HYDROTHERMAL LIQUEFACTION OF SPENT COFFEE GROUNDS FOR CRUDE BIO-OIL PRODUCTION

by

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Abstract

The extensive use of fossil fuels has intensified the energy crisis over the recent years and caused series of environmental issues. Biofuels are renewable and carbon-neutral, thus have gained increasing attention and are becoming an irreplaceable proportion in the section of renewable energy. Hydrothermal liquefaction (HTL) is a promising technology that can not only convert wet biomasses to biofuels (crude bio-oil) but also provide a potential pathway to deal with the bio-waste streams.

The first portion of this research is to investigate the HTL of spent coffee grounds (SCG) in subcritical water for crude bio-oil production. The batch-scale experiments were conducted in a 100 cm^3 stainless-steel autoclave reactor in N_2 atmosphere. The effects of operating parameters, e.g., reaction times (varied from 5 min to 25 min), reaction temperatures (varied from 200 °C to 300°C), 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, were investigated. The highest yield of the crude bio-oil (47.3 % mass fraction) was obtained at conditions of 275 °C, reaction time of 10 min 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 $MJ \cdot kg^{-1}$, much higher than that of the raw material (20.2 $MJ \cdot kg^{-1}$). GC-MS and FT-IR measurements showed that the main volatile compounds in the crude bio-oil were long chain aliphatic acids and esters.

In the second part of this research, spent K-Cups were liquefied into crude bio-oil in a water-ethanol co-solvent mixture and reaction conditions were optimized using response surface methodology (RSM) with a central composite design (CCD). The effects of three independent variables on the yield of crude bio-oil were examined, including the reaction temperature (varied from 255 °C to 350 °C), reaction time (varied from 0 min to 25 min) and solvent/feedstock mass ratio (varied from 2:1 to 12:1). The optimum reaction conditions identified were 276 °C, 3 min, and solvent/feedstock mass ratio of 11:1, giving a mass fraction yield of crude bio-oil of 60.0 %. The overall carbon recovery at the optimum conditions was 93 % in mass fraction. The effects of catalyst addition (sodium hydroxide NaOH and sulfuric acids H_2SO_4) on the yield of crude bio-oil were also investigated under the optimized reaction conditions.

The last portion of this research is to study co-liquefaction of SCG with other lignocellulose biomasses, including paper filter (PF), corn stalk (CS) and white pine bark (WPB), in subcritical water for crude bio-oil production. The effects of reaction temperature (varied from 225 °C to 325 °C) on the product distributions were investigated, aiming to maximize the crude bio-oil yield. The highest crude bio-oil yield was obtained at the reaction temperature of 250 °C when the feedstock combination mass ratio was fixed at 50 % SCG with 50 % the others. The addition of catalyst (5 % of sodium hydroxide NaOH) and various feedstock combination mass ratios were also tested at 250 °C. The results showed that synergistic effects occurred in the co-liquefaction process of these feedstocks with the addition of 5 % NaOH in terms of the crude bio-oil yield. The measurements of elemental analysis, GC-MS, GPC and viscometer revealed that positive synergistic effects appeared in their co-liquefaction process by improving the oil quality.

List of Abbreviations Used

HTL	hydrothermal liquefaction
GHG	greenhouse gas emission
PERC	Pittsburgh Energy Research Center
MSW	municipal solid waste
H^+	hydroxyl/hydrogen cations
OH^-	hydronium/hydroxide anions
Oil	crude bio-oil
SR	solid residue
WSP	water soluble product
VM	volatile matter
TOC	total organic carbon
GP	gas product
CO	carbon monoxide
Na_2CO_3	sodium carbonate
NaOH	sodium hydroxide
KOH	potassium hydroxide
H_2SO_4	sulfuric acid
THF	tetrahydrofuran
SCG	spent coffee grounds
PF	paper filter
Al	aluminum foil lid
PC	plastic container
PS	plastic seat
CS	corn stalk
WPB	white pine bark
RSM	response surface methodology
CCD	central composite design
ANOVA	analysis of variance
SE	synergistic effect
GC-MS	gas chromatography/mass spectrometry
TGA	thermogravimetric analysis
DTG	differential thermogravimetry
FTIR	Fourier transform infrared
GPC	gel permeation chromatography
dab	dry ash free basis
Y_{oil}	yield of crude bio-oil
Y_{solid}	yield of solid residues
$Y_{\mathrm{gas+WSP}}$	yield of combined gas and water soluble products
M_{n}	relative molecular mass (number average)
M_{w}	relative molecular mass (weight/mass average)
PDI	polydispersity index
dab	dry and ash free basis

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Chapter 1: Introduction

1.1 Motivation

1.1.1 Energy Crisis and Environmental Issues

In today's global energy market, fossil fuels account for ~ 80 % of the primary energy consumption and the transport sector alone takes up ~ 58 % of it (IEA, 2006). Fossil fuels, mainly including crude oil, coal and natural gas, are non-renewable resources and have been rapidly depleting (Zhao., et al., 2009). The extensive use of fossil fuel is one of the major contributors to the greenhouse gas (GHG) emissions and has caused many environmental impacts (Gullison., et al., 2007). The limited fossil resources, along with the related environmental concerns has necessarily called for renewable and sustainable energy source alternatives (Singh, et al., 2010; Prasad, et al., 2007; Nigam & Singh., 2011). Renewable energy generated from natural resources, e.g., solar, wind, biomass, hydro, geothermal, etc. has been gradually rising and developing in the past 100 years. However, most of these natural resources are only able to produce electricity while the currently available transportation infrastructure needs tremendous amounts of liquid fuels. Therefore, generating liquid biofuels from biomass has sparked the interest worldwide as they are renewable, sustainable and carbon-neutral (Bhatti, et al., 2008). In addition, biomass feedstocks are also geographically wider distributed than fossil fuels or nuclear resources, and the produced biofuels/bio-energy could thus provide a secure, independent and localized energy supply (Nigam & Singh, 2011).

1.1.2 Waste Streams for Biofuels Production

Today, the major viable commercial options for liquid biofuel production are biodiesel and bioethanol, which are derived from edible crops, e.g., corn and wheat. However, the competition between food, feed and fuels production has intensified constantly. The bio-waste streams, e.g., agricultural waste and residues, food-processing waste, forest residues, and municipal solid waste (MSW), etc., are therefore being extensively researched and showing great potential as promising feedstocks for biofuels production. Converting bio-waste streams into biofuels can also bring a number of benefits to human society and activities, such as reducing local pollution and GHG emissions, saving cost for feedstocks purchase and providing steady incomes for crop producers and agricultural products' manufacturers (when using agricultural waste and residues) (Peterson, et al., 2008; Delfort, et al., 2008; Nigam & Singh., 2011).

1.1.3 Hydrothermal Liquefaction (HTL) for Liquid Biofuels Production

Converting bio-waste to applicable biofuels is challenging and requires high-level technologies. Currently, different thermochemical conversion processes such as combustion, pyrolysis, liquefaction and gasification, have been applied to convert biomasses into various energy products (e.g., syngas and biofuels) (Goyal, et al., 2006). Among these processes, hydrothermal liquefaction (HTL) is an emerging technology that can convert high-moisture biomasses into liquid fuels and chemicals (Cantrell, et al., 2007). It is a thermochemical conversion process using high pressure and moderate temperature in sub-/supercritical water medium (near 374 °C and 22 MPa) to break down and reform the solid bio-polymeric structure of the biomasses into biofuels (the liquid fraction, hereafter referred to as crude bio-oil) (Brown, 2011; Peterson, et al., 2008). The crude bio-oil derived from HTL of biomasses can be mixed with other fuels for combustion or be further upgraded to liquid fuels comparable to petro-fuels (e.g., gasoline and diesel) (Dote, et al., 1991; Elliott, 2007; Duan and Savage, 2011a).

The HTL process has tremendous advantages over other biofuel production technologies. 1) The high water content in most biomass feedstocks, e.g., agricultural waste, forest residues and municipal sludge, has to be removed by a pre-drying process during thermochemical processes, e.g., combustion, gasification and pyrolysis, etc. However, the water drying process requires large energy consumption and increases the operational cost. The HTL is carried out in water environment and does not require a preliminary drying process (Peterson, et al., 2008), which can thus lessen the capital cost and increase the overall economic viability (Brown, 2011). 2) Fossil fuels typically have trace amounts of oxygen (under 1 % volume fraction) while the biomasses often contain 40 % to 60 % volume fraction. Removing oxygen is thus one of the important objectives of the biofuels production (Peterson, et al., 2008). The HTL has a higher oxygen removal capability compared to other thermochemical technologies, and thus, the resulting biofuels could have an increased energy content (Tekin & Karagöz, 2013; Peterson, et al., 2008). 3) For the feedstocks containing inorganic materials, e.g., nitrates, phosphates, and sulfates, the

HTL process can assist in the recycling and recovery of the inorganic chemicals in their ionic forms, which can be further used in fertilizer production (Peterson, et al., 2008). 4) In addition, the high-pressure and temperature environment in the HTL process can provide a complete sterilization process, which can destructively hydrolyze the possible pathogens, e.g., bacteria, bio-toxins, and viruses in the product streams (Peterson, et al., 2008).

Although the HTL process enables to convert a wide range of wet biomass feedstocks into a substitute for the existing petro-fuels, this technology is mainly practiced at laboratory scales with very limited commercialization to date (Pavlovic, et al., 2013). This is mainly due to the high pressure needed for the hydrothermal processing that requires special reaction and separation operations, plus the high capital investments for the construction of the full-scale plants (Peterson, et al., 2008). The challenges of processing real waste biomasses, including feedstocks delivery, catalyst deactivation and heat exchange, also need to be addressed (Pavlovic, et al., 2013). In addition, the quality of the resulting crude bio-oils needs to be improved significantly. Petroleum oil is a mixture of liquid hydrocarbons that occur naturally beneath the earth's surface (Petroleum Geology. Org., 2014). In contrast, the crude bio-oils derived from the HTL has high heteroatom contents, primarily in the form of nitrogenous and oxygenated compounds, e.g., carbonyl compounds, phenols, guaiacols, syringols, furans and nitrogen compounds (Huber, et al., 2006; Peterson, et al., 2008; Demirbas, 2009). These components result in some undesirable fuel properties, e.g., high viscosity, oil acidity and oil structures un-stability, etc. (Adjaye, et al., 1992; Speight, 2001), which have limited the direct application of these oil products.

One of the other difficulties hindering the commercialization of crude bio-oil production via HTL is the low yield of the resulting oil product, which reduces the HTL efficiency. Numerous research has been conducted to investigate the crude bio-oil production from a variety of biomasses, including agricultural and forest residues, animal waste, algae and municipal solid waste (MSW) (Akhtar & Amin, 2011). The yield of the resulting oil product in mass fraction was found to be highly associated with operating parameters (e.g., reaction temperature, reaction time, solvent/feedstock mass ratios, etc.), and more importantly to be affected by the chemical compositions of the feedstocks (e.g., content of cellulose, hemicellulose, lignin, lipid and protein). High-lignin content in feedstocks, such as woody biomasses and agricultural waste, were demonstrated to be un-desirable for the crude bio-oil production. In contrast, the feedstocks contained high-lipid and protein, e.g., algae, were reported to have a positive impact on the yield of the crude bio-oil in mass fraction. However, the correlation between the chemical compositions of feedstock and the yield/quality of the crude bio-oil are not established, and the underlying reaction mechanism and pathways in the process of HTL is still not fully characterized or well understood. The most suitable feedstocks for HTL crude bio-oil production are still under exploration. Co-liquefaction of various types of feedstock mixtures is an emerging research area developed in the past 10 years, which has potential for reducing transportation costs and improving the yield/quality of the crude bio-oil through synergetic effects between different feedstocks (Chen, et al., 2014). For example, the addition of plastic waste or high-lipid/protein materials is reported to have the positive effect on the HTL of lignocellulose biomasses, improving the oil yield and oil quality (Gai, et al., 2015; Wang, et al., 2013). However, the relevant studies focusing on the co-liquefaction of mixed feedstocks are very limited and more research is highly required.

Spent coffee grounds (SCG) are the solid waste generated from coffee brewing process. According to the record released from International Coffee Organization (ICO, 2015), about 9.6 million tons of coffee were produced in 2013/14 worldwide, and 8.6 million tons of SCG were generated accordingly then treated as a waste stream without any commercial value (Kondamudi, et al., 2008). It is essential to develop effective, efficient and economic pathways to utilize such abundant biomass. The HTL shows its great advantages in processing wet biomasses into crude bio-oil, which seems to be a promising solution for handling this high-moisture organic waste. One the other hand, SCG have higher content of lipids/fatty acids while lower content of lignin, compared to lignocellulose biomasses (Mussatto, et al., 2011; Kondamudi, et al., 2008; Ballesteros, et al., 2014). It could be a suitable feedstock for crude bio-oil production via HTL and/or could be co-liquefied with other waste materials to improve the yield and quality of the oil products.

1.2 Research Objectives

This research is focused on the evaluation of spent coffee grounds (SCG) as a new feedstock for crude bio-oil production and the exploration of co-liquefaction of SCG with other feedstocks, aiming to maximize the yield of crude bio-oil resulted from the HTL process through optimizing the reaction parameters. The specific research objectives include:

1. To identify spent coffee grounds (SCG) as a renewable feedstock for crude bio-oil

production via HTL, and to optimize the reaction parameters for maximizing the crude bio-oil yield.

2. To investigate the direct liquefaction of spent K-Cups, consisting SCG and plastic waste as the main components, for crude bio-oil production.

3. To explore the potential of co-liquefaction of SCG with other lignocellulose feedstocks from waste streams, expecting to promote the crude bio-oil production by the possible synergistic effect between SCG and the other biomasses on the oil yield and oil quality.

1.3 Thesis Organization

Chapter 2 provides a literature review of the contents relevant to this research, including fundamentals of HTL, historical development of HTL, and the effects of reaction parameters and feedstock chemical compositions on the HTL products, as well as the HTL of single and mixed feedstocks. Chapter 3 contains a description of the methods used in this study, including the batch-scale HTL experiment, product separation procedure, feedstock and product characterization and data analysis methods throughout this research. Chapter 4 presents the results of a study that investigated the potential of SCG as a suitable feedstock for crude bio-oil production via HTL. Chapter 5 presents the results of the reaction parameters optimization in spent K-Cups liquefaction for maximizing crude bio-oil yield and the impact of catalyst on the liquefaction process was discussed. Chapter 6 explores the synergistic effect between SCG and other lignocellulose feedstocks in a co-liquefaction process on the crude bio-oil yield and quality. Chapter 7 provides the overall conclusion of this study and gives recommendations for the future work.

Chapter 2: Literature Review

2.1 Fundamentals of the HTL

2.1.1 Properties of Water at Sub- and Supercritical Conditions

Hydrothermal processing of biomasses in hot-compressed water medium is able to facilitate the decomposition of the organic molecular of biomasses and re-polymerize the biomasses fragments into biofuels and bio-chemicals (Beherent, et al., 2008; Elliot, 2007). It is carried out near or above the critical point of water (temperature of 374 °C, pressure of 22 MPa). Depending on the temperature and pressure, there are three main regions in the hydrothermal processing, including liquefaction, catalytic gasification and high-temperature gasification, which are described in pressure-temperature phase diagram for pure water and presented in Fig. 2.1. In a close system, water stays in liquid phase as the temperature increases from 0 °C to 100 °C (boiling point). When the temperature increases to or near 374 °C (critical point), the liquid and vapor states of water co-exist in the system and continuously transform within two states. Liquefaction occurs generally at the temperature ranged from 250 °C to 374 °C, with the pressure ranged from 5 MPa to 22 MPa in subcritical condition. In the region of liquefaction near critical point, water is highly compressed and is kept sufficiently in a liquid state. As the temperature and pressure increases to over the critical point (374 °C, 22 MPa), gasification occurs and becomes the dominating process, maintaining the water in a vapor state in supercritical condition (Peterson, et al., 2008). In this study, liquid biofuel (crude bio-oil) is the target product, the required processing condition is therefore in the region of liquefaction, where maintains the liquid water in the processing medium, at the temperature of 250 °C to 374 °C, with the pressure of 0 MPa to 22 MPa.

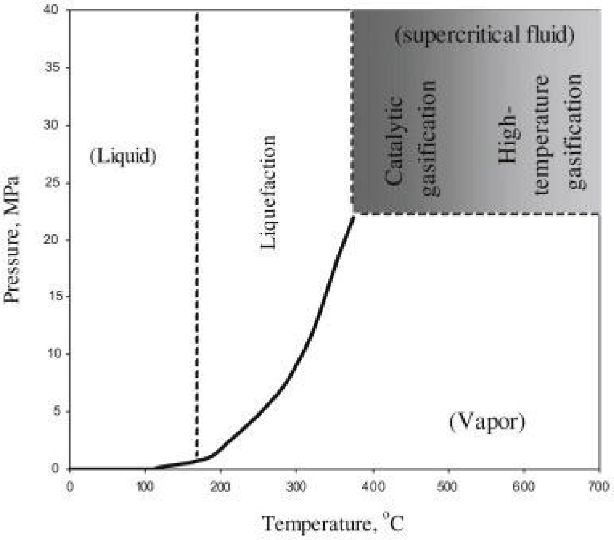


Fig. 2.1 Pressure-temperature phase diagram of water (Peterson, et al., 2008).

Water has interesting properties at the conditions near its critical points. The liquid water is an ionic reaction medium and its ionic product in subcritical range is relatively higher than that in the ambient condition (e.g., at room temperature and pressure). The ionisable compounds of liquid water will be presented as ions, including hydroxyl (H^+) and hydronium (OH^-), which is able to react via ionic mechanisms. The organic molecules in the biomass components are unreactive in the liquid water at ambient temperature and pressure, while are found to undergo chemical reactions (e.g., hydrolysis) and interact with ionic water when the temperature increases to or near the critical point (Peterson, et al., 2008).

2.1.2 Product Distribution from the HTL Process

In subcritical water medium, the biomasses/organic wastes with a high moisture content, e.g., agricultural residues, sludge, food-processing waste, etc., can be heat treated directly in the absence of oxygen at 250 °C to 374 °C under pressure up to 22 MPa. The main products of this process are water-insoluble crude bio-oil (Oil) with a relatively high energy density, char or solid residue (SR), water soluble product (WSP) and gaseous product (GP) (can be seen in Fig. 2.2).

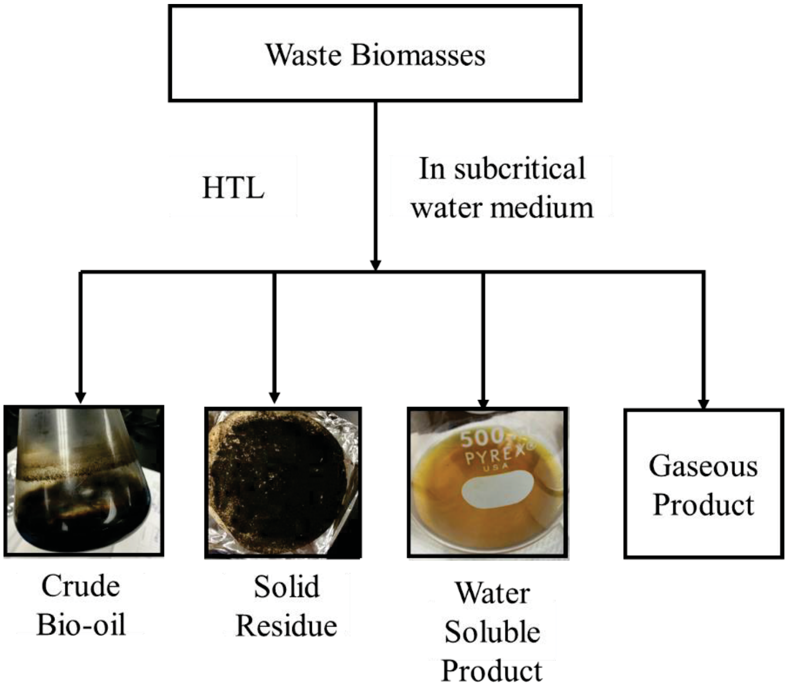


Fig. 2.2 Main products of the HTL process.

2.1.3 Possible Reaction Pathways in the HTL Reactions

During HTL, feedstocks/biomasses undergo a series of complex reactions (thermally and chemically) to form the final products. The basic reaction pathways and mechanism proposed by researchers are summarized as below and described in Fig. 2.3 (Toor, et al., 2011; Theegala & Midgett, 2012; Behrendt, et al., 2008):

1) Hydrolysis or pyrolysis of feedstock/biomasses to monomer/unit structures, e.g., monosaccharides.

2) Decompositions/degradation of the produced monomers to form intermediate products/fragments, e.g., glucose, phenolic compounds, etc. through the reactions of dehydration, dehydrogenation, cleavage, deoxygenation, deamination, decarboxylation, etc.

3) Rearrangement of the reactive intermediates/fragments through re-polymerization, condensation, cyclization, cracking/fragmentation to form final products.

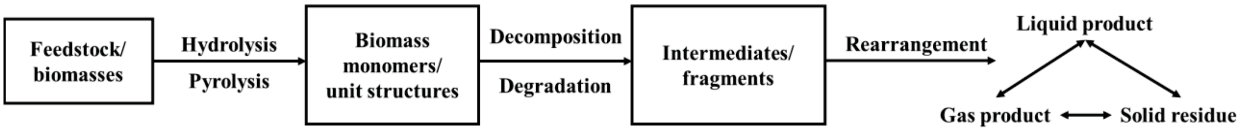


Fig. 2.3 Basic reaction pathways and mechanism of the HTL process.

2.2 Historical Development of HTL

The HTL of biomasses was developed on the basis of the pioneering work carried out at Pittsburgh Energy Research Center (PERC) in the early 70's, and a pilot plant was demonstrated at Albany Biomass Liquefaction Experimental Facility at Albany, Oregon, at a scale of 100 $kg \cdot h^{-1}$ (Behrendt, et al., 2008; Elliott, 2007). In this pilot plant, the woody powder mixed with recycle oil product was liquefied in water medium at temperature of 350 °C in the presence of reducing gas carbon monoxide (CO) and catalyst sodium carbonate (Na_2CO_3), obtaining crude bio-oil product with a relatively low oxygen content of 12 % to 14 % mass fraction. Shortly after that, the Shell Research Laboratory in Amsterdam further made significant progress. Forest residues were converted to heavy liquid oil at temperatures ranging from 300 °C to 350 °C and at pressures of 12 MPa to18 MPa in water medium without using any reducing gases or catalysts. The highest yield of the obtained crude bio-oil was 45 % mass fraction, and a higher heating value (HHV) of 35 $MJ \cdot kg^{-1}$ was achieved (Goudriaan and Peferoen, 1990). Since then, researchers have been working on the crude bio-oil production from the HTL process with a focus on operation optimization, feedstock identification, product characterization and upgrading, as well as the identification of reaction pathway and mechanisms discovering, which will be mentioned in the following sections.

2.3 Effects of Operating Parameters

Products distribution and the oil components are found to be highly influenced by the operating parameters of the HTL process, e.g., reaction temperature, reaction time and solvent to feedstock mass ratio, the addition of catalyst and organic solvents, particle size of raw materials, reducing gas/hydrogen donors etc. (Akhtar and Amin, 2011). This section only reviews the effect of the five major parameters, including reaction temperature, reaction time, solvent to feedstock mass ratio, the addition of catalyst and organic solvents on the HTL process.

2.3.1 Effects of Reaction Temperature

In general, it is accepted that reaction temperature is an important parameter having the most significant impact on the HTL process. When the heat provided by the applied temperature is larger than the activation energies for the bond formation, the organic structures of biomasses start to depolymerize/decompose. The increase of temperature is able to accelerate biomasses decomposition, which will result in a higher concentration of the free radicals in the HTL process and the probability of the biomasses fragments re-polymerization to form HTL products will be also increased (Akhtar and Amin, 2011).

Different reaction temperatures are reported to have significant effect on the product distribution. Sugano, et al., (2008) studied the HTL of plantation biomass with two kinds of wastewater from paper industry under various reaction temperatures and their results showed that the yield of crude bio-oil increased from ~ 7 % to ~ 37 % as the reaction temperature rise from 150 °C to 300 °C. A further increase of temperature to 350 °C resulted in a reduced oil yield. The yield of water soluble product obtained in their study was at an average of ~ 15 % mass fraction while the formation of solid residue decreased constitutionally from ~ 70 % to ~ 13 % as increase of temperature. Moderate temperature is found to yield a higher production of liquid crude bio-oil. The increase of temperature first triggers the crude bio-oil yield, while after reaching the highest oil yield, a further increase of temperature actually suppresses the biomasses liquefaction (Yin, et al., 2010; Sugano, et al., 2008; Xu and Lancaster, 2008). It is believed that very high temperature is not suitable for the liquid oil production in terms of the oil yield and operational cost (Akhtar and Amin, 2011). Part of the reasons is that the secondary de-compositions of oil product would reduce the oil production and the more active Bourdard gas reactions occur at high temperature, which would lead to a higher yield of gas product (El-Rub, et al., 2004). In addition, a rise of temperature could also result in the re-polymerization of the oil fragments to form higher yield of solid residues (Akhtar and Amin, 2011). Moreover, a low reaction temperature (lower than 200 °C) is not sufficient for complete biomasses decomposition that could also suppress the oil formation (Sugano, et al., 2008; Yin et al., 2010; Zhou, et al., 2010). Therefore, the selection of the optimum reaction temperature is essential in the HTL process.

2.3.2 Effects of Reaction Time

The reaction time is another important factor affecting the HTL process by resulting differences in the product distribution and liquefaction efficiency. In general, a shorter reaction time (ranged from 10 min to 30 min) is preferred in the HTL of biomasses to achieve effectively biomass degradation as the rate of decomposition and hydrolysis of biomass is fairly fast in the HTL process (Peterson, et al., 2008; Akhtar and Amin, 2011; Sasaki, et al., 2003). It was reported by the studies of Boocock and Sherman (2009) and Qu, et al., (2003) that a long reaction time suppressed the oil formation while increase the yield of solid residues and thus reduce the liquefaction efficiency. Yuan, et al., (1999) studied the liquefaction of sawdust for biofuels production and a negligible change was observed for the oil yield when a longer reaction time was applied. There may be several reasons to affect the product distribution in the HTL process. In hydrothermal medium, the chemical reactions of the intermediates are always dynamic to either drive the fragments into liquid oil, gas or solid residues (Akhtar and Amin, 2011). As a longer reaction time is applied, the previously formed oils would secondary de-polymerize to form gas and light oil, or re-polymerize to form higher-molecular solid residues (Qu, et al., 2003).

2.3.3 Effects of Solvent/Feedstock Mass Ratio

The solvent/feedstock mass ratio also plays an important role in the HTL of biomasses. It was observed that a high mass ratio of solvent to feedstock resulted in a high yield of crude bio-oil and a low yield of solid residue in mass fraction. Cheng, et al., (2010) liquefied woody biomass (white pine sawdust) in hot-compressed co-solvent of ethanol-water and it was found that an increase of solvent/feedstock mass ratio (up to 10/1) resulted in a higher yield of crude bio-oil and a lower solid residue. It is generally accepted that a higher amount of solvent (or water) would prevail throughout the HTL process and enhance the solubility and stability of the biomass fragments, which could finally lead to a higher formation of oil product and a higher feedstock conversion rate. However, a high solvent/feedstock mass ratio is not economically favorable. In contrast, a low solvent/feedstock mass ratio was reported to promote the dehydration/polymerisation of the intermediates products, which could lead to an increase yield of crude bio-oil. Gan and Yuan (2013) studied the interactive effect of the operating conditions on the HTL of corncob and their results showed that a lower solvent/feedstock mass ratio could result in a higher yield of oil product with a higher carbon recovery.

