Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production

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Abstract

Spent coffee grounds (SCG) were liquefied in hot-compressed water to produce crude bio-oil via hydrothermal liquefaction (HTL) in a 100 cm³ stainless-steel autoclave reactor in N₂ atmosphere. We investigated the effects of operating parameters such as retention times (5 min, 10 min, 15 min, 20 min and 25 min), reaction temperatures (200 °C, 225 °C, 250 °C, 275 °C and 300°C), and water/feedstock mass ratios (5:1, 10:1, 15:1 and 20:1) and initial pressure of process gas (2.0 MPa and 0.5 MPa) on the yield and properties of the resulting crude bio-oil. The highest yield of the crude bio-oil (47.3 % mass fraction) was obtained at conditions of 275 °C, 10 min retention time and water/feedstock mass ratio of 20:1 with an initial pressure of 2.0 MPa. The elemental analysis of the produced crude bio-oil revealed that the oil product had a higher heating value (HHV) of 31.0 MJ·kg⁻¹, much higher than that of the raw material (20.2 MJ·kg⁻¹). GC-MS and FT-IR measurements showed that the main volatile compounds in the crude bio-oil were long chain aliphatic acids and esters.

Keywords: hydrothermal liquefaction; spent coffee grounds; hot-compressed water; crude bio-oil

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1. Introduction

The inherent conflict between the increase of global energy demand and the depletion of fossil fuel reserves, along with the environmental concerns caused by the extensive use of fossil fuels, has necessarily called for sustainable energy alternatives [1]. Using biomass for liquid biofuels production has sparked the interest worldwide due to its abundance, renewability and carbon neutrality [2]. However, today, the major viable commercial options for producing liquid biofuels use edible crops (vegetable oils for biodiesel and corn/sugarcane for bioethanol), which has negative impacts on food and feed supplies [2, 3]. Research efforts are, therefore, re-orientated to use **the** biological waste such as agricultural and forest residues, animal manure, food processing waste and municipal waste [4-10]. Utilizing waste streams for biofuels production also has additionally environmental benefits, including reducing the local pollution, decreasing greenhouse gas emissions, and lessening the burden on landfills.

Coffee is one of the most popular beverages and widely consumed in America, Japan and Europe [11, 12]. According to the coffee trade record from **the** International Coffee Organization [13], the global coffee production has increased by 6 % since 2010, and the total coffee production in 2014 was 142 million bags, equalling 9.6 million tonnes. The amount of spent coffee grounds (SCG), the solid residues obtained from coffee brewing, therefore increases accordingly. Despite such biomass residues are generated in large quantities each year, they are mostly underutilized, being disposed in landfills or small amounts used for composting [14]. However, the complex organic substances (e.g., caffeine, tannins and polyphenols) left in the coffee residue were found to have adverse impacts on land and the environment [11]. Some industries attempted to process SCG into coffee logs or pellets for heating and electricity generation, while its combustion generated particulate matter and hazardous gases, especially high nitrogen oxidants in emissions, compared to wood pellets or briquettes. This dramatically limits the direct use of SCG as solid fuels [15, 16]. New interests are recently developed to use SCG for liquid biofuels production. Kondamudi et al. [12] extracted coffee oil from SCG for biodiesel production. However, the average oil content in SCG is fairly low, only 10-15 % mass fraction, and the **necessary solvent** extraction makes **this** option economically unfavorable. Mussatto et al. [17] evaluated the feasibility of producing bioethanol from SCG through fermentation using three different yeasts, while the ethanol production yield was only 26.0 % mass fraction. Other researchers [18-20] used a fast pyrolysis process to convert SCG into **the**

bio-oil. The results were very promising, with an oil yield as high as 54.9 % mass fraction. Unfortunately, SCG has a fairly high moisture content (50– 60 % mass fraction) [12], and thus a pre-drying process is required before SCG is fed to a pyrolysis system. This leads to a large energy consumption and decreases the overall economic viability. Moreover, the quality of the pyrolysis bio-oil is not satisfactory. A relatively high oxygen (35.2–59.5 % mass fraction) resulted in lower HHVs in a range of 17 MJ·kg⁻¹ to 23 MJ·kg⁻¹, depending on the composition of feedstock and pyrolysis conditions. Therefore, it is essential to explore other pathways to utilize this waste stream effectively, efficiently and economically.

Hydrothermal liquefaction (HTL) is an emerging technology that is able to convert wet biomass (especially waste materials) to the oil (referred to as bio-oil or biocrude), aqueous, gaseous and solid products at high pressures (5–22 MPa) and moderate temperatures (250–380 °C) in sub-/supercritical water medium [21, 22]. HTL is advantageous over other thermochemical conversion technologies such as fast pyrolysis and gasification. It is carried out at lower temperatures; more importantly, it accepts wet biomass, and thus obviates an energy-intensive pre-drying process. Also, the bio-oil obtained from the liquefaction process is hydrophobic, typically has a lower oxygen and water content, giving much higher HHV (25–35 MJ·kg⁻¹) compared to those of the fast pyrolysis bio-oil (14–20 MJ·kg⁻¹). The HTL crude bio-oil can be mixed with other fuels and used for combustion or be further upgraded to high quality hydrocarbon liquid fuels such as gasoline and diesel [22–26].

