinds of biomass were tested for the production of biofuels that can be classified basically into three categories: solid, liquid and gas. Liquid biofuels (e.g. bio-oil) are attracting much attention and investment because they can be processed and refined into a variety of transportation fuels that can be used in existing vehicles with little or no modification to engines and fueling systems. Of those different biomass feedstocks tested, algae are considered as one of the most promising and attractive energy sources. They offer many competitive advantages over terrestrial biomass, including rapid growth rates, high per-acre yield, strong ability to survive in a variety of environments, absent (or much reduced) competition with agricultural land, and high quality and versatility of the byproducts (Chisti, 2007; Brennan and Owende, 2010; Mata et al., 2010; Leite et al., 2013). Algae can be classified according to their size into two major groups: macroalgae and microalgae (Samarakoon and Jeon, 2012). Macroalgae, also known as seaweed, are multicellular plants and possess plant-like characteristics, making their harvesting more easily than that of microalgae (Maceiras et al., 2011). They usually contain high amounts of carbohydrates and thus can be used as potential feedstock for the production of bioethanol (Daroch et al., 2013). In contrast, microalgae are unicellular

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organisms less than 0.4 mm in diameter and have the ability to produce substantial amounts of lipid. Compared to macroalgae, microalgae are more favored primarily for the production of biodiesel because they have much higher lipid content, higher per hectare yield (158 vs 60–100 tons of macroalage), and shorter harvesting cycle (daily vs 3 or 6 months of macroalgae) (Chisti, 2007). The chemical compositions of macroalgae and microalgae are not an intrinsic constant factor but vary over a wide range, both depending on species and cultivation conditions such as temperature, illumination, pH, CO_2 supply, salt and nutrients (Li et al., 2008).

Both marcoalgae and microalgae have high moisture content after harvesting. Converting these high moisture algae by using conventional thermo-chemical techniques such as fast-pyrolysis and gasification usually require a dry feedstock, and thus will suffer a large energy penalty from vaporizing the moisture. Alternatively, hydrothermal liquefaction (HTL) uses high moisture biomass, and therefore saves high cost in the dewatering process and is suitable for the production of bio-oil from biomass with varying moisture content. During HTL, high moisture algae are subjected to elevated temperatures (250–350 °C) and pressures (10–20 MPa) in order to break down and reform the chemical building blocks into a "biocrude" oil that can be used for direct combustion or refined for transportation grade fuels (Toor et al., 2011). Furthermore, HTL can not only convert the lipid but also other cellular components such as protein, fiber, and carbohydrate in algae into the "biocrude" oil (Patil et al., 2008). Therefore, both high-lipid microalgae and low-lipid macroalgae are all suitable feedstocks for HTL. There has been some previous studies that separately examined microalgae and macroalage as feedstock for production of biofuels via HTL (Brown et al., 2010; Zhou et al., 2010; Zou et al., 2010; Anastasakis and Ross, 2011; Barreiro et al., 2013). These previous work suggested that higher "biocrude" oil yields were always achieved with employing microalgae as the feedstock due to their high lipid content, and the molecular composition of the "biocrude" oils produced from microalgae was also different from that of macroalgae.

Over the past few decades, many efforts had been made by researchers to examine the co-liquefaction of biomass with other uneasily degradable feedstocks such coal and polymers in different solvents (Yuan et al., 2009; Guo et al., 2011; Xiu et al., 2011; Pei et al., 2012; Shen et al., 2012; Shui et al., 2011). These previous studies suggested that the presence of biomass enhanced the conversion of coal and polymer and improved the yield and quality of liquid products (bio-oil). That is a positive synergistic effect existed during the co-liquefaction, and this synergistic effect was dependent on liquefaction conditions. Microalgae were also employed in the co-liquefaction of coal and synthetic polymer (Ikenaga et al., 2001; Yuan et al., 2009; Pei et al., 2012), respectively. During the co-liquefaction, microalgae would promote the thermal decomposition of macromolecules in coal and synthetic polymer and thus not only increased the bio-oil yield but also alleviated the severe reaction conditions (especially the liquefaction temperature). Compared to microalgae, macroalgae are more difficult to degrade due to their high carbohydrate content. Therefore, one would expect that a positive synergistic effect might also exist during the co-liquefaction of microalgae and macroalgae. To the best of the authors' knowledge, however, the literature provides no reports on the co-liquefaction of microalgae and macroalgae under hydrothermal conditions. This article provides the first such report.