2.3.4 Effects of Organic Solvent

Water is characterized by high solubility and low viscosity of hydrophobic organic compounds and thus can act as a reactant and catalyst for biomasses conversion. However, the crude bio-oil obtained from the HTL process in only water medium is viscous tarry lump which may cause trouble in handling (Yuan, et al., 2007). Also, compared with the crude oil in the market, the resulting oil products obtained from the HTL of biomasses usually have a high oxygen content and a low carbon content, which result in a lower heating value (HV) (Li, et al., 2009). To enhance the yield of crude bio-oil with a better oil quality, e.g., a lower viscosity and oxygen content, the use of organic solvents, such as ethanol, acetone, methanol and 1,4-dioxane, have been added to the reaction system (Yuan, et al., 2007; Liu, et al., 2013; Li, et al., 2009; Liu and Zhang, 2008; Zhai, et al., 2015). Although water is cheaper and more environmental friendly than organic solvents, its critical value (374 °C, 22 MPa) makes the operative condition of sub-/supercritical liquefaction difficult to achieve. When mixing organic solvent with water, the critical value of the mixture solvent can be reduced and their low dielectric constant helps to readily dissolve the biomasses with high-molecular mass, which makes the liquefaction process occur more effectively within milder reaction conditions (Yuan, et al., 2007; Yamazaki, et al., 2006).

Ethanol is considered one of the most promising organic solvents not only because it is cheap and easily available in industrial production, but also being a renewable source that can be produced from bio-conversion processes from sugars, cereals and lignocellulosic biomass (Sun and Cheng, 2005; Liu and Zhang, 2008). Sub-/supercritical ethanol can also provide an effective hydrogen donor to stabilize the free radicals generated in the liquefaction process, which could help reduce the re-polymerization reaction and improve the crude bio-oil yield (Toshiaki, et al., 1991; Sangon, et al., 2006). Co-solvent of ethanol-water (50/50, v/v) has been confirmed to positively affact the liquefaction process and the crude bio-oil yield was promoted more significantly than that in sole solvent (Liu, et al., 2013).

2.3.5 Effects of Catalysts

2.3.5.1 Effects of Alkaline Catalysts

Catalysts are important in the HTL process and the addition of alkaline or acidic catalysts are found to have remarkable impacts on the products formation (Zhou et al., 2011). Alkaline catalysts, such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and potassium hydroxide (KOH), etc., have been widely employed in the HTL of lignocellulose biomasses for improving the crude bio-oil yield and suppressing the solid residue formation (Xu and Lancaster, 2008; Song, et al., 2004; Karagöz, et al., 2006). Song, et al., (2004) studied the HTL of corn stalk with the addition of 1 % mass fraction of Na_2CO_3 and their results revealed that the yield of crude bio-oil increased from 33.4 % mass fraction to 47.2 % mass fraction as the dosage of catalyst increased. Similarly, K_2CO_3 was also found to have positive effect on the HTL of woody biomasses (sawdust from pine). A higher yield of oil product (increased from 17.8 % to 33.7 %) was achieved with a lower yield of solid residue, suggesting a higher feedstock conversion rate (Karagöz, et al., 2006). However, the mechanism of alkaline catalyst action in the HTL process has not been fully explored. One of the important catalytic action is that alkali materials could accelerate the water-gas-shift reaction in the HTL, where to favor the H_2 and CO_2 formation. The generated H_2 may act as a reducing environment to remove the oxygen in the oil product and promote the heating value (HV) and oil quality (Toor, et al., 2011).

In addition to the products distribution, alkaline catalyst is also reported to favor the lignin decomposition and enable the formation of phenolic compounds. Phenolic compounds are one type of the typical product in the crude bio-oil derived from the HTL of lignocellulosic biomasses. Liu, et al., (2006) investigate the effect of KOH on the HTL of agriculture by-product (walnut shells) at 300 °C and their results showed that the components detected in the resulting oil product were mainly phenols and their derivatives, which were readily derived from lignin in the raw materials.

2.3.5.2 Effects of Acidic Catalysts

The HTL of lignocellulose biomasses with a high cellulose content can be acid-catalyzed (Zhou, et al., 2011; Hu, et al., 2014; Wang and Chen, 2007; Zhuang, et al., 2006). The strong liquid acids, e.g., sulfuric acid (H_2SO_4) and hydrochloric acid (HCl), etc. are suggested to be used as catalysts in the HTL process to promote the hydrolysis of cellulose (Zhou, et al., 2011). Sulfuric acid has been the most frequently used acidic catalyst in the hydrolysis of lignocellulose biomasses and has demonstrated high catalytic activity in the HTL process. Zhuang, et al., (2006) investigated the cellulose hydrolysis of filter paper under low concentration sulfuric acids (0.05 % mass fraction) in hot-compressed water for liquid fuels production and their results showed that 46.6 % mass fraction of reducing sugar was produced as the typical product, indicating the high-degree hydrolysis of cellulose. Zhou, et al., (2011), Hu, et al., (2014) and Wang and Chen, (2007) also suggested that acidic catalysts could retard the re-condensation reactions and reduce the formation of solid residue. The reaction mechanism of the acid-catalyzed hydrolysis of cellulose is relevant to the promotion of hydrogen cations (H^+) and hydroxide anions (OH^-) spited from water molecular in the HTL process, where the de-polymerisation of lignocellulose biomasses is accelerated by obtaining more hydrolytic products (e.g., reducing sugars) (Zhou, et al., 2011).

2.4 HTL of Various Types of Feedstocks

2.4.1 Effects of Feedstock Chemical Compositions

In addition to the operating parameters, different chemical compositions of the biomass feedstocks, e.g., cellulose, hemicellulose, and lignin, have significantly impacts on the yield of the HTL products and also determine the resulted oil components (Huang and Yuan, 2015). Biomasses/organic wastes consist of holocellulose (cellulose and hemicellulose), lignin, protein and lipid (Pavlovic, et al., 2013). Various biomasses/organic wastes have different proportion of each component, leading to different behaviors in the HTL process.

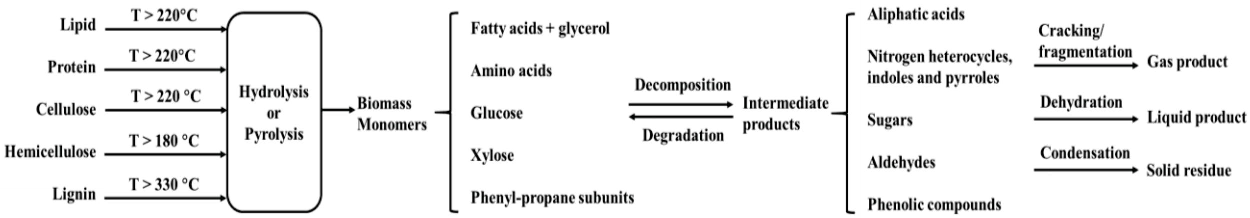
It is generally believed that the presence of a high lipid and protein in the feedstocks can yield the crude bio-oil. For example, Toor, et al., (2013) investigated the HTL of two types of microalgae (*Nannochloropsis salina* and *Spirulina platensis*) with various lipid content for crude bio-oil production. Their results showed that *Nannochloropsis salina* with higher lipid content resulted in a higher yield of crude bio-oil (46 % mass fraction) than *Spirulina platensis* (38 % mass fraction). The HTL of *Litsea cubeba* seed was also found to result in a high yield of oil product (56.9 % mass fraction) due to its large amount of lipids in the oil seeds (Wang, et al., 2013). The high content of holocellulose (cellulose and hemicellulose) is found to favor the formation of water soluble product (light oils) instead of crude bio-oil (water insoluble). Wang et al. (2008) liquefied four types of agriculture waste (cotton stalk, cornstalk, legume straw and wheat straw) into crude bio-oil via deoxy-liquefaction process (a special liquefaction process designed for oxygen removal), where the cotton stalk with the highest holocellulose content was found to achieve the highest feedstock conversion rate (65.7 % mass faction) while result in a lowest oil yield (5.2 % mass fraction). A high content of lignin has been widely reported to result in a low yield of crude bio-oil and reduced the overall feedstock conversion rate. Zhong and Wei (2004) studied the HTL of four woody biomasses (*C. lanceolate, Fraxinus mandshurica*, *Pinus massoniana Lamb.* and *Populus tomentosa Carr*.) and found that the feedstock with a lower lignin content showed a better potential in yielding oil while the solid formation showed the opposite tendency. Minowa et al. (1998) investigated the HTL of several agricultural waste/forest residues and a correlative coefficients (R) between the products distribution and the feedstock components were calculated. A high correlation between the yield of solid residue and lignin content was observed with an R = 0.702, indicating a strong positive relation between solid residue formation and lignin content.

The different behaviors of each feedstock component in the HTL process are resulted from the variation of their decomposition potentials which owes to their chemical structures (Akhtar and Amin, 2011; Toor, et al., 2011; Palovic, et al., 2013). Lipids (oils or fats) are one of the most important raw materials in food and agriculture industries. They are non-polar compounds and are referred to triacylglycerides connected by the structures of fatty acids (93 % to 98 % of the lipids mass) and glycerol (2 % to 7 % of the lipids mass). It can gradually dissolve in hot-compressed water as the temperature increases (above 200 °C) with more fatty acids generated. The resulting fatty acids can further degrade in the HTL process and be converted into long-chain hydrocarbons structured similar with petro-fuels (Watanabe, et al., 2006). Proteins are the major compounds in animal and microbial biomasses, with the amino acids as the basic unit interlinked by the peptide bond. Peptide bond can be rapidly hydrolyzed in the HTL process and the resulting amino acids can further degrade when the temperature is above 250 °C (Peterson, et al., 2008, Toor, et al., 2011). Cellulose is a linear biopolymer consisting of glucose units interlinked with β- (1-4) glucosidic bonds. The crystalline structures and the relatively intermediate degree of polymerization (ranged from 500 to 10,000) renders it insoluble in water at standard conditions. However, it can rapidly dissolve in water starting at 180 °C and be hydrolyzed to constituent sugars at higher temperatures (~ 220 °C). The decomposition of hemicellulose is easier than cellulose due to its amorphous structure, where the hydrolysis occurs when the temperature is above 180 °C (Akhtar and Amin, 2011). Lignin is a major components in woody biomasses. It is difficult to degrade/decompose even at a high temperature due to its complex branching structures and the high degree of polymerization (>10,000) (Peterson, et al., 2008). The dissolution and hydrolysis of lignin starts in near sub-/supercritical condition. Therefore, the HTL behavior of each individual biomasses component is strongly dependent on their chemical structure and the potential of yielding crude bio-oil can be generally described as: lipids > proteins > holocellulose > lignin.

The variations of the biomasses chemical compositions could also alter the intermediate products of HTL or the major components in the resulting crude bio-oils (Huang, et al., 2015; Akhtar and Amin, 2011). Hydrothermal decomposition of the feedstocks with a high content of lipids results in a formation of long-chain aliphatic acids, e.g., n-Hexadecanoic acid and Octadecanoic acid. The crude bio-oil derived from high-protein materials contains large amount of nitrogen heterocycles, indoles, and pyrroles. Differently, holocellulose produces a high content of sugars and aqueous decomposition products, e.g., fructose, glucose, and furfurals, while the crude bio-oil obtained from the HTL of lignin mainly contains phenolic compounds.

The overall conversion steps of these feedstock compositions in HTL process are summarized as below in Fig. 2.4:

Fig. 2.4 Feedstock compositions conversion steps in the HTL process.



2.4.2 HTL of Single Feedstock

Many efforts have been made in applying the HTL to produce crude bio-oil from a wide range of biomasses, with most of the work focused on the oil production from single feedstock. Table 2.1 illustrates examples of crude bio-oil production from different types of single feedstock, including agricultural waste, forest residues, livestock waste, and sewage sludge and pulping by-product by using HTL. Table 2.2 showed that the crude bio-oil production from HTL process is usually carried out at temperature ranged from 200 °C to 374 °C or near critical point, final pressures ranged from 2 MPa to 30 MPa in the reaction time ranged from 10 min to 70 min. The crude bio-oil yield varies from 13 % mass fraction to 68 % mass fraction with a higher content of carbon and hydrogen while a lower level of oxygen, compared with the raw materials. The oil product obtained from the HTL of waste biomasses generally has a higher heating value (HHV) of 20 $MJ \cdot kg^{-1}$to 40 $MJ \cdot kg^{-1}$, which is much higher than that of the feedstocks (ranged from 10 $MJ \cdot kg^{-1}$ to 20 $MJ \cdot kg^{-1}$). The results suggest that HTL is a promising method for the treatment of organic wastes and has a good potential in yielding oil product. It can also upgrade the biomass feedstocks with low-heating values to liquid fuels (crude bio-oils) with higher heating values (Demirbas, 2009).

Compositions of the crude bio-oil resulted from the HTL process are generally very complex, including straight and branched aliphatic compounds, aromatics and phenolic derivatives, carboxylic acids, esters, and nitrogenous ring structures (Vardon, et al., 2011). These compounds result in undesirable biofuel qualities such as high viscosity, polymerization, oil acidity and high-boiling distribution (Adjaye, et al., 1992; Speight, 2001). The class of compounds identified in the HTL crude bio-oil is reported to be influenced by the feedstock nutritional profile, such as the proportion of protein, lipid, and carbohydrate in the feedstock, which has been also mentioned in the section 2.4. In general, high amount of carbohydrates and lipids/proteins (microalgae, animal and fish wastes) in the feedstock can result in a higher yield of crude bio-oil while the presence of lignin content could promote the solid residue formation and reduce the yield of oil product (Pavlovic, et al., 2013). Therefore, exploring or creating the most suitable feedstock for crude bio-oil production via HTL is critical and considered priority.

Table 2.1. A Summary of the operation conditions, yield and higher heating value (HHV) of the crude bio-oil resulted from the HTL of various types of waste biomasses.

Categories	Feedstock	Temp. (°C)	Time (min)	Gas Eviron.	Catalyst	Solvent	Oil yield (%)	HHV (MJ·kg^{-1})	Ref.
Agric-waste and residues	Cellulose	310	30	N_2	Na_2CO_3	Water	44.0	-[a]	Fang, et al., 2004
	Empty palm fruit birch	270	20	N_2	K_2CO_3	Water	68.0	-	Akhtar, et al., 2010
	Cotton stalk	380	30	CO	Wood vinegar	Water	54.0	37.6	Wu, et al., 2014
	Rice husk	270	20	N_2	NaOH	Ethanol	24.2	24.8	Huang, et al., 2013
	Rice husk	260	20	NP	-	Ethanol -water	21.5	27.0	Liu, et al., 2013
	Rice stalk	200	60	N_2	-	Ethanol	55.0	32.5	Li, et al., 2014
	Corn stalk	380	30	CO	-	Water	-	36.7	Peng, et al., 2013
Forest residues	White birch Barks	300	30	N_2	-	Ethanol -water	67.0	39.0	Feng, et al., 2014
	Jack pine powder	350	40	H_2	$FeSO_4$	Ethanol	63.0	29.3	Xu and Excheverr, 2008
	Pinewood sawdust	375	60	N_2	Alkali salts	Ethanol	30.8	27.4[b]	Wang, et al., 2013
	Beech wood powder	377	25	-	-		28.0	31.7	Demirbas, 2005
Livestock waste	Cattle manure	310	15	N_2	-	Water	48.8	37	Yin, et al., 2010
	Swine manure	240	70	N_2	-	Water	33.0	-	Dong, et al., 2009
Sewage, pulping by-product; MSW	Sludge powder	350	60	H_2	$Ca(OH)_2$	Water	26.0	36.0	Xu and Lancanster, 2008
	Sewage sludge	330	10	-	K_2CO_3 & ZrO_2	Water	13.0	34.0	Hammerschmidt, et al., 2011
	Garbage	340	30	-	Na_2CO_3	Water	27.6	-	Minowa, et al., 1995

[a] not detected or provided

[b] Higher heating value calculated by the *Dulong* formula: HHV (MJ·kg^{-1}) = 0.3383C + 1.442 (H-(O/8)) (Liu, et al., 2013).

2.4.3 Co-liquefaction of Various Types of Feedstocks

The HTL of mixed feedstocks (co-liquefaction) is an emerging research area, aiming to identify the best feedstock combinations for crude bio-oil production. It could be a feasible pathway to promote the crude bio-oil production by obtaining a higher oil yield with a better oil quality. In the past 10 years, few attempts have been made to co-liquefy various types of feedstocks for crude bio-oil production via HTL, which are briefly summarized in Table 2.2.

Table 2.2. The summaries of co-liquefying various types of feedstocks for crude bio-oil production.

Feedstock combination	Temp. (^oC)	Time (min)	Gas environ.	Catalyst	Solvent	Oil yield (%)	HHV ($MJ\cdot kg^{-1}$)	Ref.
Micro-algae (*Spirulina*) & Synthetic polymer (HDPE)	340	-[a]	-	-	Ethanol	44.8	48.4	Pei, et al., 2012
Micro-algae (*Spirulina platensis*) & Macro-algae (*Entermorpha profera*)	340	40	-	-	Water	21.6	35.3	Jin, et al., 2013
Woody biomass & Synthetic polymer (HDPE)	380	20	-	-	Water	60.0	45.2	Yuan, et al., 2009
Swine manure & crude glycerol	340	15	-	-	Water	68.0	36.0	Xiu, et al., 2011
Swine manure & fatty acids	340	15	N_2	-	Water	80.0	-	Ye, et al., 2012
Secondary pulp/paper-mill sludge & waste newspaper	350	20	-	HCO(2)H	Water	34.4	29.5	Zhang, et al., 2011
Rice husk & microalgae	300	10	N_2	-	Water	23.4	-	Gai, et al., 2015

[a] not detected or provided

In the studies presented in Table 2.2, synergetic effects (positive and negative) on the product distributions and oil compositions were observed in their co-liquefaction process, e.g., using the mixture of swine manure with fatty acids, paper sludge with newspaper, and microalgae with plastic waste, etc.

Synthetic polymers (e.g. polyethylene and polypropylene) from plastic waste were recognized as a good hydrogen donor in co-liquefaction process, which could yield synergistic effects and increase the production of bio-crude oil. Pei, et al., (2012) investigated the co-liquefaction of microalgae with plastic waste in subcritical ethanol and their results showed that the oil yield in mass fraction increased with a higher ratio of plastic in the feedstock mixture. A positive synergistic effect on the oil quality was also found in their co-liquefaction process by obtaining an oil product with a reduced oxygen content and the higher heating value (HHV) of the oil product was also increased. Therefore, plastic waste could be a feasible addition to be co-liquefied with other biomasses waste and result in a higher oil yield with a better quality. Positive synergistic effect was also found in the liquefaction of lignocellulose biomass with the addition of high-lipid/protein materials. Gai, et al., (2015) investigated the co-liquefaction of rice husk with microalgae in subcritical water, where the oil quality was improved.

However, the relevant researches to co-liquefaction are still limited. Only a few types of biomasses have been tested as shown in Table 2.2. The effect of the reaction conditions, e.g., feedstock combination mass ratio, reaction temperature, reaction time, etc., on the products distribution and oil composition are largely unexplored. The reaction mechanism and pathways in the process of co-liquefaction is uncharacterized or unknown. Co-liquefaction of waste mixtures can promote the crude bio-oil production and also provide an effective way to reduce the logistics costs associated with the feedstock collecting and transportation. More comprehensive studies related to co-liquefaction is highly required. In this study, co-liquefaction of SCG with plastic waste (Spent-K-Cup liquefaction) or other lignocellulose biomasses are explored for crude bio-oil production. The reaction parameters and feedstock combination mass ratios are optimized and the relevant results are presented in Chapter 5 and 6.

Chapter 3: Materials and Methods

The purpose of this chapter is to describe the bench-scale experiment carried out for the HTL reaction, products separation procedures, the characterization methods for both feedstocks and HTL products, and also the data analysis methods that are common throughout Chapter 4, 5 and 6. Three studies were carried out based on the sub-objectives mentioned in section 1.2. Spent coffee grounds (SCG) were selected as the main and basic raw material in this research while the SCG used in each study were collected from different waste streams. The specific materials used in each study, including biomasses feedstocks, chemicals and solvents will be described in each chapter.

3.1 Batch-scale Experiment

The HTL experiments in this research were carried out following in the standard procedures developed by Dr. Chunbao (Charles) Xu's research group (Zhang, et al., 2011; Feng, et al., 2014; Naleh, et al., 2015). The HTL reactor used in this study was 100 cm^3 stainless-steel autoclave (Parr 5513 Micro Bench top reactor) with a maximum working temperature and pressure of 500 °C and 5000 psi, respectively (Fig. 3.1B). The schematic diagram of the reactor is shown in Fig. 3.1A. In a typical run, desired amount of biomasses and solvents were mixed based on the pre-set solvent to feedstock mass ratios and were fed into the reactor. The occupation of the reactor volume was maintained between 40 cm^3 to 60 cm^3 by considering the reaction efficiency and lab safety. The reactor was then sealed and purged with high purity nitrogen several times to remove the residue air. Then, the reactor was pressurized with 0.5/2 MPa nitrogen and heated up under stirring at 4.8 Hz, to the pre-set temperature at a heating rate of 10 $°C\cdot min^{-1}$. The pressure inside the reactor during reaction varied between 0.5 MPa to 10 MPa, depending on the reaction temperature and the solvent been used. As soon as the pre-set temperature was reached, the reactor was hold at that temperature for a desired reaction time. After the time elapsed, the reaction was rapidly stopped by quenching the reactor with water/ice bath. The detailed HTL procedure carried out in each study was varied dependent on their different feedstocks and reaction conditions used, which will be described in each respective chapter.

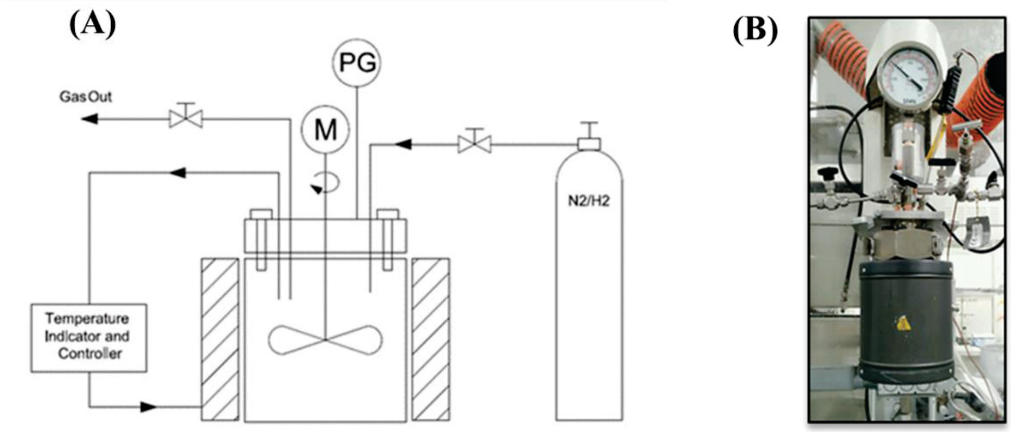


Fig. 3.1. (A) Schematic diagram (Nazari, et al., 2015) and (B) practical 100 cm^3 batch reactor.

3.2 Product Separation Procedure

Fig. 3.2 generally described the procedure used for separating the products from the HTL process, e.g., crude bio-oil (Oil), water soluble product (WSP), solid residue (SR) and gas product (GP). After the reactor was cooled down to room temperature (< 30 °C), the gaseous product (GP) in the reactor was first released and collected into a 1.0 dm^3 gas bag for GC-TCD (Agilent Micro-GC 3000) analysis with 120 cm^3 of air injected to the gas bag as an internal standard. Then the reactor was opened. The contents in the reactor (solid and water phase mixture) were transferred into a beaker and rinsed by distilled water followed by a vacuum filtration using Buchner funnel and a pre-weighted filter paper. The filtrate were collected and obtained as water soluble product (WSP). Then the reactor, the stirrer and the solid contents left on the filter paper was further rinsed by acetone several times to recover the oil phase. The slurry of oil and acetone was then transferred to a pre-weighed Erlenmeyer flask to remove acetone and solvents left using a rotary evaporator. The black matter attached on the inner wall of the flask was weighted and obtained as crude bio-oil (Oil). The acetone insoluble fraction was dried at 105 °C for 24 h in an oven to obtain a solid residue (SR). The detailed procedures for products separation for each study will be also described in their respective chapter.

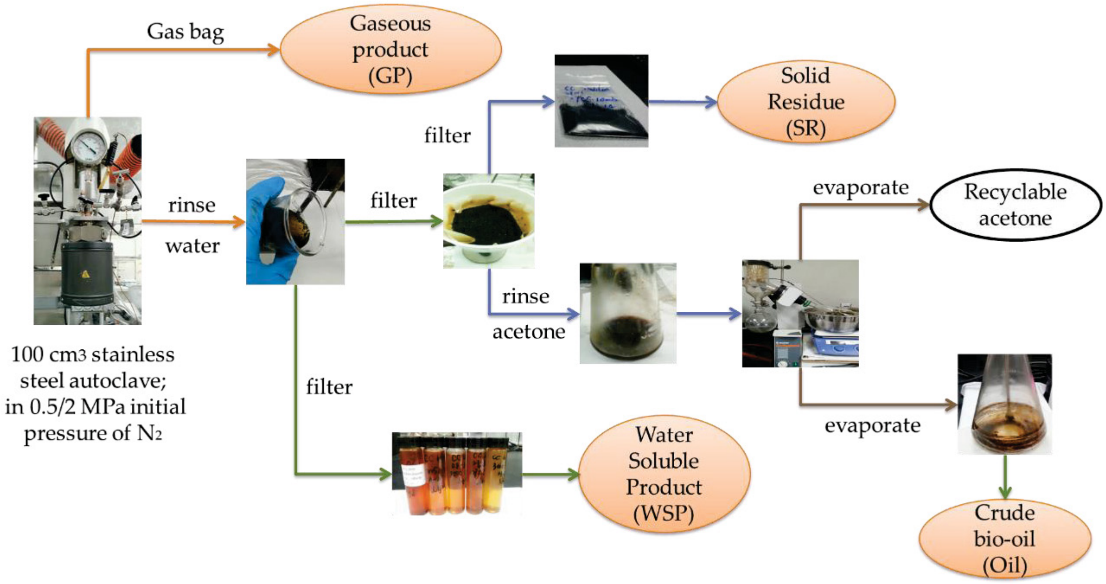


Fig. 3.2 HTL products separation procedure.

