



## Co-liquefaction of swine manure and mixed-culture algal biomass from a wastewater treatment system to produce bio-crude oil



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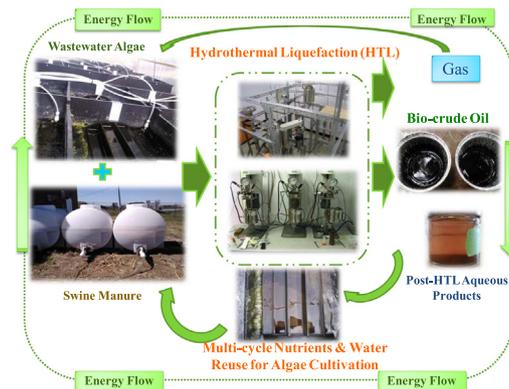
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### HIGHLIGHTS

- The first work co-liquefied swine manure and algae from wastewater into bio-crude oil.
- Demonstrated comparable energy consumption ratios in contrast to HTL of pure algae.
- The highest bio-crude oil yield was 35.7% based on dry matter.
- Thermal gravimetric analysis showed both light oils and heavy crudes were produced.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This study explored the feasibility of combining two types of feedstocks, swine manure (SW) and mixed-culture algae (AW) from wastewater treatment systems, for bio-crude oil production via hydrothermal liquefaction. The effect of feedstock combination ratios on the bio-crude oil yields and qualities were investigated. SW to AW ratios (dry weight basis) were 1:3, 1:1 and 3:1 with a total solids content of 25%. Pure SW and AW were also hydrothermally converted at the same reaction condition for comparison. By combining 75% SW with 25% AW, the highest bio-crude oil yield was achieved (35.7% based on dry matter). By mixing 25% SW with 75% AW, the highest heating value (27.5 MJ/kg) was obtained. GC–MS spectra and thermal gravimetric analysis of bio-crude oils revealed that both light oils and heavy crude were produced, averaging 25% and 20% of the bio-crude oil, respectively. Analysis of energy consumption ratios indicated that co-liquefaction of AW and SW is energetically feasible and could be an economically competitive system for bio-crude oil production.

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## 1. Introduction

Algal feedstock is viewed as a favorable feedstock for next generation bio-energy products. Algae can grow in most water sources (fresh, salty, wastewater, etc.) and on marginal lands, which can reduce competition with food crops for arable lands. To date, algal biofuels research has predominantly focused on culturing algal species with high lipid content for extraction and transesterification to biodiesel. Low lipid content algae, however, typically have higher biomass productivity than high lipid algae and are much more tolerant with stressful conditions such as growing in wastewater [1,2]. This capability also provides an opportunity to combine bio-energy production and waste treatment to mitigate environmental pollution such as eutrophication [1,3]. This new paradigm of integrating bioenergy production with bio-waste treatment using low lipid algae [2,4] is referred to here and elsewhere as Environment-Enhancing Energy (E<sup>2</sup>-Energy). This type of system cannot only uptake nutrients from wastewater sources but can also re-release most of the nutrients to support multiple cycles of algae growth and bioenergy production [2,5].

Hydrothermal liquefaction (HTL) converts biomass feedstock into bio-crude oil with high temperatures and pressures. The macromolecules in the feedstock are first depolymerized into light molecules. Subsequently, the unstable fractions are repolymerized into oil compounds [6]. HTL can directly convert feedstock into energy-dense products without drying and thus is more suitable for treating wet feedstocks (e.g. algae) than other thermochemical conversion processes such as gasification or pyrolysis [4,7–9]. In a previous HTL test of *Chlorella* algae, liquefaction produced a self-separating bio-crude oil product when the reaction temperature reached approximately 240 °C. Below 240 °C, green/brown slurries and bio-char were formed instead [4]. Reaction time is another significant factor affecting the formation of bio-crude oil. Swine manure (SW) and algae typically require at least 15 and 10 min, respectively, to form products similar to crude oil or bitumen [10].

Low-lipid algae are a suitable candidate to produce bio-energy via HTL [4,11,12]. While previous studies have concentrated mostly on food grade or pure-culture (axenic) algae, large-scale algal cultivations are difficult to grow consistently as monocultures, particularly for algae cultured in wastewater. Our previous work has demonstrated that mixed-culture algal biomass from wastewater treatment systems (AW) can be an appropriate HTL feedstock for bio-crude oil production [5,13], and several other studies have noted that waste treatment and algal biomass production should be integrated to achieve a net positive energy balance [1,2,14]. With abundant nutrients, such as nitrogen and phosphorus, the liquid fraction of swine manure is an advantageous medium for algae cultivation. Thus, it is expected that swine manure bio-solids and algal biomass could both be available at the same locations, and it would

be advantageous to process them both using the same HTL process. Some amount of manure bio-solids will likely be entrained in the algal biomass grown in manure liquids [15,16]. Therefore, this study aims to explore the co-liquefaction of SW and AW for bio-crude oil production in order to help establish an energy-efficient and economically viable approach to treat these biomass mixtures.

