Improvement in bio-crude yield and quality through co-liquefaction of algal biomass and sawdust in ethanol-water mixed solvent and recycling of the aqueous by-product as a reaction medium

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ABSTRACT

Co-liquefaction of algal biomass (AB) and sawdust (SD) was investigated in ethanol-water mixed solvent for the production of bio-crude. Effects of temperature (200–300 °C), residence time (30–120 min), ethanol-water mixed solvent composition (0/100–100/0 wt/wt), and AB/SD mass ratio (0/100–100/0) on the products distribution were explored. The results indicated that both AB/SD and ethanol/water exhibited positive synergistic effects on the co-liquefaction process. The highest bio-crude yield of 58 wt% was obtained from co-liquefaction of AB and SD (50/50, wt/wt) in ethanol-water (75/25, wt/wt) mixed solvent at 250 °C for 60 min. In addition, the bio-crude produced from the mixed feedstocks contained a higher fraction of light oil components than that produced from only AB or SD. In addition, this work demonstrated the promise of recycling the aqueous by-product form the co-liquefaction process as a reaction medium for the process, aiming to reduce overall waste generation and increase the bio-crude quality.

1. Introduction

Due to the shortage of fossil fuels and severe environmental issues, bio-fuels from renewable resources have gained increasing attention. Generally, bio-fuels can be classified into first, second, and third generation categories. First and second-generation bio-fuels can be produced from food crops (e.g., corn, soybean, and sugarcane) and non-food crops (e.g., rice husk and wood chip), respectively. While, the development of first and second-generation bio-fuels are limited owing to the land availability and the competition with crop production [1]. Recently, algae as third-generation biomass have been widely applied for the production of liquid fuels. Algae have several advantages, such as high growth rate, high lipid content, be able to sequester atmospheric CO_2, and can be cultivated in non-arable land [2]. Until now, numerous technologies have been developed for converting algal biomass into renewable fuels, including transesterification [3], pyrolysis [4], and hydrothermal liquefaction [5]. Compared to conventional technologies, hydrothermal liquefaction (HTL) has been identified as a more suitable conversion route for high water-containing feedstocks, due to the elimination of drying/dewatering the feedstock.

HTL as a thermochemical conversion technology is commonly performed in sub- or near-critical water at 250–350 °C and 5–15 MPa for 5–120 min with or without catalyst [6]. Recently, some researchers have co-liquefied algae and lignocellulosic biomass in subcritical water [7,8]. For instance, Gai et al. [9] investigated co-liquefaction of *C. pyrenoidosa* and rice husk in hot-compressed water at 200–350 °C for 10–90 min and found positive synergistic effects existed in the co-liquefaction of two feedstocks in terms of better quantity and quality of bio-crude produced. However, as suggested by previous studies, there remain several limitations regarding the use of water. On one hand, more than half of carbon and hydrogen in the feedstock migrated into aqueous phase rather than in the oily phase when liquefaction was carried out in water [10]. To solve this problem, various organic solvents (e.g., ethanol, methanol, acetone, and 1,4-dioxane, etc.) have been applied for algal liquefaction [1,11,12]. Among them, ethanol is reported to be the most desirable reaction medium, which can be explained as follows, (i) enhanced degradation of macromolecules due to a lower dielectric constant than water [13]; (ii) can act as a hydrogen donor solvent [14]; (iii) can achieve a high bio-crude yield at mild operating conditions [1]; and (iv) can be derived from renewable sources [13]. In literature, the ethanol-water mixed solvent has demonstrated positive effects on the liquefaction of microalgae with respect to bio-crude yield [6,13,15]. Ji et al. [15] studied the effect of ethanol-water mixed solvent composition on the products distribution from liquefaction of *Spirulina* at 300 °C for 45 min. It was reported that the bio-crude yield reached its maximum level when the liquefaction

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was conducted in ethanol-water (75/25, v/v) mixed solvent. Hence, in this study, the ethanol-water mixed solvent rather than pure ethanol was introduced into liquefaction system.

On the other hand, the aqueous phase derived from HTL process needs to be treated as it contains high total organic carbon (TOC) and some environmentally toxic compounds (e.g., 2-piperidinone, 2-pyrrolidinone, and pyridine, etc.) [9]. Although the aqueous phase could be used as feedstock for production of methane via anaerobic digestion or supercritical water gasification [16], a more environmentally benign and cost-effectively approach was demo0nstrated by Ramos-Tercero et al. [17] and Hu et al. [18] where the aqueous phase from HTL of algae was recycled and reused as the liquefaction medium for the HTL process. The results indicated that the recycled aqueous phase demonstrated positive effects on the oil formation, achieving even higher yield of bio-crude. To the best of our knowledge, however, no study has investigated on co-liquefaction of an algal biomass and woody biomass in ethanol-water mixed solvents while recycling the aqueous phase from the process.

Therefore, in this study, algal biomass and sawdust (a typical forestry residue available in great amount in Canada [28]) were co-liquefied in ethanol-water mixed solvents under various reaction conditions. Furthermore, for the first time in the literature, the aqueous phase from the algae-wood co-liquefaction process was recycled as the reaction medium for the process, aqueous phase from co-liquefaction process.