The yield of each product was calculated in mass fraction on a dry basis and is defined as:

$$Yield\ of\ Oil\ (\%) = \frac{Mass\ of\ crude\ bio\text{−}oil}{Mass\ of\ feedstock} \times 100\% \tag{1}$$

$$Yield\ of\ SR\ (\%) = \frac{Mass\ of\ solid\ residue}{Mass\ of\ feedstock} \times 100\% \tag{2}$$

$$Yield\ of\ Gas\ (\%) = \frac{Mass\ of\ gaseous\ product}{Mass\ of\ feedstock} \times 100\% \tag{3}$$

$$Yield\ of\ WSP\ (\%) = 100 - Yield\ of\ Oil - Yield\ of\ Gas - Yield\ of\ SR \tag{4}$$

$$Feedstock\ Conversion\ rate\ (\%) = 100 - Yield\ of\ SR \tag{5}$$

$$Energy\ Recovery\ rate\ (\%) = \frac{\text{HHV of crude bio−oil} \times \text{mass of crude bio−oil}}{\text{HHV of feedstock} \times \text{mass of feedstock}} \times 100\% \tag{6}$$

The mass of gaseous product was calculated by the assumption of the mass of each gas component. The mass of each gas was calculated based on the volume of each gas component calculated using ideal gas law ($PV = nRT$). Wherein, the volume of the each gas was determined by the volume percentage of each gas component obtained by Micro-GC analysis with a known volume of gas as an internal standard to the gas bag. In this research, 120 cm^3 of air was injected to the gas bag and 21 % volume fraction of oxygen was used as the internal standard as no oxygen was released from the HTL process.

3.3 Feedstock and Product Characterization

Different analysis has been performed for the feedstock and product characterization. The analysis methods are described and summarized in Table 3.1.

Table 3.1. A summary of feedstock and product characterization methods.

Analysis	Equipment	Description
Feedstock		
Moisture content (%)	Oven	Drying the sample for at least 12 h (based on ASTM E1756-08)
Ash content (%)	Muffle Furnace	Burning the sample at 575 °C for 3 h (based on ASTM E1755-1)
Volatile matter (VM)	TGA	Thermo-gravimetric Analyzer
Elemental analysis	Elemental Analyzer (CHN)	For determining the C, H, and N contents in the feedstock; O content is calculated by difference
Chemical compositions	-	Determined according to the methods of Chemical Analysis and Testing Task Laboratory Analytical Procedure (LAP)
Higher Heating Value (HHV)	Bomb Calorimeter	Or calculated by the *Dulong* formula: HHV ($MJ\cdot kg^{-1}$) = 0.3383C + 1.442 (H-(O/8)) (Liu, et al., 2013); C, H, N, O obtained from elemental analysis.
Products		
Gas components	GC-TCD	Agilent Micro-GC 3000
Total Organic carbon (TOC)	TOC analyzer	For determining total carbon content in water soluble product
Gas Chromatography-Mass Spectrometry (GC-MS)	GC-MS analyzer	For determining the volatile compounds in crude bio-oil
Gel Permeation Chromatography (GPC)	GPC analyzer	For determining the relative molecular mass of crude bio-oil
Fourier Transform Infrared Spectroscopy (FTIR)	FTIR analyzer	For determining functional groups in crude bio-oil
Karl-Fischer	Karl-Fischer titration	For determining water percentage in crude bio-oil
Elemental analysis	Elemental Analyzer (CHN)	For determining the C, H, and N contents in the crude bio-oil; O content is calculated by difference
Higher Heating Value (HHV)	Bomb Calorimeter	Or calculated by the *Dulong* formula: HHV ($MJ\cdot kg^{-1}$) = 0.3383C + 1.442 (H-(O/8)) (Liu, et al., 2013); C, H, N, O obtained from elemental analysis.
pH value	pH meter	For determining the pH value of crude bio-oil
Viscosity	Viscometer	For determining the fluidity of crude bio-oil

3.4 Data Analysis

All the HTL experiments were conducted in triplicate, unless explained otherwise, in order to ensure the repeatability of the results and to minimize the experimental errors (< 5%). The mean values of the data along with the corresponding error bars representing standard deviations are presented in all figures in Chapter 4, 5 and 6. In Chapter 5, statistical analysis was done by using Design Expert 7.0 combined with Minitab 17.0 software. Specific data analysis for each study will be described in their respective chapters.

Chapter 4: Hydrothermal Liquefaction (HTL) of Spent Coffee Grounds (SCG) in Water Medium for Crude Bio-oil Production

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Contribution statement:

I was responsible for collecting and preparing raw materials, designing and performing all the experiments, samples analysis, and data analysis and manuscript preparation.

4.1 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 (Nigam & Singh, 2011). Using biomass for liquid biofuels production has sparked the interest worldwide due to its abundance, renewability and carbon neutrality (Peterson, et al., 2008). 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 (Peterson, et al., 2008; Minowa, et al., 1998). 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 (Appell, et al., 1972; Savage, et al., 2010; Panisko, et al., 2015; Wang, et al., 2014; Azadi & Farnood, 2011; Luo, et al., 2014; Theegala & Midgett, 2012). 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 (Mussatto, et al., 2011; Kondamudi, et al., 2008). According to the coffee trade record from the International Coffee Organization (ICO, 2015), 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 (Liu & Price, 2011). 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 (Mussatto, et al., 2011). 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 (Sprules, 1999; Limousy, et al., 2013). New interests are recently developed to use SCG for liquid biofuels production. Kondamudi et al., (2008) 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., (2012) 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 (Romeiro, et al., 2012; Bok, et al., 2012; Li, et al., 2014) 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) (Kondamudi, et al., 2008), 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 $\mathrm{MJ \cdot kg^{-1}}$ to 23 $\mathrm{MJ \cdot kg^{-1}}$, 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 crude bio-oil or bio-crude), aqueous, gaseous and solid products at high pressures (5–22 MPa) and moderate temperatures (250–380 °C) in sub-/supercritical water medium (Behrendt, et al., 2008; Toor, et al., 2011). 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 crude 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 (Toor, et al., 2011; Elliott, 2007; Demirbas, 2011; Huber, et al., 2006; Goudriaan & Peferoen, 1990).

Many researchers have been focusing on the crude bio-oil production via the HTL process from a wide variety of biomass, including woody biomass, mainly forest residues (Cheng, et al., 2010; Wang, et al., 2013; Xu & Lad, 2008; Zhu, et al., 2014), agricultural waste such as barley straw, corn stalk, corncob and rice husk (Zhu, et al., 2015; Peng, et al., 2014; Gan & Yuan, 2013; Liu, et al., 2013), animal manure (Cantrell, et al., 2007; Xiu, et al., 2010; Yin, et al., 2010), municipal solid waste (Minowa, et al., 1995; Hammerschmidt, et al., 2011; Xu & Lancaster, 2008) and most recently microalgae (Brown, et al., 2010; Valdez, et al., 2012; Jena & Das, 2011; Biller & Ross, 2011; Barreiro, et al., 2015; Barreiro, et al., 2014; Barreiro, et al., 2013). Through these studies, it was found that the yield and quality of the crude bio-oil resulting from the HTL process were highly associated with the operating parameters such as the reaction temperature, reaction time, ratio of feedstock and solvent, etc., as reviewed by Akhtar and Amin (2011) as well as the experimental results reported in the previous literatures. 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 crude bio-oil yield. With an increase in the liquefaction temperature, the yield of crude bio-oil increases while the solid residue decreases. However, at the temperature higher than 300°C, for most feedstocks, a decreased crude bio-oil yield and increased gas fraction yield are observed due to a secondary decomposition of the crude bio-oil and Bourdard gas reactions. However, the solid residue yield may also increase, being caused by the re-polymerization of the crude bio-oil components and/or re-combination of high-concentration free radicals to form bio-char. Retention time is another key factor influencing the crude bio-oil production and the overall biomass conversion. Generally, a short retention time (10–30 min) is preferred, giving a relatively high crude 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 crude 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 crude 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 (Cheng, et al., 2010; Wang, et al., 2013; Xu & Lad, 2008; Zhu, et al., 2014; Demirbas, 2005). The HHVs of the HTL crude bio-oils obtained from the lignocellulose biomass (without using any catalysts and organic solvents) are in the range of 30–36 $MJ \cdot kg^{-1}$, 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 crude bio-oil production. Recently, it was observed that high lipid and protein contents in feedstock benefited the yield and the quality of the crude bio-oil (Brown, et al., 2010; Valdez, et al., 2012; Jena & Das, 2010; Biller & Ross, 2011; Biller, et al., 2011; Barreiro, et al., 2015; Barreiro, et al., 2014; Barreiro, et al., 2013; Wang, et al., 2013; Teri, et al., 2014).

A thorough literature review encouraged us to explore the feasibility of converting the spent coffee grounds (SCG) to crude 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 (Mussatto, et al., 2011; Kondamudi, et al., 2008; Ballesteros, et al., 2014). It might be a promising feedstock for the crude bio-oil production using the HTL technology. More attractively, the size of SCG is in the range of 200–300 μm (Bok, et al., 2012), 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 N_2 atmosphere. Effects of the reaction time (varied from 5 min to 30 min), reaction temperature (varied from 200 °C to 300 °C), and 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 our knowledge, this is the first to examine SCG as a feedstock for the crude bio-oil production via a HTL process.

4.2 Experimental

4.2.1 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.

4.2.2 Hydrothermal Liquefaction Procedure

The experiments were carried out following the procedures descried in section 3.1. In a typical run, 2.5 g to 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 cm^3 to 60 cm^3. 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 4.8 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 $°C \cdot min^{-1}$. After the system reached the desired temperature, the reactor was kept at the temperature for a specified reaction time (between 5 min to 30 min).

4.2.3 Separation of Reaction Products

Once the reaction was completed, the reactor was cooled down to room temperature in an ice water bath, and the products were separated following the steps mentioned in section 3.2. The yields of crude bio-oil (Oil), solid residue (SR) and gaseous product (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 % – Oil yield – SR yield – GP yield). The biomass conversion rate was calculated by (100 % – SR yield).

4.2.4 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 H_2, N_2, O_2, CO_2, CO, CH_4, C_2H_4, C_2H_6, C_3H_8, and C_3H_6. 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 $°C \cdot min^{-1}$, 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 $cm^3 \cdot min^{-1}$. 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 (Liu, et al., 2013):

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

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) (Biller & Ross, 2011):

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

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

4.3 Results and Discussion

4.3.1 Effects of Reaction Time

Reaction time in a HTL process impacts the product yield and distribution. It is generally believed that a shorter reaction time is preferred to degrade biomass effectively as the rate of decomposition and hydrolysis of biomass is fairly fast in the HTL process (Akhtar & Amin, 2011; Sasaki, et al., 2003; Peterson, et al., 2008).

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. 4.1. 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. 4.1, 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 reaction time of 10 min, then started decreasing to 22.68 % as the reaction 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 reaction 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 reaction 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 reaction 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 reaction 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 (Akhtar & Amin, 2011; Qu, et al., 2003).

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 reaction 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.

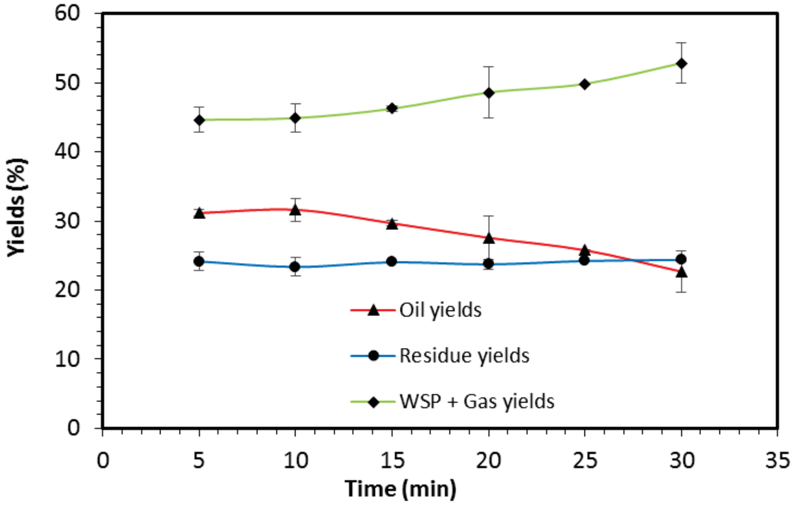

Fig. 4.1. Yields of crude bio-oil, solid residue, WSP, and gas obtained under different reaction time (temperature of 300 °C and water/feedstock mass ratio of 5:1 with 2.0 MPa initial N_2 pressure).

4.3.2 Effects of Temperature

Compared to the effects of the reaction time, the influence of the reaction temperature on SCG liquefaction was more significant with a wider range of crude bio-oil yields from 16.58 % to 35.29 %.

Fig. 4.2 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 gas products resulting from the SCG liquefaction in 10 min with a water/feedstock mass ratio of 5:1. As seen from Fig. 4.2, 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 supress 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 $g \cdot mol^{-1}$ to 479 $g \cdot mol^{-1}$ 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 (El-Rub, et al., 2004). These results are consistent with the research reported in the literature (Xu & Lad, 2008; Zhu, et al., 2015; Gan & Yuan, 2013; Xu & Lancaster, 2008; Akhtar & Amin, 2011). For example, Akhtar and Amin (2011) 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 (2008) 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 reaction time of 10 min and the water/feedstock mass ratio of 5:1.

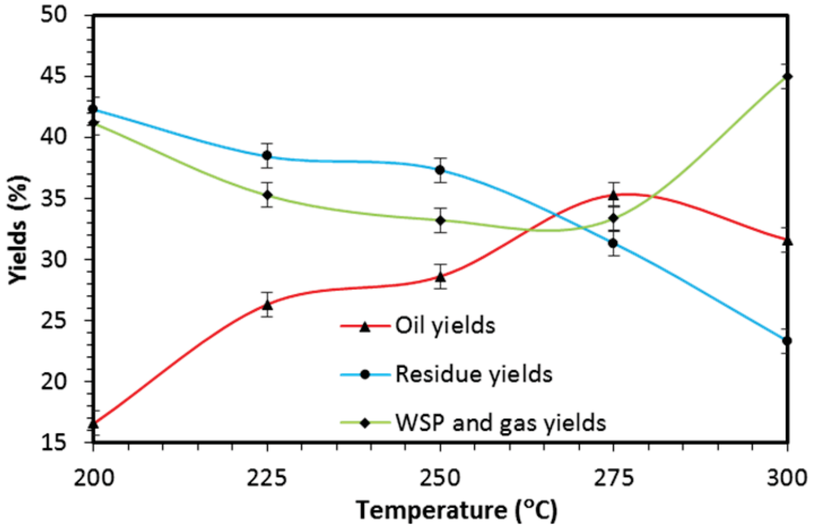

Fig. 4.2. Yields of crude bio-oil, solid residue, WSP, and gas obtained from the HTL of SCG at various reaction temperatures (reaction time of 10 min and water/feedstock mass ratio of 5:1 with 2.0 MPa initial N_2 pressure).

4.3.3 Effects 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 N_2 pressure. Fig. 4.3 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 (Cheng, et al., 2010; Wang, et al., 2013; Gan & Yuan, 2013; Liu, et al., 2013; Xiu, et al., 2010). 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 (Brown, et al., 2010). On the contrary, higher water concentration would prevail throughout the whole process, which might accelerate the sovolysis, 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 (Cheng, et al., 2010; Xu & Lancaster, 2008). 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 N_2 pressure was 2.0 MPa.

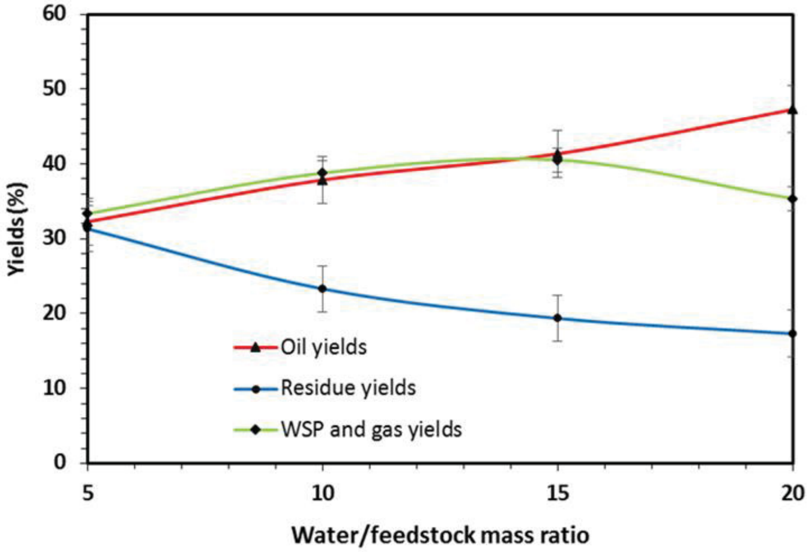

Fig. 4.3. Yields of crude bio-oil, solid residue, WSP, and gas obtained from the HTL of SCG with various water/feedstock mass ratios (reaction time of 10 min and temperature of 275 °C with 2.0 MPa initial N_2 pressure).

4.3.4 Effects of N_2 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. (2011) and Goudriaan and Peferoen (1990), 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.

4.3.5 Crude Bio-oil Characterizations

In addition to the yield, the properties of the resulting crude 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 N_2 pressure, was characterized as a representative and reported in the following sections.

4.3.5.1 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 4.1. 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 CO_2 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 crude 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.

Table 4.1. Elemental analyses of SCG and crude bio-oil obtained under the reaction condition of 275 °C, 10 min, 20:1 water/feedstock mass ratio with 2.0 MPa initial N_2 pressure.

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	72.6
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	

[a] by mass difference; [b] Higher heating value calculated by the *Dulong* formula: HHV (MJ·kg^{-1}) = 0.3383C + 1.442 (H-(O/8)); [c] 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.

4.3.5.2 GC-MS

The chemical composition of the crude bio-oil derived from SCG was further identified by a GC-MS analysis. Table 4.2 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 N_2 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 C_{16} – C_{18} 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 C_{20} aliphatic acids (eicosanoic acid). They were mainly derived from the decomposition and re-polymerization of lipids in the raw materials. Little amounts of C_{25} 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 (Xiu, et al., 2010; Wang, et al., 2013).

Table 4.2 Major compounds in the crude bio-oil derived from the HTL of SCG (temperature of 275 °C, reaction time of 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N_2 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

4.3.5.3 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 N_2 pressure are illustrated in Fig. 4.4. 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 (Wang, et al., 2013). 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 (Cheng, et al., 2010). 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.

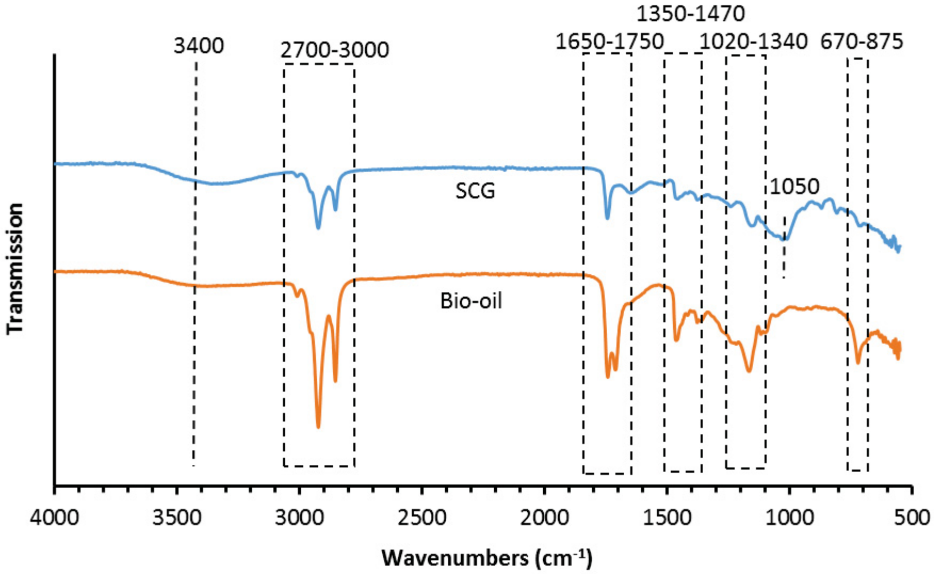

Fig. 4.4 FT-IR spectrum of SCG and the crude bio-oil derived from the HTL of SCG (temperature of 275 °C, reaction time of 10 min and water/feedstock mass ratio of 20:1 with 2.0 MPa initial N_2 pressure).

4.3.6 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 4.3 provides the properties of crude 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 4.3, 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 (Brown, et al., 2010; Valdez, et al., 2012; Jena & Das, 2010; Biller & Ross, 2011; Biller, et al., 2011; Barreiro, et al., 2015; Barreiro, et al., 2014; Barreiro, et al., 2013; Wang, et al., 2013; Teri, et al., 2014). 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 lignocellulosic 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.

Table 4.3. Properties of crude bio-oils derived from the HTL of SCG and other biomass.

Feedstock	Liquefaction conditions	C%	H%	O%	N%	HHV ($MJ \cdot kg^{-1}$)	Max Oil yield (% mass fraction)	Main product distribution from GC-MS analysis	Ref.
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	Xu & Lad, 2008
Tea waste	377°C, 25 min, -[a]	71.6	5.6	22.8	0.0	33.6	22.6	-	Demir-bas, 2005
Corn stalk	380°C, 30 min, N_2	77.8	6.9	14.9	0.0	33.5	36.0	-	Peng, et al., 2014
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	Xiu, et al., 2010
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	Xu & Lancaster, 2008
Microalgae (*Nannochloropsis sp.*)	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	Brown, et al., 2010
***Litsea cubeba* seed**	290°C, 60 min, -[a]	76.2	11.9	10.4	3.9	40.8	56.9	Toluene, fatty acids and their derives	Wang, et al., 2013

[a] not detected or provided

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 4.4 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 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 the 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.

Table 4.4. Properties of oil products derived from SCG.

Oil products from SCG	C%	H%	O%	N%	O/C	HHV ($MJ\cdot kg^{-1}$)	Max Oil yield (% mass fraction)	Water content (%)	pH	Ref.
HTL	71.2	7.1	18.7	3.0	0.2	31.0	47.3	2.1	4.8	Current research
Fast pyrolysis	54.3	7.4	35.3	3.1	0.4	20.4	54.9	31.1	3.1	Bok, et al., 2012
Biodiesel	-[a]	-	-	-	-	-	15.0	-	-	Kondamudi, et al., 2008

[a] not detected or provided

4.4 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, reaction 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 $MJ\cdot kg^{-1}$, much higher than that of SCG which was only 20.2 $MJ\cdot kg^{-1}$. The energy recovery percentage was 72.6%. Our results suggested that SCG could be a suitable feedstock for crude bio-oil production in terms of the crude bio-oil yield. However, large amount of aliphatic acids were found in the oil compounds and the oxygen content was relatively high, indicating that the resulting oil needs to be further upgraded to petroleum-like fuel.

4.5 Transition Section: Co-liquefaction of SCG with Plastic Waste (Spent K-Cups Liquefaction)

The addition of plastic waste was found to provide hydrogen donor in the liquefaction of biomasses, which have positive effect on the yield of crude bio-oil (as mentioned in section 2.7.3). Therefore, co-liquefaction of SCG with plastic waste attracted our interest. Spent K-Cups are the waste produced from K-Cup coffee brewing system and have raisin more and more concerns due to their environmental impact. Spent K-Cups consist over 80 % mass fraction of SCG and over 10 % mass fraction of un-recyclable plastic, which provide us the raw materials for co-liquefaction. Therefore, our next step is to study the liquefaction of spent K-Cups for crude bio-oil production, which will be presented in Chapter 5.

Chapter 5: Production of Crude Bio-oil via Direct Liquefaction of Spent K-Cups

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Contribution statement:

I was responsible for collecting and preparing raw materials, designing and performing all the experiments, samples analysis, data analysis and manuscript preparation.

5.1 Introduction

Liquefaction is a thermochemical process for the transformation of lignocellulosic biomasses or organic waste into liquid biofuels and bio-chemicals under reaction conditions of temperature and pressure in sub-/supercritical water or organic solvents/co-solvent mixture (Behrendt, et al., 2008). Liquefaction has proven to be an efficient route not only for the production of renewable fuels but also for the treatment of waste materials (Zhai, et al., 2015; Liu, et al., 2013; Zhang, et al., 2011; Xu and Lancaster, 2008; Yin, et al., 2010; Barreiro, et al., 2013; Barreiro, et al., 2015; Subagyono, et al., 2015). Most of the current liquefaction processes are carried out heterogeneously, requiring rigorous reaction conditons in terms of reaction temperature, pressure, reaction time and solvent/feedstcok ratio, etc. (Long, et al., 2012; Valdez, et al., 2012). Lignocellulosic biomasses can be easily depolymerized/liquefied in the presense of alkaline/acidic catalysts in a suitable solvent (Mahmood, et al., 2015; Zhu, et al., 2015). Hot compressed or sub-/supercritical water has been widely used for biomass liquefaction (Behrendt, et al., 2008; Zhang, et al., 2011; Subagyono, et al., 2015; Valdez, et al., 2012; Cheng, et al., 2010), however, the resulting crude bio-oil was found to be very viscous and tarry lump, which may cause handling problems (Yuan, et al., 2007). Also, the obtained oily products generally have high oxygen content and low carbon content, leading to lower heating values (Li, et al., 2009), compared to bio-oils obtained from liquefaction processes using alcohols or alcohol-water as solvents

(Zhai, et al., 2015; Liu, et al., 2013; Yuan, et al., 2007; Li, et al., 2009; Liu, et al., 2008; Wang, et al., 2013).

K-Cup, the main product of Keurig Green Mountain, Inc., is a popular single-serve coffee brewing system in North-America (KGM-S, 2014). As it grows in popularity, the waste produced from this "convenient" process, referred to as spent K-Cups, has raised concern over their potential environmental impact, and thus disposal and/or utilization have attracted increasing attention (KGM-S-RPW, 2004). One spent K-Cup (with a total mass of ~ 16.5 g) consists of five components, namely, spent coffee grounds (SCG), a paper filter (PF), an aluminum foil lid (Al), a plastic container (PC), and a plastic seat (PS). It is generally difficult and/or expensive to separate five components from one another (Harris, 2015). The K-Cup's outer container (PC) is made of #7 non-recyclable plastic, and although the other parts of K-Cups are recyclable individually, the existence of PC results in the spent K-Cup being typically disposed of as a whole unit in landfills (Oatman, 2014). In 2013, Keurig Green Mountain produced 8.3 billion K-Cups, enough to wrap around the equator 10.5 times, a figure which increased to 9.8 million in 2014 (Godoy, 2015). Therefore, there is an urgent need to identify alternative ways to recycle these plastic coffee pods and address the environmental concern caused by the K-Cup system (Allen, 2011). Until now, only a few successful steps have been made in Canada, the Lafarge cement plant in Kamloops, B.C. combusted 1.4 million spent K-Cups for energy supply with the residual ash used in the production of cement (CBC News, 2015). The Holcim cement plant in Joliette, Quebec, also used spent K-Cup packs as an alternative to fossil fuels (mainly through incineration process for energy purposes) (KGM-S, 2014). However, direct combustion of spent K-Cups generates hazardous emissions such as NOx, due to a higher nitrogen content in the spent coffee grounds than typically found in other fuels, which may require the additional expensive gas scrubber to purify the flue gas before it is released to the atmosphere. Therefore, it is essential to develop more efficient and effective methods for disposing of K-Cups with potential inherent benefits of energy recovery.

Liquefaction of spent K-Cups employing sub-/supercritical ethanol or its co-solvent with water could be a viable route for the production of crude bio-oil and also for effective waste management. Ethanol under sub-/supercritical conditions acts as an effective hydrogen donor to stabilize the free radicals generated during the liquefaction process, reduce the condensation/repolymerization reaction, and thus improve the yield of crude bio-oil (Kabe, et al., 1991; Sangon, et al., 2006). An ethanol-water mixture (50/50, v/v) has demosntrated a synergistic effect on the liquefaction of lignocellulosic biomasses (Liu, et al., 2013), and hence improved the yield of crude bio-oil.