Although SW and AW are each individually viewed as promising feedstocks for bio-crude oil production via HTL [2,5,7,17], co-liquefaction of these two mixed feedstock has not been previously reported. This study explored the product distribution, physico-chemical properties, nutrient recovery, and energy balance in the co-liquefaction of SW and AW. To the best of our knowledge, this present study is the first of its kind to systematically evaluate the production of bio-crude oil from combined biomass feedstock of SW and AW. When using wastewater (e.g. liquid portion of swine manure) to culture algae, the contamination by competing microorganisms during the algae cultivation is typically encountered [2,18,19]. The co-liquefaction of swine manure and mixed-culture algal biomass into bioenergy products allows for using two different types of biomass sources and thus can help resolve the contamination of target algal species (e.g. high-lipid algae) during the algae cultivation, and facilitate increased efficiency in converting two renewable resources into sustainable bio-energy products.

## 2. Experimental procedures

### 2.1. Feedstock

A mixed-culture algal biomass from wastewater (AW) was directly harvested from a full-scale mixed algal wastewater treatment plant (One Water Inc., Indianapolis, IN) and therefore had a relatively high ash contents (47.5%). Similar ash contents were also found in the algae feedstocks directly harvested from a retention pond and a local wastewater treatment plant (Urbana-Champaign Sanitary District, Champaign, IL) [13,20]. The mixture algal biomass contained microalgae, macroalgae, bacteria and other organisms. The swine manure (SW), which was the same type used in the previous studies [11,20–22], was collected directly from the floor of a grower-finisher barn. Prior to HTL experiment, proper ratios of mixed algal biomass and swine manure were mixed and homogenized using a commercial blender (MX 1000XT, Waring Commercial Inc., Torrington, CT) and then stored in a refrigerator at 4 °C. The total solids of AW and SW were measured as the dry residue at 105 °C, and the corresponding ash contents were measured as the combustion residue at 550 °C. The other macromolecules and chemical compositions such as acid detergent fiber, neutral detergent fiber and lignin were analyzed using the methods of the Association of Official Analytical Chemists (AOAC). Detailed analyses of AW and SW were summarized in Table 1.

**Table 1**  
Characteristics of swine manure (SW) and mixed-culture algal biomass from wastewater (AW).

Feedstock	Proximate analysis (d.w.%) <sup>b</sup>		Ultimate analysis (d.w.%) <sup>b</sup>						
	VM <sup>a</sup>	Ash	C	H	N	O <sup>c</sup>	H/C	O/C	N/C
AW	52.5	47.5	27.9 ± 2.6	3.01 ± 0.5	3.90 ± 0.4	65.2	1.29	1.75	0.12
SW	83.7	16.3	41.1 ± 0.2	5.42 ± 0.09	3.36 ± 0.1	50.1	1.58	0.92	0.07
Chemical composition (d.w.%) <sup>b</sup>									
	Crude fat		Crude protein		Hemicellulose		Cellulose		Lignin
AW	1.70		27.2		3.50		14.4		5.70
SW <sup>d</sup>	20.3 ± 1.5		24.5 ± 1.8		27.3 ± 2.2		3.8 ± 1.4		3.6 ± 1.3

<sup>a</sup> Volatile matter.

<sup>b</sup> Dry weight basis.

<sup>c</sup> O (wt%) = 100 – (C + H + N) (wt%).

<sup>d</sup> Average values were reported based on the previous studies [11,20–22] because the chemical compositions were found to be stable in the same type of swine manure.

Major inorganic chemicals (e.g. Sodium) of AW and SW were also available in [supplementary data](#).

## 2.2. HTL experiments

The HTL experiments were performed according to the previously reported method [4,22], using a stainless steel cylinder reactor of 100 ml capacity with a magnetic drive stirrer and removable vessel (Model 4593, Parr Instrument Co., Moline, IL) in a batch mode. HTL was processed at 300 °C and 1 h reaction time, which are previously determined optimum conditions for converting AW into bio-crude oil [5]. Dry AW combined with various ratios of dry SW was mixed with tap water to make a slurry feedstock containing 25% total solid content by weight for each HTL experiment. A total 30 g of slurry feedstock (containing 7.5 g solids and 22.5 water) was placed in the reactor and the reactor was subsequently sealed and purged with nitrogen 3 times to remove the residual air. Nitrogen gas was again added to the reactor to build 0.69 MPa gauge pressure inside the reactor headspace to prevent water boiling during the tests. After the HTL reaction at the given temperature and reaction time, the reactor was cooled down to room temperature in 0.5 h by circulating tap water through the cooling coil located outside the reactor. For each reaction condition, at least two independent experiments were conducted and the average values and the standard deviations were reported.

