Co-liquefaction of microalgae and lignocellulosic biomass in subcritical water

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HIGHLIGHTS

- Co-liquefaction of *C. pyrenoidosa* and rice husk in subcritical water.
- Effects of operation conditions and combined mass ratio on product distribution.
- Major chemical compositions of the bio-crude oils were identified.
- A positive synergistic interaction was observed during the co-liquefaction process.

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ABSTRACT

This study investigated co-liquefaction of microalgae (*Chlorella pyrenoidosa*, CP) and lignocellulosic biomass (Rice husk, RH) in subcritical water for bio-oil production. The effects of liquefaction temperature (200–350 °C), residence time (10–90 min), solid concentration (10–30 wt.%) and mass ratio of CP/RH on product distribution were investigated. The results showed that the highest yield of bio-crude oils at the combination of 50% CP with 50% RH was obtained at 300 °C temperature, 60 min residence time and 20 wt.% solid concentration. The oil yields increased gradually with the increased mass ratio of CP/RH. The major compounds identified in bio-crude oils from hydrothermal liquefaction (HTL) of RH were cyclic oxygenates (20.62%), followed by esters, ketones and alcohols (17.19%). As for CP, the main components were straight & branched amides (28.38%). A synergistic interaction was observed between CP and RH during co-liquefaction, resulting in decreased acidity and nitrogen content of bio-crude oils.

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1. Introduction

Energy crisis has intensified over recent years due to the unrestrained exploitation of fossil fuels. To ensure energy security and reduce our appetite for fossil fuels, renewable energy in terms of solar, wind and biomass have gained increasing attention. Biomass is a cheap and abundant renewable source, which can be converted into biofuels through two main technologies: thermo-chemical conversion such as pyrolysis, gasification and liquefaction, and bio-chemical conversion like anaerobic digestion and alcoholic fermentation (Scholz et al., 2013). Liquefaction of biomass in sub- or supercritical water, which is also called hydrothermal liquefaction (HTL), offers several potential advantages, including high conversion efficiency, high throughputs, and

the ability to use mixed feedstock without drying (Kanauija et al., 2014; Peterson et al., 2008).

In recent years, algal biomass has been recognized as one of the most promising feedstocks for biofuel production, especially for microalgae. Many studies have been carried out concerning hydrothermal processing of microalgae for bio-oil production (Anastasakis and Ross, 2015; Jazrawi et al., 2015; Tommaso et al., 2015; Gai et al., 2014; Toor et al., 2013). Recently, several papers have been published concerning the co-liquefaction of microalgae with other uneasily degradable materials like coal or synthetic polymer (Pei et al., 2012; Yuan et al., 2009). The results indicate that the presence of microalgae enhanced the conversion efficiency, alleviated the reaction conditions and improved the quality of products. Lignocellulosic biomass is the most widely used feedstock for bio-oil production via HTL such as berley straw (Zhu et al., 2015) and miscanthus (Hafez and Hassan, 2015). Previous studies indicate that the bio-oil yield of hydrothermal processing of algal biomass is usually higher than that of lignocellulosic biomass. According to Huang et al. (2013), microalgae of *Spirulina* and

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lignocellulosic biomass of rice straw were liquefied in subcritical ethanol under identical operating conditions, and it was observed that the biocrude oil yield for *Spirulina* (34.5%) was higher than that of rice husk (21.1%). The different oil yields were ascribed to the different major components of these two kinds of biomass. Proteins, lipids and carbohydrates are the major composition of microalgae, which are less thermal resistant compared to those of main components of lignocellulosic biomass including cellulose, hemicellulose and lignin (Karagöz et al., 2005). Besides, the conversion rates of lipid and protein are higher than those of cellulose and lignin in hydrothermal environment (Biller and Ross, 2011; Gai et al., 2014; López-González et al., 2014). Therefore, it is expected that the co-liquefaction of microalgae and lignocellulosic biomass may also promote the efficiency in converting two renewable resources into sustainable biofuels.

Extensive studies have been carried out about HTL of microalgae or lignocellulosic biomass in literature. However, to the best of our knowledge, few information is available about the co-liquefaction of these two biomass feedstock. Therefore, this study aims to explore the co-liquefaction of microalgae (*Chlorella pyrenoidosa*, CP) and lignocellulosic biomass (rice husk, RH) for bio-crude oil production. The effects of operating conditions and combined mass ratio on the co-liquefaction characteristics of CP and RH were investigated. The operating conditions for bio-crude oil production were optimized, and the main composition of oil compounds was analyzed. In addition, the interactions between CP and RH were determined during co-liquefaction process.