The objective of this work is to produce crude bio-oil via liquefaction of spent K-Cups employing a water-ethanol mixture (50/50, v/v), and to optimize reaction conditions using a statistical method, Response Surface Methodology (RSM). Three input variables, reaction temperature, reaction time and solvent to feedstock mass ratio were studied to determine their impact on the yield of crude bio-oil. The effects of catalysts sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were also investigated at the optimized reaction conditions.

5.2 Experimental

5.2.1 Materials

The spent K-Cups used in this study were Caffè Verona (dark roast) produced by Starbucks (Fig. 5.1A) and were collected from home waste streams. The five components (SCG, PC, PS, PF, Al) of the spent K-Cups were carefully separated. With the exception of the SCG inside the container, the other components were cleaned, crushed, ground and sieved at 0.841 mm (20 mesh) (Fig. 5.1B). All of the samples were oven-dried at a temperature of 105 °C in air over several days. The dried samples were kept in sealed bags separately and stored in a refrigerator at 4 °C. For every experiment, each spent K-Cup component was further dried in the oven at 105 °C overnight before use, and mixed based on the respective component mass ratio (i.e., 84 % SCG, 9.6 % PC, 3.3 % PS, 1.5 % PF, and 0.8 % Al). Other chemicals used included denatured ethanol, NaOH, H_2SO_4, and acetone, all CAS reagent grade, purchased from the Sigma-Aldrich and used without further purification. The physical characteristics of the feedstock components used in the present experiment are shown in Table 5.1.

Fig. 5.1. (A) Spent K-Cup (B) ground powder of each spent K-Cup component.

Table 5.1. Physical characteristics of spent K-Cup components

Sample	Proximate analysis (%)[a,b]			Ultimate analysis (%)[c]				HHV[d] (MJ·kg^{-1})
	Volatiles	Ash	Moisture	C	H	N	O[e]	
SCG	77.3	1.4	4.38	40.3	8.3	3.3	47.9	17.0
Spent K-Cup	78.8	8.8	10.4	46.0	8.4	2.8	41.1	20.2

[a] On a dry basis

[b] Determined by thermogravimetric analysis (TGA) in N_2 at 10 °C ·min^{-1} to 800 °C, and 800 °C in air for 15 min.

[c] On a dry and ash free basis

[d] Higher heating value calculated by the *Dulong* formula: HHV (MJ·kg^{-1}) = 0.3383C + 1.442 (H-(O/8))(Liu, et al., 2013)

[e] By difference

5.2.2 Liquefaction of Spent K-Cups

Thermochemical liquefaction experiments were carried out following the procedures mentioned in section 3.1. In a typical run, dried samples from each spent K-Cup component were mixed (based on the respective mass ratio in the spent K-Cup) as desired and loaded in the reactor, followed by the addition of a certain amount of denatured ethanol and distilled water, with the pre-set solvent/feedstock mass ratios (varied from 2:1 to 12:1). The total volume of feedstock and solvent loading was kept constant at 40 cm^3. The reactor was sealed and purged 3 times with high purity nitrogen to remove any air and pressurized to an initial pressure of 0.5 MPa. The reactor was then heated up to the targeted temperature (varied 255 °C to 350 °C) at a heating rate of 10 °C·min^{-1} and hold constant for the desired reaction time (varied from 0 min to 25 min) while stirred (4.8 Hz). After the pre-set retention time had elapsed, the reactor was immediately quenched with water to stop further reaction. Once the system reached a lower temperature (near room temperature), the gas was collected in a gas bag. The products were separated following in the methods described in section 3.2. The yields of each product were on a dry and ash free basis (dab). The yield (Y) of each product in mass percentage was defined as:

$$Y_{oil}(\%) = (\frac{m_{oil}}{m_{K-Cup}} \times 100\%)/(1 - ash\%) \tag{1}$$

$$Y_{solid}(\%) = (\frac{m_{solid}}{m_{K-Cup}} \times 100\%)/(1 - ash\%) \tag{2}$$

$$Y_{gas+WSP}(\%) = (\frac{m_{gas+WSP}}{m_{K-Cup}} \times 100\%)/(1 - ash\%) \tag{3}$$

where Y_{oil}, Y_{soild}, and $Y_{\mathrm{gas+WSP}}$ denote the yield of crude bio-oil, solid residues, combined gas and water soluble product, respectively, in mass percentage, on a dry and ash free basis; m_{oil}, $m_{\mathrm{K\text{-}Cup}}$, m_{solid}, $m_{\mathrm{gas+WSP}}$ denote the mass of crude bio-oil, spent K-Cup samples, solid residue, and gas and water soluble product, respectively, on a dry basis; $ash\,\%$ denotes the mass fraction of ash in the spent K-Cup sample. The overall carbon recovery for liquefaction products were estimated according to the method descried by Yu and co-workers (2011).

5.2.3 Experimental Design

Response surface methodology (RSM) with a central composite design (CCD) was used to study the effects of independent variables and interaction of these variables on the response, and further to determine the optimum reaction conditions of spent K-Cups during liquefaction. It is an effective second-order design for any number of design factors, and has a number of desirable properties for process optimization (Myers, et al., 2009; Montgomery, 2013). Three independent variables were reaction temperature (X_1), reaction time (X_2) and solvent/feedstock mass ratio (X_3) at five coded levels ($-\alpha$, – 1, 0, +1, $+\alpha$), and the response was the yield of crude bio-oil. The alpha value depends on the number of factors (variables) in the factorial design and is determined by Eq. (4).

$$\alpha = \left[2^n\right]^{1/4} \tag{4}$$

where, *n* is the number of factors and alpha is presented at – 1.682 and + 1.682. The reaction temperature (X_1), reaction time (X_2) and solvent/feedstock mass ratio (X_3) in coded units were calculated by Eq. (5)

$$X_i = \frac{x_i - x_0}{\Delta x_i} \tag{5}$$

where X_i is the coded independent variable, x_i is the actual value of the independent variable, x_0 is the actual value of the independent variable at the center point and Δx_i is the change between each actual variable. The ranges of the independent variables were selected based on our preliminary experiments and the relevant research reported in the literature. The reaction temperature was in the range of 255 °C to 350 °C, the reaction time was set from 0 min to 25 min, and the solvent/feedstock mass ratio was set in the range of 2:1 to 12:1, as presented in Table 5.2.

Table 5.2 The range and levels of independent factors.

Factors	Coded variables	Range and levels of independent factors				
		–1.682 (-α)	–1	0	+1	+1.682 (+α)
Temperature (°C)	X_1	255	275	303	330	350
Reaction time (min)	X_2	0	5	13	20	25
Solvent/feedstock mass ratio	X_3	2	4	7	10	12

Design Expert 7.0 Statistical Software was used to determine the response surface and optimize the reaction condition. A second-order polynomial equation was developed and obtained from response surface analysis of deviation (ANOVA). The overall fitness of the model was validated by examining the coefficient of determination (R^2) value. The significance (*p*-value) of each factor was determined by an *F*-test with $\alpha = 0.05$ (or 95 % confidence level). The second order polynomial equation correlating the response to the factors is shown in Eq. (6).

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 \ldots \tag{6}$$

where, Y is the response; a_0 the model intercept; $X_{`1}$, $X_{`2}$, and $X_{`3}$ are the input variables; a_1, a_2 and a_3 are the linear coefficients; a_{12}, a_{13} and a_{23} are the interaction coefficients, and a_{11}, a_{22} and a_{33} are the quadratic coefficients.

5.2.4 Characterizations

Thermogravimetric analysis (TGA) was carried out using Perkin Elmer (Pyris 1 TGA) instrument. The feedstock, spent K-Cups with particles size of 0.84 mm (20 mesh) were heated at a heating rate of 10 $°C \cdot min^{-1}$ from 40 °C to 800 °C under nitrogen atmosphere, and then at 800 °C in air for 15 min. The elemental composition of feedstock and the resulting crude bio-oil were analyzed using an Elemental Analyzer (C, H, N), while oxygen content was calculated by difference. The higher heating value (HHV) of the resulting crude bio-oil was calculated according to the *Dulong Formula* described in section 4.2.4. The compositions and functional groups of the obtained crude bio-oil were determined by GC-MS and FT-IR. The specific running programs were described in section 4.2.4.

5.3 Results and Discussions

5.3.1 Statistical Analysis

5.3.1.1 Model Fitting

A 5-level-3-factor CCD design requires a total of 20 experiments, which include 8 factorial points, 6 axial points and 9 central points. The matrix corresponding to the CCD design including three experimental variables along with the actual and predicted values are shown in Table 5.3. Using different combinations of reaction conditions, the yield of crude bio-oil varied from 17.5 % to 59.3 %. The actual values of the independent variables and the 20 experimental responses were used to develop a regression model, and the resulting quadratic equation (Eq. (7) in un-coded values) was shown to be:

$$Y_{oil} = 1907.53 - 11.39X_1 - 48.77\,X_2 - 250.47\,X_3 + 0.16\,X_1X_2 + 1.74\,X_1X_3 + 0.02\,X_1^2 + 1.84\,x_2^2 - 0.54\,X_3^2 \qquad (7)$$

Where, Y is the yield of crude bio-oil (mass fraction in percentage); X_1 is the reaction temperature (°C); X_2 is the reaction time (min); X_3 is the solvent/feedstock mass ratio.

The ANOVA analysis was summarized in Table 5.4 which aimed to explain the effects of the independent variables (X_1, X_2 and X_3) on the response (Y) at $\alpha = 0.05$ level of significant in terms of their linear, interaction and quadratic contributions. The Fisher F-test values (F-value), p-value, lack of fit, regression coefficient R-square (R^2) were used to evaluate the fitness of the generated model. Generally, a well-fitted regression model indicates a successful correlation between the response and independent variables.

The ANOVA analysis demonstrated that the fitted model was valid, with $R^2 = 0.9945$ and p-value of $0.0001 \ll \alpha$. All the model terms, including linear model terms (X_1, X_2 and X_3); quadratic model term (X_1^2, X_2^2 and X_3^2) and interaction model terms (X_1X_2, and X_1X_3) are significant with p-values $\ll \alpha$. The linear effect of X_1 (reaction temperature) and X_3 (solvent/feedstock mass ratio) is more significant than X_2 (reaction time) with lower p-values and higher F-values, suggesting that the reaction temperature and solvent/feedstock mass ratio affect the yield of crude bio-oil more significantly. The lack of fit of the model was non-significant with a p-value of $0.2751 \gg 0.05$, indicating that the model is adequate and reliable. Fig. 5.2 shows the comparison between the predicted response values using the quadratic model and the actual response values obtained from experiments. The adequate correlation to the linear regression fit, with R^2 values of 0.9945 for the yield of crude bio-oil, demonstrating that the fitted model covered the experimental range of studies sufficiently.

Table 5.3. The central composite design matrix along with the predicted/actual responses.

Coded independent variable levels							Response	
	X_1	X_2	X_3	X_1	X_2	X_3	Y	
				Temp (°C)	Time (min)	Ratio	Y_{oil}[a] (%)	
							Actual	Predicted
1	–1	–1	–1	275	5	4	55.1	54.32
2	+1	–1	–1	330	5	4	20.2	20.50
3	–1	+1	–1	275	20	4	45.7	46.31
4	+1	+1	-1	330	20	4	19.6	19.14
5	–1	–1	+1	275	5	10	59.3	58.80
6	+1	–1	+1	330	5	10	21.9	20.33
7	–1	+1	+1	275	20	10	50.5	50.79
8	+1	+1	+1	330	20	10	17.5	18.97
9	–1.682	0	0	255	13	7	48.7	48.84
10	+1.682	0	0	350	13	7	25.4	25.60
11	0	–1.682	0	303	0	7	44.3	45.80
12	0	+1.682	0	303	25	7	39.1	37.92
13	0	0	–1.682	303	13	2	17.8	17.95
14	0	0	+1.682	303	13	12	43.5	44.58
15	0	0	0	303	13	7	43.0	44.58
16	0	0	0	303	13	7	46.3	44.58
17	0	0	0	303	13	7	44.5	44.58
18	0	0	0	303	13	7	43.4	44.58
19	0	0	0	303	13	7	45.0	44.58
20	0	0	0	303	13	7	45.2	44.58

[a] Yield of crude bio-oil in mass percentage.

Table 5.4. ANOVA for response surface quadratic model at $\alpha = 0.05$ for Y_{oil} (yield of crude bio-oil in mass percentage).

% Y_{oil}[a]					
Source	Degrees of freedom (DOF)	Sequential sum of squares (SS)	Mean square (MS)	*F*-value	*p*-value
Model	8	3281.93	328.19	169.44	<0.0001
X_1[b]	1	270.36	270.36	139.58	<0.0001
X_2[c]	1	75.15	75.15	38.80	0.0002
X_3[d]	1	330.51	330.51	170.64	< 0.0001
X_1X_2	1	22.07	22.07	11.4	0.0082
X_1X_3	1	10.80	10.80	5.58	0.0425
X_1^2	1	97.58	97.58	50.38	< 0.0001
X_2^2	1	13.40	13.40	6.92	0.0274
X_3^2	1	341.90	341.90	176.52	< 0.0001
Residual	9	17.43	1.94		
Error	5	7.26	1.45		
Lack of fit	4	10.17	2.54	1.75	0.2751
Pure error	5	7.26	1.45		
Total	19	26.25			
R^2	0.9945				

[a] Yield of crude bio-oil in mass percentage
[b] Reaction temperature
[c] Reaction time
[d] Solvent/feedstock mass ratio

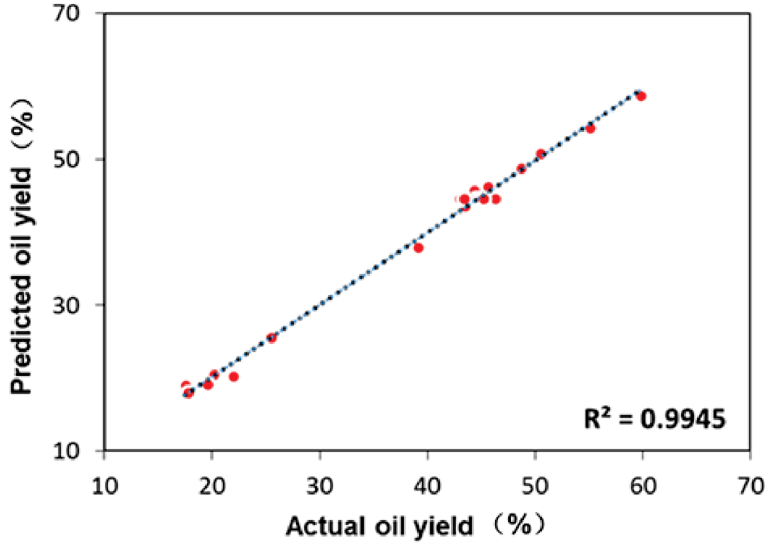


Figure 5.2. Actual vs. predicted values of Y_{oil} (yield of crude bio-oil in mass percentage).

5.3.1.2 Main Effects Plots

The main effects plots were obtained from ANOVA analysis using Minitab 17.0, the differences between the level means of each factor and how the levels of the factors affected the response differently were examined. Fig. 5.3 represents the main effects plots of three independent variables on the response, the crude bio-oil yield. It shows that the crude bio-oil yield increases from 48.7 % to 54.3 % as X_1 (reaction temperature) increases from 255 °C to 275 °C. However, further increase of temperature (275 °C<X_1<330 °C) led to a significant reduction in the bio-oil yield (from 54.3 % to 19.8 %), most likely due to the secondary decomposition/depolymorization of the generated oil to smaller molecules and fromation of gas and water soluble products. When a low reaction temperature (< 330 °C) was applied, plastic components (PC and PS) were clumped and remained in the solid residue, suggesting that the plastics were not liqufied at low temperature and the resulting crude bio-oil was mainly derived from SCG and PF. With a further increase in temperature above 330 °C, the yield of crude bio-oil increased from 19.8 % (330 °C) to 25.4 % (350 °C) with less plastic clumps observed in the final product, indicating that the plastic components (PC and PS) partilly decomposed and were very likely contributing to the crude bio-oil formation.

Compared to the effect of reaction temperature, the influence of reaction time on spent K-Cup liquefaction was less significant. Fig. 5.3 shows that a decreasing trend of the yield of oil product was observed as X_2 (reaction time) increases. The oil yield decreased from 44.3 % to 33.3 % when the reaction time increased from 0 min to 20 min then increased to 39.1 % with a further increase in time. The results indicated that a shorter reaction time was preferred for feedstock liquefaction and oil formation. With the increase of reaction time, the formed crude bio-oil would subsequently decompose into smaller molecular products and thus reduce the oil yield (Valdez, et al., 2012).

Fig. 5.3 also illustrates that a higher mass ratio of solvent to feedstock has positive impact on the yield of crude bio-oil. As X_3 (solvent/feedstock mass ratio) increased from 2:1 to 12:1, the resulting yield of oil increased significantly from 17.8 % to 43.5 %, which is likely due to the accelerated sovolysis, hydration and hydrolysis reactions when the solvent concentration was high, and would further lead to an increased yield of bio-oil (Yin, et al., 2010).

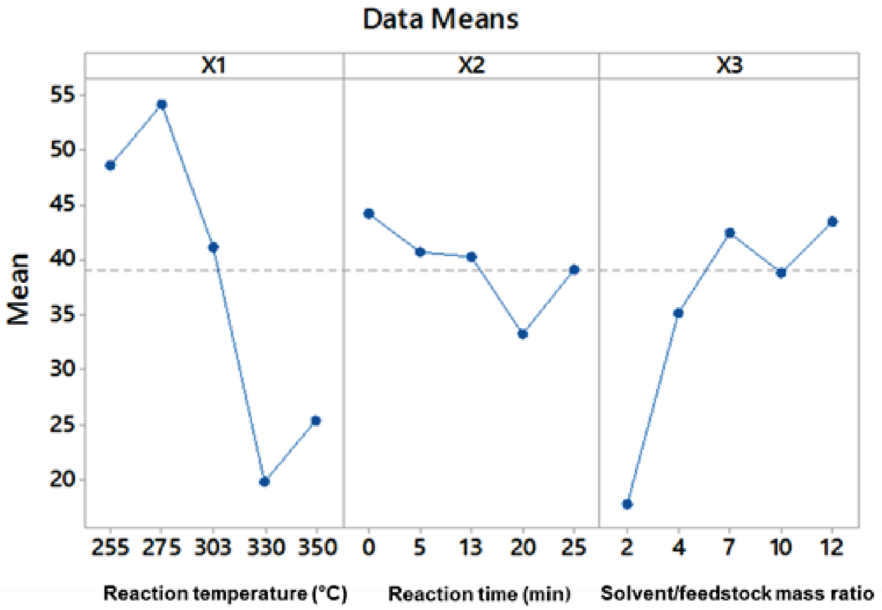


Fig. 5.3. Main effect plots of three independent variables on response of Y_{oil} (yield of crude bio-oil in mass percentage) in actual units.

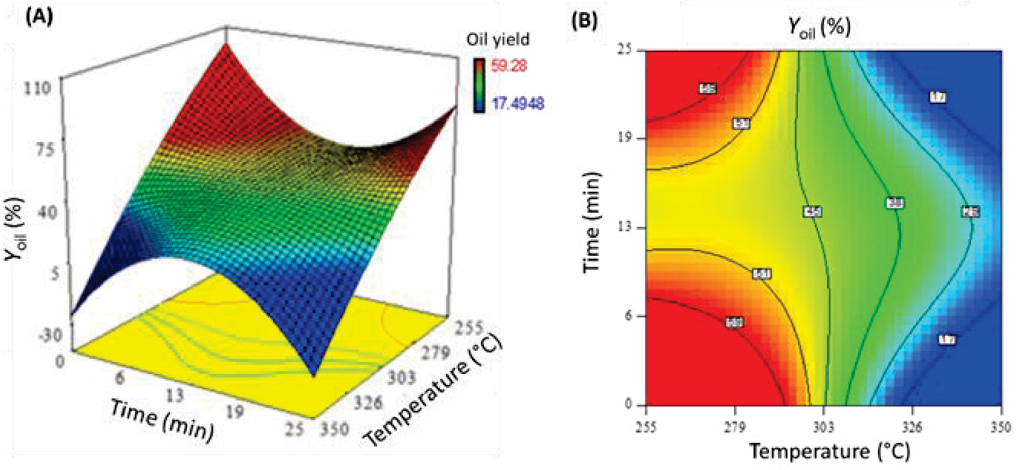
5.3.1.3 Response Surface/contour Plots

The interaction effects of three variables on the yield of crude bio-oil were evaluated using response surface and contour plots. One factor is held constant in each diagram, which enables us to understand how the other two factors interact with each other. The third non-targeted variable was kept at its middle value, i.e., temperature, X_1 = 303 °C, reaction time, X_2 = 13 min, and mass ratio, X_3= 7.

Fig. 5.4 A and B depicts the interactions between reaction temperature and reaction time in response to the yield of crude bio-oil at a constant value of solvent/feedstock mass ratio 7:1. The colors on the response surface plots are diversely covered, indicating that the interaction effects of the two factors on the yield of crude bio-oil are significant. Fig. 5.4A shows that the yield of oil product increases significantly with decreasing temperature and reaction time, suggesting that a higher yield of oil could be obtained at a lower temperature with a shorter reaction time. Fig. 5.4B shows that when the reaction temperature is lower than 279 °C with a reaction time of <6 min, 59 % of oil product can be obtained as predicted.

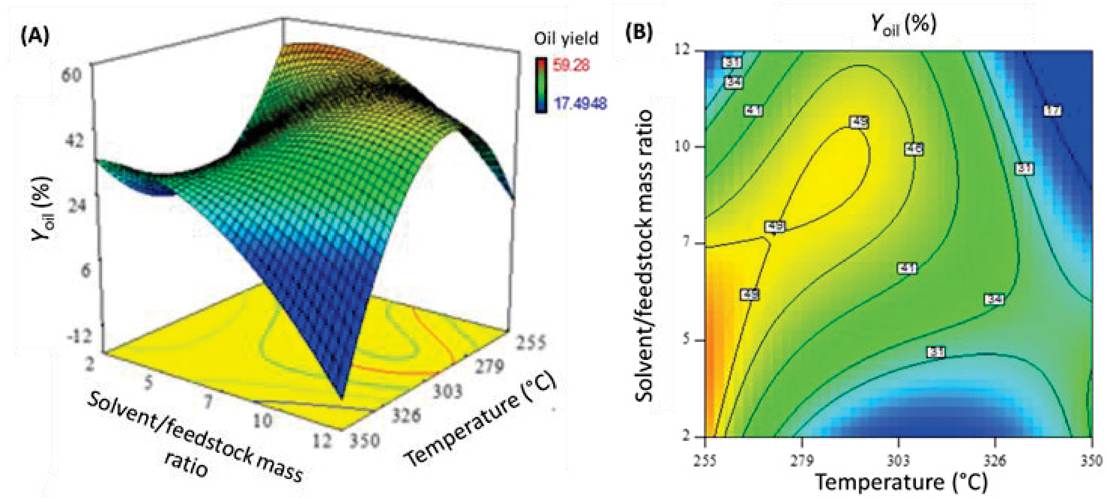
Fig. 5.5A and B presents the interaction effect of reaction temperature and solvent/feedstock mass ratio on the yield of crude bio-oil at a fixed reaction time of 13 min. Fig. 5.5A shows that the yield of crude bio-oil decreases sharply when a high temperature and solvent/feedstock mass ratio is used. However, by decreasing the temperature and maintaining a high solvent/feedstock mass ratio results in a high yield of oil, indicating that high reaction temperature has a negative effect on the bio-oil formation while a high solvent concentration could benefit the bio-oil formation under low temperatures. Fig. 5.5B depicts a nearly elliptical shaped circle on the contour plot, suggesting that high yield of crude bio-oil (49 %) could be achieved when the temperature is between 255 °C and 303 °C when the solvent/feedstock mass ratio varied from 5:1 to 11:1 at a constant reaction time of 13 min.

Fig. 5.6A and B illustrates the interaction between reaction time and solvent/feedstock mass ratio on the yield of oil at a fixed temperature of 303 °C. Fig. 5.5A shows that when we increase the solvent/feedstock mass ratio with a long reaction time, the bio-oil yield at first increases significantly and then decreases slowly after the optimum value. This suggests that a long reaction time is not favorable for maximizing the crude bio-oil. In Fig. 5.6B, a circle counter plot is observed, which indicated that the maximal predicted crude bio-oil yield appears when solvent/feedstock mass ratio is around 10:1 if using a reaction time of 2 min to 6 min.



Fixed level: Solvent/feedstock mass ratio (X_3) = 7:1

Fig. 5.4. Surface (A) and contour (B) plots showing the effect of reaction temperature and reaction time on Y_{oil} (yield of crude bio-oil in mass percentage) with solvent/feedstock mass ratio of 7:1.



Fixed level: reaction time (X_2) = 13 min

Fig. 5.5. Surface (A) and contour (B) plots showing the effect of reaction temperature and solvent/feedstock mass ratio on Y_{oil} (yield of crude bio-oil in mass percentage) with 13 min reaction time.

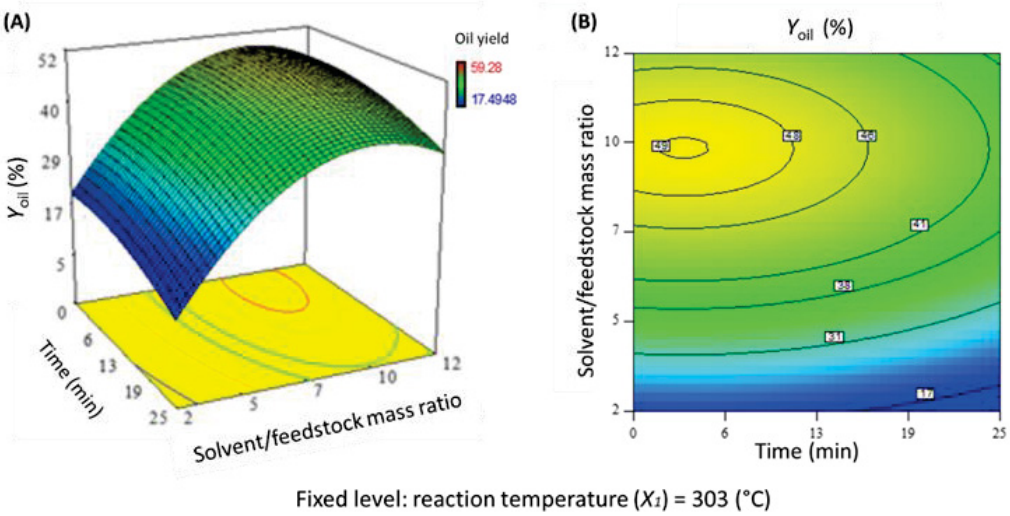


Fig. 5.6. Surface (A) and contour (B) plots showing the effect of reaction time and solvent/feedstock mass ratio on Y_{oil} (yield of crude bio-oil in mass percentage) with 303 °C reaction temperature.