## 2.3. Analysis of HTL products

During each HTL test, the initial/final pressures/temperatures were recorded. After the reactor was cooled down to room temperature, the gas products were collected through a control valve into a Tedlar® gas sampling bag (CEL Scientific CORP., Cerritos, CA). Since the headspace remained the same after the reactor cooled down to room temperature, the gas production of the HTL can be calculated using the ideal gas law. The rest of the products were first separated by filtration with Whatman® 55 mm glass-fiber filters (Whatman®, Cat. No. 1822-055). The aqueous portion was defined as the water soluble portion, which can pass through the filter, while the rest of the filtration cake was defined as the raw oil, which is the water insoluble part. The moisture content of the water insoluble product was measured using a distillation apparatus based on ASTM Standard D95-99 [23], whereas the solid residue fraction of the raw oil product was determined via Soxhlet extraction according to ASTM Standards D473-02 [24] and D4072-98 [25]. The recovery procedure was summarized in Fig. 1.

Products distribution was calculated on the dry weight (d.w.) of the mass of feed (AW + SW) by the following equations:

$$\text{Bio-crude oil yield (d.w.\%)} = \frac{W_{\text{oil}}}{W_{\text{feed}}} \times 100 \quad (1)$$

$$\text{Solid residue yield (d.w.\%)} = \frac{W_{\text{residue}}}{W_{\text{feed}}} \times 100 \quad (2)$$

$$\text{Gas yield (d.w.\%)} = \text{Based on the ideal gas law equation} \quad (3)$$

$$\begin{aligned} \text{Aqueous product yield (d.w.\%)} \\ = 100 - (\text{bio-crude oil} + \text{solid residue} + \text{gas}) \end{aligned} \quad (4)$$

The gas composition was analyzed in a Varian CP-3800 Gas Chromatograph equipped with an Alltech HayeSep D 100/120 column and a thermal conductivity detector (TCD). The bio-crude oil and the solid residue were respectively dried at room temperature in the fume hood and at 105 °C in the oven for a 24-h prior to the

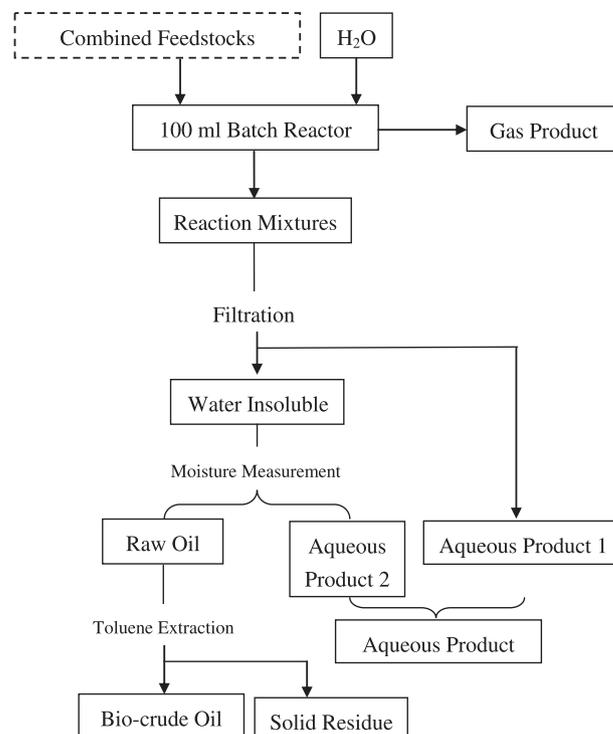


Fig. 1. Experimental process schematic for separation of co-liquefaction products.

elemental tests. Elemental compositions of the raw materials, bio-crude oil, and solid residue were determined using a CE 440 elemental analyzer (Exeter Analytical, Inc., North Chelmsford, MA).

The higher heating value (HHV) of the bio-crude oil was calculated using the Dulong formula based on the elemental composition:  $\text{HHV} = 0.3383 \times C + 1.422 \times (H - O/8)$  [4,26]. The energy recovery was defined as the HHV of the bio-crude oil divided by that of the combined feedstock; the nutrients recovery (e.g. carbon recovery) for liquefaction products were estimated according to the nutrient contents (e.g. carbon) of various products divided by that of the combined feedstock. Detailed equations of the energy recovery and nutrients recovery were described in the previous relevant studies [4,5]. The energy consumption ratio (ECR) was calculated for each tested HTL condition using Eq. (5),

$$\text{ECR}_{\text{co-HTL}} = \frac{[W_i C_{pw} T + (1 - W_i) C_{pm} T][1 - R_h]}{Y(\text{HHV})(1 - W_i)R_c} \quad (5)$$

where  $W_i$  is the moisture content of the initial feedstock prior to conversion,  $C_{pw}$  is the specific heat of water (4.18 kJ/kg K),  $C_{pm}$  is the specific heat of dry feedstock (for algae: 1.25 kJ/kg K; for swine manure: 1.09 kJ/kg K) [27],  $T$  is the difference between the designated reaction temperature and the initial temperature (assumed to be 25 °C),  $Y$  is the bio-crude oil yield, HHV is the higher heating value of bio-crude oil,  $R_h$  is the efficiency of heat recovery assumed to be 0.5,  $R_c$  is the efficiency of available combustion energy assumed to be 0.6 [8,20]. An ECR of less than 1.0 indicates a net energy gain for the system [28].

