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Effect of operating conditions on direct liquefaction of low-lipid microalgae in ethanol-water co-solvent for bio-oil production

Changhao Ji [a], Zhixia He [a,b,*], Qian Wang [a,*], Guisheng Xu [a], Shuang Wang [a], Zhixiang Xu [a], Hengsong Ji [a]

[a] School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013, China
[b] Institute for Energy Research, Jiangsu University, Zhenjiang 212013, China

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ABSTRACT

In this work, the direct liquefaction (DL) of low-lipid microalgae Spirulina was investigated in a 50 ml autoclave reactor with ethanol and water as co-solvent. The objective of this research was carried out to examine the effect of operating conditions such as reaction temperature, reaction time, solvent/microalgae (S/M) ratio and ethanol-water co-solvent (EWCS) composition on product distribution and bio-oil characterization. The results revealed that the optimal operating conditions for bio-oil yield and conversion rate were reaction temperature of 300 °C, reaction time of 45 min, ethanol content of 50 vol.% and S/M ratio of 40/4 ml/g, which gave the bio-oil yield of 59.5% and conversion rate of 94.73%. Conversion rate in EWCS was significantly higher than that in pure water or ethanol, suggesting the synergistic effect between ethanol and water during microalgae DL. Distinct difference in composition and relative content of compound among bio-oils in different solvents were observed by GC–MS and FT-IR. Compared with hydrothermal liquefaction, the most abundant compounds in bio-oil from both EWCS and pure ethanol were esters. The presence of ethanol could enhance the bio-oil yield and improve bio-oil quality by promoting the formation of esters.

1. Introduction

Nowadays, energy is playing a crucial role in economic growth and development of modern industrial society. However, energy crisis and environmental concerns have become increasingly serious due to unrestrained utilization of limited fossil fuels [1]. To ensure energy security and alleviate environmental problems, accelerating the development and utilization of clean and renewable energy sources has gained increasing attention over the past decades [2]. Biomass is currently regarded as the fourth largest primary energy source followed by coal, petroleum and natural gas in the world [3]. As an energy source, biomass is also considered to be a potential substitute with low carbon intensity for fossil fuels because of its abundant reserves, wide distribution and carbon neutral [4]. Fuels derived biomass, called "biofuels" for short, can be classified basically into the first, second and third generation categories according to their difference in raw materials [5]. Generally, the first and second generation biofuels can be produced from food crops such as corn, cassava and soybean, and non-food crops like rape straw and pine sawdust, respectively [6]. Considering competition with food crops and land resources of the first and second generation biofuels respectively, the third generation biofuels derived from microalgae show attractive promise by saving arable lands and stabilizing effective food supplies [7].

Traditional lipid extradition of microalgae for biodiesel by means of trans-esterification can only utilize the lipid fraction and require high-lipid content in microalgae. However, most microalgae distributed widely in nature belongs to low-lipid microalgae, usually accompanied by higher biomass yield and better environment adaption [8]. Rapid pyrolysis and direct liquefaction (DL), the two main thermochemical conversions which can lead to full use of the whole microalgae regardless the lipid content, are gradually employed to convert microalgae biomass into easily storable and transportable liquid fuels [9]. Microalgae contains approximately 80–90% moisture content, namely called wet microalgae. The rapid pyrolysis of microalgae involves the consumption of a great deal of energy for effective drying and dewatering steps to reduce the moisture content since the rapid pyrolysis process is suited for conversion of dry feed stocks with moisture content below 10% [10]. Therefore this technology limits the application of microalgae for bio-oil production, especially for wet microalgae. In contrast, the typical DL process, as the most promising technique for producing biofuels from wet microalgae, has lower reaction temperature and higher energy efficiency than

* Corresponding authors. Tel.: +86 13776476205 (Z. He); Tel.: +86 13912802056 (Q. Wang).
E-mail addresses: zxhe@ujs.edu.cn (Z. He), qwang@ujs.edu.cn (Q. Wang).

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that of rapid pyrolysis process because energy intensive drying and dewatering steps are not imperative [11]. Therefore this technology will become the mainstream direction of microalgae thermochemical conversion for bio-oil production. Liquefaction of microalgae in hot compressed or sub- and supercritical water at elevated temperature and pressure is usually called hydrothermal liquefaction (HTL). Extensive researches have been investigated to produce bio-oil from HTL of microalgae [12–14]. Although water is an ideal and environmentally friendly medium, using water as a solvent has the following drawbacks: (1) water reached up to critical value (374.3 °C, 22.1 MPa) need higher energy consumption due to the large specific heat [15,16]; (2) Bio-oil obtained from HTL contains high amount of oxygen and nitrogen, and thus limits its application for transport fuels [17].

To ease the severe requirement of reaction condition and enhance the quality of bio-oil, addition of various organic solvents with lower critical value and dielectric constant to sub- and supercritical water have been adopted for liquefaction of microalgae, including alcohol (ethanol, glycol, methanol and butanol), acetone, and 1,4-dioxane [18,19]. It has been proved that organic solvent-water co-solvents have obviously synergistic effects on liquefaction of biomass. Compared to water as sole solvent, co-solvents can not only decrease the critical temperature and pressure of reaction system but also enhance the bio-oil yield with lower oxygen content [20]. Furthermore, some alcohol-water co-solvents can serve as hydrogen donor by providing and transferring active hydrogen free radicals. Yuan et al. reported that the presence of alcohol, which promotes the decomposition of relatively high-molecular-weight in microalgae, can readily react with acidic components in the bio-oil to obtain biodiesel-like esters [21].