5.3.2 Process Optimization

The mathematical model was developed by the response optimizer (available within Design Expert 7.0) to determine the optimum reaction conditions for the liquefaction of spent K-Cup for maximizing the yield of crude bio-oil. The optimal operating conditions from the models are: reaction temperature of 276.12 °C, reaction time of 2.67 min and solvent/feedstock mass ratio of 11.23:1. The theoretical yield of crude bio-oil predicted by the quadratic model was 61.9 %. Verification experiments were performed under these suggested conditions, and the experimental value of oil yield was found to be 60.0 %, indicating that the generated model was reliable.

5.3.3 Effects of Catalyst on the Liquefaction of Spent K-Cup

5.3.3.1 Effects of Alkaline Catalyst

The liquefaction process of lignocellulosic biomass can be highly influenced by adding alkaline or acidic catalysts (Zhou, et al., 2011). Alkaline catalysts, such as NaOH, Na_2CO_3, K_2CO_3, and KOH, have been widely employed in the direct liquefaction of forest/agricultural biomass to improve oil yield and suppress the formation of solid residues (Yang, et al., 2009; Minowa, et al., 1998a; Minowa, et al., 1998b; Karagöz, et al., 2005; Xu & Lancaster, 2008). The effects of catalysts, NaOH, on the liquefaction of spent K-

Cup was investigated under the pre-optimized reaction conditions (at temperature 276°C, reaction time of 3 min and 11:1 of solvent/feedstock mass ratio). The results in Table 5.5 showed that the addition of NaOH had a positive effect on the liquefaction of spent K-Cups. The yield of solid residues decreased from 36.5 % to 23.5 %, as NaOH loading was in the range of 0 % to 15 % (mass ratio of NaOH to spent K-Cups), indicating an enhancement to liquefaction. While the bio-oil yield was not necessarily increasing accordingly. When a small amount of NaOH was introduced, i.e., 2.5 % and 5 %, there was no significant increase in crude bio-oil yield. As the dosage of NaOH was increased from 5 % to 15 %, the yields of crude bio-oil increased considerably from 61.3 % to 72.9 %. The possible reason might be that NaOH can not only catalyze the decomposition of biomass but also suppress the unfavorable condensation/re-polymerization reactions (Mahmood, et al., 2015; Yang, et al., 2009; Huang, et al., 2013). A further increase in the catalyst loading, no significant improvement in the bio-oil yield was observed. As the dosage of NaOH influences a variety of chemical reactions occurred during liquefaction, the final product profile generally results from a competition among a series of reactions such as decomposition, hydrolysis, re-polymerization and condensation etc. (Huang, et al., 2013; Mahmood, et al., 2015; Behrendt, et al., 2008). Unfortunately, to date, these possible reaction pathways were still not well understood.

The reported experimental results demonstrated that NaOH was a promising catalyst for the liquefaction process of spent K-Cup in the water/ethanol mixture with a suitable dosage in the range of 10 % to 15 % under our experimental scope.

5.3.3.2 Effects of Acidic Catalyst

Liquefaction of lignocellulose biomass can be also acid-catalyzed (Zhou, et al., 2011; Yao, et al., 1993; Hu, et al., 2014; Wang & Chen, 2007; Zhang, et al., 2012). Sulfuric acid was the most commonly used acidic catalyst and has demonstrated high catalytic activity in liquefaction processes. It was believed that acidic catalysts could effectively accelerate hydrolysis, retard re-condensation reactions and thus achieve a high feedstock conversion rate (Zhou, et al., 2011; Hu, et al., 2014; Wang & Chen, 2007). Liquefaction of spent K-Cups was carried out in a water/ethanol mixture (50/50 v/v) at pre-optimized reaction conditions using 2.5 %, 5 % and 10 % (mass ratio of H_2SO_4 to spent K-Cups) dosage H_2SO_4 as a catalyst. Surprisingly, in this study, the addition of H_2SO_4 showed a negative effect on the liquefaction of spent K-Cups. As shown in Table 5.5, when the catalyst loading was 2.5 %, 5 % and 10 %, a remarkable decrease in the oil yield was observed from 60.0 % (without adding H_2SO_4) to 50.7 %, 41.7 % and 38.8 %, respectively. The yield of solid residues increased from 36.5 % (without H_2SO_4) to 36.7 %, 40.9 % and 43.3 %. This observation cannot be elucidated sufficiently in this study. The possible reasons could be attributed to the concentrated acidic medium, which could increase the risk of re-condensation/re-polymerization of the unstable intermediate fragments produced through the secondary de-polymerization of oil compounds, may decrease the crude bio-oil yield but increase the yield of solid residue (Yao, et al., 1993; Zhang, et al., 2012).

Table 5.5. Y_{oil} (yield of crude bio-oil in mass percentage) and Y_{solid} (yield of solid residue in mass percentage) with the type and dosage of catalysts under the reaction condition of 276 °C, 3 min and solvent/feedstock mass ratio of 11:1.

Catalyst	Dosage[a] (%)	Y_{oil}[b] (%)	Y_{solid}[c] (%)
None	0	60.0	36.5
NaOH	2.5	59.4	30.2
	5	61.3	28.8
	7.5	64.4	25.2
	10	72.0	23.6
	15	72.9	23.4
H_2SO_4	2.5	50.7	36.7
	5	41.7	40.9
	10	38.8	43.3

[a] Dosage of catalyst calculated by the ratio of the mass of catalyst to spent K-Cup sample, on a dry basis.
[b] Yield of crude bio-oil in mass percentage, on a dry and ash free basis.
[c] Yield of solid residue in mass percentage, on a dry and ash free basis.

5.3.4 Product Characterization

Feedstock and the resulting crude bio-oil obtained under the optimized reaction conditions (reaction temperature of 276 °C, reaction time of 3 min and solvent/feedstock mass ratio of 11:1, were characterized and reported in the following sections.

5.3.4.1 Thermogravimetric Analysis

The thermal behavior of each component of the feedstock (SCG, PC, PS, PF, and Al) was studied by using Thermo-analytical techniques (TGA and DTG) and the results are shown in Fig. 5.7. For SCG and PF, three steps of weight losses in mass fraction were observed as illustrated in Fig. 5.7A: the first one (~200 °C) corresponding to water and volatile compounds evaporation, the second one (250-350 °C) representing the degradation of hemicellulose and cellulose, and the last one (350-500 °C) corresponding to the combustion process of lignin. The devolatilization curves (DTG) in Fig. 5.7B shows that SCG decomposes in the temperature range of 250 °C to 400°C with the maximum rate of decomposition occurring at around 300 °C. A similar profile of DTG curves in the case of PF is also observed while the maximum rate of decomposition is at higher temperature (around 350 °C). In the case of plastic components (PC and PS), a single stage degradation in the temperature range of 300-480 °C was observed with a maximum weight loss (nearly 100 % mass fraction) at around 440 °C, representing the decomposition of hydrocarbon polymers. Fig. 5.7A also shows that the aluminum foil undergoes a single-stage degradation from 300 to 500 °C with a 23 % mass fraction of weight loss, corresponding to the carbon content in the foil. The weight of the remaining component was constant when the temperature is higher than 500 °C, indicating the remainder was metal. Our thermo-analysis results suggest that biomass degradation occurred at lower temperatures than plastics.

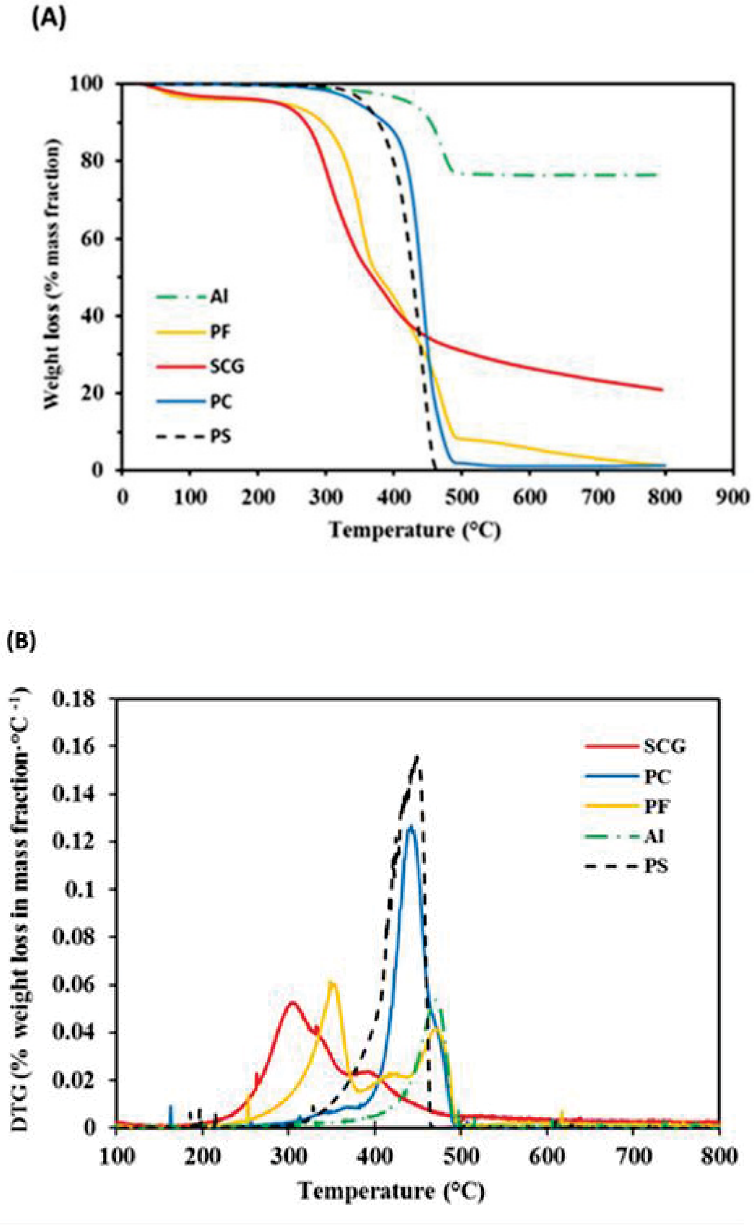


Fig. 5.7. Thermogravimetric curves corresponding to the spent K-Cup components (SCG, PC, PS, PF, and Al).

5.3.4.2 Elemental Analysis

The elemental compositions (C, H and N) of SCG, spent K-Cups and the crude bio-oil obtained under the optimized reaction conditions are presented in Table 5.6. The results showed that spent K-Cups contained higher content of carbon and low nitrogen and oxygen than SCG. This is because that the carbon content in the plastic components (PC and PS) is high. In the resulting crude bio-oil, the carbon content was increased and oxygen was decreased, leading to a HHV 24.7 MJ·kg^{-1}, slightly higher than that of spent K-Cup (20.2 MJ·kg^{-1}).It was concluded that the water-ethanol co-solvent liquefaction process can convert spent K-Cups to crude bio-oil with a bio-oil yield, close to 60 %, however, the improvement of energy density (HHV) was not significant.

Table 5.6. Elemental analyses of SCG, spent K-Cup and crude bio-oil obtained under the reaction condition of 276 °C, 3 min and solvent/feedstock mass ratio of 11:1.

Sample	Elemental compositions, (%)				HHV[b] (MJ·kg^{-1})	H/C (molar ratio)	O/C (molar ratio)
	C	H	N	O[a]			
SCG	40.3	8.3	3.3	47.9	17.0	2.3	0.9
Spent K-Cup	46.0	8.4	2.8	41.1	20.2	2.2	0.7
Crude bio-oil[c]	57.6	7.5	3.4	31.4	24.7	1.6	0.4

[a] by mass difference

[b] Higher heating value calculated by the *Dulong* formula: HHV (MJ·kg^{-1}) = 0.3383C + 1.442 (H-(O/8))

[c] The crude bio-oil derived from spent K-Cup liquefaction in water-ethanol (50/50, v/v) at the temperature of 276 °C in the reaction time of 3 min with solvent/feedstock mass ratio of 11:1.

5.3.4.3 GC-MS

GC-MS analysis was conducted to identify the chemical composition of the resulting crude bio-oil. Table 5.7 illustrates the major compounds in the crude bio-oil derived from spent K-Cup liquefaction under the conditions of 276 °C, 3 min and solvent/feedstock mass ratio of 11:1. The area % (percentage of each compound's chromatographic area out of total area) represented the relative concentration of each compound in the derived crude bio-oil as shown in Table 5.7. The major compounds in the crude bio-oil were long-chain (C_{16}-C_{18}) aliphatic acids (48.88 %), including 30.12 % of n-hexadecanoic acid, 6.97 % of octadecanoic acid and 11.79 % of 9,12-octadecadienoic acid (Z,Z)-. Nearly 29 % of long-chain (C_{16} – C_{20}) esters were also found in the crude bio-oil, such as 9.98 % of hexadecanoic acid, ethyl ester, 4.71 % of hexadecanoic acid, methyl ester, 6.11 % of octadecanoic acid, ethyl ester and 4.63 % of linoleic acid ethyl ester. Additionally, oxygenated aromatic compounds (22.14 %), were identified, including 11.99 % of phenol and 10.15 % of anisole. In general, the presence of aliphatic acid were mainly derived from lipids in the raw materials and the ester compounds were from the thermal degradation of carbohydrates. The aromatic compounds were most likely from the decomposition and re-polymerization of lignin. The similar carboxylic acids or esters are also observed in the crude bio-oil derived from liquefying SCG solely in water solvent in our previous study.

Table 5.7. Major compounds in the crude bio-oil derived from spent K-Cup liquefaction in water-ethanol (50/50, v/v) under the reaction condition of 276 °C, 3 min and solvent/feedstock mass ratio of 11:1.

Peak	RT (min)	Compound name	Formula	Area %
1	4.5018	Anisole	C_7H_8O	10.15
2	5.8378	Phenol	C_6H_8O	11.99
3	10.9974	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	4.71
4	11.3028	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$	9.98
5	11.4491	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	30.12
6	11.9645	Methyl stearate	$C_{19}H_{38}O_2$	1.71
7	12.0026	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$	1.85
8	12.2380	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$	6.11
9	12.2699	Linoleic acid ethyl ester	$C_{20}H_{34}O_2$	4.63
10	12.3780	Octadecanoic acid	$C_{18}H_{36}O_2$	6.97
11	12.4353	9,12-Octadecadienoic acid (Z,Z)-	$C_{18}H_{32}O_2$	11.79
Total area %				100.0

5.3.4.4 FT-IR Analysis

The FTIR spectra of each feedstock component and the resulting crude bio-oil are presented in Fig. 5.8. Similar functional groups were observed in the crude bio-oil and biomass feedstock, suggesting that the crude bio-oil was mainly derived from SCG and PF. For the crude bio-oil, a broad vibration at around 3400 cm^{-1} was attributed to O–H stretching vibrations, indicating the presence of phenols or alcohols derived from lignin content of the biomass feedstock. SCG and PF also showed a strong absorbance at the wave number of 3400 cm^{-1}, indicating a high content of carbohydrates in the biomass feedstock. However, as for PC, PS and Al, it shows no signal at such a wave number range. The absorption peaks between 2800 and 2950 cm^{-1} were typical attributed from C–H stretching vibration which was assigned to alkyl groups, indicating the presence of hydrocarbons in both crude bio-oil and feedstock. Moreover, strong signals at 1650–1750 cm^{-1} were attributed to C=O stretching vibration, corresponding to carboxylic acids in the crude bio-oil (Griffiths & Haseth, 2007; Lievens, et al., 2011). For SCG and PF, weaker signals at the wavenumber of 1650–1750 cm^{-1} were observed, suggesting that more carboxylic acids were formed in liquefaction process. Meanwhile, there was no signals observed at such wavenumber range for PC, PS and Al. The C-H bending at 1350–1470 cm^{-1} representing alkane groups were also observed in all samples. The absorption between 905 cm^{-1} and 1200 cm^{-1} were attributed to C-O stretching vibration, corresponding to carboxylic acids or esters present in the crude bio-oil and biomass feedstock. However, C-O groups were not detected in PC, PS and Al. Additionally, absorption at 670-875 cm^{-1} representing phenyl ring substitution was observed in FP, PC and Al while not detected in other samples. FTIR results provided additional evidence to our observation that plastic components in the feedstock were not decomposed completely made no significant contribution to the crude bio-oil formation under out experimental reaction conditions.

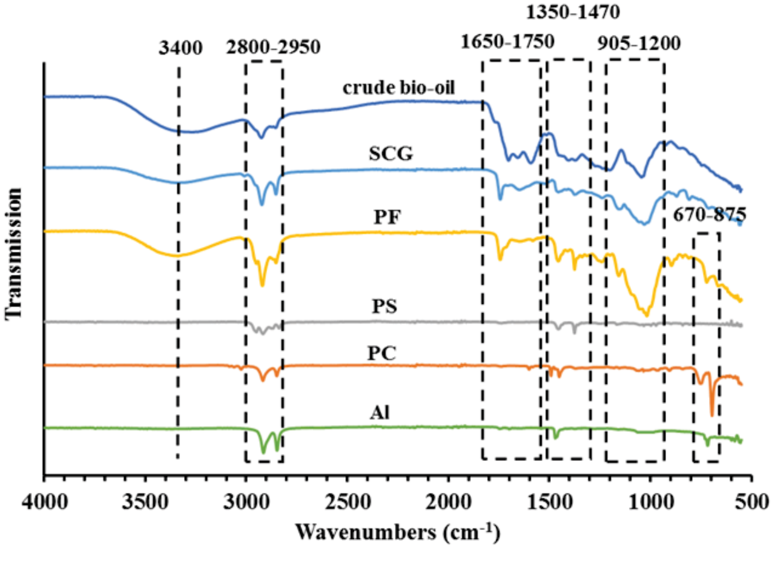


Fig. 5.8. FT-IR spectrum of spent K-Cup components and the crude bio-oil derived from liquefaction process in water-ethanol (50/50, v/v) under the reaction condition of 276 °C, 3 min and solvent/feedstock mass ratio of 11:1.

5.4 Conclusions

Liquefaction of spent K-Cups for the production of crude bio-oil were conducted in sub-/supercritical water-ethanol mixture of 50/50 (v/v). The optimum reaction conditions for maximizing crude bio-oil yield were determined to be a temperature of 276 °C, reaction time of 3 min and solvent/feedstock mass ratio of 11:1, giving the crude bio-oil yield of 60.0 %. The volatile compounds in the resulting crude bio-oil identified using GC-MS and FT-IR were long-chain aliphatic acids, esters and aromatic compounds. The crude bio-oil was mainly derived from the liquefaction of biomass compounds (SCG and PF), while the plastic components (PC and PS) had no significant contribution to the bio-oil formation under the experimental conditions in this study. The presence of catalyst, NaOH promoted the decomposition of feedstock and thus significantly enhanced the bio-oil production and liquefaction efficiency. However, the addition of acidic catalyst, H_2SO_4 showed a negative impact on the liquefaction process, decreasing the crude bio-oil yield.

5.5 Transition Section: Co-liquefaction of SCG with other Lignocellulosic Biomasses

High-lipid/protein materials were also reported to have positive effect on the liquefaction of lignocellulose biomasses (as mentioned in section 2.3.7), especially showing improvement in the quality of the resulting crude bio-oil. SCG has a higher lipid content (~ 15 %), compared with other lignocellulose biomasses, e.g., woody biomass, which could be a feasible material added to the HTL process and co-liquefied with other lignocellulose biomasses. Therefore, co-liquefaction of SCG with other lignocellulose biomasses from different waste streams, e.g., agricultural/forest residues and food-processing waste, are investigated for promoting crude bio-oil production, and will be presented in Chapter 6.

Chapter 6: Co-liquefaction of Spent Coffee Grounds (SCG) and other Lignocellulosic Feedstocks for Crude Bio-oil Production

A version of this chapter is under preparation for the submission to the Journal of Applied Energy 2016.

Contribution statement:

I was responsible for collecting and preparing raw materials, designing and performing all the experiments, samples analysis, data analysis and manuscript preparation.

6.1 Introduction

Fossil fuels (particularly petroleum and natural gas) are the major resources for the production of chemicals and liquid transportation fuels. However, the depletion of non-renewable fossil resources with the resulting adverse effects on global warming and environmental issues has attracted increasing attention. Alternative sources for chemicals and fuels production are sought (Nigam and Singh, 2011). Biomass from waste streams is one of the most abundant and bio-renewable resources for sustainable and green energy production with less or no greenhouse gas emission to the environment due to its carbon neutral life-cycle (Peterson, et al., 2008). The term biomass refers to organic wastes, such as agricultural waste, forest residues, food-processing waste, some animal waste and organics in municipal solid waste. Biomass waste contains carbohydrates, proteins, oils and fats, and lignin (woody biomass) which is therefore a renewable energy source with stored chemical energy that can be potentially recovered by thermochemical processes (Zhou, et al., 2011).

Hydrothermal liquefaction (HTL) is a thermochemical process that converts biomass feedstocks or organic wastes into crude bio-oil using moderate temperature (250–380 °C) and high pressure (5-22 MPa) in sub/supercritical water medium (Beherent, et al., 2008). It is advantageous over most conventional thermochemical processes, such as incineration, pyrolysis and gasification, etc., as it can directly transform wet biomasses into an energy-dense product (crude bio-oil) and eliminate the energy-and-capital-intensive pre-drying process (Furness and Hoggett, 2000). Lignocellulose biomasses from waste streams, including agricultural/forest waste and food-processing waste, were the most widely used feedstocks for crude bio-oil production via HTL, such as corn stalk (Liu, et al., 2013) and barks (Feng, et al., 2014). However, the yields of the resulting crude bio-oil are relatively low with an average value of ~ 28 % mass fraction. In addition, high heteroatom contents in the oil products, including carbonyl compounds, phenols, furans, etc., result in undesirable biofuel quality, such as low heating value, high viscosity and oil acidity, which have limited the application of these products (Peterson, et al., 2008). Therefore, the yield and quality of the resulting crude bio-oil from HTL needs to be significantly improved.

Co-liquefaction of various types of waste materials was found to be an effective way to facilitate the production efficiency in converting waste streams into sustainable bio-energy products and also reduce logistics costs associated with collecting and transporting feedstocks to a center processing plant (Chen, et al., 2014). Liquefaction of lignocellulose feedstocks combined with other types of materials was found to improve the crude bio-oil yield and quality (Yuan, et al., 2009; Gai, et al., 2015). It is an emerging research area with in the last 10 years and very few studies have been reported. Yuan and co-workers (2009) investigated the co-liquefaction of biomass with plastic waste in sub-/supercritical water (from 340 °C to 440 °C). Their results showed that the oil yield increased with a higher proportion of plastic in the feedstock mixture and a significant synergistic effect was found in the co-liquefaction process by resulting in an oil product with a reduced oxygen content and higher heating value (HV). However, a high reaction temperature region (> 380 °C) was required for plastic de-polymerization, which would negatively reduce the energy efficiency and increase operational cost. The addition of high-lipid/protein materials was also found to have positive synergistic effects on the HTL of lignocellulose biomasses. Gai, et al., (2015) studied the co-liquefaction of rice husk with microalgae in subcritical water (from 200 °C to 350 °C), where the oil yields increased gradually as the mass ratio of microalgae/risk husk increased. The oil yield obtained from the co-liquefaction of 60/40 microalgae/rice husk was ~ 40 %, very close to the highest oil yield derived from 100 % microalgae, indicating that the feedstock combination of 60 % microalgae and 40 % rice husk gave a significant positive synergistic effect on the oil yield. A positive synergistic interaction between rice husk and microalgae was also observed in their co-liquefaction process by achieving a better oil quality (reducing acidity and nitrogen content in the oil products). Their results suggested that the different yield and quality of the resulting oil is highly associated with the variation of feedstock chemical compositions. High-lipid and -protein feedstocks (e.g., microalgae and oil seeds) are less thermal resistant than lignocellulose biomasses (with cellulose, hemicellulose and lignin as major compositions), which can decompose more easily in subcritical water, resulting in a higher oil yield (Wang, et al., 2013; Teri, et al., 2014; Liu, et al., 2013; Feng, et al., 2014). In addition, the chemical interaction between biomass fragments may result in the synergistic effect between different feedstocks in the co-liquefaction process.

Spent coffee grounds (SCG) are solid residue obtained from the coffee brewing process and their quantities are considerable resulting from the extremely popular coffee consumption (Bedmutha, et al., 2011). In our previous study presented in Chapter 4, SCG has been investigated as a promising feedstock for crude bio-oil production via HTL by achieving an optimum oil yield of ~ 47 % mass fraction in subcritical water. Compared to other lignocellulose biomasses, SCG contains higher mass of protein (≈ 17 %) and lipid (≈ 15 %), while a lower mass of lignin (≈ 24 %) (Kondamudi et al., 2008; Ballesteros, et al., 2014). Therefore, it is expected that co-liquefaction of SCG with other lignocellulose feedstocks may also promote crude bio-oil production and improve oil quality.

Although HTL of SCG or lignocellulosic biomass has been separately reported, to the best of our knowledge, co-liquefaction of SCG with other lignocellulose biomasses consisting of various chemical compositions has not been reported in the literature. This study explored the co-liquefaction of SCG with other lignocellulose feedstocks from waste streams, including paper filter (PF), corn stalk (CS) and white pine bark (WPB) for crude bio-oil production. The effects of reaction temperature on the product distributions were investigated, aiming to maximize the crude bio-oil yield. The addition of catalyst (Sodium hydroxide NaOH) and various feedstock combination ratios were also tested under the optimum reaction temperature, expecting to produce synergistic effects between these feedstocks during co-liquefaction process. The characterization of resulting crude bio-oils, including elemental analysis, higher heating value, chemical compositions and relative molecular weight, etc., were determined and the synergistic effect on the oil qualities were also explored.

6.2 Experimental

6.2.1 Materials

In the present study, SCG, PF, CS and WPB were selected as representative lignocellulosic biomasses with different chemical compositions, including holocellulose, lignin, protein and extractives. The wet SCG were collected from Tim Hortons, Truro, Canada, after coffee brewing. The PF typically used for coffee filter were selected and purchased from Dollarama, London, Canada, and were crushed and grounded. The CS and WPB were kindly provided by a local sawmill in Northwestern Ontario, Canada. All of the feedstocks were air dried, and ground into particles sieved as 0.841 mm (20 mesh) (Fig. 6.1), then oven-dried at 105 °C in air for several days. All of the dried samples were kept in sealed bags separately and stored in a refrigerator at 4 °C.

The proximate, elemental content and chemical compositions of each dried feedstock were analyzed with the results listed in Table 6.1. Volatile matters were determined by thermogravimetric analysis (TGA) in N_2, heated to 800 °C at 10 °C $\cdot min^{-1}$, then kept at 800 °C in air for 15 min. The volatile matters were calculated by the weight loss below 200 °C. The ash content was determined by combusting feedstocks at 575 °C for 3 h, according to ASTM E1755-01. The elemental compositions were determined by using an Elemental Analyzer (vario EL cube Elementar). The holocellulose content was determined using the modified Chlorination method (ASTM D1104) and the protein content was calculated based on the nitrogen composition from elemental analysis using the nitrogen factor of 6.25. Extractives content was determined by using Soxhlet extraction according to the method of Chemical Analysis and Testing Task Laboratory Analytical Procedure (LAP-010). The lignin (Klason) content was determined through sulfuric acid hydrolysis according to the method of Chemical Analysis and Testing Task Laboratory Analytical Procedure (LAP-003). The chemicals used included acetone and NaOH, all CAS reagent grade, were purchased from the Sigma-Aldrich and were used as received.

