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Research article

The impact of downstream processing methods on the yield and physiochemical properties of hydrothermal liquefaction bio-oil

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ABSTRACT

Hydrothermal liquefaction (HTL) is considered as a promising thermochemical conversion technology for crude bio-oil (biocrude) production from biomass. However, the influence of downstream processing methods (such as biocrude recovery methods and solvents used) has not been investigated fully to date. In this investigation we examined the effect of solvents and extraction methods on the yield and physiochemical properties of biocrude from *Chlorella* sp. (*C.* sp.), spent coffee grounds (SCG), and a mixture of the two. It was found that the extraction method did not have a significant effect on the yield and physiochemical properties of biocrude derived from the feedstock of interest in this study. However, the solvents used for biocrude recovery had crucial effects, in which dichloromethane (DCM) was determined to the most favorable one from biocrude yield and chemical yield perspective. It was also noticed that the synergetic effects claimed for co-liquefaction of *C.* sp. and SCG were highly dependent on the solvent used to recover bio-crude. Overall, it is expected that this study could attract more attention on the impact of various recovery procedures on the yield/physiochemical properties of bio-oil resulting from hydrothermal liquefaction processes.

1. Introduction

Hydrothermal liquefaction (HTL) is an emerging thermochemical conversion technology, which is able to directly process a broad spectrum of wet biomass feedstocks. In an HTL process, biomass can be converted into crude bio-oil in water or organic solvent media at moderate to high temperature (250–350 °C) and high pressure (5–25 MPa) [1,2]. Extensive efforts have been centering around investigating the effects of operation parameters on the yield/quality of biocrude [3–7], modelling for biocrude yield prediction [8–10] and catalytic upgrading of biocrude [11–13]. In these studies, different downstream processing procedures were applied to recover biocrude including separation methods, solvents used, and extraction conditions etc. as illustrated in Table 1. Different recovery procedures can cause significant variations on the yield and physiochemical properties of the resulting biocrude, making the literature results less comparable even for the same feedstock and similar liquefaction conditions, and thus hinder facilitating process optimization and better understanding of reaction mechanisms under HTL conditions.

Filtration, followed by solvent dissolving was commonly used to collect biocrude [6,7,13]; Soxhlet extraction was also applied to recover the biocrude from product mixtures after HTL conversion [3,4]; and ultrasound-assisted extraction was used in some studies [14]. Unfortunately, there is no literature available that investigates the influence of extraction methods on the yield/physicochemical properties of HTL biocrude. Apart from the extraction method, organic solvents for extraction vary widely from one study to another [5,8,15–17]. Very limited research has studied the effects of using different recovery solvents on the yield and properties of biocrude. Valdze et al. [18] conducted the first research, examining the solvents' influence on the yields of bioproduct fractions in a liquefaction of microalgae, *Nannochloropsis* sp. They found that the amount of fatty acids in the crude bio-oil was highly dependent on the solvents used, and the polar solvents garnered more fatty acids than non-polar solvents. Organic solvents used in their study included hexane, cyclohexane, hexadecane, decane, methoxycyclopentane, chloroform and dichloromethane, of which had similar dielectric constants (low to moderate). The solvent's dielectric constant is closely related to its polarity, and has proven to be an influential factor for the extraction efficiency in many fields such as food science [19,20] and the pharmaceutical industry [21]. It is therefore necessary to use solvents with a broader dielectric constant range (low to high) to thoroughly study the impact extraction solvents on the yield and physiochemical properties of HTL biocrude.

The yield/properties of HTL biocrude are also highly associated

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Table 1
Various downstream processing procedures used to recover crude bio-oil after hydrothermal liquefaction (HTL) conversion.

Feedstock	Downstream extraction method	Extraction solvent	Solvent evaporation	References
Microalgae and swine manure	Soxhlet extraction	Toluene	Room temperature for 24 h within fume hood	[3,4]
Microalgae	Ultrasound-assisted, 30 min	Acetone	Under atmosphere at 75 °C for 12 h	[14]
Microalgae	Vigorously shake, 30 min	Acetone	Unavailable details	[5]
Barley straw	Centrifuge	Acetone	Rotary vacuum under 60 °C and 556 mbar	[6,22]
Microalgae	Filtration	DCM	Rotary vacuum at 40 °C, unknown pressure	[11,12,23]
Microalgae	Filtration	Chloroform	Rotary vacuum at 40 °C, unknown pressure	[24–26]
Microalgae and model compounds	Filtration	DCM	Unavailable details	[15,27]
Microalgae and model compounds	Centrifuge then filtration	DCM	Nitrogen gas purging for 8 h	[16,28]
Microalgae and model compounds	Centrifuge	DCM	Nitrogen gas purging for 1.5 h	[8,29]
Woody biomass	Filtration	Acetone	Rotary vacuum at 50 °C, unknown pressure	[13,30]

Note: DCM = dichloromethane.