Many researchers have been focusing on the bio-oil production via the HTL process from a wide variety of biomass, including woody biomass, mainly forest residues [27–30], agricultural waste such as barley straw, corn stalk, corncob and rice husk [31–34], animal manure [35–37], municipal solid waste [38–40] and most recently microalgae [41–48]. Through these studies, it was found that the yield and quality of the bio-oil resulting from the HTL process were highly associated with the operating parameters such as the reaction temperature, retention time, ratio of feedstock and solvent, etc., as reviewed by Akhtar and Amin [49] as well as the experimental results reported in the literature [27–48]. The commonly used temperature range is from 250 °C to 400 °C; and usually around 300 °C, the maximum bio-oil yield was obtained. At a low temperature, an incomplete decomposition of biomass gives a relatively high solid residues yield and a low bio-oil yield. With an increase in the liquefaction temperature, the yield of bio-oil increases while the solid residue decreases. However, at the temperature higher than 300°C, for

most feedstocks, a decreased bio-oil yield and increased gas fraction yield are observed due to a secondary decomposition of the bio-oil and Bourdard gas reactions. However, the solid residue yield may also increase, being caused by the re-polymerization of the bio-oil components and/or re-combination of high-concentration free radicals to form bio-char. Retention time is another key factor influencing the bio-oil production and the overall biomass conversion. Generally, a short retention time (10–30 min) is preferred, giving a relatively high bio-oil yield. The ratio of feedstock and solvent also plays an important role in the biomass liquefaction process. It was observed that a low ratio of feedstock and solvent led to a high bio-oil yield, however it was not economically favorable. In contrast, some researchers also found that a higher biomass concentration might promote the dehydration/polymerisation of the intermediates products, which resulted in an increase of the bio-oil yield. Despite enormous studies conducted and significant progress made, the underlying mechanism of the effects of operating parameters on HTL process was so far not fully understood. The optimization of reaction conditions and knowledge of the interaction of operating parameters have to be obtained by experiments.

In addition to operating parameters, the nature of biomass, i.e., different components of cellulose, lignin, protein and fat, significantly impacts the yield and chemical composition of the HTL products. To date, most of studies examined the lignocellulose-based feedstock (e.g., forest residues, agricultural wastes), which contains a relatively high content of lignin while low contents of lipid and protein [27-30, 50]. The HHVs of the HTL bio-oils obtained from the lignocellulose biomass (without using any catalysts and organic solvents) are in the range of 30–36 MJ·kg⁻¹, and the oil yields are relatively low (20 % to 36 % mass fraction). These studies indicated that a high content of lignin in feedstock was not desirable for the bio-oil production. Recently, it was observed that high lipid and protein contents in feedstock benefited the yield and the quality of the bio-oil [41-48, 51, 52].

A thorough literature review encouraged us to explore the feasibility of converting the spent coffee grounds (SCG) to bio-oil via HTL. SCG has higher contents of lipid (≈ 15 %) and protein (≈ 17.4 %), while a lower content of lignin (≈ 23.9 %), compared to the lignocellulose biomass [11, 12, 53]. It might be a promising feedstock for the bio-oil production using the HTL technology. More attractively, the size of SCG is in the range of 200–300 μm [19], which makes it suitable for being directly fed to the HTL reactor without a prior energy-intensive grinding process.

In this study, SCG was liquefied in hot-compressed water in N₂ atmosphere. Effects of the retention time (varied from 5 min to 30 min), reaction temperature (varied from 200 °C to 300 °C), water/feedstock mass ratio (varied from 5:1 to 20:1) and initial pressure (0.5 MPa and 2.0 MPa) on the yield of product fractions were investigated, with an expectation of maximizing the oil yield. The properties of the resulting bio-oil (e.g., elemental composition, higher heating value, and chemical composition) were characterized. To the best of our knowledge, this is the first to examine SCG as a feedstock for the bio-oil production via a hydrothermal liquefaction process.

2. Experimental

2.1 Materials

The wet SCG for this study were collected after coffee beans (*Coffea arabica*) brewing from Tim Hortons, London, Canada, and were first air-dried at room temperature over several days, and then were oven dried at 105 °C. The dried SCG were kept in sealed bags and stored in refrigerator at 4 °C. For each experiment, the required amount of raw material was dried further in an oven at 105 °C overnight. The proximate and ultimate analyses of dried SCG are respectively listed below: 82.3 % volatiles, 1.4 % ash, 4.0 % moisture and 50.4 % C, 7.2 % H, 2.1 % N, and 40.3 % O (calculated by difference). The solvents used were distilled water and reagent grade acetone, purchased from Caledon laboratories Ltd., which was used as received.