The chemical composition of the bio-crude oils and aqueous products were analyzed using GC-MS (Agilent Technologies, Santa Clara, CA). All data were normalized according to internal standards: 0.1 μM 3-methyl butanoic acid for aqueous extracts; and 0.5 μM pentadecanoic acid methyl ester for the bio-crude oil product extracted in toluene (see Fig. 1). Detailed analytical methods were described in previous literature [5]. Thermal gravimetric analysis (TGA) of each bio-crude oil sample was performed on a Q50 TGA (TA Instruments, Schaumburg, IL) from 110 °C to 800 °C

in 50 ml/min N<sub>2</sub> at 10 °C/min to determine its boiling point distribution [12,26,29].

### 3. Results and discussion

#### 3.1. Products distribution

The distribution of liquefaction products is shown in Fig. 2. Liquefaction product yields obtained from pure AW and SW were also listed for comparison. The highest bio-crude oil yield (35.7% d.w.) of the co-liquefaction process was obtained from the combination of 25% AW and 75% SW. Although the bio-crude oil yield of pure SW was higher than pure AW biomass, the bio-crude oil yields did not increase as the SW fraction of the feedstock increased from 0% to 50%. Instead, the average bio-crude oil yields decreased slightly from 25.8% to 22.0% as the addition of SW increased from 25% to 50%. When the SW fraction was increased to 75%, the bio-crude oil yield increased to 35.7%. This reveals that when the ash content of feedstock was too high (in this case, above 30% d.w.), the feedstock combinations may be preferentially converted into aqueous or solid products rather than bio-crude oils. In addition, there is some evidence showing that higher feedstock ash contents can obstruct the bio-crude oil formation. A previous study about converting different kinds of algae and bio-waste into bio-crude oil also demonstrated that when the ash content was higher than 20% in the dry feedstock, the bio-crude oil yields began to decrease [20]. However, the details of how the ash content interacts with other feedstock components during HTL conversions require additional research to elucidate.

The lowest bio-crude oil yield was obtained at the combination ratio of 50% SW with 50% AW, which indicated that the reaction pathways were fine tuned for the synthesis of other liquefaction products (e.g. aqueous products) rather than bio-crude oil. This may be impacted by the great increase of hemicellulose (from 3.50% in pure AW to 15.4% in AW:SW = 1:1) and crude fat (from 1.70% in pure AW to 11.0% in AW:SW = 1:1) in the feedstock. GC–MS results (details in section 3.3.) demonstrated that, with the combination ratio of 50% SW with 50% AW, there were more hemicellulose-derived compounds (e.g. cyclic oxygenates) in the bio-crude oil and the aqueous products (e.g. ketones) as compared to other feedstock combination ratios. Additionally, the crude fat can be saponified under a basic environment. In this study, the high ash content might provide an alkaline environment for the saponification and thus the crude fat may undergo saponification rather than hydrolysis, which turned out to form more aqueous products instead of solid products or bio-crude oil. The pH of aqueous products obtained from various combination ratios of feedstock (Fig. 2) also reveals this indication. Similar results were

observed in Muangrat's study on transforming different food for hydrogen gas production during subcritical water via gasification [30]. Another example is Ren's work regarding the hydrothermal process on the variations of the lipids in the restaurant garbage. They also found that saponification may involve in the hydrothermal process [31].

As the SW fraction was increased from 25% to 75%, the solid residue yield dramatically decreased from 50.3% to 24.1% and then to 17.1%, which implied that the interaction between AW and SW led liquefaction products to be more favorably converted into aqueous products rather than solid residue. This may also be affected by the pH of the co-liquefaction system. As the addition of SW increased from 0% to 75%, the pH of aqueous product was decreased from 7.4 to 6.8, but the pH was relatively stable from 0% to 50% SW. The dilute acidic environment with 75% SW may facilitate the hydrolysis of hemicellulose and the disruption of lignin structure [32], followed by some water-soluble products such as phenols. A similar observation was also presented in He's work about converting SW into bio-crude oil [33]. Furthermore, the generation of esters and water as products (esterification), may become more dominant in the co-liquefaction system as the SW fraction increases because it contains more crude fat, which serves as a source of fatty alcohols. Thus, the feedstock tended to be preferentially transformed into aqueous products when the ratio of SW increased. Previous literature also demonstrated that the esterification became more dominant when using the methanol or ethanol as the reaction media [26,34].