with the chemical composition of the subject feedstock. Biomass feedstocks typically consist of protein, lipid and carbohydrates. Co-liquefying feedstocks with different biochemical compositions might enhance biocrude yield via chemical reactions between biochemical components at hydrothermal condition. For instance, Maillard reactions between protein and carbohydrates [31], and amide formation between protein and lipid were observed previously [32,33]. There is an increasing research interest in blending various feedstock for co-liquefaction such as paper-mill sludge with waste newspaper [34], sewage sludge with teacake [35], swine manure with algal biomass [3] and others [17,36–39]. One motivation is to explore possible existing synergetic effects in co-liquefaction, which might enhance the yield and tailor the properties of the resulting bio-crude oil. Positive synergetic effects were observed in some of these studies even though the underlying synergistic effects from blending this biomass were not well understood [36,40,41]. For example, Xiu et al. [40] co-liquefied swine manure with crude glycerol and used acetone to recovery biocrude, they reported that a significantly higher biocrude yield (68%) was obtained from HTL with a blend of feedstock, compared to those of individual crude glycerol (28%) and swine manure (24%). Jin et al. [42] carried out co-liquefaction of microalgae (*Spirulina platensis*, SP) and macroalgae (*Entermorpha prolifera*, EP) and used dichloromethane to recover biocrude; a positive synergy effect (3.2 wt% increase on biocrude yield) was observed. However, each study used different biocrude recovery solvents, and this kind of inconsistency makes it difficult to gain insight into the benefits of co-liquefaction. The synergetic effect (SE) is generally defined as a comparison of the actual yield of mixed feedstock to the mass-averaged yield of individual feedstock, being considered as a positive SE if the actual yield of a mixture is higher than the mass-averaged one. If the yield of biocrude is strongly affected by the solvent used, the reported results in the literature might be biased due to extraction solvents used, and thus make it difficult to truly reflect SE that takes place in the process of co-liquefaction. Some mixed feedstock that did not show synergetic effect using certain solvents, might exhibit significant synergetic effect using other extraction solvents. There are currently no appropriate ways to address this fundamental research limitation with HTL as researchers can only rely on the extracted bio-oil to evaluate the performance of liquefaction. However, it is essential to examine the influence of extraction solvents on the research outcomes of synergetic effects in co-liquefaction, which could provide more information, and potential discovery of some hidden synergetic effects and prevent underestimation of the advantages of certain feedstock combinations.

This study aims to explore the effects of downstream extraction methods/solvents on biocrude yield and its physiochemical properties. Three commonly used extraction methods were examined including filtration (solvent dissolving at room temperature), Soxhlet extraction and microwave-assisted extraction. Hexane, acetone, dichloromethane (DCM), and tetrahydrofuran (THF) were selected as extraction solvents, representing varied degrees of polarity. *Chlorella* sp. microalgae (*C.* sp.), spent coffee ground (SCG) and *C.* sp./SCG (50/50 by mass) were liquefied under identical reaction conditions, to assess whether co-liquefaction (*C.* sp./SCG) can produce more desirable biocrude or not as compared to that of individual *C.* sp. and SCG. Biocrude yield, chemical yields and dynamic viscosity were used to evaluate the influence of extraction procedures and feedstock used. The impact of extraction solvents on the research results of co-liquefaction synergetic effects was investigated as well. It is expected that this study will raise awareness of the impact of inconsistent recovery procedures on the study of HTL and encourage researchers to critically reference research results/conclusions reported in the literature.

2. Materials and methods

2.1. Materials

Wet spent coffee grounds were collected from Tim Hortons, Truro, Canada, and oven dried at 105 °C for 24 h. Dried microalgae (*Chlorella.* sp.) was purchased from Buy Algae, Meridian, American. ACS reagent grade hexane and acetone were purchased from Fisher Scientific Ltd. Dichloromethane (ACS reagent grade), inhibitor-free tetrahydrofuran ($>$ 99.9%) and naphthalene D8 standard were purchased from Sigma Aldrich Ltd. All chemicals were used as received.

2.2. Biomass feedstock characterization

The proximate analysis and feedstock chemical composition analysis of *C.* sp. and SCG were conducted by SGS lab (Guelph) at Ontario, Canada. The moisture, ash, lipid, protein, lignin, acid detergent fiber (ADF) and neutral detergent fiber (NDF) content were measured by following methods, AOAC 930.15, AOAC 942.05, AOAC 945.16, AOAC 990.03, AOAC 973.18, NFTA 4.1 and NFTA 5.1 respectively. The cellulose and hemicellulose content were calculated based on the ADF and NDF percentage. The lignin, cellulose and hemicellulose for SCG was 24.01%, 26.77% and 22.50% respectively. Unfortunately, the lignin, ADF and NDF percentage for *C.* sp. (very fine powder) were not obtained due to the crucible clogging problems during testing. The element analysis of *C.* sp. and SCG was conducted in a Perkin Elmer 2400 CHNS elemental analyzer on Agricultural Campus, Dalhousie University. The obtained results from feedstock characterization are presented in Table 2.

2.3. Hydrothermal liquefaction processes

Hydrothermal liquefaction experiments were carried out in a 100 mL stainless-steel autoclave (Parr Instrument, 4590 micro-reactor) equipped with an A2140HC magnetic stirrer and a 4848 reactor controller. In a typical conversion process, 5 g of dried feedstock were weighed and loaded into the reaction vessel, followed by the addition of 40 g distilled water, giving a water/feedstock mass ratio of 9:1. The reaction vessel was then sealed and transferred to the autoclave support stand, and the magnetic stirrer was started. The reaction vessel was