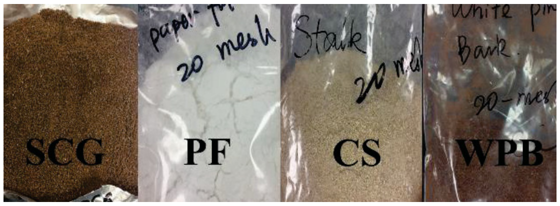


Fig. 6.1. Dried grounded powder of SCG, PF, CS and WPB.

Table 6.1. Characterization of SCG, PF, CS and WPB.

	SCG	PF	CS	WPB
Proximate analysis (%)[a]				
Volatile matter[b]	75.2	79.4	68.9	70.5
Ash[c]	1.1	0.5	2.4	1.1
Elemental compositions (%)[d]				
Carbon	51.4	50.1	44.4	42.7
Hydrogen	7.7	6.2	6.3	6.8
Nitrogen	2.1	0.2	0.5	0
Oxygen[e]	38.8	43.5	48.9	50.5
Chemical compositions (%)[a]				
Holocellulose[f]	61.4	91.5	67.9	44.1
Protein[g]	13.0	1.2	3.1	-
Extractives[h]	10.5	7.3	1.3	5.1
Lignin[i]	27.7	0.7	18.6	49.7

[a] On dry mass basis; in mass fraction.

[b] Determined by thermogravimetric analysis (TGA) in N_2 at 10 °C $\cdot$min^{-1} to 800 °C, and 800 °C in air for 15 min.

[c] Determined by biomass combustion at 575 °C for 3 h, according to ASTM E1755-01.

[d] Determined by elemental analyzer; on dry and ash free basis.

[e] By difference

[f] Determined according to the modified Chlorination method (ASTM D1104).

[g] Calculated based on nitrogen composition from elemental analysis using the nitrogen factor of 6.25.

[h] Determined according to the method of Chemical Analysis and Testing Task Laboratory Analytical Procedure (LAP-010).

[i] Determined according to the method of Chemical Analysis and Testing Task Laboratory Analytical Procedure (LAP-003).

6.2.2 Co-liquefaction Procedure

In this study, co-liquefaction experiments were carried out following the HTL procedures described in section 3.1. In a typical run, dried SCG combined with powder of PF, CS or WPB in various mass ratios were mixed with distilled water to make a feedstock slurry with water/feedstock mass ratio of 5:1. A total of 60 g feedstock slurry (containing 10 g solids and 50 g distilled water) was loaded in the reactor. The reactor was subsequently sealed and purged with high purity nitrogen three times to remove the residual air. Then, the reactor was pressurized with 0.5 MPa nitrogen and heated while being stirred at 4.8 Hz, to the pre-set temperature (varied from 225 °C to 325 °C) and held for 10 min.

6.2.3 Separation of Co-liquefaction Products

After 10 min, the liquefaction reaction was immediately stopped and the reactor was quenched with iced water. After the system had been cooled down to room temperature (< 30 °C), the products were separated following the procedures mentioned in section 3.2. The yields of each product were calculated in mass percentage on a dry basis and defined as follows:

$$Y_{oil}(\%) = \frac{m_{oil}}{m_{feedstock}} \times 100 \quad (1)$$

$$Y_{SR}(\%) = \frac{m_{SR}}{m_{feedstock}} \times 100 \quad (2)$$

$$Y_{gas+WSP}(\%) = 1 - Y_{oil} - Y_{SR} \quad (3)$$

$$Y_{conversion}(\%) = 1 - Y_{SR} \quad (4)$$

where Y_{oil}, Y_{SR}, and $Y_{gas+WSP}$ denote the yield of crude bio-oil, solid residues, combined gas and water soluble product, respectively, in mass percentage, on a dry basis; m_{oil}, $m_{feedstock}$, m_{SR}, $m_{gas+WSP}$ denote the mass of crude bio-oil, feedstock loading to the reactor, solid residue, and gas and water soluble product, respectively, on a dry basis; $Y_{conversion}$ denotes to the feedstock conversion rate of liquefaction process.

The value of synergetic effect (*SE*) of various feedstock combinations in co-liquefaction process can be calculated as follows:

$$SE(\%) = Y_{actual} - Y_{theo} = Y_{actual} - (Y_{SCG} \times Y_{oil-SCG} + (1 - Y_{SCG}) \times Y_{oil-other}) \quad (5)$$

where Y_{actual} and Y_{theo} denote the actual yield of bio-crude oil from co-liquefaction and the theoretical value of crude bio-oil yield, respectively; $Y_{oil\text{-}SCG}$ and $Y_{oil\text{-}other}$ denote the crude bio-oil yields obtained from the liquefaction of pure SCG and pure PF, CS or WPB, individually, under the same operation conditions; Y_{SCG} denotes the mass percentage of SCG in the feedstock mixture.

6.2.4 Crude Bio-oil Characterization

The elemental composition (C, H and N), of the feedstocks and the resulting crude bio-oils were analyzed using an Elemental Analyzer, with oxygen content (O) calculated by difference. The higher heating value (HHV) of the feedstocks, and the crude bio-oils were calculated using the *Dulong* formula based on the elemental compositions described in section 4.2.4. The volatile compositions of the resulting crude bio-oils were analyzed using GC-MS. The relative molecular mass *M*n (number average), *M*w (weight average) and polydispersity index (PDI = *M*w:*M*n) of the resulting crude bio-oils were analyzed using GPC. The specific running programs were described in section 4.2.4. The viscosity of the resulting oil products were measured by Brookfield CAP 2000+ Viscometer and the measurements were recorded at 80 °C.

6.3 Results and Discussions

6.3.1 Effects of Temperature on Product Distributions

During the HTL process, reaction temperature is found to be the most important operating parameter affecting product yields and distributions (Akhtar and Amin, 2011). Consequently, co-liquefaction of SCG with PF, CS and WPB was examined when varying the reaction temperature from 225 °C to 325 °C. Fig. 6.2 illustrates the effect of reaction temperature on product distributions in 10 min reaction times, water/feedstock mass ratio of 5:1 and feedstock combination mass ratios of 50 % SCG with 50 % PF, CS and WPB. As the gas yields were low (less than 1 %) for all experiments, they were added to WSP and presented together as gas + WSP yield.

In general, an incremented reaction temperature ranging from 225 °C to 325 °C, the yield of different products obtained from the co-liquefaction process produced different trends. As shown in Fig. 6.2, when the temperature increased from 225 °C to 250 °C, the yield of resulting crude bio-oil increased from 13.8 %, 10.2 % and 15.5 % to 18.3 %, 21.6 % and 15.6 % for the co-liquefaction of SCG with PF, CS and WPB, respectively. However, a further increase of the temperature led to a slight decrease of oil yield to 15.2 %, 16.7 %, and 15.4 %, as the temperature reached 325 °C. These results reveal that the biomass decomposition was accelerated by the increase of the temperature and the highest oil yields were obtained at 250 °C for the co-liquefaction of all kinds of feedstock combinations. When a higher temperature was applied (> 250 °C), the crude bio-oil yields decreased. This is likely due to the de-polymerization of the oil compounds/intermediates at a higher temperature, reducing the oil formation. With an increase in the reaction temperature, the yields of gas and WSP increased from 32.6 %, 38.8 % and 32.6 % to 55.8 %, 56.6 % and 51.3 %, which was re-formed by the secondary decomposed oil fragments. In contrast, the yields of SR decreased gradually from 53.6 %, 51.0 % and 52.0 % to 28.0 %, 26.8 % and 32.3 % with the increasing temperature, indicating an increased biomass conversion rate and liquefaction efficiency. These results are consistent with the studies reported in the literature (Xu & Lad, 2008; Zhu, et al., 2015; Gan & Yuan, 2013; Xu & Lancaster, 2008; Akhtar & Amin, 2011).

Fig. 6.2 also shows the different performance of various feedstock combinations in the co-liquefaction process. SCG and CS was found to be the most suitable feedstock combination by obtaining the highest crude bio-oil yield while forming the lowest SR under various reaction temperatures. For instance, the yields of the crude bio-oil resulted from the co-liquefaction of SCG with CS were 21.6 %, 20.1 %, and 17.5 % at 250 °C, 275 °C and 300 °C, respectively, which were all higher than that resulted from the co-liquefaction of SCG with PF or WPB. The SR yields obtained from the co-liquefaction SCG with CS were 36.8 %, 30.3 % and 26.6 % under such temperatures, which were all lower than those obtained from the co-liquefaction of SCG with PF or WPB. The co-liquefaction of SCG with PF and WPB resulted in similar oil yields with an average value of ~ 15 % under various temperatures. Particularly, as for the co-liquefaction of SCG with WPB, the SR yield was higher than that obtained from the co-liquefaction of SCG with PF and CS, while the gas and WSP yield was lower. The higher SR yield is likely due to the higher lignin content in WPB (~ 50 %), which is more difficult to decompose in subcritical water, compared to other biomass components (Pavlovic, et al., 2013). The higher proportion of incomplete biomass de-polymerization could consequently lead to a higher yield of SR (Akhtar, et al., 2011). In addition, WPB had the lowest holocellulose content of 44.1 %, leading to a lower yield of WSP (Akhtar, et al., 2011; Sakaki, et al., 1996).

These results suggest that 250 °C is the most suitable reaction temperature for the co-liquefaction of SCG with PF, CS and WPB, giving the highest yield of crude bio-oil with 18.3 %, 21.6 % and 15.6 %, respectively. Therefore, a reaction temperature of 250 °C was used in the following work to investigate the effects of catalyst on the co-liquefaction process.

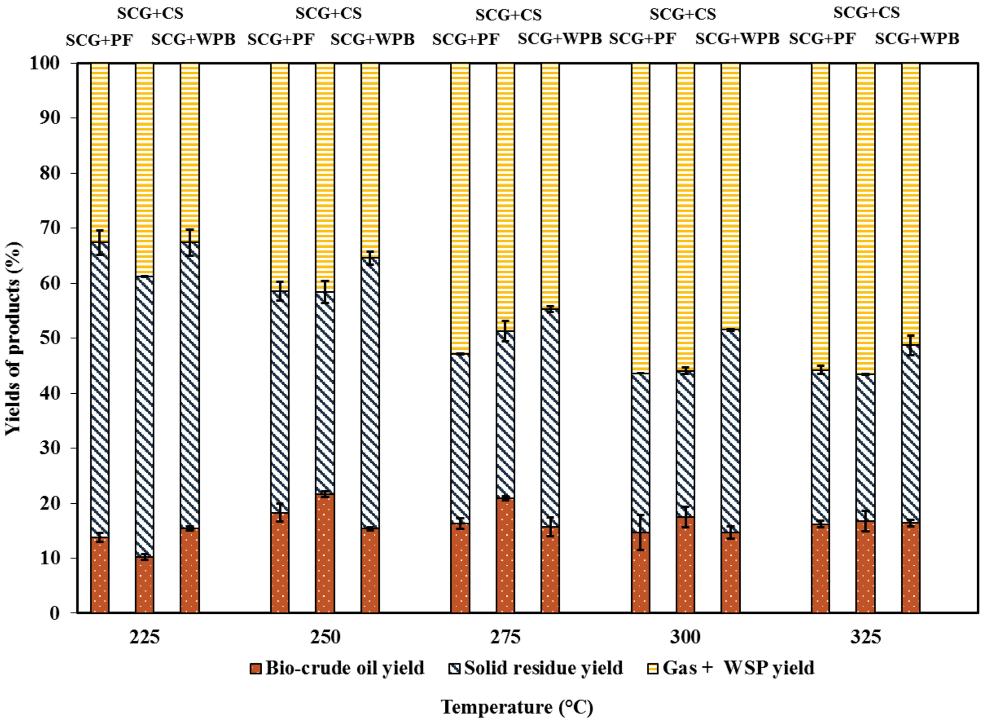


Fig. 6.2. Yields of crude bio-oil, solid residue, gas and WSP obtained from co-liquefaction of 50 % SCG with 50 % PF, CS and WPB at various reaction temperatures.

6.3.2 Effects of Catalyst on Crude bio-oil Yield

The addition of alkaline catalysts, for example, NaOH, Na_2CO_3 and KOH, has been widely reported to have positive effects on crude bio-oil production and enhance biomass conversion rate (Feng, et al., 2014; Karagöz, et al., 2005; Minowa, et al., 1998 a and b; Yang, et al., 2009). In this study, sodium hydroxide (NaOH) was added as a catalyst in the co-liquefaction process, with an expectation of resulting in a significant synergistic effect on the crude bio-oil yield. Fig. 6.3, 6.4, and 6.5 show the effects of NaOH (5 % mass ratio to feedstock, determined from the preliminary experiments trying various NaOH dosage) on the crude bio-oil yields obtained from the co-liquefaction of SCG with PF, CS and WPB, respectively, at 250 °C.

In the absence of 5 % NaOH, the crude bio-oil obtained from the HTL of pure SCG, PF and CS were similar, shown as 19.6 %, 16.8 % and 20.8 %, respectively (Fig. 6.3 and 6.4). In contract, the HTL of WPB gave a low crude bio-oil yield of 6.8 % (Fig. 6.5). The difference of the resulting crude bio-oil yields could be associated with the variation of the chemical compositions in the feedstocks. For instance, SCG, PF and CS contained over 70 % of holocellulose, protein, and extractives in each individual feedstock, which can easily decompose at a low temperature, leading to a higher oil formation (Pavlovic, et al., 2013). In contrast, the de-polymerization of the high-lignin content (~ 50 %) in WPB was difficult at low temperature, consequently resulted in a low oil yield. As for the co-liquefaction, the crude bio-oil yields obtained from the feedstock combinations of SCG with CS, PF, and WPB were 18.3 %, 21.4 % and 15.9 %, respectively, which were all close to the theoretical values (18.2 %, 20.2 % and 13.2 %). These results suggest that no synergistic effect occurred within the co-liquefaction process in terms of the crude bio-oil yields in the absence of 5 % NaOH.

The effects of 5 % NaOH on the co-liquefaction of these feedstock combinations are also presented in Fig. 6.3, 6.4, and 6.5. Fig. 6.3 shows a positive effect of 5 % NaOH on the HTL of pure SCG, by obtaining a higher yield of crude bio-oil (26.7 %), compared with that (18.3 %) obtained in the absence of the catalyst. Such an increase in the oil yield likely resulted from the greater lipid decomposition accelerated by the addition of alkaline material. Similar results were also reported in Chapter 5. The addition of 5 % NaOH also promoted the HTL of WPB, by achieving a ~ 9 % increase of the oil yield (Fig. 6.5), however, little effect was observed on the HTL of pure PF and CS (Fig. 6.3 and 6.4). These results suggest that NaOH can enhance the de-polymerization of lignin in WPB, leading to a higher oil formation, but have little influence on the decomposition of PF and CS with a high holocellulose content.

The addition of 5 % NaOH in the co-liquefaction of SCG with PF and CS resulted in an increased oil yield by ~ 5 % and ~ 8 %, respectively (Fig. 6.3 and 6.4). However, no effects were seen on the co-liquefaction of SCG and WPB, where similar yields of crude bio-oil (~ 16 %) was obtained (Fig. 6.5). Interestingly, the synergistic effects on the co-liquefaction were observed with the addition of 5 % NaOH. Fig. 6.3 and 6.4 show that the actual oil yield obtained from the co-liquefaction of SCG with PF and CS were ~ 23 % and ~ 29 %, respectively, which are higher than the theoretical values (~ 20 % and 24 %). These results indicate that a positive synergistic effect occurred (possibly between lipids and holocellulose) in their co-liquefaction process with the presence of 5 % NaOH, which improved the oil formations. However, a negative effect was observed in the co-liquefaction of SCG with WPB, resulting in a reduced oil yield (~ 17 %), compared with the theoretical value (~ 21 %), which was possibly due to the negative interaction between lipids and lignin with the presence of 5 % NaOH. This result suggests that the addition of 5 % NaOH can not only enhance the crude bio-oil formation, but also promote the appearance of synergistic effect on the co-liquefaction process. More specific synergistic effects of the co-liquefaction of these feedstocks were further investigated in the following section by varying feedstock combination mass ratios.

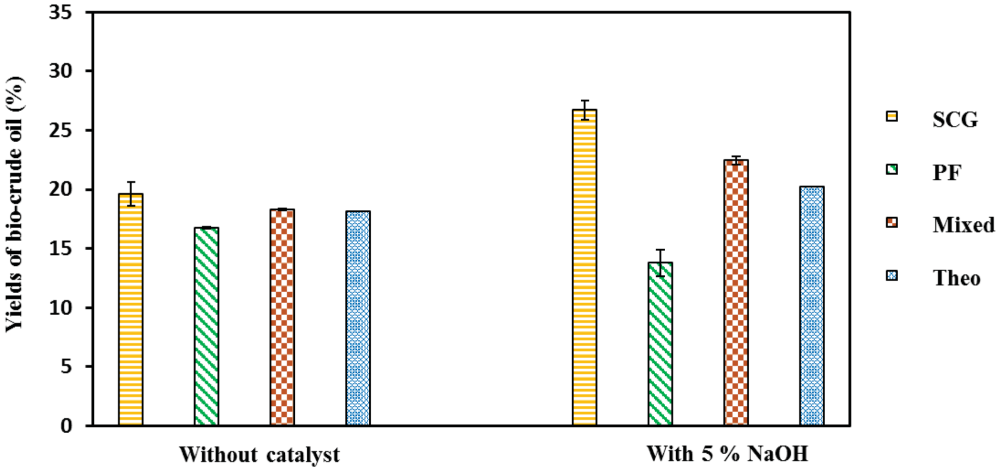


Fig. 6.3. Yields of crude bio-oil obtained from co-liquefaction of SCG and PF at 250 °C with/without adding 5 % NaOH.

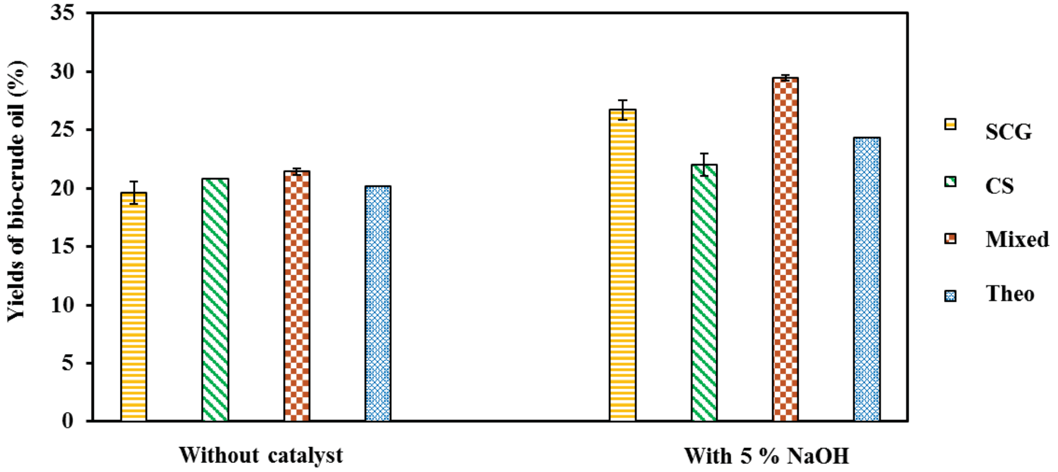


Fig. 6.4. Yields of crude bio-oil obtained from co-liquefaction of SCG and CS at 250 °C with/without adding 5 % NaOH.

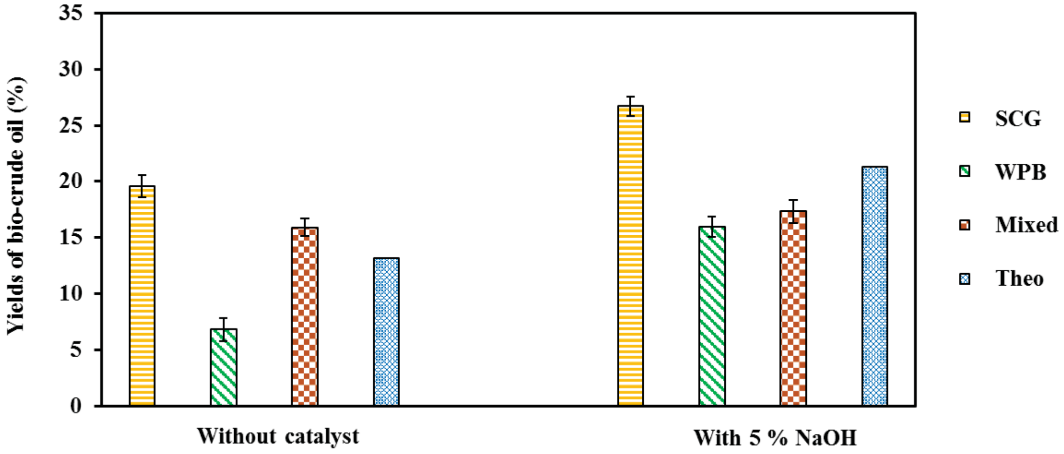


Fig. 6.5. Yields of crude bio-oil obtained from co-liquefaction of SCG and WPB at 250 °C with/without adding 5 % NaOH.

6.3.3. Effects of Feedstock Combination Mass Ratio on Product Distributions

Fig.6. 6, 6.7 and 6.8 presented the effects of various feedstock combination mass ratios on the product distributions of the co-liquefaction of SCG with PF, CS and WSP, respectively, at 250 °C with the addition of 5 % NaOH.

Fig. 6.6 illustrates the product distributions of the co-liquefaction of SCG and PF. As the mass ratio of PF increased, the resulting crude bio-oil yield decreased constantly from 26.7 % at the combination of 0 % PF with 100 % SCG to 13.8 % at the combination of

100 % PF with 0 % SCG. These results suggest that the higher proportion of SCG in the feedstock led to a higher yield of crude bio-oil, which resulted from a greater decomposition of the lignin content in SCG (~ 28 %) facilitated by the addition of alkaline. The SR yield obtained from the co-liquefaction process remained constant at ~ 31 % as the mass ratio of PF increased from 0 % to 50 %. When the mass ratio of PF further increased to 100 %, the SR yield rose from ~ 31 % to ~ 40 %, then decreased to 16.1 %. In contrast, the yield of gas and WSP increased significantly from 44.3 % to 70.1 % with an increase of PF proportion from 70 % to 100 %, which could resulted from the decomposition of the high holocellulose content in PF. The un-monotonic trend of SR and gas plus WSP fractions suggest that synergistic interactions could occur in the co-liquefaction of SCG and PF, which altered the product distributions.

Fig. 6.7 present the effects of CS mass ratios on the product distributions in the co-liquefaction of SCG with CS. As the mass ratio of CS increased, the yield of crude bio-oil gradually increased from 26.7 % at the combination of 0 % CS with 100 % SCG to 29.7 % at the combination of 50 % CS with 50 % SCG, then decreased to 23.0 % as the CS proportion continuously increased. Fig. 6.7 shows that SCG and CS had similar potentials in crude bio-oil production, by resulting a close crude bio-oil yield of 26 % and 23 %, respectively. This is likely due to the similar chemical compositions in these two biomass materials. The SR yield shows a concave trend as the mass ratio of CS increased from 0 % to 100 % and the lowest SR formation of 25.4 % was obtained at the combination of 50 % SCG with 50 % CS. In contrast, the yield of gas and WSP shows a protruding curve by obtaining the maximum yield of 47.8 % at the combination of 70 % SCG with 30 % CS. With the particular interest of maximizing the yield of oil product, the best performance was noted for the feedstock combination mass ratio of 50 % SCG with 50 % CS, at which the oil formation reached the highest level (29.7 %), coinciding with a lowest yield of SR. The results illustrated in Fig. 6.7 strongly indicate the existence of positive synergistic effects the co-liquefaction of SCG with CS, which was further investigated by oil characterization.

The product distributions of the co-liquefaction of SCG with WPB in various feedstock combination mass ratios are illustrated in Fig. 6.8. The results show that the yield of crude bio-oil obtained from the HTL of pure SCG and WPB was 26.7 % and 16.0 %, respectively, with SR yields of 30.7 % and 50.9 %. The possible reason for these two feedstocks resulting in different yields of crude bio-oil and SR was likely due to the difference of their feedstock chemical compositions. Specifically, higher holocellulose/lipid contents (71.9 % in SCG vs. 49.1 % in WPB) could decompose more easily in subcritical water, resulting in a greater oil formation. In contrast, a higher content of lignin in biomass materials (49.7 % in WPB vs. 27.7 % in SCG) could lead to a higher yield of SR. Fig. 6.8 also show that the crude bio-oil yield obtained from the co-liquefaction of SCG with WPB decreased consistently from 26.7 % to 16.0 % as the mass ratio of WPB increased from 0 % to 100 %. The yield of gas and WSP also reduced from 42.6 % to 33.2 %. In contrast, the SR yield rose gradually from 30.7 % to 50.9 % as the proportion of WPB increased. The monotonic trends of the product distributions suggest that no significant synergistic effect appeared in the co-liquefaction of SCG and WPB.

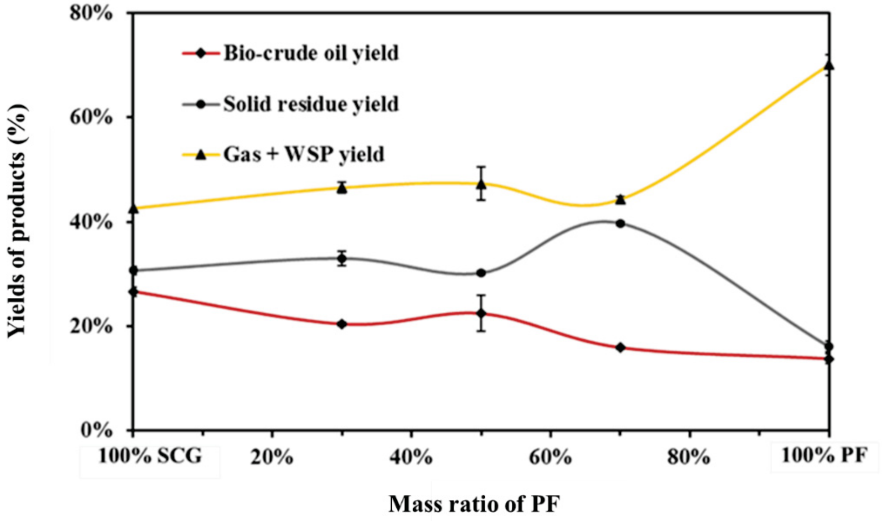


Fig. 6.6. Yields of crude bio-oil, solid residue, gas and WSP obtained from co-liquefaction of SCG and PF at 250 °C with adding 5 % NaOH in various feedstock combination mass ratios.