2.2 Hydrothermal liquefaction procedure

The experiments were carried out in a 100 cm³ stainless-steel autoclave (Parr Instrument, 5513) equipped with a stirrer. In a typical run, 2.5-10 g dried SCG were weighed and loaded into the reactor, followed by the addition of certain amount of distilled water with desired water/feedstock mass ratios 5:1, 10:1, 15:1 and 20:1, respectively. The occupation of reactor volume was maintained between 50 cm³ to 60 cm³. The reactor with the suspension of feedstock and distilled water was oscillated in an ultrasonic bath for 3 min to ensure the suspension was well-mixed. The reactor was then sealed and the air inside the reactor was displaced by purging nitrogen several times. The reactor was pressurized to 0.5 or 2.0 MPa with high purity nitrogen. The stirring speed was set at 4.5 Hz, the reaction mixture was then ramped up to the pre-set

temperature (200 °C, 225 °C, 250 °C, 275 °C and 300°C), at a heating rate of 10 °C·min⁻¹. After the system reached the desired temperature, the reactor was kept at the temperature for a specified retention time (between 5 min to 30 min).

2.3 Separation of reaction products

Once the reaction was completed, the reactor was cooled down to room temperature in an ice water bath, and the gaseous product (GP) inside the reactor was collected with a pre-vacuumed gas bag. In each run, the gas bag was injected with 120 cm³ air as an internal standard for Micro-GC analysis. The reactor was opened. Solid and water phase mixture were carefully collected, rinsed by 30 cm³ distilled water and separated by vacuum filtration through a pre-weighed filter paper. The filtrate was designated as water soluble product (WSP), containing dissolved organic compounds. The reactor, the stirrer and the solid remained on the filter paper was further rinsed using acetone several times to fully recover oil phase. The resulting suspensions were filtered through the same filter paper. The solid residue (SR) product and filter paper was dried in the oven at 105 °C overnight and then weighed to determine the mass of SR. Acetone in the filtrate was then removed by rotary evaporator under vacuum at 55 °C, resulting in the liquid product referred to as “crude bio-oil”. Yields of the crude bio-oil, SR and GP, all were expressed as percentage in a mass basis, and were calculated by the ratio of the mass of each product to the mass of SCG (dry basis) loaded to the reactor. The yields of WSP were determined by difference (100 % – crude bio-oil yield – SR yield – GP yield). The biomass conversion rate was calculated by (100 % – SR yield). All experiments were conducted in triplicate in order to ensure the repeatability of the results and to minimize the experimental errors (< 5%). In all figures, the mean values of the data along with the corresponding error bars (for the yields of crude bio-oil, SR, WSP and GP) were presented.

2.4 Product characterization

The composition of gaseous products was analyzed using GC-TCD (Agilent Micro-GC 3000) and the system employed in this study was able to analyze the gas species, including H₂, N₂, O₂, CO₂, CO, CH₄, C₂H₄, C₂H₆, C₃H₈, and C₃H₆. The volatile compositions of the crude bio-oils were analyzed by a Gas Chromatograph-Mass Spectrometer (GC-MS, Agilent Technologies, 5977A MSD) with a SHRXI -5MS column (30 m × 250 µm × 0.25 µm) and a temperature

program as follows: 60 °C held for 2 min, then heated to 320 °C at a rate of 20 °C·min⁻¹, held for 5 min. Compounds in the produced crude bio-oils were identified by means of the NIST database 2011. The functional groups of the crude bio-oils were confirmed by PerkinElmer FT-IR spectrometer within the wavelength range of 4000–550 cm⁻¹. The relative molecular mass and their distribution of crude bio-oils were analyzed by Waters Breeze gel permeation chromatography (GPC). The analysis was conducted on a 1525 Binary High Performance Liquid Chromatography (HPLC), equipped with a UV detector at a wavelength of 270 nm and a Waters Styrange HR 1 column. The column temperature was 40 °C, and the mobile phase was tetrahydrofuran (THF), the flow rate of which was 1 cm³·min⁻¹. Linear polystyrene standard was used for calibrating the relative molecular mass of the samples. The pH values were measured by a pH meter (SympHony, H10P, VWP) and the water contents of the crude bio-oil were determined in accordance with American Society for Testing and Materials (ASTM) standard. Elemental composition (C, H and N) of SCG and crude bio-oil were analyzed using an elemental analyzer (Flash EA 1112 analyzer). The composition of oxygen (O) was calculated by difference and the sulphur content (S) in samples was assumed negligible. The Higher Heating Values (HHV) of SCG, and crude bio-oils were calculated according to Eq. (1) the Dulong formula [34]:

$$\text{HHV (MJ}\cdot\text{kg}^{-1}) = 0.3383C + 1.442 (H - (O/8)) \quad (1)$$

Where C, H and O are mass percentages of carbon, hydrogen, and oxygen in the crude bio-oil, respectively, obtained from the elemental analysis.

