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Hydrotreatment of bio-oil distillates produced from pyrolysis and hydrothermal liquefaction of duckweed: A comparison study

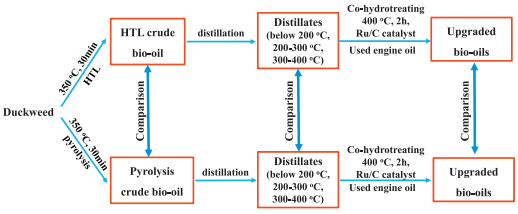
Feng Wang, Ye Tian, Cai-Cai Zhang, Yu-Ping Xu, Pei-Gao Duan *

College of Chemistry and Chemical Engineering, Department of Energy and Chemical Engineering, Henan Polytechnic University, No. 2001, Century Avenue, Jiaozuo, Henan 454003, PR China

HIGHLIGHTS

- HTL of duckweed produces a higher crude bio-oil yield than pyrolysis at 350 °C.
- Total yield of distillates below 400 °C of HTL oil is larger than pyrolysis oil.
- HTL oils and their distillates show much difference in properties from pyrolysis.
- N removal of distillates from pyrolysis oil is easier than from HTL oil.
- Aromatics and alkanes constitute a large proportion in most of upgraded bio-oils.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive comparison of hydrothermal liquefaction (HTL) to the pyrolysis of duckweed was conducted to determine the yields and components of the crude bio-oils and their distillates. The upgrading behaviors of the distillates were thoroughly investigated with the use of used engine oil as a solvent. With all other variables fixed, HTL produced crude bio-oil with a lower H/C ratio (1.28 ± 0.03) than pyrolysis did (1.45 ± 0.04). However, its distillates had a higher H/C ratio (1.60 ± 0.05) and total yield (66.1 ± 2.0 wt%) than pyrolysis (1.46 ± 0.04 and 47.2 ± 1.4 wt%, respectively). Phenolics and nitrogenous heterocycles constituted relatively major proportions of the two crude bio-oils and most of their distillates. Obvious differences in molecular composition between the two crude bio-oils and their distillates were ascribed to the distinct impacts of HTL and pyrolysis and were affected by the distillate temperature. Co-hydrotreating with used engine oil (UEO) provided the upgraded bio-oils much higher H/C ratios (~1.78 ± 0.05) and higher heating values (~45.5 ± 1.4 $MJ \cdot kg^{-1}$), as well as much lower contents of N, O and S compared to their initial distillates. Aromatics and alkanes constituted a large proportion in most of upgraded bio-oils. N removal from the pyrolysis distillates was easier than from the HTL distillates. Distinct differences in yields and molecular compositions for the upgraded bio-oils were also attributed to the different influences associated with the two conversion routes.

1. Introduction

Due to the gradual exhaustion of fossil fuel resources and their negative impact on the environment, biofuels, as a renewable and environmentally friendly form of energy, have received worldwide attention (Dang et al., 2013). Biofuel generation has been supported by various biomass feedstocks. Compared to terrestrial biomass, aquatic biomass has many desirable properties, including high productivity, minor requirements for additional energy, and, especially, the avoidance of the "food vs fuel" competition (Chen et al., 2014; Chiaramonti et al., 2017). Therefore, aquatic biomass, especially algal biomass, has become the focus of attention for many scholars.

In most cases, of the possible routes for thermochemical processing of algae biomass into liquid biofuels, pyrolysis and hydrothermal liquefaction (HTL) have been extensively studied. The two routes are also

* Corresponding author.
E-mail address: pgduan@hpu.edu.cn (P.-G. Duan).

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considered to be the leading processing options to produce fuel precursor-crude bio-oil (Chiaramonti et al., 2017; Yang et al., 2016). Pyrolysis is normally performed at atmospheric pressure and temperatures ranging from 300 to 700 °C or higher, and can be used to achieve thermal decomposition of biomass without oxygen to obtain bio-oil, gas and coke (Chiaramonti et al., 2017). The pre-drying process of biomass is necessary for the pyrolysis process, especially for the fast and flash pyrolysis processes, in which high heating rates, sufficient temperature control and the reduction of phase separation are critical. HTL can convert biomass into crude bio-oil via thermochemical reactions in and with liquid water at elevated temperatures (280–370 °C) and pressures (10–25 MPa) (Elliott et al., 2013). Water at high temperatures exhibits peculiar properties, including a lower dielectric constant, higher native H^+ concentration, and a higher solubility for small organic compounds. Therefore, water can serve as solvent, catalyst and reactant in the HTL process (Savage, 1999). Furthermore, HTL can directly convert wet biomass into crude bio-oil, obviating the energy-intensive dewatering and drying processes that are necessary for pyrolysis (Toor et al., 2013). Both pyrolysis and HTL are effective in achieving full component conversion of algae, not only including the lipid fraction but also proteins, carbohydrates and other organic components (Chiaramonti et al., 2017; Biller and Ross, 2011). The two thermochemical processes for treating algae biomass have gained the attention of researchers, and an enormous number of studies have been extensively reported (Grierson et al., 2009; Borges et al., 2014; Pan et al., 2010; Xu and Savage, 2017; Li et al., 2014; Shakya et al., 2017).