2. Experimental

2.1. Materials

C. pyrenoidosa (CP) and rice husk (RH) were selected as representative microalgae and lignocellulosic biomass in the present study. Powder CP was purchased from a health-food store as food-grade material (NOW FOODS, Bloomingdale, IL) and RH was locally obtained with the pretreatment of crushing and sieving. The moisture, volatile content, ash and calorific value of the materials were determined following standards ISO 589:2003, ISO 562:2010, ISO 1171:2010 and ISO 1928:2009, respectively. Elemental analysis of CP and RH was conducted on an elemental analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA). The chemical compositions were determined according to the methods of the Association of Official Analytical Chemists (AOAC). Table 1 presented the properties of two feedstock.

2.2. Experimental procedure and characterization

In the present study, three stainless autoclave with 100 ml capacity were applied to the HTL experiments. During each test, 30 g feedstock slurries with biomass and deionized water were added to the reactor. The reactor was sealed and then was heated by an electric heater up to a preset temperature and maintained for a certain residence time based on the experimental design. Finally, the reactor was cooled down to room temperature. The gas in the reactor was first sampled into a Tedlar® gas sampling bag (CEL Scientific CORP., Cerritos, USA) through a control valve. Afterwards, the reactor was opened and the remaining mixture was separated by physical filtration using a Whatman® 55 mm glass-fiber filter (Whatman®, Cat, No. 1822-055). The water-soluble portion was defined as the aqueous fraction while the left product was defined as the raw oil. Soxhlet extraction using the solvent of toluene was used to extract the toluene soluble fraction from the raw oil, which was defined as the bio-crude oil in the present study. The toluene insoluble fraction was then oven dried

Table 1

Proximate, ultimate and chemical analysis of the CP and RH.

	CP	References	RH	References
<i>Proximate analysis (d.wt.%)</i>				
Volatile matter	94.3	94.4 (Yu et al., 2011)	81.1	81.2 (Mansaray and Ghaly, 1998)
Ash	5.7	5.6 (Yu et al., 2011)	18.9	18.8 (Mansaray and Ghaly, 1998)
<i>Elemental composition (d.wt.%)</i>				
Carbon	51.2	51.4 (Yu et al., 2011)	41.6	43.1 (Liu et al., 2013)
Hydrogen	6.8	6.6 (Yu et al., 2011)	5.2	6.1 (Liu et al., 2013)
Nitrogen	11.3	11.1 (Yu et al., 2011)	4.7	4.3 (Liu et al., 2013)
Oxygen ^a	30.7	30.9 (Yu et al., 2011)	48.5	46.6 (Liu et al., 2013)
<i>Chemical composition (d.wt.%)</i>				
Protein	71.5	71.3 (Yu et al., 2011)	–	–
Lipid	0.2	0.1 (Yu et al., 2011)	–	–
Non-fibrous carbohydrates	22.5	22.0 (Yu et al., 2011)	–	–
Cellulose	–	–	29.2	25.9 (Mansaray and Ghaly, 1998)
Hemicellulose	–	–	20.1	18.1 (Mansaray and Ghaly, 1998)
Lignin	–	–	28.2	31.4 (Mansaray and Ghaly, 1998)

^a By difference.

and viewed as the solid residue. The chemical compositions of bio-crude oil were analyzed using GC/MS (Agilent 7890A GC-5975C MS, Agilent Technologies, USA) equipped with flame ionization detector (FID) and HP-5 column. Pentadecanoic acid, methyl ester was selected as the internal standard for bio-crude oil. The main peaks in the total ion chromatograms of the bio-crude oil were identified using an NIST mass spectral database (NIST08).

3. Results and discussion

3.1. Effect of temperature on product distribution

During hydrothermal processing, temperature is the most important factor affecting product distribution (Peterson et al., 2008; Gai et al., 2015). Consequently, the effect of temperature was firstly valued on the product distribution from co-liquefaction

Fig. 1. Effect of temperature on product distribution (at 20 wt.% solid concentration, 60 min residence time and the combination of 50% CP with 50% RH).

of CP and RH. The aqueous fractions were calculated by difference in the present study. Fig. 1 illustrated the effect of temperature on the distribution of products at 20 wt.% solid concentration, 60 min residence time and the combination of 50% CP with 50% RH. With the increment of temperature from 200 to 350 °C, the yields of different products had various trends. Specifically, the yield of bio-crude oil increased from 15.5% at 200 °C to 37.6% at 300 °C, and then decreased slightly to 33.1% at 350 °C. The yield of solid residue was decreased with the increasing temperature from 34.9% at 200 °C to 10.8% at 350 °C, while in the case of the gaseous product, its yield gradually increased from 7.1% at 200 °C to 21.1% at 350 °C.