The energy recovery expressed in % of the crude bio-oil was calculated by the Eq. (2) [44]:

$$\text{Energy recovery (\%)} = \frac{\text{HHV of crude bio-oil} \times \text{mass of crude bio-oil}}{\text{HHV of SCG} \times \text{mass of SCG}} \times 100 \quad (2)$$

Where HHV is the higher heating value, calculated by Eq. (1).

3. Results and Discussion

3.1 Effects of retention time

Retention time in a HTL process impacts the product yield and distribution. It is generally believed that a shorter residence time is preferred to degrade biomass effectively as the rate of decomposition and hydrolysis of biomass is fairly fast in the HTL process [2, 49,54].

In this study, SCG liquefaction was examined by varying retention times from 5 min to 30 min in a hot-compressed water medium and the results are illustrated in Fig. 1. As the gas yields

were very low (less than 1% mass fraction) under these experimental conditions, they were lumped with the water soluble product as WPS + gas yields. As shown in **Fig. 1**, at a constant temperature of 300 °C and a water/feedstock mass ratio of 5:1, the crude bio-oil yield reached the highest point of 31.63 % at a retention time of 10 min, then started decreasing to 22.68 % as the retention time was increased to 30 min. The results indicated that 10 min was sufficient to break down biomass and achieve the highest yield of crude bio-oil. When a longer retention time was applied, the crude bio-oil would be decomposed into smaller and lighter products and gases, as evidenced by a decrease in the average relative molecular mass of crude bio-oil from 479 g·mol⁻¹ to 433 g·mol⁻¹ when the retention time increased from 10 min to 30 min. This speculation can be further supported by the observation that yields of WSP and gases showed a continuously increasing trend from 44.91 % to 52.62 % when the retention time changed from 10 min to 30 min. This indicated that most of the organic matters in the raw material were converted into the crude bio-oil, WSP and GP within 10 min. In terms of SR, the yield remained constant at about 24.03 % from 5 min to 25 min, and only showed a slight increase at a longer retention time (30 min). This might be caused by the re-polymerization of the crude bio-oil compounds into the solid residues, resulting in the decrease yield of the crude bio-oil. Our experimental results showed that a long retention time impacted the yield of SR less significantly, however favored the formation of WSP, leading to a lower yield of the crude bio-oil product. Similar results were observed in the reported studies from other researchers [49, 55].

Under our experimental scope, the highest yield of crude bio-oil of 31.63 % was achieved with a reaction time of 10 min. Therefore, the retention time of 10 min was used in the following work to investigate the effects of the temperature, water/feedstock mass ratio and initial pressure on the SCG liquefaction.

[Here] **Fig. 1**. Yields of bio-oil, solid residue, WSP, and gas under different retention time (temperature of 300 °C and water/feedstock mass ratio of 5:1 with 2.0 MPa initial N₂ pressure).

3.2 Effect of temperature

Compared to the effects of the retention time, the influence of the reaction temperature on SCG liquefaction was more significant.

Fig. 2 illustrates the effects of the reaction temperature ranging from 200 °C to 300 °C on the yields of the crude bio-oil, SR, WSP and GP products resulting from the SCG liquefaction in 10 min with a water/feedstock mass ratio of 5:1. As seen from **Fig. 2**, the crude bio-oil yields increased continuously from 16.58 % to 35.29 % as the temperature increased from 200 °C to 275 °C, however it started dropping remarkably to 31.63 % when the temperature was further increased to 300 °C. The yield of SR decreased consistently from 42.33 % to 23.53 % as the temperature increased. The results indicated that, at a low temperature, the decomposition of biomass was incomplete and left a large amount of unreacted biomass which may suppress the crude bio-oil formation. The rise in temperature was able to accelerate the decomposition of the feedstock and benefited the crude bio-oil formation; however, a further increase in temperature, higher than 275 °C in our experiments, would break down the previously formed crude bio-oil/intermediates to smaller molecules (WSP and GP), and thus led to a decrease in the crude bio-oil yield. GPC analyses showed that the relative molecular mass of the crude bio-oil decreased remarkably from 769 g·mol⁻¹ to 479 g·mol⁻¹ with increasing temperature, suggesting that the HTL reaction was a thermally-controlled process and the high temperature would decompose biomass to products with a low relative molecular mass. The reducing yield of the SR suggested an increase of the overall biomass conversion when increasing the temperature from 200 °C to 300 °C. As for the yield of the WSP and GP, they showed an initially decreasing and then increasing trend in the temperature range of 200 °C to 300 °C. At a lower temperature, volatile compounds were readily evaporated and partially dissolved in the water medium, giving a relatively high yield of WSP and GP. As the temperature increased, these components may react with the decomposed biomass to form oil compounds through a series of reactions such as condensation, polymerization and depolymerisation etc., thus the fraction of WPS product decreased. When temperature was higher than 275 °C, the oil product was secondarily cracked into lighter products and resulted in an increasing in the WSP yield. In addition, the Bourdar gas reaction might become more active at the higher temperatures and lead to the formation of more gaseous products and less crude bio-oil [56]. These results are consistent with the research reported in the literature [29, 31, 33, 40, and 49]. For example, Akhtar and Amin [49] stated that the temperature was one of the most important factors influencing the biomass liquefaction and a moderate temperature (from 250 °C to 300°C) generally yielded a higher amount of crude bio-oil.