However, a direct comparison of the chemical properties of the crude bio-oil resulting from the two processes has rarely been reported for the same algae biomass. To the best of our knowledge, there are only two articles that provide a more detailed, direct comparison of the pyrolysis and HTL processes using the same algae feedstock. Vardon et al. (2012) compared HTL and slow pyrolysis of *Spirulina*, raw and defatted *Scenedesmus*, respectively. Sharp differences between bio-oils obtained via HTL and pyrolysis were reported in their mean molecular weights and the percentage of low-boiling fractions. A comparison of HTL and pyrolysis for *C. reinhardtii* was conducted by Hognon et al. (2015). In their research, the bio-oils from the two processes revealed different compositions; that is, the pyrolysis bio-oils mainly consisted of protein-derived compounds, whereas HTL bio-oils mainly consisted of lipid-, protein- and carbohydrate-derived compounds. These studies confirmed the great influence of conversion process on the physiochemical characteristics of crude bio-oils. These studies also inspired our interest in performing a thorough comparison of the HTL and pyrolysis processes when using the same biomass and reaction parameters.

Crude bio-oils from both pyrolysis and HTL of algae cannot be directly used due to their high contents of N, O and S, and their high viscosity. Therefore, further treatment is required to upgrade the quality of crude bio-oils, including increasing the content of hydrocarbon molecules and decreasing the N, O and S contents and the viscosity. The ultimate aim is for the upgraded bio-oils to reach the standard of liquid transportation fuel (Duan and Savage, 2011). Various technologies have been developed for upgrading crude bio-oil, and hydrotreating is the most common (Saber et al., 2016). Duan and Savage (2011) demonstrated pioneering work on the upgrading of crude bio-oil from HTL of microalgae in supercritical water (SCW). With a Pt/C catalyst and high-pressure H_2, the upgraded bio-oil presented a marked increase in hydrocarbon molecules and decrease in N, O and S contents, as well as in total acid number (TAN). Subsequent studies have further confirmed that the catalyst is a crucial factor that affects the fraction of nitrogenous and oxygenated compounds and saturated hydrocarbons (Duan et al., 2013a; Bai et al., 2014; Xu et al., 2015). Different from the direct upgrading of the entire crude bio-oil, Nam et al. (2017) performed a catalytic upgrade of microalgae distillates. In their research, light (20–120 °C) and middle (120–200 °C) fractions were physically distilled and then subjected to catalytic upgrading with temperature and pressure ranges of 130–250 °C and 4.1–8.3 MPa, respectively. Compared to direct catalytic upgrading, upgraded bio-oil from the distillates presents better qualities including a higher H/C ratio, higher HHV and lower TAN. There have been many previous studies of upgrading methods for crude algae bio-oils from both HTL and pyrolysis, but few that compared the upgrading behaviors of crude bio-oils from the two processes. The study mentioned above also triggered our interests in probing the different effects between pyrolysis and HTL on the distillates of bio-oils and their behaviors in the upgrading process.

In this text, we attempted to perform pyrolysis and HTL for the same biomass. The purpose was to directly compare the effects of the two methods on the yields and components of the resultant crude bio-oils and their distillates. The upgrading behaviors of the distillates were also included. Duckweed, a small aquatic plant that floats on the surface of ponds, is the biomass selected for our study. This aquatic biomass has attracted great attention from researchers due to its desirable properties such as rapid multiplication, strong adaptability and low processing costs (Landolt et al., 1998; Muradov et al., 2010; Xiao et al., 2013; Xu et al., 2011). Duckweed can be recovered from the cultivation medium using simple mechanical separation, which is in sharp contrast to microalgae (Muradov et al., 2010). In addition, the ability to accumulate starch, which is required for creating biofuels, make duckweed a promising candidate for biofuel feedstock (Xiao et al., 2013; Xu et al., 2011). The composition of duckweed is distinctly different from that of microalgae, mainly because of the relative content of lipid, protein, and hydrocarbons (Yan et al., 2016; Vardon et al., 2012). These differences in composition are likely to affect the effects of the two routes on the yield and composition of the crude bio-oils and on their upgrading behaviors. The study comparing the two routes of duckweed conversion, combined with the previous studies on microalgae, may help us to understand the effects of the biomass composition on the two routes. The pyrolysis and HTL of duckweed have been investigated in several studies (Muradov et al., 2010; Muradov et al., 2012; Duan et al., 2013b; Yan et al., 2016). The upgrading process of crude HTL oil of duckweed has also been demonstrated in our previous studies (Zhang et al., 2014). However, to the best of our knowledge, no literature has reported a direct comparison between the two processes for duckweed.

In the hydrotreating of crude bio-oil, solvents, especially hydrogen donor solvents, are typically used with a goal to reduce mass-transfer limitations, to effectively retard the formation of coke precursors and to extract them from catalyst pores in situ (Arpa et al., 2010). In this study, used engine oil (UEO) was used as solvent in the upgrading process because of its ideal performance, including its high availability, low price, and omitting separation from the product oil, which was proven in our previous studies (Wang et al., 2016; Wang et al., 2017a).

In this study, duckweed was converted into crude bio-oil by HTL and pyrolysis under the same reaction conditions, to the extent possible. The two crude bio-oils were then distilled into three fractions with different temperature ranges of <200, 200–300, and 300–400 °C. A comprehensive comparison between the two methods was conducted for the yields and components of the crude bio-oils and their distillates. The upgrading behaviors of the distillates were also thoroughly compared, using UEO as a solvent. The objective of the study is to explore the impacts of HTL and pyrolysis on the yields and properties of crude bio-oils. Because no equivalent study for duckweed has been reported thus far, the current study can expand the understanding of the effectiveness and applicability of the two routes on duckweed conversion.

2. Experimental section

2.1. Materials

Duckweed *Lemma minor* (*L. minor*) was collected from a paddy field in the Hebei Province, North China and was received in sun-dried form. The proximate and ultimate analyses of the duckweed are listed in Table 1. Before use, the duckweed sample was further washed, dried