The gas yields were least affected by the feedstock combination ratios, suggesting that the gas yields were relatively constant under the operating condition with different compositions of feedstocks. Similar results were reported in previous literature [4,22,35]. These studies indicated that HTL gas yields were primarily impacted by the reaction temperature under supercritical HTL conditions. For instance, Li's work [36] demonstrated that as the reaction temperature increased from 320 °C to 380 °C, the gas yields were drastically increased.

#### 3.2. Elemental analysis and higher heating value (HHV) of bio-crude oils

Table 2 displays the elemental analysis and HHV of bio-crude oils as well as the toluene solubility of raw oils obtained from various combination ratios of SW and AW at 300 °C and 1 h reaction time. The H/C ratios of bio-crude oils were all greater than the feedstock of AW but were slightly lower than SW. On the contrary, the O/C and N/C ratios of all the bio-crude oils were lower than the two feedstocks, confirming that partial deoxygenation and denitrogenation occurred during the HTL process [4]. The deoxygenation can proceed through decarboxylation of protein, lignocelluloses and fatty acids while the denitrogenation can occur via deamination of proteins [37,38]. Deamination can remove nitrogen and hydrogen from the amino acids and produce hydroxyacid. Similar findings were observed by converting low-lipid microalgae, brown macro-alga, and cattle manure into bio-crude oils via HTL [4,12,35].

Although Table 2 shows that increasing the SW fraction in the co-liquefaction system increased the toluene solubility of raw oils, the quality of bio-crude oils in terms of energy density, carbon and hydrogen contents were not improved. This may be due to the relatively high ash content in the co-liquefaction system compared to other HTL work using pure feedstocks. Xiu also found that co-liquefying SW with crude glycerol did not improve the bio-crude oil quality because the ash content was increased in the co-liquefaction system [17]. The highest HHV of the bio-crude oil converted from combined feedstocks (AW:SW = 3:1) was 27.5 MJ/kg, which was comparable to previous research using macroalgae and corn-cobs as HTL feedstocks [36,39,40], but it was lower than those

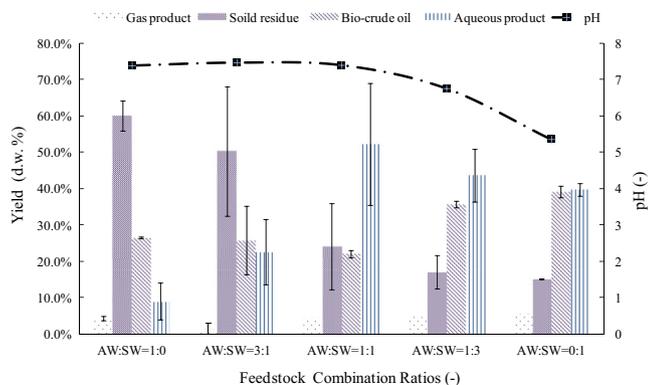


Fig. 2. The effect of feedstock combination ratios on yields of liquefaction products based on dry feedstock; AW = mixed-culture algae from wastewater; SW = swine manure.

**Table 2**

Ultimate analysis of HTL bio-crude oils and the toluene solubility of raw oils obtained at 300 °C for 1 h reaction time with various AW:SW ratios.

Component (d.w.%)	AW:SW = 1:0	AW:SW = 3:1	AW:SW = 1:1	AW:SW = 1:3	AW:SW = 0:1
C	59.4 ± 0.05	61.7 ± 0.5	54.2 ± 0.3	48.5 ± 0.2	76.6 ± 0.6
H	7.79 ± 0.02	8.00 ± 0.02	7.10 ± 0.02	6.28 ± 0.005	10.3 ± 0.1
N	2.50 ± 0.1	3.53 ± 0.03	2.68 ± 0.03	2.50 ± 0.03	3.76 ± 0.05
O <sup>a</sup>	30.3	26.8	36.0	42.7	9.4
H/C atomic ratio	1.57	1.56	1.57	1.55	1.61
O/C atomic ratio	0.38	0.33	0.50	0.66	0.09
N/C atomic ratio	0.04	0.05	0.04	0.04	0.04
Heating value (MJ/kg)	25.8	27.5	22.0	17.8	38.8
Toluene Solubility	35.5	55.0	63.3	71.8	72.6

<sup>a</sup> Calculated by difference.