It can be seen in Fig. 1 that when the temperature exceeded the specific point (300 °C), more gas products were generated while the bio-crude oil yields decreased slightly. This is because at temperatures lower than 300 °C, organic matters in the samples are more thermally degraded into oil phase while with further increased temperature, polymerization reactions of intermediates to form the char are dominated, resulting in decreased bio-crude oil yields. In addition, secondary decompositions may be triggered to transform some bio-crude oils into gaseous compounds at high temperatures (Valdez et al., 2012). It was also verified by the constant increase of gas yield from 300 to 350 °C in the present study. Chen et al. (2014) investigated the hydrothermal liquefaction of mixed-culture algal biomass from wastewater treatment and it was observed that the gas products greatly increased when the temperature exceeding 300 °C. These trends of product distribution are also consistent with the HTL results of microalgae of *Spirulina platensis* (Jena et al., 2011) and lignocellulosic biomass of cornelian cherry stone (Akalın et al., 2012). The optimum condition for the yield of bio-crude oil was observed to be 300 °C for the given reactor. Therefore, this optimum temperature was chosen for studying the effect of residence time.

3.2. Effect of residence time on product distribution

Fig. 2 demonstrated the effect of residence time on the distribution of products at 300 °C temperature, 20 wt.% solid concentration and the combination of 50% CP with 50% RH. It is clear that with an increase in residence time, bio-crude oil yield increased until 60 min, then decreased slightly with a further increase in residence time. This observation indicates that a 60 min residence time is sufficient for the formation of oil compounds, while a time longer than 60 min will bring about the further recondensation or repolymerization of bio-crude oils. The yield of solid residue

underwent a fall after an increment of residence time from 10 to 90 min while in the case of gaseous product, its yield decreased from 10 to 30 min and then increased again from 30 to 90 min. Compared to reaction temperature, the residence time showed less effect on the yield variations of solid residue and gaseous product.

The optimum residence time for the oil yield during the HTL process is mainly affected by the chemical composition of the feedstock. For example, HTL of microalgae *Dunaliella tertiolecta* cake was investigated by Zou et al. (2010), and it was reported that the oil yield increased up to 1 h. However, liquefaction of lignocellulosic biomass of *Cunninghamia lanceolata* in subcritical water (Qu et al., 2003) showed that a residence time of 10 min was enough to produce the highest oil yield. In addition, residence time is also closely linked to reaction temperature and higher temperature requires shorter residence time, and vice versa. For example, during the HTL of microalgae *Desmodesmus* (García Alba et al., 2012), a residence time of only 5 min at 375 °C produced the highest oil yield while a residence time of 120 min at 280 °C was optimum for the oil yield during liquefaction of microalgae *Chlorella* (Yu et al., 2011).

3.3. Effect of solid concentration on product distribution

Fig. 3 showed the effect of solid concentration on product distribution at 300 °C, 60 min residence time and the combination of 50% CP with 50% RH. It can be observed that with the increased solid concentration from 10 to 30 wt.%, the yields of bio-crude oil increased slightly then decreased, and the highest yield was achieved at 20 wt.%. In hydrothermal environment the water acts both as a medium of heat-transfer and as a reactant of hydrogen donor. According to Akhtar and Saidina Amin (2011), the increased solid concentration may inhibit the interactions between molecules of biomass and water, suppressing the dissolution of the biomass components. Thus the yield of bio-crude oil was decreased at higher solid concentration. This observation agrees with the reported liquefaction of lignocellulosic biomass of *C. lanceolata* in subcritical water (Qu et al., 2003) and rice husk in subcritical ethanol (Huang et al., 2013). However, as for the liquefaction of brown macro-alga *Laminaria saccharina* (Anastasakis and Ross, 2011), it was reported that the maximum oil yield was obtained at a solid concentration of 10 wt.% (i.e. 3 g of seaweed with 30 ml of water) and further increase of solid loading did not influence the yields. It suggests that the effect of solid concentration is also affected by the feedstock chemical composition.