In the present study, co-liquefaction of microalgae (*Spirulina platensis*, SP) and macroalgae (*Entermorpha prolifera*, EP) in subcritical water were examined. Effects of reaction temperature (varied from 250 to 370 °C), time (varied from 5 to 120 min), SP/EP mass ratio (varied from 0 to 1.0), and water/algae mass ratio (varied from 1:1 to 6:1) on the yields of product fractions were determined, aiming to explore how these parameters affect the co-liquefaction behavior and the possible synergistic effects between SP and EP. Finally, the properties of the bio-oils were characterized by using Gas chromatography–Mass spectroscopy (GC–MS), elemental analysis and Fourier transform infrared spectrometry (FT-IR), respectively.

2. Methods

2.1. Materials

Spirulina platensis (SP) *and Entermorpha prolifera* (EP) are all commercially available. They were sun dried as received and pulverized into a fine powder with particle size >100 mesh by using a multi-functional pulverizer (SB-02). The algae powder was stored in a sealed glass bottle isolated from the air contact and clearly labeled until further use. Table 1 lists their proximate and ultimate analysis along with other properties. Quantification methods of evaluating the moisture, ash, crude protein, and crude lipid in the algae powder were described as previously (Duan et al., 2013a). Freshly deionized water, prepared in the lab, was used throughout the experiments. All other chemicals used in this research were obtained commercially and used as received.

The reactors, which were fabricated from stainless-steel Swagelok tube fitting, had an internal volume of 25 mL and were used in all experiments. The body of the reactor consisted of 1-in. port connector sealed with two 1-in. caps at both ends. Prior to their use in experiments, the metal reactors were loaded with water and conditioned at 400 °C for 1 h to remove any lubricants/oils that remained from the manufacture of the Swagelok parts.

2.2. Procedure

In a typical run, 2.5 g algal biomass (1.25 g SP, 1.25 g EP) and desired amount of freshly deionized water were loaded into two identical reactors. The water loadings were selected such that 95% of the total reactor volume would be occupied with liquid phase if water were the sole component. The reactors were sealed by traditional wrenches after they were loaded.

Hydrothermal reactions were carried out by placing the loaded reactors into a custom made molten-salts (consists of KNO_3 and $NaNO_3$ at a mass ratio of 5:4) tank pretreated to the desired temperature which was controlled by using an Omega type temperature controller. The reactors stayed in the molten-salts tank for a desired total holding time, and then were removed and cooled by cold water. The reactors were taken out of the water when they reached room temperature and thoroughly dried by an electric hair dryer. The dried reactors were weighted and depressurized, and the gaseous products were vented. Most of the aqueous phase

Table 1
Proximate and ultimate analysis of SP and EP.

Properties	SP	EP
Water content (wt.%)	15.4 ± 0.8	15.0 ± 0.7
Ash content (wt.%)	17.5 ± 0.9	38.0 ± 0.5
Organic content (wt.%)	67.1 ± 1.7	47.0 ± 1.2
Protein (wt.%)	26.8 ± 0.6	23.8 ± 0.4
Carbohydrate (wt.%)	29.3 ± 0.4	18.2 ± 0.6
Crude lipid (wt.%)	11.0 ± 0.7	5.0 ± 0.2
HHV (MJ/kg)	14.6 ± 0.5	13.6 ± 0.5
Elemental composition (wt.%)		
C	34.5 ± 0.6	28.0 ± 0.3
H	5.1 ± 0.1	4.5 ± 0.3
O[a]	24.2 ± 0.9	10.7 ± 1.0
N	3.4 ± 0.1	3.8 ± 0.4

[a] Calculated by difference.