Xu and Lancaster [40] also suggested that the temperature was the most critical parameter in the overall biomass conversion in the HTL process.

Under our experimental conditions, 275 °C was identified to be the most suitable temperature for the SCG liquefaction, producing the highest bio-oil yield of 35.29 % in the hot-compressed water with the retention time of 10 min and the water/feedstock mass ratio of 5:1.

[Here] **Fig. 2.** Yields of bio-oil, solid residue, WSP, and gas from the liquefaction at various reaction temperatures (retention time of 10 min and water/feedstock mass ratio of 5:1 with 2.0 MPa initial N₂ pressure).

3.3 Effect of water/feedstock mass ratio

The effects of different water/feedstock mass ratios (5:1, 10:1, 15:1 and 20:1) were also investigated in HTL of SCG under the reaction condition of 275 °C, 10 min with 2.0 MPa initial N₂ pressure. **Fig. 3** clearly illustrated that larger mass ratios of water to SCG had positive impacts on the crude bio-oil yield and total biomass conversion rate. As the mass ratio of water/SCG increased from 5:1 to 20:1, the corresponding crude bio-oil yield increased from 35.29 % to 47.28 % and the solid residue reduced from 31.34 % to 17.33 %.

Similar results were also observed in other studies showing that higher mass ratio of water/feedstock resulted in higher yield of crude bio-oil and lower solid residues [27, 28, 33, 34, and 36]. A generally accepted explanation for this observation is that a lower oil yield at a lower solvent/biomass ratio was caused by an insufficient mixing of reactants due to a limited amount of water. This would lead to unfavourable heat/mass transfer conditions inside the reactor, and hence, slow down the liquefaction process and solvolysis reaction, and finally generate less bio-oil and more solid residues [41]. On the contrary, higher water concentration would prevail throughout the whole process, which might accelerate the solvolysis, hydration, and hydrolysis reaction of the raw material and finally result in an increased yield of crude bio-oil and also achieved a higher biomass conversion [27, 40]. However, high mass ratio of water/feedstock, implying a low process capacity, is economically unfavorable. In real application, a good balance should be struck taking oil yield/batch, overall processing capacity and operating costs into consideration.

Based on above experimental results obtained in our work, the highest crude bio-oil yield of 47.28 % was achieved under the reaction condition of 275 °C, 10 min and 20:1 water/feedstock mass ratio, when the initial N₂ pressure was 2.0 MPa.

[Here] Fig. 3. Yields of bio-oil, solid residue, WSP, and gas from the liquefaction with various water/feedstock mass ratios (retention time of 10 min and temperature of 275°C with 2.0 MPa initial N₂ pressure).

3.4 Effect of N₂ initial pressure

Nitrogen was used as a process gas in this study and was believed to be inactive in the HTL of SCG, considering the reaction temperature, retention time and water/feedstock mass ratio involved. When lowered the initial pressure from 2.0 MPa to 0.5 MPa under the reaction condition of 275 °C, 10 min and 20:1 of water/feedstock mass ratio, the yields of crude bio-oil, WSP + gas and SR were 44.33 %, 38.08 % and 17.59 %, respectively. The standard deviations of the product yields between 0.5 and 2.0 MPa initial pressure were all below 2 %, indicating that the change of initial pressure had very little impact on the products distribution. The final pressures after heating under both conditions were close to 6.0 MPa, also suggesting the little effect of initial pressure on the HTL of SCG. The possible reason could be that more water in the reactor evaporated at low temperature, which led to the increase of the final pressure. However, it took a longer time for the reactor to reach the desired temperature when decreased the initial pressure. This also agrees with the results of studies from Yu, et al. [57] and Goudriaan and Peferoen [26], in which the elevated initial pressure had no effect on HTL of biomass but only prevent the water from boiling so that the reaction will take place in single-phase and avoid large heat supply and longer heating time for maintaining the temperature of the system.

3.5 Bio-oil characterizations

In addition to the yield, the properties of the resulting bio-oil are also important in this work. The crude bio-oil obtained under conditions of the reaction temperature 275 °C, reaction time of 10 min, water/feedstock mass ratio of 20:1 and 2.0 MPa of initial N₂ pressure, was characterized as a representative and reported in the following sections.