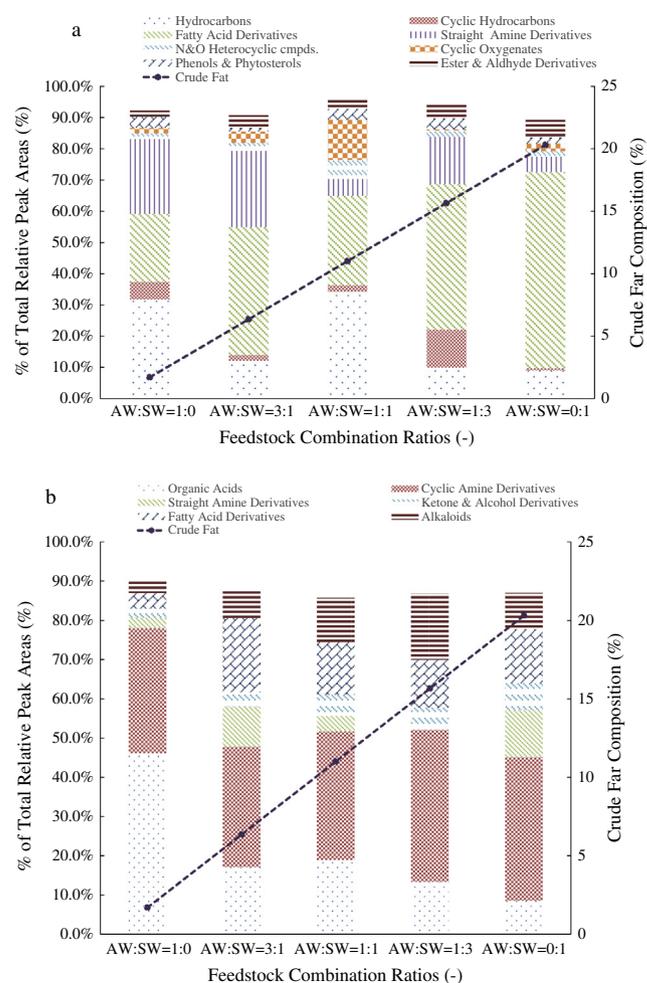
employing microalgae [4,28]. Nonetheless, upgrading would be necessary to improve the bio-crude oil quality for use in transportation fuel applications.

### 3.3. GC–MS analysis of bio-crude oil and aqueous products

In order to examine if the co-liquefaction of AW and SW would change the composition of liquefaction products, GC–MS analysis of bio-crude oils and aqueous products was performed. Components characterized by GC–MS were categorized into several groups including cyclic oxygenates (e.g. oxirane derivatives), hydrocarbons and straight amine derivatives. Compounds containing more than one functional group were classified into only one category. For example, 2-piperidinone consists of both C=O and N–H functional groups and it was classified as cycle amine derivatives based on its chemical property. For each bio-crude oil and aqueous product sample, approximately 90% of the peak area for identified compounds was grouped. GC–MS spectra and the major compounds (>1% relative total peak area) of the bio-crude oils and aqueous products are summarized in the [Supplementary Data](#).

Fig. 3(a) shows the GC–MS results for the bio-crude oils. Notably, as the crude fat increased with the addition of SW, the amount of hydrocarbons in the bio-crude oil decreased or remained constant. Typically, fatty acids would undergo decarboxylation to produce hydrocarbons and carbon dioxide under HTL conditions. However, this reaction may be suppressed under hydrothermal conditions [38,41]. For example, the decarboxylation of stearic acid was retarded in a previous hydrothermal experiment [38]. Another example is that the decarboxylation of carboxyl acid model compounds (e.g. benzoic acids) was found to be completed until HTL reaction temperature increased from 305 °C to 390 °C; before 390 °C, the decarboxylation of carboxyl acids appeared to be suppressed [38]. Simultaneously, about 2–5% of esters, aldehydes and alcohols derived from fatty acids were observed in the bio-crude oils converted from mixed feedstock and pure SW, which also reveals that decarboxylation of fatty acids was restrained in this study. On the other hand, it is generally believed that the decarboxylation reaction can be strongly improved by adding catalyst such as KOH [38]. In order to further elaborate the reaction pathway of fatty acids at sub-critical conditions, additional HTL studies using model compounds such as lactic acids are recommended.

Fig. 3(b) provides the GC–MS results for the aqueous HTL products. Notably, the organic acids (e.g., acetic acid) were greatly reduced after SW was added into the co-liquefaction system, suggesting that either the degradation of lignocellulose or proteins was suppressed. The reduction of cyclic oxygenates (e.g. oxirane derivatives) in the bio-crude oil obtained with 75% SW and pure SW also supports this argument. Cellulose from different biological sources has different structure and physicochemical properties that can affect its reactivity [38]. Surprisingly, the alkaloids group (mainly pyrazine derivatives) increased as the fraction of SW was



**Fig. 3.** Effect of feedstock combination ratios on the composition of (a) bio-crude oil; and (b) aqueous products at 300 °C and 1 h reaction time.

increased. This might be due to the fact that chloride was naturally present in manure and the chloride might facilitate the synthesis of pyrazines via self-condensation [42–44]. Additionally, Fig. 3(b) reveals that further utilization of the aqueous products would be advantageous. For instance, there were significant amounts of nitrogen-containing compounds such as urea, which is an excellent nutrient source for culturing microorganisms or algae.