Fig. 2. Effect of residence time on product distribution (at 300 °C temperature, 20 wt.% solid concentration and the combination of 50% CP with 50% RH).

Fig. 3. Effect of solids concentration on product distribution (at 60 min residence time, 300 °C temperature and the combination of 50% CP with 50% RH).

The variations of yields for solid residue and gas were similar, which were both increased with the increment of solid concentration. According to Sato et al. (2003), lower solid concentration enhanced the extraction by the denser solvent medium during the HTL process, thus reducing the amount of solid residues and gas.

3.4. Effect of CP/RH mass ratio on product distribution

Fig. 4 presented the effect of mass ratio of CP/RH on the distribution of products at 20 wt.% solid concentration, 300 °C temperature and 60 min residence time. With the increment of mass ratio of CP/RH, the bio-crude oil yield increased constantly from 13.9% at the combination of 0 CP with 100% RH to 43.6% at the combination of 100% CP with 0 RH. Karagöz et al. (2005) investigated the liquefaction of woody biomass of sawdust and non-woody biomass of rice husk in the subcritical water at 280 °C for 15 min and 16 wt.% solid concentration. It was reported that the oil yield of rice husk and sawdust was 8.3% and 8.6%, respectively. Jena et al. (2011) investigated the hydrothermal liquefaction of microalgae of *S. platensis*. It was concluded that the highest bio-crude yield of 39.9% could be obtained at 350 °C for 60 min and 20 wt.% solid concentration. Taking into account the differences in the chemical compositions of biomass material and operating conditions, the result in the present study is consistent with the results obtained in literature.

In the present study, the yields for solid residue gradually decreased from 19.8% to 1.2% with increased mass ratio of CP/RH from the combination of 0 CP with 100% RH to the combination of 100% CP with 0 RH. The solid residue is mainly composed of ash and bio-char, and Table 1 demonstrated that the ash content for CP and RH was 5.7% and 18.91%, respectively. The yield of solid residue decreased gradually due to the increased proportion of microalgae with low ash content in the samples. Another reason is that in hydrothermal environment, the composition of lignin contributes more to the formation of solid residue compared to other substituents. According to Karagöz et al. (2005), 60 wt.% of the lignin were converted into the solid residue in hydrothermal environment, which is far higher than that of cellulose (29.9 wt.%). It should be noted in Fig. 4 that the variations of yields for gas and aqueous fractions were both not monotonic with the increased mass ratio of CP/RH. A possible reason may be that during hydrothermal processing, the interactions between CP and RH may alter the product distribution, and it indicates that a

synergistic interaction may exist during the co-liquefaction process, which is further investigated by GC/MS.

3.5. Characterization of bio-crude oil

The seven samples of bio-crude oils obtained at different mass ratios of CP/RH were analyzed using GC/MS to identify the major components. As shown in Fig. 5, the major compounds identified were categorized into six classes based on the functional groups: (1) hydrocarbons such as alkanes, alkenes and derivatives, (2) organic acids like short-chained acids, aromatic acids or long-chained fatty acids, (3) straight & branched amides, (4) cyclic oxygenates in terms of phenol, phenol derivatives and fused ring compounds, (5) N&O-heterocyclic compounds, (6) esters, ketones and alcohols. It should be noted that each component was categorized into only one group, although many compounds contained more than one function group. The major components with a relative percentage of peak areas higher than 1% for the bio-crude oils were available in supplementary information (Table S1).

The mass ratio of CP/RH showed different effects on chemical composition of the bio-crude oils. With the increasing percentage of CP in mixed feedstock from 0% to 100% (Sample 1–7), the content of straight & branched amides and N&O-heterocyclic gradually increased while the concentration of cyclic oxygenates and esters, ketones and alcohols constantly decreased. The major compounds identified in bio-crude oils from HTL of RH (Sample 1) were cyclic oxygenates (20.62%). It mainly contained phenolic compounds and its derivatives (i.e. 2-methoxy-phenol and 4-ethyl-phenol), which are likely derived from the lignin of RH. Lignin is one of the major components of the carbohydrates in the lignocellulosic biomass. It is an aromatic heteropolymer consisting of phenylpropanoid compounds in terms of *p*-coumaryl alcohol, coniferyl alcohol and sinapylalcohol. Phenols and methoxy phenols can be formed by hydrolysis of ether-bonds or methoxy groups in the hydrothermal environment. For example, Wahyudiono Kanetake et al. (2007) investigated the lignin model compounds in near-critical water and it was reported that the main products were catechol (40.73%), phenol (14.18%) and *o*-cresol (4.45%). Karagöz et al. (2005) concluded that lignin-derived oil mainly contained phenolic compounds under hydrothermal treatment. Phenol and its derivatives are also observed to be the major components of the bio-crude oils from hydrothermal processing of other lignocellulosic biomass such as bamboo (Yip et al., 2009) and barley straw (Zhu et al., 2015).