3.5.1 Properties of the resulting crude bio-oil

The crude bio-oil obtained from the HTL process of SCG were coffee-brown, viscous and possessed a coffee-aromatic odor with a water content of 2.1 % and pH of 4.8. The elemental composition (C, H and N) of the raw material and the representative crude bio-oil product was determined by an elemental analyzer and presented in Table 1. The results showed that the SCG crude bio-oil contained a higher content of carbon and a less oxygen content than those of the raw materials. The oxygen content of SCG was greatly reduced from approximately 40 % down to 19 % mass fraction, and the O/C molar ratio dropped from 0.6 to 0.2. This was expected since the oxygen was removed in the form of CO or CO₂ through decarbonylation reaction and decarboxylation reaction, respectively, in the process of liquefaction. This resulted in a significant increase in the higher heating value, as presented in Table 1, in which the HHV of the bio-oil was 31.0 MJ·kg⁻¹, much higher than that of SCG (20.2 MJ·kg⁻¹). Additionally, the energy recovery of the resulting oil at such conditions was fairly high with a value of 72.6 %, indicating that a large percentage of the energy in the feedstock was recovered in the oil phase. It was thus concluded that HTL is a suitable technology to convert SCG to a more energy-rich bio-oil with the potential to be used as a renewable energy source.

[Here] Table 1. Elemental analyses of SCG and crude bio-oil under the reaction condition of 275 °C, 10 min, 20:1 water/feedstock mass ratio with 2.0 MPa initial N₂ pressure.

3.5.2 GC-MS

The chemical composition of the crude bio-oil derived from SCG was further identified by a GC-MS analysis. Table 2 illustrates the major compounds in the SCG-derived crude bio-oil under the liquefaction condition of 275 °C, 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N₂ pressure. The area % was defined by the percentage of the chromatographic area of each compound out of the total area. They showed the relative concentration of each compound in the derived crude bio-oil. It should be noted that only volatile compounds in the crude bio-oil passing through the GC column were identified and reported here. According to the results given by GC-MS, the main volatile chemical components in the crude bio-oil were C₁₆ – C₁₈ aliphatic acids with long carbon chain hydrocarbons (96 %), including 48.15 % of n-hexadecanoic acid, 32.99 % of 9,12-octadecadienoic acid (Z,Z)-, 15.46 % of octadecanoic acid

and a small amount of C₂₀ aliphatic acids (eicosanoic acid). They were mainly derived from the decomposition and re-polymerization of lipids in the raw materials. Little amounts of C₂₅ esters were also detected, which were from the carbohydrates in the feedstock. The similar carboxylic acids components of the crude bio-oil were also observed in the bio-oils derived from other lipids/protein containing feedstock, such as *Litsea cubeba* seed and swine manure [36, 51].

[Here] Table 2 Major compounds in the crude bio-oil derived from SCG liquefaction (temperature of 275 °C, retention time of 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N₂ pressure).

3.5.3 FT-IR Analysis

FTIR spectra for SCG and the crude bio-oil derived from SCG liquefaction under the liquefaction conditions of 275 °C, 10 min, water/feedstock mass ratio of 20:1 with 2.0 MPa initial N₂ pressure are illustrated in Fig. . Similar functional groups presented in both the SCG and crude bio-oil. A broad absorbance was displayed at around 3400 cm⁻¹ for the raw material, which indicated a high content of carbohydrates and proteins [51]. The crude bio-oil showed a weaker absorbance at the wavenumber of 3400 cm⁻¹, suggesting that both carbohydrates and proteins were decomposed in HTL process. Absorption between 2700 cm⁻¹ and 3000 cm⁻¹ was ascribed to O-H stretching vibration and the bond of O-H, mainly from long-chain carboxylic acids in the bio-oil. The absorption peaks between 1650–1750 cm⁻¹ were attributed to the C=O stretching from carboxylic acids and ester groups in the crude bio-oil. A weaker absorbance in this wavenumber range was also observed for the raw material, indicating that more carboxylic acid groups were formed during HTL process. The bands from 1350 cm⁻¹ to 1470 cm⁻¹ were ascribed to C-H bending, which indicated alkyl groups in the obtained oil. Absorption between 1020 cm⁻¹ and 1340 cm⁻¹ was attributed to C–N bands, most likely showing the presence of amines groups which might be in non-volatile compounds thus were not detected by GC-MS. Meanwhile, the absorption profiles between 670 cm⁻¹ and 870 cm⁻¹ implied the presence of phenyl rings and substituted phenyl rings [27]. The bond at 1050 cm⁻¹ only appeared in the

absorption profile of SCG, which could be C–O connected with hydroxyl groups and were dehydrated after liquefaction.

[Here] Fig. 4. FTIR spectrum of SCG and the crude bio-oil derived from SCG liquefaction (temperature of 275 °C, retention time of 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N₂ pressure).