### 3.4. Thermal gravimetric analysis (TGA) of bio-crude oils

The boiling point distribution of the bio-crude oils was determined using TGA. TGA applied in simulated distillation is regarded as a miniature distillation and it can provide an estimate of the

boiling range of the bio-crude oil [12,26,29]. The bio-crude oils were dried naturally at room temperature in a fume hood for 24 h and then subjected to TGA. The weight loss of the bio-crude oils before 110 °C was only about 1.5%, implying that the drying process efficiently removed the toluene solvent (Table 3). The amount of distilled fractions between 110 °C and 550 °C, which can generally enter the petroleum refineries, of the bio-crude oil obtained with a combination of 25% SW and 75% AW feedstock were comparable to previous work employing microalgae and pure macroalgae as HTL feedstock [12,20]. As the addition of SW increased, the distilled fraction between 200 °C and 300 °C was decreased in the bio-crude oil, indicating that more heavy crude oils were formed rather than light oils. However, the bio-crude oil converted from pure SW contained a larger light portion (between b.p. of 200 °C and 300 °C), which reveals that the formation of light oils was suppressed in the co-liquefaction system with 50% and 75% SW fractions. Comparing with other published information, the bio-crude oils obtained with 50% and 75% SW fractions have a TGA curve similar to the phenolic resin from petroleum and the bio-resin converted from lignocellulosic materials via direct liquefaction [45]. Thus, it is speculated that the bio-crude oils converted from the above two conditions may be used as resins. Moreover, the residues obtained from TGA might be used as carbon fiber, which has to be prepared at about 1000 °C [46]. Additional studies such as elemental tests and scanning electronic microscopy (SEM) are suggested to further investigate the residues obtained from TGA tests.

### 3.5. Nutrient recovery, distribution and energy balance

Carbon recovery (CR) and nitrogen recovery (NR) into the various liquefaction products is shown in Fig. 4. Compositions of crude fat, lignocellulose and protein of AW and SW were also provided to indicate how the reaction environment may change as the co-liquefaction AW to SW ratio was adjusted. Notably, the CR of the bio-crude oils (Fig. 4(a)) did not increase as the crude fat increased in the feedstock, indicating that there may be antagonisms between SW and AW in terms of oil formation. In contrast, when the cellulose content increased in the co-liquefaction system, CR of the solid residue increased as well. This suggests that there is a positive correlation between the amount of cellulose and solid residue [48,49]. Fig. 4(b) shows that as the addition of SW increased, the NR of bio-crude oil increased from 16.8% to 43.9%, implying that protein derivatives may tend to react with crude fat derivatives when the crude fat was drastically increased in the co-liquefaction system. GC–MS results also demonstrated the straight amide derivatives increased as the crude fat increased. However, when the pH was changed from slightly basic to slightly acidic, the formation of amide derivatives may be suppressed because the release of ammonium groups, one of the reactants for amide formation, is unfavorable for amino acids under acidic conditions [50]. The above observation also reveals that the NR of bio-crude oil could be decreased by removing the crude fats in the reaction system prior to HTL. A previous study using

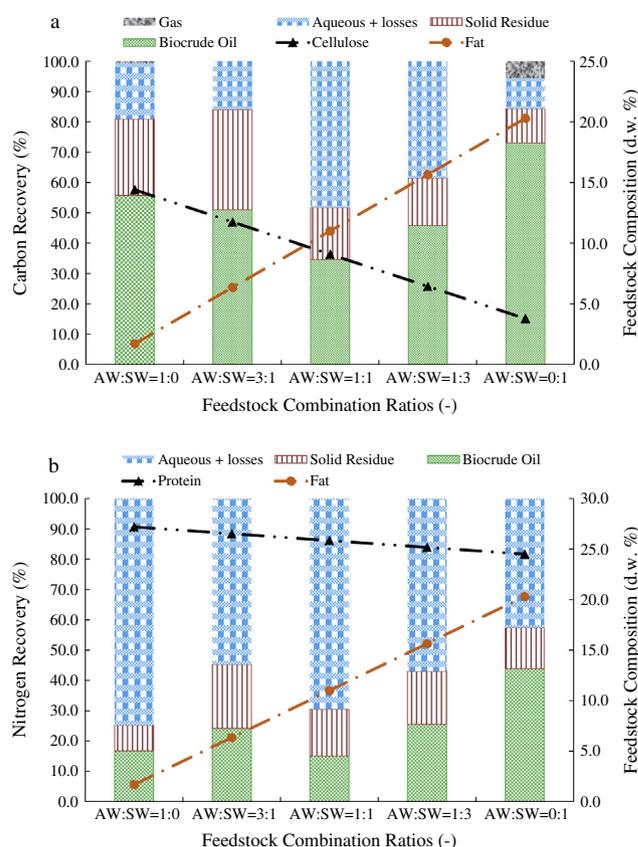


Fig. 4. The effect of AW:SW feedstock combination ratios on (a) carbon recovery; and (b) nitrogen recovery distributed in various HTL products at the operating condition of 300 °C and 1 h reaction time; and protein and cellulose contents in the feedstock.