2. Materials and methods

2.1. Materials

Algal biomass (AB), *Chlorella*, was purchased from PureBulk, Inc (Roseburg, USA) as food-grade material in powder form (0.2 mm particle size). Aspen wood sawdust (SD) was supplied from a lumber mill (Thunder Bay, Canada), with the pre-treatment of crushing and sieving to 0.5 mm particle size. Dichloromethane (DCM) and ethanol were purchased from Caledon Laboratory Ltd (Georgetown, Canada). The characteristics of AB and SD were summarized in Table 1.

2.2. Experimental procedure

The co-liquefaction experiments were performed in a 100 mL benchtop autoclave reactor coupled with a magnetic stirrer (Parr 4590, Moline, USA). In a typical run, 3.0 g of the mixed feedstock (AB + SD) and 30.0 g of ethanol–water mixed solvent were loaded into the reactor.

Table 1
Proximate and elemental analysis of algal biomass and sawdust.

	Algal biomass	Sawdust
Proximate analysis (wt.%)		
Moisture	3.48 ± 0.62	0.38 ± 0.05
Ash	7.15 ± 0.10	0.58 ± 0.10
Organics[a]	89.37	99.04
Elemental analysis (%)[b]		
C	46.54	48.12
H	7.37	6.91
O[c]	29.87	44.32
N	8.59	0.07
S	0.48	0.00
H/C (mol/mol)	1.90	1.72
O/C (mol/mol)	0.48	0.69
N/C (mol/mol)	0.16	0
HHV (MJ/kg)[d]	20.97	18.22

[a] Determined by difference.
[b] On dry basis.
[c] Estimated by 100% -%Ash-%C-%H-%N-%S.
[d] Calculated by Eqn. (2).

The reactor was tightly closed and flushed with pure nitrogen to remove residual air inside the reactor. After that, pure nitrogen at 0.69 MPa was purged into the reactor to prevent the mixed reaction medium from boiling during the heating process. The reactor was then heated up to the pre-set temperature at a heating rate of ~5 °C/min. This temperature was then kept for a designated residence time. The agitation speed was set at ~250 rpm throughout the whole co-liquefaction process. The reaction conditions investigated in this study were as follows: temperatures (200 °C, 225 °C, 250 °C, 275 °C, and 300 °C), residence times (30 min, 60 min, 90 min, and 120 min), ethanol–water mixed solvent compositions (0/100, 25/75, 50/50, 75/25, and 100/0 w/w,), and AB/SD mass ratios (0/100, 25/75, 50/50, 75/25, and 100/0).

At end of the reaction, the reactor was quenched in a water bath. After the reactor was cooled to room temperature, the gaseous products inside the reactor were vented through a control valve into fume hood. In a typical co-liquefaction experiment: AB/SD (50/50, wt/wt) in ethanol-water (50/50, wt/wt) mixed solvent at 250 °C for 60 min, the gaseous products were collected in a gas bag and were analyzed with a gas chromatograph equipped with a thermal conductivity detector (GC-TCD, Agilent Micro-GC 3000). In order to quantify the volume of the gaseous products, 200 mL air was injected into the gas bag as an internal standard. The resultant gas yield (mainly consists of CO_2) was found to be negligible (< 1%) likely due to the very mild reaction temperatures (200–300 °C), so the gaseous products were not analyzed in this work.

The reaction mixture was collected from the reactor by washing with a proper amount of ethanol, followed by filtration to separate the solid residue. The solid residue was then dried in an oven at 105 °C for 24 h. The filtrate was transferred to a 500 mL round bottom flask to remove ethanol via rotary evaporation at 45 °C under reduced pressure. Afterwards, the remaining mixture was transferred into a separatory funnel, and 100 mL of dichloromethane (DCM) was added to extract bio-crude. Leaving the upper layer containing water and aqueous by-product, the bottom layer was transferred into a 500 mL pre-weighed round-bottom flask to remove DCM using a rotary evaporator at 40 °C under reduced pressure, and the remaining dark material was denoted as bio-crude.

Furthermore, multiple co-liquefaction experiments were conducted at the optimal reaction conditions where the water phase products from these multiple runs were collected and mixed. The obtained water phase mixture in a sufficient amount was then filtered under vacuum to remove some undissolved materials, and used as the reaction medium in the water phase recycling studies for co-liquefaction of the feedstocks with the same solid/solvent mass ratio of 1/10.

The bio-crude and solid residue yield were expressed in wt.% and calculated on a dry basis. The combined yield of gas and aqueous phase was defined as "others yield", and simply determined by the weight difference. The energy recovery (%) of co-liquefaction process was calculated by Eq. (1).

$$Energy recovery\,(\%) = \frac{HHV_{bio-crude} \times Weight_{bio-crude}}{HHV_{AB} \times Weight_{AB} + HHV_{SD} \times Weight_{SD}} \quad (1)$$

2.3. Analytical approaches

The moisture content was measured by drying the feedstocks in an oven at 105 °C overnight. The ash content was determined by combusting the dried feedstocks in a muffle furnace at 575 °C for at least 3 h until the weight reached a constant level. The particle size was analyzed using a particle size analyzer (HELOS/BF, Sympatec GmbH). The elemental analysis (CHNS) of raw material, bio-crude, solid residue, and water-soluble products was performed via an elemental analyzer (Vario EL Cube, Elementar, Germany). The water-solubles were obtained by removing water from aqueous phase using a rotary evaporator under reduced pressure. The higher heating values (HHVs) of original