3.6 Comparison with the relevant studies

A variety of low value biomass have been investigated as feedstock for the crude bio-oil production via HTL, including agricultural and forest residues, food-processing waste, animal manure and municipal solid waste (MSW), etc. Our present study was a first attempt to produce the crude bio-oil from SCG, therefore, it is necessary to compare the results obtained with other studies in this field to evaluate the feasibility and the promise of SCG liquefaction. It is important to point out that this comparison is a generally qualitative comparison, as each feedstock was liquefied under different conditions as reported in the literature. We made our best effort to select the cases in which liquefaction conditions were close to our experimental conditions (water as a medium and in nitrogen atmosphere without any catalysts application).

Table 3 provides the properties of bio-oils derived from the HTL of SCG and other representative biomass. In general, the crude bio-oil derived from SCG liquefaction has a much higher yield (47.28 %) and a slightly lower HHV(31.0 MJ·kg⁻¹), compared to the crude bio-oils derived from lignocellulose-based biomass such as Jack pine wood sawdust, corn stalk, tea waste, and pulp/paper sludge. However, the reaction condition employed in the HTL of SCG is milder or more favorable than the HTL of lignocellulose biomass, for example, a lower temperature and a shorter retention time. In terms of the composition, the crude bio-oil from SCG is composed of long-chain carboxylic acids. No phenolic compounds were detected, which is very different from the crude bio-oils generated from other lignocellulose feedstock. This may be attributed to a low lignin content in the SCG and various liquefaction conditions. Microalgae and oilseeds demonstrated themselves as excellent feedstocks for the HTL process. As shown in **Table 3**, microalgae, *Nannochloropsis sp*, was liquefied at 350 °C, giving a fairly high yield of the crude bio-oil (43.0 %) and a HHV of 39.0 MJ·kg⁻¹. HTL of *Litsea cubeba* seed achieved an even

higher yield of the oil product (56.9 %) with a HHV value of 40.8 MJ·kg⁻¹, both of which are much higher than those of the crude bio-oil from SCG liquefaction (oil yield of 47.3 %, HHV of 31.0 MJ·kg⁻¹). This is not surprising because *Nannochloropsis sp.* and *Litsea cubeba* seed contains high contents of lipid (28.0 % and 41.0 %, respectively) and protein (52.0 % and 35.0 %, respectively), which was believed to be able to enhance the crude bio-oil yield in the HTL processes [44-48,51,52]. However, high lipid content materials can be converted into biodiesel comparable to petro-diesel, through a process known as transesterification, less costly than HTL. More concerning, the cultivation of algae and *Litsea cubeba* requires additional energy inputs. On the contrary, SCG, a waste stream does not require extra energy for the feedstock plantation. The above comparison suggests that SCG can become a promising feedstock for HTL. The yield of crude bio-oil from HTL of SCG is much higher than those of lignocellulose feedstock and its HHV is comparable or slightly lower than that of lignocellulose feedstock. However, SCG bio-oil is still not competitive to the bio-oils derived from the protein/lipid rich biomass such as microalgae and oilseeds in terms of yield and higher heating value.

[Here] Table 3 Properties of crude bio-oils derived from HTL of SCG and other biomass.

Alternatively, other processing methods such as lipid extraction and fast pyrolysis have also been exploited to utilize SCG for the liquid fuel production. Thus, it is worthwhile to compare the HTL with other pathways. Table 4 presents the properties of the oil derived from SCG by using HTL, fast pyrolysis and solvent extraction, respectively. Compared to the fast pyrolysis oil, the crude bio-oil obtained from the HTL process has a higher content of carbon and hydrogen while a lower content of water and oxygen, consequently an oil product with a higher HHV. It is concluded that the HTL can provide a larger capability of water and oxygen removal and a more hydrophobic bio-oil product with a lower acidity than fast pyrolysis, while the fast pyrolysis is able to obtain a higher yield of the crude bio-oil (54.9 %) than HTL (47.3 %). However, achieving such a high oil yield requires a high temperature (> 500 °C). More importantly, HTL is advantageous over the fast pyrolysis in that it can utilize feedstock with any moisture level without any pre-drying processes. Compared to the coffee oil extraction for biodiesel production with a yield of 15.0 %, HTL produced a higher yield of oil product. It not only can “extract” lipid content but also generate oil from other components such as carbohydrate and

protein in SCG. The comparison indicates HTL to be a more suitable technology to produce liquid fuels from SCG.

[Here] Table 4 Properties of oil products derived from SCG.

4. Conclusions

HTL was identified to be a promising technology for the crude bio-oil production from SCG. The preferable liquefaction conditions were determined as: the reaction temperature of 275 °C, retention time of 10 min and water/feedstock mass ratio of 20:1. Under such reaction conditions, the highest crude bio-oil yield of 47.3 % mass fraction was achieved with a higher heating value (HHV) of 31.0 MJ·kg⁻¹, much higher than that of SCG which was only 20.2 MJ·kg⁻¹. The energy recovery percentage was 72.6%. This work is an attempt to utilize the waste stream from the coffee industries for the bio-oil production via HTL. More research is needed and recommended, including the liquefaction process conducted in other solvents or co-solvents, and the investigation on the effects of catalysts on the yield and composition of the resulting bio-oil.