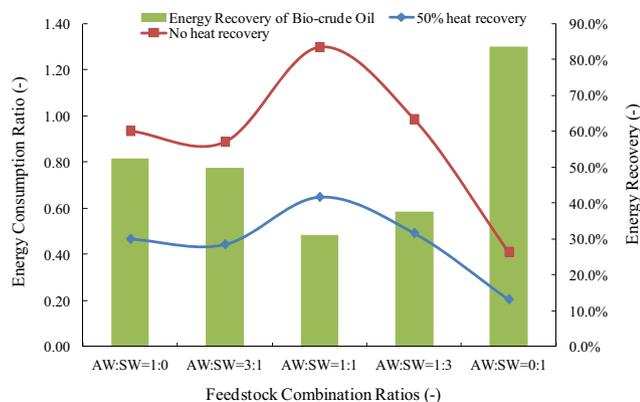
microwave irradiation to extract the crude fats from microalgae also exhibited a similar finding—the NR of the bio-crude oil was reduced but the bio-crude oil yield converted via HTL was also reduced at the same time [51].

The highest energy recovery (ER) of the bio-crude oils converted from mixed feedstocks was 49.9% (Fig. 5), which was comparable to previous studies using a higher reaction temperature (320–340 °C) and pure macroalgae as an HTL feedstock [34,36]. Although the ER obtained from the co-liquefaction tests was lower than that from pure AW or SW, Fig. 5 shows that the energy consumption ratio (ECR), the energy required for thermochemical conversion against the energy that can be recovered from bio-crude oil combustion, of the co-liquefaction system with 25% SW plus 75% AW was lower than that of pure AW. This ECR value is also lower than several studies using food grade microalgae (e.g. *Porphyridium* and *Spirulina*) as an HTL feedstock [28]. The above observation suggests that more net energy gain was obtained in the co-liquefaction system.

Table 3  
Boiling point distributions of bio-crude oils gained with different feedstock combination ratios at 300 °C with 1 h (%).

Distillate range (°C)	AW:SW = 1:0	AW:SW = 3:1	AW:SW = 1:1	AW:SW = 1:3	AW:SW = 0:1	Typical applications <sup>a</sup>
25–110	0.79	1.30	1.66	2.62	0.91	Bottle gas and chemicals
110–200	5.13	4.84	4.64	2.58	4.05	Gasoline
200–300	26.31	26.58	18.23	8.20	43.91	Jet fuel, fuel for stoves and diesel oil
300–400	19.02	19.22	15.02	12.27	30.98	Lubricating oil for engines and fuel for ships
400–550	19.15	20.21	22.56	25.76	9.74	Lubricants and candles and fuel for ships
550–700	1.91	1.46	0.92	3.15	0.54	Fuel for factories and central heating
700–800	1.03	1.06	0.72	1.21	0.15	Asphalt and roofing material
>800	26.66	25.33	36.25	44.21	9.72	Residues

<sup>a</sup> Adopted from handbook of petroleum product analysis [47].



**Fig. 5.** The energy recovery (ER) of bio-crude oils and energy consumption ratios (ECR) for the co-liquefaction system (operated at 300 °C and 1 h reaction time) with different feedstock combination ratios.

Overall, Fig. 4 illustrated that there were about 60% and 70% of carbon and nitrogen distributed to the rest of liquefaction products including solid residues and aqueous products, indicating the recovery of carbon and nitrogen in the by-products will play a key role to a sustainable scale-up [4,12]. In an E<sup>2</sup>-Energy paradigm, the nutrients and carbon in the post HTL aqueous stream can be recycled multiple times to increase bio-energy production and hence achieve a sustainable bio-energy generation system [2].

#### 4. Conclusion

It was shown in this study that co-liquefaction of SW and AW could serve as a feasible approach for bio-crude oil production. At 300 °C and 1 h reaction time, a bio-crude oil yield was the highest (37.5% d.w.) with a combination of 75% SW and 25% AW, but the highest HHV (27.5 MJ/kg) and net energy recovery was obtained at a combination of 25% SW and 75% AW. GC–MS and TG analyses of the bio-crude oils demonstrated that both light oils and heavy crudes were produced in this study. The decomposition of fatty acids, lignocelluloses and proteins might be suppressed in the co-liquefaction system. Energy consumption ratios suggest that co-liquefaction of AW with SW was a competitive alternative system for bio-crude oil production.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2014.04.068>.

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