As one of the most universal alcohols applied in industry, ethanol has relatively lower critical value (240.8 °C, 6.14 MPa) and dielectric constant compared to other organic solvents [22]. Additionally, ethanol is cost-effective and reproducible, and can be obtained from biomass fermentation. All these merits make ethanol-water co-solvent (EWCS) a promising liquefaction solvent. Although several efforts have been devoted to investigating the liquefaction of lignocelluloses biomass in mixed solvent [23,24], to the best of our knowledge, there is only limited information yet available on Liquefaction of low-lipid microalgae in EWCS, especially on Liquefaction of Spirulina. More importantly, it was worth noted that the main components of microalgae, which contains proteins, lipids and carbohydrates, are different from those of lignocelluloses biomass including cellulose, hemicellulose and lignin [25]. Besides, microalgae is more easily to decompose than that of lignocellulose biomass due to its low thermal stability. Thus, it is essential to further research low-lipid microalgae liquefaction with EWCS as the medium.

The objectives of this work were to investigate the DL of low-lipid microalgae Spirulina by replacing water with ethanol and water as the co-solvent, and to explore the effects of reaction temperature, reaction time, solvent/microalgae (S/M) ratio and EWCS composition on DL characteristics of Spirulina, especially on the product distribution and bio-oil yield and properties.

2. Materials and methods

2.1. Materials

Spirulina powder with particle size less than 100 mesh used in this work was supplied from Shandong Binzhou Tianjian Biotechnology Co., Ltd. (Shandong, China). Prior to use in experiments, the sample was firstly dried in a vacuum oven at 105 °C for 24 h to a constant weight, and then stored in a sealed plastic bag. The results of proximate and ultimate analysis along with other properties of microalgae sample are presented in Table 1. All chemical reagents throughout the whole experiments were commercially available and analytical grade, and used as received.

Table 1
Proximate, ultimate and chemical composition analyses of Spirulina sample.

Proximate analysis	(wt.%)	Ultimate analysis	(wt.%)	Chemical composition	(wt.%)
Moisture	10.3	C	46.9	Protein	70.3
Ash	8.5	H	6.9	Lipid	5.8
Volatiles	69.4	N	10.7	Carbohydrate	23.9
Fixed carbon	10.8	O[a]	35.5	HHV (MJ/kg)	18.5

[a] By difference.

2.2. Experimental apparatus

The DL system was comprised of the autoclave reactor and some associated auxiliary equipment, such as electric furnace, controller, rotary evaporator, inlet or outlet valve and cooling coil, as clearly shown in Fig. 1. The reactor with 50 ml internal volume made of 316 stainless steel had a maximum pressure and operating temperature of 40 MPa and 400 °C, respectively. All DL experiments of Spirulina were conducted in the reactor and an electric furnace was used to provide heat for the reactor. Temperature was monitored by a controller equipped with an internal thermocouple. Extraction agents were recovered using a rotary evaporator under reduced pressure.

2.3. Experimental procedures

The DL experiments of Spirulina were performed in the autoclave reactor mentioned above. In a typical run, 4 g Spirulina powder and 40 ml EWCS with different ethanol content were firstly added to the reactor. Then, the reactor was sealed firmly with six evenly distributed bolts. The electric furnace was firstly heated to the desired temperature with a heating rate of 10 °C min^{-1}. Subsequently, reactor was placed into it and reaction was initiated for given reaction time. Finally, the reactor was immediately removed from the electric furnace, then it was cooled down to the room temperature using an electric fan and cooling coil located outside the reactor. Table 2 summarizes the detailed operating conditions used for the DL experiments. At least three duplicate runs were performed to ensure the experimental errors for the liquefaction yields and conversion rate within 5% and the mean values were presented.

After the typical run, microalgae powder was finally transformed into various products including gas, bio-oil, solid residue

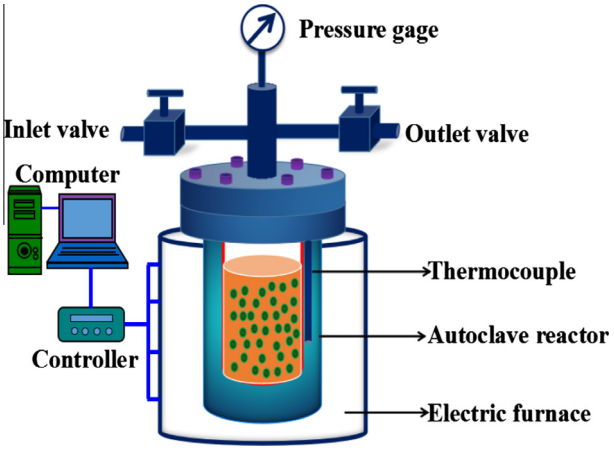

Fig. 1. Schematic diagram of the DL system.