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634 **Table 1.** Elemental analyses of SCG and crude bio-oil under the reaction condition of 275 °C, 10
635 min, 20:1 water/feedstock mass ratio with 2.0 MPa initial N₂ pressure.
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Sample	Elemental compositions, %				HHV ^b (MJ·kg ⁻¹)	H/C (molar ratio)	O/C (molar ratio)	Energy Recovery ^c (%)
	C	H	N	O ^a				
Spent coffee grounds ^d	50.4	7.2	2.1	40.3	20.2	1.7	0.6	
Crude bio-oil (W/F mass ratio = 1:20; 275 °C; 10min)	71.2	7.1	3.0	18.7	31.0	1.2	0.2	72.6

^a by mass difference; ^b Higher heating value calculated by the Dulong formula: $\text{HHV (MJ}\cdot\text{kg}^{-1}) = 0.3383C + 1.442 (H-(O/8))$; ^c $\text{Energy recovery (\%)} = \frac{\text{HHV of crude bio-oil} \times \text{mass of crude bio-oil}}{\text{HHV of SCG} \times \text{mass of SCG}} \times 100$. ^d On a dry basis.

Table 2. Major compounds in the crude bio-oil derived from SCG liquefaction (temperature of 275 °C, retention time of 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N₂ pressure).

Peak	RT (min)	Compound name	Formula	Area %
1	11.5066	n-Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	48.15
2	12.4227	Octadecanoic acid	C ₁₈ H ₃₆ O ₂	15.46
3	12.4863	9,12-Octadecadienoic acid (Z,Z)-	C ₁₈ H ₃₂ O ₂	34.43
4	13.2816	Eicosanoic acid	C ₂₀ H ₄₀ O ₂	1.58
5	15.2665	Octanoic acid, heptadecyl ester	C ₂₅ H ₅₀ O ₂	0.38
Total area %				100.0

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Table 3. Properties of crude bio-oils derived from HTL of SCG and other biomass.

Feedstock	Liquefaction conditions	C%	H%	O%	N%	HHV (MJ·kg ⁻¹)	Max Oil yield (% mass fraction)	Main product distribution from GC-MS analysis	Reference
SCG	275°C, 10 min, N ₂	71.2	7.12	18.7	2.95	31.0	47.3	Long chain carboxylic acids	In this study
Jack pine wood sawdust	340°C, 30 min, N ₂	76.3	6.7	17.1	0.0	32.3	36.0	Phenolic compounds, carboxylic acids/esters	[29]
Tea waste	377°C, 25 min, - ^a	71.6	5.6	22.8	0.0	33.6	22.6	-	[50]
Corn stalk	380°C, 30 min, N ₂	77.8	6.9	14.9	0.0	33.5	36.0	-	[32]
Swine manure	340°C, 15 min, N ₂	72.6	9.76	13.2	4.5	36.1	24.2	Aromatic hydrocarbons, phenol, carboxylic acids, alkenes, nitrogenous compounds	[36]
Pulp/paper sludge powder	280°C, 60 min, N ₂	75.5	8.5	12.1	3.9	35.4	20.3	Carboxylic acids, heterocyclic nitrogen compounds, phenolic compounds	[40]
Microalgae (<i>Nannochloropsis sp.</i>)	350°C, 60 min, He	76.0	10.3	9.0	3.9	39.0	43.0	Phenol, N-containing compounds, long-chain fatty acids, alkanes and alkenes	[41]
<i>Litsea cubeba</i>	290°C, 60	76.2	11.9	10.4	3.9	40.8	56.9	Toluene, fatty acids	[51]

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and their derives

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^a not detected or provided

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Table 4 Properties of oil products derived from SCG.

Oil products from SCG	C%	H%	O%	N%	O/C	HHV (MJ·kg ⁻¹)	Max Oil yield (% mass fraction)	Water content (%)	pH	Ref.
Crude bio-oil obtained in this study	71.2	7.1	18.7	3.0	0.2	31.0	47.3	2.1	4.8	Current research
Fast pyrolysis oil	54.3	7.4	35.3	3.1	0.4	20.4	54.9	31.1	3.1	[19]
Biodiesel	- ^a	-	-	-	-	-	15.0	-	-	[12]

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^a

not

detected

or

provided

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Fig. 1. Yields of bio-oil, solid residue, WSP, and gas under different retention time (temperature of 300 °C and water/feedstock mass ratio of 5:1 with 2.0 MPa initial N₂ pressure).

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Fig. 4. FTIR spectrum of SCG and the crude bio-oil derived from SCG liquefaction (temperature of 275 °C, retention time of 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N_2 pressure).