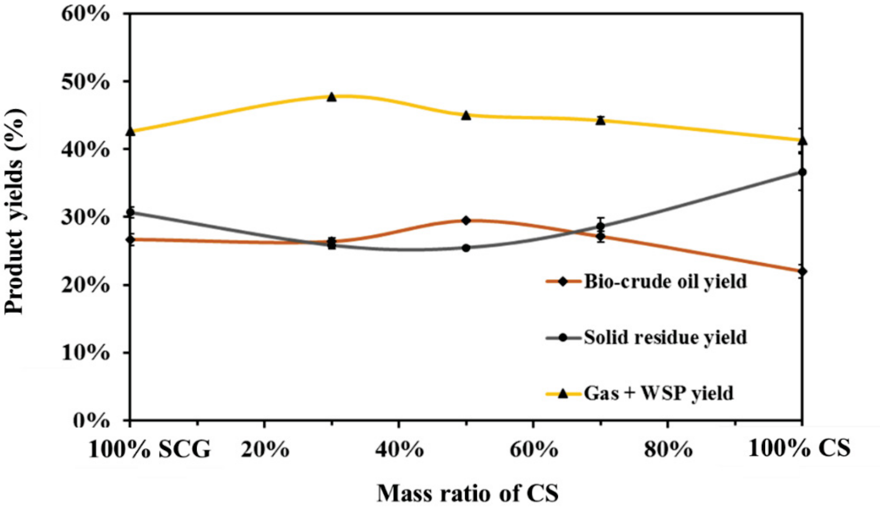


Fig. 6.7. Yields of crude bio-oil, solid residue, gas and WSP obtained from co-liquefaction of SCG and CS at 250 °C with adding 5 % NaOH in various feedstock combination mass ratios.

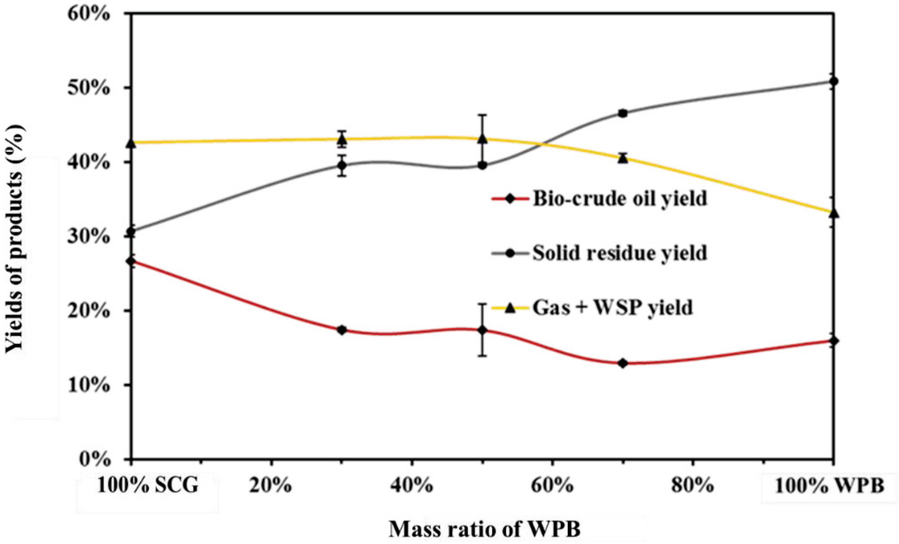


Fig. 6.8. Yields of crude bio-oil, solid residue, gas and WSP obtained from co-liquefaction of SCG and WPB at 250 °C with adding 5 % NaOH in various feedstock combination mass ratios.

6.3.4 Characterization of Crude Bio-oil

6.3.4.1 Elemental Analysis

In order to investigate the synergistic effect of the co-liquefaction of SCG with PF, CS and WPB on the oil quality, elemental analysis of the feedstocks and the resulting crude bio-oils obtained at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios were determined.

Table 6.2 displays the elemental compositions of SCG, PF, and the resulting crude bio-oils derived from the co-liquefaction of SCG and PF. The results show that SCG and PF had similar contents of carbon and hydrogen, while SCG contained a lower content of oxygen, resulting in a slightly higher HHV of 21.5 $MJ \cdot kg^{-1}$, compared with that of PF (18.1 $MJ \cdot kg^{-1}$). In the absence of 5 % NaOH, the crude bio-oil derived from the HTL of SCG had higher contents of carbon and hydrogen and a reduced oxygen content, leading to a significant increase in the HHV to 40.4 $MJ \cdot kg^{-1}$. However, the HHV of the oil derived from the HTL of PF was not remarkably improved. The HHV of the resulting crude bio-oils derived from the co-liquefaction of 50 % SCG and 50 % PF was 25.6 $MJ \cdot kg^{-1}$, which was lower than the theoretical HHV (30.7 $MJ \cdot kg^{-1}$). This result indicates that negative synergistic effects occurred in the co-liquefaction of SCG with PF in terms of the oils' HHVs in the absence of 5 % NaOH.

Table 6.2 also shows the effects of 5 % NaOH on the elemental compositions and the HHVs of the resulting bio-crude oils derived from co-liquefaction of SCG with PF. In the presence of 5 % NaOH, the contents of carbon and hydrogen in the oil products derived from the HTL of SCG was reduced, while the oxygen content increased, resulting in a lower HHV of 31.9 $MJ \cdot kg^{-1}$, compared with that in the absence of 5 % NaOH (40.4 $MJ \cdot kg^{-1}$). These results suggest that 5 % NaOH had a negative impact on the HHVs of the SCG oil. However, the addition of 5 % NaOH shows a slight positive effect on the HTL of PF by obtaining a crude bio-oil with a HHV of 22.1 $MJ \cdot kg^{-1}$, higher than that in the absence of the catalyst (18.1 $MJ \cdot kg^{-1}$). The HHVs of the oil products derived from the co-liquefaction of 70 % SCG with 30 % PF, 50 % SCG with 50 % PF, and 30 % SCG with 70 % PF were 32.1 $MJ \cdot kg^{-1}$, 27.3 $MJ \cdot kg^{-1}$, and 28.9 $MJ \cdot kg^{-1}$, respectively, which were all higher than the theoretical values of 29.0 $MJ \cdot kg^{-1}$, 27.0 $MJ \cdot kg^{-1}$, and 25.0 $MJ \cdot kg^{-1}$. These results reveal that positive synergistic effects appeared in the co-liquefaction of SCG and PF on the oils' HHVs in the presence of 5 % NaOH. Among them, 70 % SCG with 30 % PF was found to be the optimal SCG to PF mass ratios by resulting in a crude bio-oil with the highest HHV of 32.1 $MJ \cdot kg^{-1}$.

Table 6.2. Elemental analysis of SCG, PF and crude bio-oils derived from co-liquefaction of SCG and PF at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Sample	*Elemental compositions, %*				HHV^b $(MJ \cdot kg^{-1})$	HHV_{theo}^c $(MJ \cdot kg^{-1})$
		C	H	N	O^a		
Feedstock[d]	SCG	51.4	7.7	2.1	38.8	21.5	-
	PF	50.1	6.2	0.2	43.5	18.1	-
Without catalyst	Oil from SCG	73.9	12.3	0.8	13.0	40.4	40.4
	Oil from SCG:PF (5:5)	60.4	7.4	1.7	30.5	25.6	30.7
	Oil from PF	56.4	6.0	0	37.6	20.9	20.9
With 5% NaOH	Oil from SCG	66.6	9.2	2.3	21.9	31.9	31.9
	Oil from SCG:PF (7:3)	67.6	9.0	2.3	21.1	32.1	29.0
	Oil from SCG:PF (5:5)	62.3	7.8	1.6	28.2	27.3	27.0
	Oil from SCG:PF (3:7)	65.3	7.8	2.0	24.9	28.9	25.0
	Oil from PF	56.5	6.7	0.1	36.8	22.1	22.1

[a] by mass difference; [b] Higher heating value calculated by the *Dulong* formula: HHV $(MJ \cdot kg^{-1})$ = 0.3383C + 1.442 (H-(O/8)); [c] Theoretical higher heating value calculated by: $HHV_{theo} = HHV_{oil-SCG} \times Y_{SCG} + HHV_{oil-PF} \times (1 - Y_{SCG})$; [d] On a dry basis.

Table 6.3 displays the elemental analysis of SCG, CS and the crude bio-oils derived from the co-liquefaction of SCG and CS. SCG had a higher HHV (21.5 $MJ \cdot kg^{-1}$) than CS (15.2 $MJ \cdot kg^{-1}$). In the absence of 5 % NaOH, the contents of carbon and hydrogen in the oil products derived from the HTL of SCG and CS both increased along with a decreased oxygen content. This resulted in an increase in the oils' HHVs with the values of 40.4 $MJ \cdot kg^{-1}$ and 27.9 $MJ \cdot kg^{-1}$, which were both higher than that of SCG and CS. As for the co-liquefaction of SCG with CS, the HHV of the resulting oil (34.2 $MJ \cdot kg^{-1}$) was close to the theoretical value (33.3 $MJ \cdot kg^{-1}$), indicating no synergistic effect in the co-liquefaction of the SCG with CS in the absence of 5 % NaOH.

Table 6.3 also shows that the addition of 5 % NaOH had no impact on the HTL of CS by resulting the crude bio-oil with a HHV of 27.0 $KJ \cdot kg^{-1}$, close to that as absence (27.9 $MJ \cdot kg^{-1}$). In addition, the interaction effect on the oil's HHVs in the co-liquefaction of SCG with CS was insignificant. For instance, when the feedstock combination mass ratios were 70 % SCG with 30 % CS, 50 % SCG with 50 % CS, and 30 % SCG with 70 % CS, the HHVs of the resulting oil products were 30.4 MJ·kg^{-1}, 29.1 MJ·kg^{-1}, and 30.7 MJ·kg^{-1}, respectively, which were all close to the theoretical values of 30.4 MJ·kg^{-1}, 29.5 MJ·kg^{-1} and 28.5 MJ·kg^{-1}. These results suggest that despite the positive effects on the crude bio-oil yield, co-liquefaction of SCG and CS showed no interaction impact on the oils' HHVs in the presence of 5 % NaOH.

Table 6.3. Elemental analysis of SCG, CS and crude bio-oils derived from co-liquefaction of SCG and CS at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Sample	*Elemental compositions, %*				HHV^{b} (MJ·kg^{-1})	HHV$_{theo}$^{c} (MJ·kg^{-1})
		C	H	N	O^{a}		
Feedstock^{d}	SCG	51.4	7.7	2.1	38.8	21.5	-
	CS	44.4	6.3	0.5	48.9	15.2	-
Without catalyst	Oil from SCG	73.9	12.3	0.8	13.0	40.4	40.4
	Oil from SCG:CS (5:5)	71.7	8.5	1.9	17.9	33.3	34.2
	Oil from CS	67.3	6.7	0.9	25.1	27.9	27.9
With 5% NaOH	Oil from SCG	66.6	9.2	2.3	21.9	31.9	31.9
	Oil from SCG:CS (7:3)	65.0	8.8	2.0	24.1	30.4	30.4
	Oil from SCG:CS (5:5)	65.0	8.1	1.7	25.2	29.1	29.5
	Oil from SCG:CS (3:7)	68.5	7.9	1.7	21.8	30.7	28.5
	Oil from CS	64.7	6.9	1.0	27.3	27.0	27.0

[a] by mass difference; [b] Higher heating value calculated by the *Dulong* formula: HHV (MJ·kg^{-1}) = 0.3383C + 1.442 (H-(O/8)); [c] Theoretical higher heating value calculated by: $HHV_{theo} = HHV_{oil-SCG} \times Y_{SCG} + HHV_{oil-CS} \times (1 - Y_{SCG})$; [d] On a dry basis.

The elemental analysis of SCG, WPB and the resulting crude bio-oils derived from the co-liquefaction of SCG with WPB are summarized in Table 6.4. As for the feedstocks, SCG had a higher HHV (21.5 MJ·kg^{-1}) than WPB (15.1 MJ·kg^{-1}). Also, the HHV of the resulting oil product derived from the HTL of SCG (40.4 MJ·kg^{-1}) was higher than that derived from the HTL of WPB (25.6 MJ·kg^{-1}). As for the co-liquefaction of SCG with WPB, the HHV of the resulting oil product was 26.2 MJ·kg^{-1}, which was lower than the theoretical value of 33.0 MJ·kg^{-1}. This indicates that negative effects occurred in the co-liquefaction of SCG with WPB in the absence of 5 % NaOH.

Similarly to the HTL of CS, the addition of 5 % NaOH showed no impact on the HTL of WPB. The HHV of resulting crude bio-oil derived from the HTL of WPB in the presence of 5 % NaOH was 26.1 MJ·kg^{-1}, which was close to that obtained as absence (25.6 MJ·kg^{-1}). The HHVs of the resulting crude bio-oil derived from the co-liquefaction of SCG and WPB in various feedstock combination mass ratio were 29.0 MJ·kg^{-1}, 31.6 MJ·kg^{-1}, and 28.6 MJ·kg^{-1}, which were all similar to the theoretical values of 30.2 MJ·kg^{-1}, 29.0 MJ·kg^{-1}, and 27.8 MJ·kg^{-1}. This result reveals that no synergistic effect was observed in the co-liquefaction of SCG with WPB in terms of the oils' HHVs in the presence of 5 % NaOH.

Table 6.4. Elemental analysis of SCG, WPB and crude bio-oils derived from co-liquefaction of SCG and WPB at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Sample	***Elemental compositions, %***				**HHV^{b} (MJ·kg^{-1})**	**HHV$_{theo}$^{c} (MJ·kg^{-1})**
		C	**H**	**N**	**O^{a}**		
Feedstock^{d}	SCG	51.4	7.7	2.1	38.8	21.5	-
	WPB	42.7	6.8	0	50.5	15.1	-
Without catalyst	Oil from SCG	73.9	12.3	0.8	13.0	40.4	40.4
	Oil from SCG:WPB (5:5)	61.9	7.3	2.0	28.8	26.2	33.0
	Oil from WPB	61.9	7.1	0.3	30.7	25.6	25.6
With 5% NaOH	Oil from SCG	66.6	9.2	2.3	21.9	31.9	31.9
	Oil from SCG:WPB (7:3)	62.9	8.7	2.0	26.4	29.0	30.2
	Oil from SCG:WPB (5:5)	66.3	9.3	1.0	23.4	31.6	29.0
	Oil from SCG:WPB (3:7)	61.9	8.9	0.8	28.4	28.6	27.8
	Oil from WPB	64.0	6.7	0.2	29.0	26.1	26.1

[a] by mass difference; [b] Higher heating value calculated by the *Dulong* formula: HHV (MJ·kg^{-1}) = 0.3383C + 1.442 (H-(O/8)); [c] Theoretical higher heating value calculated by: $HHV_{theo} = HHV_{oil-SCG} \times Y_{SCG} + HHV_{oil-WPB} \times (1 - Y_{SCG})$; [d] On a dry basis.

6.3.4.2 GC-MS

In order to examine the synergistic effects of the co-liquefaction of SCG with PF, CS and WPB on the chemical compositions of the resulting crude bio-oils, GC-MS analysis was conducted to identify the major compounds of the oil products. Fig. 6.9, 6.10, and 6.11 summarize the distributions of the volatile compounds characterized by GC-MS in the oil products resulting from the co-liquefaction of SCG with PF, CS and WPB at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios. As shown in Fig. 6.9, 6.10 and 6.11, the major compounds were categorized into five classes based on the functional groups, including (1) long-chain carboxylic acids, (2) hydrocarbons (e.g., alkanes, alkenes and their derivatives), (3) N & O-heterocyclic compounds, (4) esters, ketones, alcohols and aldehydes, and (5) cyclic oxygenates (e.g., phenols and their derivatives). It should be noted that the compounds containing more than one functional group were categorized into only one group. The major compounds of the resulting oil products with the relative total peak area higher than 1 % are summarized and available in supplementary data presented in Appendix.

Fig. 6.9 illustrates the chemical components of the oil products obtained from the co-liquefaction of SCG with PF. In the absence of 5 % NaOH, the main volatile compounds in the crude bio-oil obtained from the HTL of SCG were long-chain carboxylic acids (98.98 %), mainly including n-Hexadecanoic acid (46.23 %) and 9,12-Octadecadienoic acid (Z,Z)- (50.83 %), which were likely derived from lipids/proteins in the SCG. As for the HTL of PF, 100 % of 5-HMF (aldehydes) were detected in the resulting oil product, which could be derived from the high content of holocellulose (91.5 %) in PF. Interestingly, the major compounds in the oils obtained from the co-liquefaction of SCG with PF were similar to that in the SCG oil, by having long-chain carboxylic acids (94.64 %) with n-Hexadecanoic acid (45.40 %) and Octadecadienoic acid (Z,Z)- (46.82 %) included. Only little amount of 5-HMF (2.55 %) and N & O heterocyclic compounds (i.e., 2.84 % of 1,2,4-Oxadiazole, 5-methyl-3-(1-piperidylmethyl)-) was detected. These results indicate that the oil obtained from the co-liquefaction of SCG and PF was mainly derived from the decomposition/de-polymerization of lipid content in the SCG in the absence of 5 % NaOH.

Fig. 6.9 also provides the major compounds in the crude bio-oils resulted from the co-liquefaction of SCG with PF in the presence of 5 % NaOH. The results show that the SCG oil mainly contained 98.83 % of carboxylic acids, similar to that as absence. As for the HTL of PF, no volatile compounds were detected, indicating that the addition of alkaline catalyst could suppress the formation of aldehyde compounds in the oil product. Another reason could be due to the enhancement of alkaline catalyst on the formation of non-volatile compounds which was not detected by GC-MS. In addition, the chemical compositions of the resulting crude bio-oils derived from the co-liquefaction of SCG with PF showed no difference when varied feedstock combination mass ratios, all of which contained carboxylic acids as their major compounds.

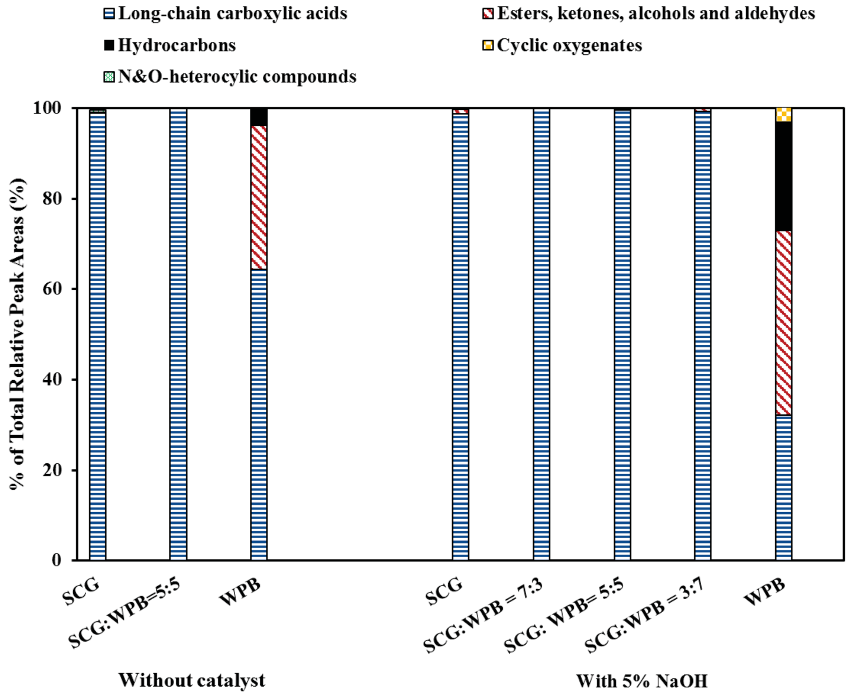


Fig. 6.9. Effects of catalyst and feedstock combination mass ratio on the major compositions of crude bio-oils derived from co-liquefaction of SCG and PF at 250 °C.

Fig. 6.10 provides the chemical compositions of the resulting crude bio-oils derived from the co-liquefaction of SCG with CS. It can be seen from Fig. 6.10 that the major compounds in the oil product derived from the HTL of CS in the absence of 5 % NaOH were aldehydes (30.38%) (i.e., 5-HMF, and Vanillin), long-chain carboxylic acids (32.6 %)

(i.e., n-Hexadecanoic acid and Octadecadienoic acid (Z,Z)-), and cyclic oxygenates (25.74 %) (i.e., Phenol, 4-ethyl- and Phenol, 2,6-dimethoxy-). The aldehydes and carboxylic acids were likely derived from the holocellulose in CS, and the cyclic oxygenates, mainly containing phenols and its derivations, were mainly derived from the lignin content. As for the co-liquefaction of the SCG with CS, the major compounds in the oil product were also carboxylic acids, similar to that obtained from the co-liquefaction of SCG with PF.

In the presence of 5 % NaOH, the resulting crude bio-oil obtained from the HTL of CS contained higher amount of carboxylic acids (64.1 %) and lower amount of aldehydes (8.9 %), compared with that obtained as absence. This result suggests that the addition of the alkaline catalyst could enhance the decomposition of lipids and form more carboxylic compounds while inhabit the aldehydes formation. When the mass ratio of CS increased from 0 % to 100 %, the amount of carboxylic acids in the oil product reduced from 100 % to 64.1 %. This might be likely due to the reduced proportion of SCG in the feedstock, which led to a lower content of lipid, consequently reducing the carboxylic acids formation. In contrast, higher amount of aldehydes and phenols were detected as the CS proportion increased, which was possibility due to the higher content of holocellulose in CS and the greater lignin decomposition enhanced by the alkaline material.

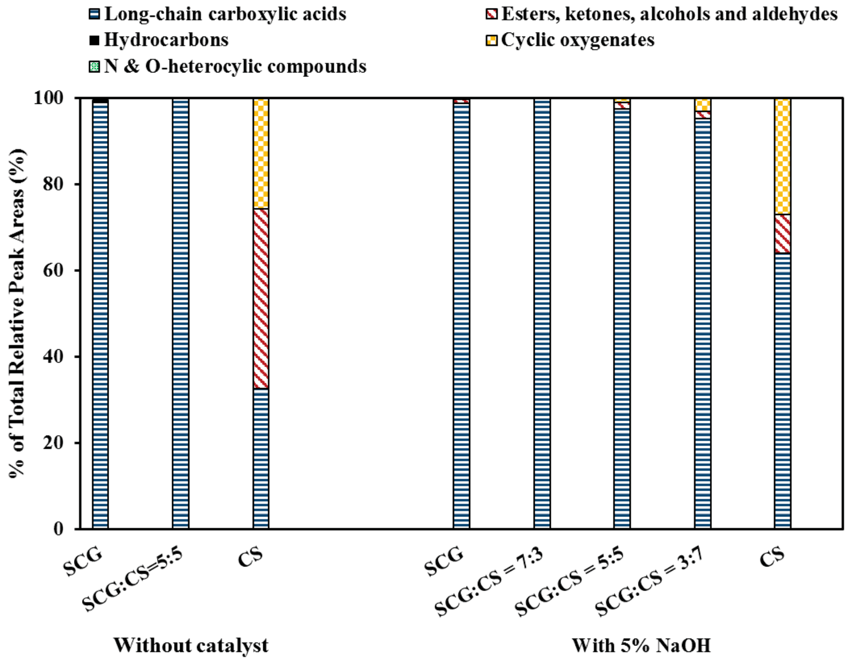


Fig. 6.10. Effects of catalyst and feedstock combination mass ratio on the major compositions of crude bio-oils derived from co-liquefaction of SCG and CS at 250 °C.

The effects of 5 % NaOH and various feedstock combination mass ratios on the chemical compositions of the resulting crude bio-oils obtained from the co-liquefaction of SCG and WPB were illustrated in Fig. 6.11. In the absence of 5 % NaOH, the major components in the crude bio-oil derived from the HTL of WPB were long-chain carboxylic acids (64.34 %), 5-HMF (31.89 %) and hydrocarbons (3.76 %, i.e., Methyl 9,12-heptadecadienoate). Interestingly, no phenols/derivations were detected even WPB had high content of lignin of ~ 50 %. This might be due to the insufficient decomposition/de-polymerization of the lignin content in the WPB at a low reaction temperature (at 250 °C in this study), which resulted in an insignificant formation of cyclic oxygenates. Similarly to the combination of SCG with PF or CS, large amount of carboxylic acids were detected in the oil product obtained from the co-liquefaction of SCG and WPB, which were derived from the lipid content in the SCG. In contrast, no contribution of WPB to the oil formation was observed.

In the presence of 5 % NaOH, the amount of aldehyde, hydrocarbon and phenol compounds in the oil product resulted from the HTL of WPB all increased from 31.89 %, 3.76 % and 0 % to 40.79 %, 24.01 % and 5.97 %, respectively. However, the carboxylic acids decreased significantly from 64.34 % to 32.17 %. These results reveal that the addition of alkaline material could enhance the dynamics of intermediate reactions, where the carboxylic acids de-polymerized to form more hydrocarbons and aldehydes. Also, the decomposition of lignin was enhanced by the addition of 5 % NaOH, resulting in a formation of phenol compounds. Similarly to the co-liquefaction of SCG and PF, the difference of feedstock combination mass ratios showed no effects on the oil compositions with carboxylic acids as the major components.

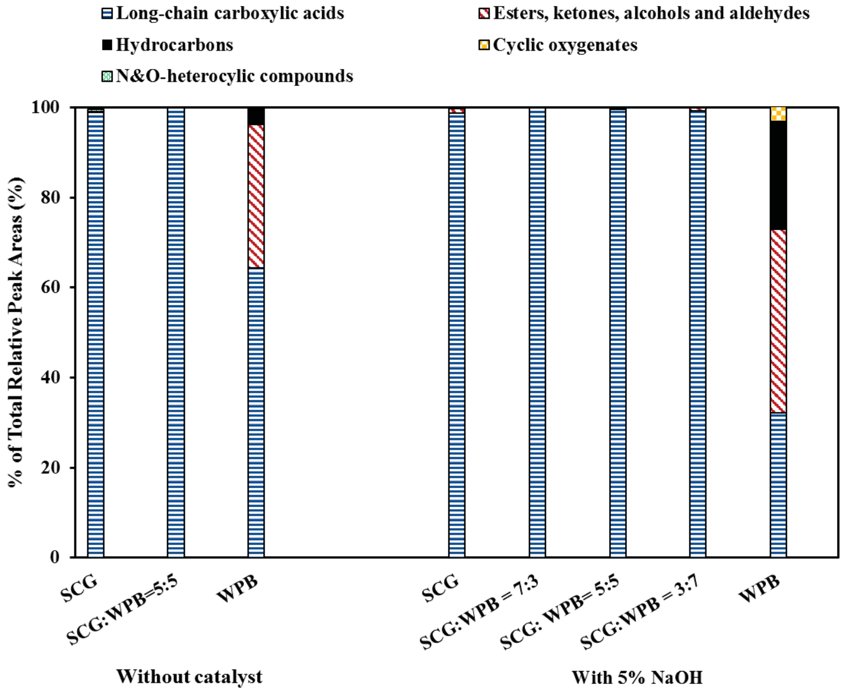


Fig. 6.11. Effects of catalyst and feedstock combination mass ratio on the major compositions of crude bio-oils derived from co-liquefaction of SCG and WPB at 250 °C.

6.3.4.3 GPC

The relative molecular mass of the crude bio-oils was reported to have significant impact on the properties of the oil product, such as viscosity and HHV (Cheng, et al., 2010). More importantly, it is a key property for its application as a future liquid fuel replacing for market petro-fuels. Therefore, the relative molecular mass and distributions for the resulting crude bio-oil resulting from the co-liquefaction of SCG with PF, CS and WPB were measured using GPC and summarized in Table 6.5, 6.6 and 6.7.