Fig. 4. Effect of mass ratio of CP/RH on product distribution (at 300 °C temperature, 60 min residence time and 20 wt.% solid concentration).

Fig. 5. Distribution of major compounds identified in bio-crude oils obtained at different mass ratios of CP/RH.

In addition, the content of esters, ketones and alcohols (17.19%) for RH was observed to be higher than other compounds, which are primarily derived from the retro-aldol condensation (Matsuoka et al., 2012) during the hydrothermal liquefaction of cellulose in lignocellulosic biomass. Besides, a certain amount of phenol and derivatives may also be derived from the condensation of cellulose or hemicellulose (Karagöz et al., 2005).

In the case of bio-crude oils of CP (Sample 7), its content of nitrogenous compounds detected was much higher than that of RH (Sample 1). It is mainly due to the high protein content in CP. Specifically, the straight & branched amides (28.38%) were the major compounds for CP (Sample 7). Similar observations have been reported from HTL of *Spirulina* (Vardon et al., 2011). In hydrothermal environment, protein and lipid are first hydrolyzed to amino acids and long-chained fatty acids, respectively. Afterwards, the hydroxyl groups in fatty acids are replaced by ammonia from deamination of amino acids to produce straight & branched amides (i.e. hexadecanamide or octadecanamide identified in the present study). Additionally, the content of N&O heterocyclic compounds of CP was much higher than that of RH. During hydrothermal processing, N&O-heterocyclic compounds are mainly produced from the Maillard reaction between amino acids from hydrolysis of the proteins in microalgae and reducing sugars from hydrolysis of carbohydrates (Peterson et al., 2008).

It can also be observed in Fig. 5 that the variations of organic acids and hydrocarbons were opposite with respect to the increase of the CP/RH mass ratio. This is because the organic acids are mainly formed from the hydrolysis of cellulose and hemicellulose in lignocellulosic biomass or the hydrolysis of proteins and lipids in microalgae. Hydrocarbons are partially produced from organic acids via decarboxylation. Interestingly, with the increase of the CP/RH mass ratio, the content of organic acids declined gradually while the hydrocarbons increased correspondingly. For example, the Sample 5 obtained at the combination of 60% CP with 40% RH was observed to have 23.44% hydrocarbons and 8.57% organic acids. In addition, the content of cyclic oxygenates (6.36%) for Sample 5 was not as high as that of Sample 1 (20.62%), while the content of straight & branched amides (13.6%) and N&O-heterocyclic compounds (6.08%) were far lower than that of sample 7 (28.38% and 11.87%), respectively. The decrease of content of organic acids can reduce acidity and improve the HHVs of bio-crude oil due to the lower oxygen content, and a higher content of hydrocarbons contributes to higher bio-oil HHVs (Mullen et al., 2009). The lower content of nitrogenous compounds in bio-crude oil is also preferable due to the lower NO_x emissions during combustion. Therefore, it can be concluded that a positive synergistic interaction occurred between CP and RH during co-liquefaction process and as a result, fuel property of the bio-crude oil was significantly improved. Additionally, as shown in Fig. 5 that the six classes of major compounds in bio-crude oils were not linearly proportional to the feedstock combination ratios, implying the complex nature of synergistic interaction. The detailed interaction involved in co-liquefaction between CP and RH requires further investigation based on different model compounds of biomass substrates.

4. Conclusions

Co-liquefaction of CP and RH in subcritical water was investigated, and the maximum yield of bio-crude oils was obtained at 300 °C temperature, 60 min residence time and 20 wt.% solid concentration. Major compounds identified in the bio-crude oil of RH were cyclic oxygenates while straight & branched amides were most abundant for that of CP. The optimum bio-crude oil was obtained at CP/RH mass ratio of 60/40 and composed of 23.44%

hydrocarbons, 8.57% organic acids, 13.6% straight & branched amides, and 6.08% N&O-heterocyclic compounds. The synergistic interaction occurred between CP and RH improved the fuel quality of bio-oil.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2015.03.015>.

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