Table 6.5 presents the average molecular mass (M_w and M_n) of the crude bio-oils derived from the co-liquefaction of SCG and PF at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios. The results show that the relative molecular mass and distributions of the oil products obtained under all reaction conditions were similar, where the M_n, M_w and PDI was in the range of 278 g/mol to 306 g/mol, 394 g/mol to 793 g/mol, and 1.60 to 2.62, respectively. The crude bio-oil obtained from the HTL of SCG had a higher relative molecular mass than that of the PF oil. For instance, the SCG oil obtained in the presence/absence of 5 % NaOH had an M_w of 705 g/mol and 793 g/mol, respectively, both of which were higher than that of the PF oil with an M_w of 466 g/mol and 394 g/mol. Surprisingly, the molecular mass of the oil products obtained from the co-liquefaction of SCG with PF was in the range of 458 to 471 g/mol, which was similar to the PF oil while lower than that of the SCG oil. These results suggest that positive synergistic effects occurred in the co-liquefaction of SCG with PF, resulting in a reduced relative molecular mass of the oil products.

Table 6.6 illustrates the average molecular mass of the crude bio-oils obtained from the co-liquefaction of SCG and CS in various feedstock combination ratios. The results show that the oils obtained from the HTL of SCG and CS had a similar M_w, with the values of 793 g/mol and 611 g/mol, respectively, indicating the similar chemical compositions in SCG and CS. In the presence of 5 % NaOH, the M_w of the resulting oil products obtained from the co-liquefaction of SCG with CS in various feedstock combination mass ratios was in the range of 502 g/mol to 561 g/mol, which was lower than that obtained from the HTL of SCG or CS. These results also demonstrate the existence of the positive synergistic effects in the co-liquefaction of SCG and CS.

Similarly to the co-liquefaction of SCG with PF or CS, slightly positive effects were also observed in the co-liquefaction of SCG and WPB. Table 6.7 shows that the M_w of the crude bio-oils obtained from the co-liquefaction of SCG with WPB was in the range of 510 g/mol to 583 g/mol, which was slightly lower than that obtained from the HTL of SCG or WPB. In the absence of 5 % NaOH, the WPB oil had a lower M_w of 379 g/mol, than SCG oil. In the presence of 5 % NaOH, the M_w of the WPB oil increased from 379 g/mol to 622 g/mol, while less effect was observed on the SCG oil.

Table 6.5. Average molecular mass of crude bio-oils obtained from co-liquefaction of SCG and PF at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Sample	M_n	M_w	PDI
without catalyst	Oil from SCG	303	793	2.62
	Oil from SCG:PF (5:5)	242	475	1.97
	Oil from PF	202	394	1.95
with 5% NaOH	Oil from SCG	306	705	2.30
	Oil from SCG:PF (7:3)	278	466	1.68
	Oil from SCG:PF (5:5)	284	471	1.66
	Oil SCG:PF (3:7)	284	458	1.61
	Oil from PF	291	466	1.60

Table 6.6. Average molecular mass of crude bio-oils obtained from co-liquefaction of SCG and CS at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Sample	M_n	M_w	PDI
without catalyst	Oil from SCG	303	793	2.62
	Oil from SCG：CS (5:5)	290	520	1.79
	Oil from CS	313	611	1.95
with 5% NaOH	Oil from SCG	306	705	2.3
	Oil from SCG:CS (7:3)	294	513	1.74
	Oil from SCG:CS (5:5)	312	561	1.8
	Oil from SCG：CS (3:7)	305	502	1.65
	Oil from CS	349	706	2.02

Table 6.7. Average molecular mass of crude bio-oils obtained from co-liquefaction of SCG and WPB at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Sample	M_n	M_w	PDI
without catalyst	Oil from SCG	303	793	2.62
	Oil from SCG:WPB (5:5)	259	542	2.1
	Oil from WPB	212	379	1.78
with 5% NaOH	Oil from SCG	306	705	2.3
	Oil from SCG:WPB (7:3)	302	567	1.88
	Oil from SCG:WPB (5:5)	288	583	2.02
	Oil from SCG:WPB (3:7)	297	510	1.72
	Oil from WPB	359	622	1.73

6.3.4.4 Viscosity

Viscosity is another important property being part of the oil quality evaluations. It represents the fluidity of liquid fuels, a lower viscosity results in a higher fluidity. Therefore, the viscosity of the resulting crude bio-oils obtained from the co-liquefaction of SCG with PF, CS and WPB at 250 °C was also measured and summarized in Table 6.8.

Table 6.8 shows that the viscosity of the SCG oil in the absence of 5 % NaOH was 409 cP, which was much lower than that of PF oil (2989 cP), CS oil (3251 cP) and WPB oil (11374 cP). These results suggest that the oils obtained from the HTL of SCG were better than that obtained from the HTL of PF, CS and WPB, in terms of the oil viscosity and fluidity. As for the co-liquefaction of SCG with PF, CS and WPB, the viscosities of the resulting crude bio-oils were 169 cP, 1420 cP, and 480 cP, respectively, which were much lower than that of the oils derived from pure PF, CS and WPB. This result indicates that the addition of SCG had positive effects on the oil viscosity.

The effect of 5 % NaOH on the oil viscosity is also presented in Table 6.8. The results show that the presence of 5 % NaOH had negative impacts on the fluidity of the oil products obtained from the HTL of PF and CS, by increasing the viscosities from 2989 cP and 3251 cP, to 8044 cP and 11926 cP, respectively. In contrast, such an impact on the crude bio-oils derived from the HTL of SCG and WPB was less significant. With the increase of SCG proportion in the feedstock, the viscosities of the oils obtained from the co-liquefaction of SCG with PF and CS were both reduced. For instance, the viscosities of the oil products obtained from the co-liquefaction of 70 % SCG with 30 % PF or CS were 2592 cP and 6531 cP, respectively, both of which were lower than that obtained from the co-liquefaction of 30 % SCG with 70 % PF or CS. In contrast, as for the co-liquefaction of SCG with WPB, the increase of SCG proportion led to a higher oil viscosity. Interestingly, 50 % SCG with 50 % PF, CS and WPB appeared to be the most suitable feedstock combination mass ratios, where the lowest oil viscosities of 1845 cP, 964 cP and 375 cP were obtained, indicating the highest oil fluidity. These results also suggest that the co-liquefaction had significant interaction effects on the oil viscosity.

Table 6.8. Viscosity of crude bio-oils obtained from co-liquefaction of SCG with PF, CS and WPB at 250 °C with/without adding 5 % NaOH in various feedstock combination mass ratios.

	Without catalyst			With 5% NaOH				
Feedstock	SCG	SCG:PF (5:5)	PF	SCG	SCG:PF (7:3)	SCG:PF (5:5)	SCG:PF (3:7)	PF
Viscosity 80°C (cP)	409	169	2989	375	2592	1845	6599	8044
Feedstock	SCG	SCG:CS (5:5)	CS	SCG	SCG:CS (7:3)	SCG:CS (5:5)	SCG:CS (3:7)	CS
Viscosity 80°C (cP)	409	1420	3251	375	6531	964	9120	11926
Feedstock	SCG	SCG:WPB (5:5)	WPB	SCG	SCG:WPB (7:3)	SCG:WPB (5:5)	SCG:WPB (3:7)	WPB
Viscosity 80°C (cP)	409	480	11374	375	7118	375	2681	10821

6.4 Conclusions

Co-liquefaction of SCG with PF, CS and WPB from waste streams were carried out in subcritical water at reaction temperature varying from 225 °C to 325 °C for crude bio-oil production. The optimal reaction temperature for maximizing the crude bio-oil yield obtained from the co-liquefaction of 50 % SCG with 50 % PF, CS and WPB was determined to be 250 °C, giving the highest crude bio-oil yields of 18.3 %, 21.6 % and 15.6 %, respectively. SCG with CS was found to be the best feedstock combination by obtaining a higher yield of oil and a lower yield of solid residue. In this study, no synergistic effect was observed in the co-liquefaction process in terms of the oil yield in the absence of a catalyst. Major volatile compounds in the oil products resulted from the co-liquefaction process with various feedstock combination mass ratios were identified using GC-MS, where the high amount of carboxylic acids suggested that the co-liquefaction could facilitate the de-polymerization of lipids while suppress the lignocellulose decomposition.

The addition of 5 % NaOH was found to promote the appearance of synergistic effects in the co-liquefaction process and the most significant effects occurred in the co-liquefaction of SCG with CS. The highest oil yield of 29.7 % was achieved at a combination mass ratio of 50 % SCG with 50 % CS, with the highest feedstock conversion rate of 75.6 %. The co-liquefaction process also reduced the relative molecular mass of the oil products, with the lowest oil viscosity obtained at the feedstock combination ratio of 50 % SCG with 50 % PF, CS and WPB. This study strongly suggests that the synergistic effects occurred in the co-liquefaction of SCG and the other lignocellulose biomasses improved the oil yield and quality.

Chapter 7: Overall Conclusions and Future Work

7.1 Overall Conclusions

In this research, HTL was demonstrated a promising technology to utilize the bio-waste streams to produce high-energy-density crude bio-oil. SCG was for the first time identified as a suitable feedstock for the crude bio-oil production *via* HTL, with the highest crude bio-oil yield of 47.3 % mass fraction. The higher heating value (HHV) of the resulting crude bio-oil was much higher than that of SCG. The yield of the crude bio-oil derived from the HTL of SCG was higher than those of many lignocellulose feedstocks and the HHV of the resulting oil was comparable to that of lignocellulose feedstocks.

Liquefaction of spent K-Cups in water-ethanol mixture has been demonstrated being a suitable option to treat spent K-Cups waste streams. The reaction conditions were optimized to obtain the highest crude bio-oil yield of ~ 60.0 %, indicating that liquefaction had great potential in converting spent K-Cups to bioenergy. The oil compositions identified from GC-MS and FT-IR showed that the crude bio-oil was mainly derived from the liquefaction of SCG (and other biomass compounds) while little amount of plastic component in the spent K-Cups feedstock was liquefied under the optimized reaction condition. This results also suggested that a higher reaction temperature was required in the liquefaction of plastics.

Co-liquefaction of SCG with lignocellulose biomasses (PF, CS and WPB) was also conducted for crude bio-oil production in the processes with/without the addition of catalysts. SCG with CS were identified as the best feedstock combination, giving the highest yield of crude bio-oil (21.4 % without catalyst; 29.7 % with catalyst) and the feedstock conversion rate (63.2 % without catalyst; 74.6 % with catalyst). Significant synergistic effect was observed between SCG and the other lignocellulose biomass in their co-liquefaction process when alkaline material was added as catalysts. The oil yield and quality was highly improved at the mixing ratio of SCG and the other lignocellulose feedstock of 1:1. This results suggested that co-liquefaction of various feedstock mixtures could be an effective way to enhance the crude bio-oil production, and also reduce logistics costs associated with collecting and transporting feedstocks to a center processing plant.

7.2 Future Work

HTL is an emerging technology that is able to convert biomasses to crude bio-oils and it is currently researched and developed on a lab-scale. More research related to the improvement of the energy and cost efficiency are highly required for a pilot-scale or commercialization in a long term run. The study presented in Chapter 4 is the first attempt to utilize the waste stream from the coffee industries for the crude bio-oil production via HTL. More research is needed and recommended, including the liquefaction process conducted in other solvents (e.g., ethanol, acetone, etc.) or co-solvents, the use of reducing gas (e.g., H_2, CO), and the investigation on the effects of catalysts on the yield and composition of the resulting crude bio-oil. The chemical compositions of the water soluble product derived from HTL of SCG is also recommended to be analyzed and organic components are suggested to be recovered.

Future research on the co-liquefaction of SCG with plastic waste should be further investigated in a wider range of reaction temperature after the design of the batch-scale reactor with higher-pressure tolerance. The chemistry of synergistic effect between SCG and plastic in their co-liquefaction process on the oil yield and oil quality should be also studied. In addition, the use of other types of organic solvents (e.g., acetone, methanol, etc.) or co-solvents are encouraged to apply in the liquefaction of spent K-Cups in order to promote the crude bio-oil production and increase the liquefaction efficiency.

Co-liquefaction of SCG and lignocellulose has demonstrated promises in enhancement of crude bio-oil yield. The mixtures of SCG with other types of waste materials, e.g., animal manure, microalgae, etc., should be also investigated. The effect of solvent/feedstock mass ratios are recommended to be further studied to find the potential synergistic effect in the co-liquefaction process without adding catalysts. Identifying the liquefaction mechanism and possible reaction pathways between various feedstock compositions is very challenging however is highly recommended to be further explored.

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Appendices:

Supplementary Material:

Table S1. Major compounds of the resulting crude bio-oils derived from co-liquefaction of SCG and PF at 250 °C in 10 min reaction time with the water/feedstock ratio of 5:1 in various feedstock combination mass ratios with/without adding 5 % NaOH.

Peak	RT (min)	Compound name	Area (%)							
			Without catalyst			With 5%NaOH				
			SCG	SCG:PF (5:5)	PF	SCG	SCG:PF (7:3)	SCG:PF (5:5)	SCG:PF (3:7)	PF
1	8.2872	5-Hydroxymethylfurfural	-	2.55	100.00	-	-	-	-	-
2	10.4821	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, [1R-(1.alpha.,2.beta.,5.alpha.)]-	-	-	-	-	0.69	-	-	-
3	11.4368	n-Hexadecanoic acid	46.23	45.40	-	40.77	44.81	40.55	47.11	-
4	12.2002	4-Decene, 8-methyl-, (E)-	0.16	-	-	-	-	-	-	-
5	12.2383	2,2-Dimethyl-4-ethynyl-tetrahydrothiopyran-4-ol	0.39	-	-	0.86	-	-	-	-
6	12.3657	cis-13-Octadecenoic acid	13.08	13.70	-	12.16	9.84	11.11	5.64	-
7	12.4229	9,12-Octadecadienoic acid (Z,Z)-	37.75	33.12	-	44.71	43.56	46.71	47.25	-
8	12.5120	Methyl 9,12-heptadecadienoate	-	-	3.76	-	-	-	-	24.01
9	13.2563	Eicosanoic acid	1.92	2.39	-	1.19	1.10	1.63	-	-
10	14.5220	1,2,4-Oxadiazole, 5-methyl-3-(1-piperidylmethyl)-	-	2.84	-	0.29	-	-	-	-

Table S2. Major compounds of the resulting crude bio-oils derived from co-liquefaction of SCG and CS at 250 °C in 10 min reaction time with the water/feedstock ratio of 5:1 in various feedstock combination mass ratios with/without adding 5 % NaOH.

Peak	RT (min)	Compound name	Area							
			Without catalyst			With 5%NaOH				
			SCG	SCG:CS (5:5)	CS	SCG	SCG:CS (7:3)	SCG:CS (5:5)	SCG:CS (3:7)	CS
1	7.2756	Phenol, 4-ethyl-	-	-	6.75	-	-	-	3.01	4.87
2	7.8545	Phenol, 4-ethyl-2-methoxy-	-	-	8.39	-	-	-	-	4.85
3	8.2872	5-Hydroxymethylfurfural	-	-	12.29	-	-	-	-	-
4	8.7007	Phenol, 2,6-dimethoxy-	-	-	10.60	-	-	1.06	-	17.27
5	9.2606	Vanillin	-	-	15.32	-	-	-	-	-
6	9.7568	Cyclohexanol, 1-methyl-4-(1-methylethylidene)-	-	-	5.30	-	-	-	-	-
7	10.2276	4,5,6,6a-Tetrahydro-2(1H)-pentalenone	-	-	3.54	-	-	-	-	-
8	10.8002	2,5-Dimethoxy-4-ethylbenzaldehyde	-	-	2.45	-	-	-	-	-
9	10.9465	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	-	-	2.77	-	-	-	1.69	-
10	10.9912	Hexadecanoic acid, methyl ester	-	-	-	-	35.23	0.35	-	-
11	11.2520	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	-	-	-	-	-	0.77	-	8.90
12	11.2710	1-Cyclohexene-1-propanoic acid, 2,6,6-trimethyl-	-	-	3.61	-	-	-	-	-
13	11.4368	n-Hexadecanoic acid	46.23	44.99	15.79	40.77	-	41.57	36.35	31.72

Peak	**RT (min)**	**Compound name**	**Area**							
			Without catalyst			**With 5%NaOH**				
			SCG	**SCG:CS (5:5)**	**CS**	**SCG**	**SCG:CS (7:3)**	**SCG:CS (5:5)**	**SCG:CS (3:7)**	**CS**
14	11.6718	2-Hydroxymethyl-1H-benzoimidazole-5-carboxylic acid	-	-	2.89	-	0.22	-	-	-
15	11.9837	1,4-Methanoazulen-7-ol, decahydro-4,8,8,9-tetramethyl-, (+)-	-	-	-	-	-	0.42	-	-
16	12.2002	4-Decene, 8-methyl-, (E)-	0.16	-	-	-	-	-	-	-
17	12.2383	2,2-Dimethyl-4-ethynyl-tetrahydrothiopyran-4-ol	0.39	-	-	0.86	-	-	-	-
18	12.3657	cis-13-Octadecenoic acid	13.08	14.00	3.84	12.16	11.89	12.67	10.02	7.43
19	12.4229	9,12-Octadecadienoic acid (Z,Z)-	37.75	38.15	6.47	44.71	49.60	41.65	46.98	24.95
20	13.2563	Eicosanoic acid	1.92	2.85	-	1.19	1.15	1.54	1.95	-
21	14.4648	Cholest-7-en-3-ol, 2,2-dimethyl-, (3.beta.,5.alpha.)-	-	-	-	0.29	-	-	-	-
22	15.3622	Benzaldehyde, 2,4-dihydroxy-	-	-	-	-	1.91	-	-	-

Table S3. Major compounds of the resulting crude bio-oils derived from co-liquefaction of SCG and WPB at 250 °C in 10 min reaction time with the water/feedstock ratio of 5:1 in various feedstock combination mass ratios with/without adding 5 % NaOH.

Peak	RT (min)	Compound name	Area (%)							
			Without catalyst			With 5%NaOH				
			SCG	SCG:WPB (5:5)	WPB	SCG	SCG:WPB (7:3)	SCG:WPB (5:5)	SCG:WPB (3:7)	WPB
1	6.6205	Phenol, 2-methoxy-	-	-	-	-	-	-	-	5.97
2	8.2872	5-Hydroxymethylfurfural	-	-	31.89	-	-	-	-	-
3	10.0242	1-(4-methylthiophenyl)-2-propanone	-	-	-	-	-	-	-	40.79
4	10.6923	2-Butanol, 4-(2,2-dimethyl-6-methylenecyclohexylidene)-	-	-	-	-	-	0.42	0.72	-
5	11.4368	n-Hexadecanoic acid	46.23	49.36	43.05	40.77	51.12	49.68	47.43	32.17
6	12.2002	4-Decene, 8-methyl-, (E)-	0.16	-	-	-	-	-	-	-
7	12.2383	2,2-Dimethyl-4-ethynyl-tetrahydrothiopyran-4-ol	0.39	-	-	0.86	-	-	-	-
8	12.3657	cis-13-Octadecenoic acid	13.08	12.75	-	12.16	9.58	10.69	9.74	-
9	12.4229	9,12-Octadecadienoic acid (Z,Z)-	37.75	37.89	21.29	44.71	37.47	38.05	42.10	-
10	12.5120	Methyl 9,12-heptadecadienoate	-	-	3.76	-	-	-	-	24.01
11	13.2563	Eicosanoic acid	1.92	-	-	1.19	1.83	1.16	-	-
12	14.5220	1,2,4-Oxadiazole, 5-methyl-3-(1-piperidylmethyl)-	-	-	-	0.29	-	-	-	-

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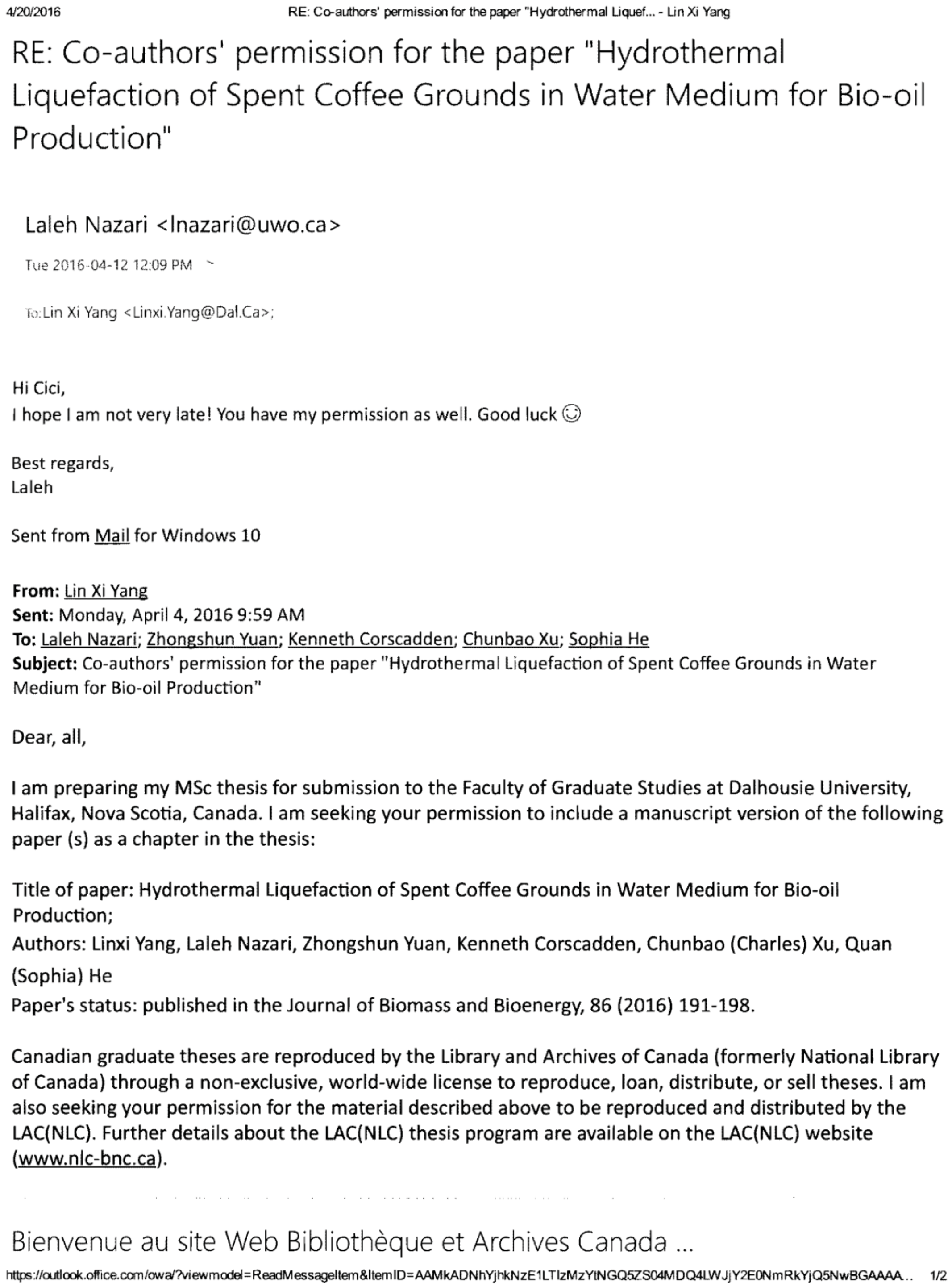

RE: Co-authors' permission for the paper "Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production"

Laleh Nazari <lnazari@uwo.ca>

Tue 2016-04-12 12:09 PM

To: Lin Xi Yang <Linxi.Yang@Dal.Ca>;

Hi Cici,
I hope I am not very late! You have my permission as well. Good luck ☺

Best regards,
Laleh

Sent from Mail for Windows 10

From: Lin Xi Yang
Sent: Monday, April 4, 2016 9:59 AM
To: Laleh Nazari; Zhongshun Yuan; Kenneth Corscadden; Chunbao Xu; Sophia He
Subject: Co-authors' permission for the paper "Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production"

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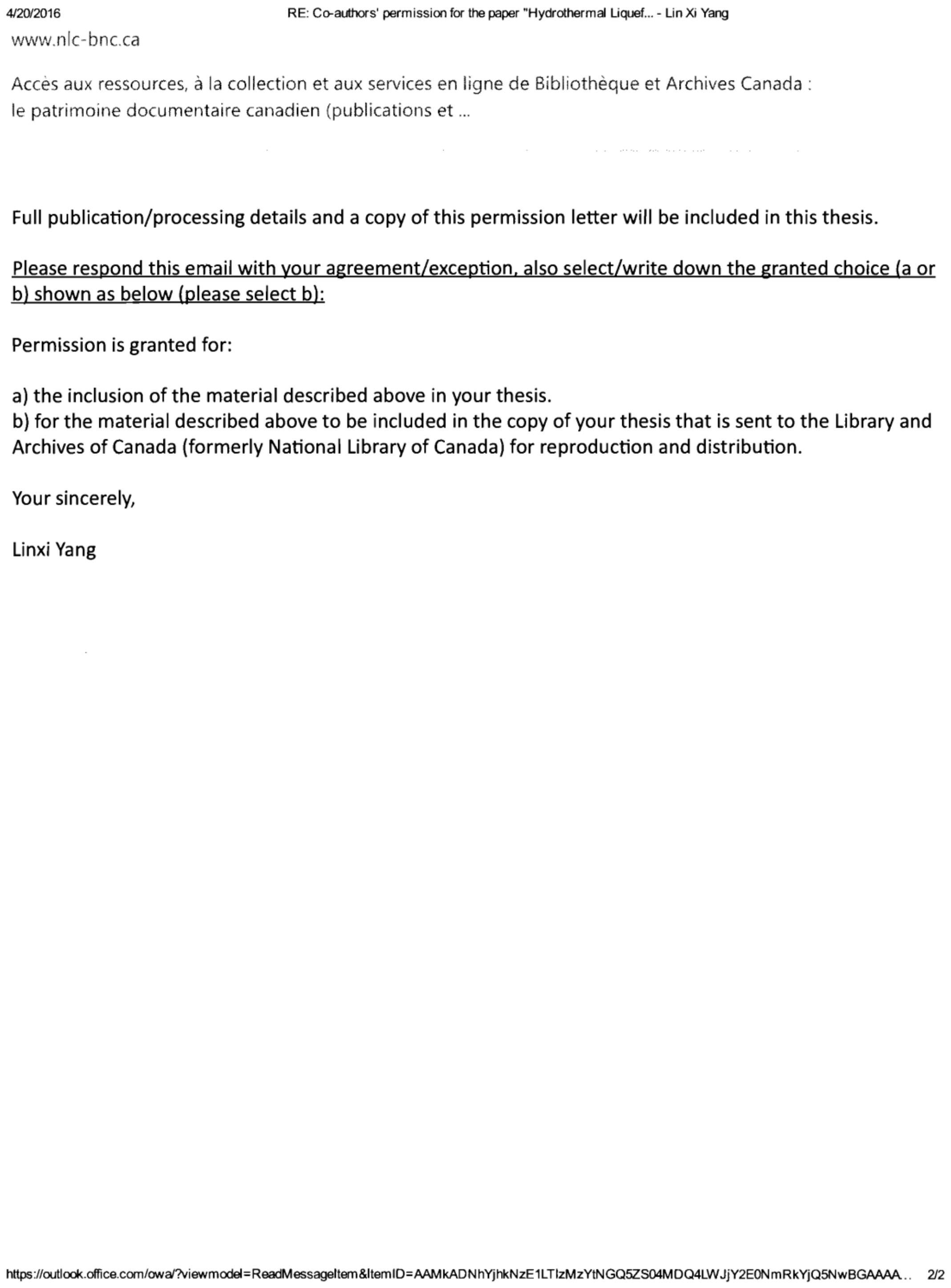

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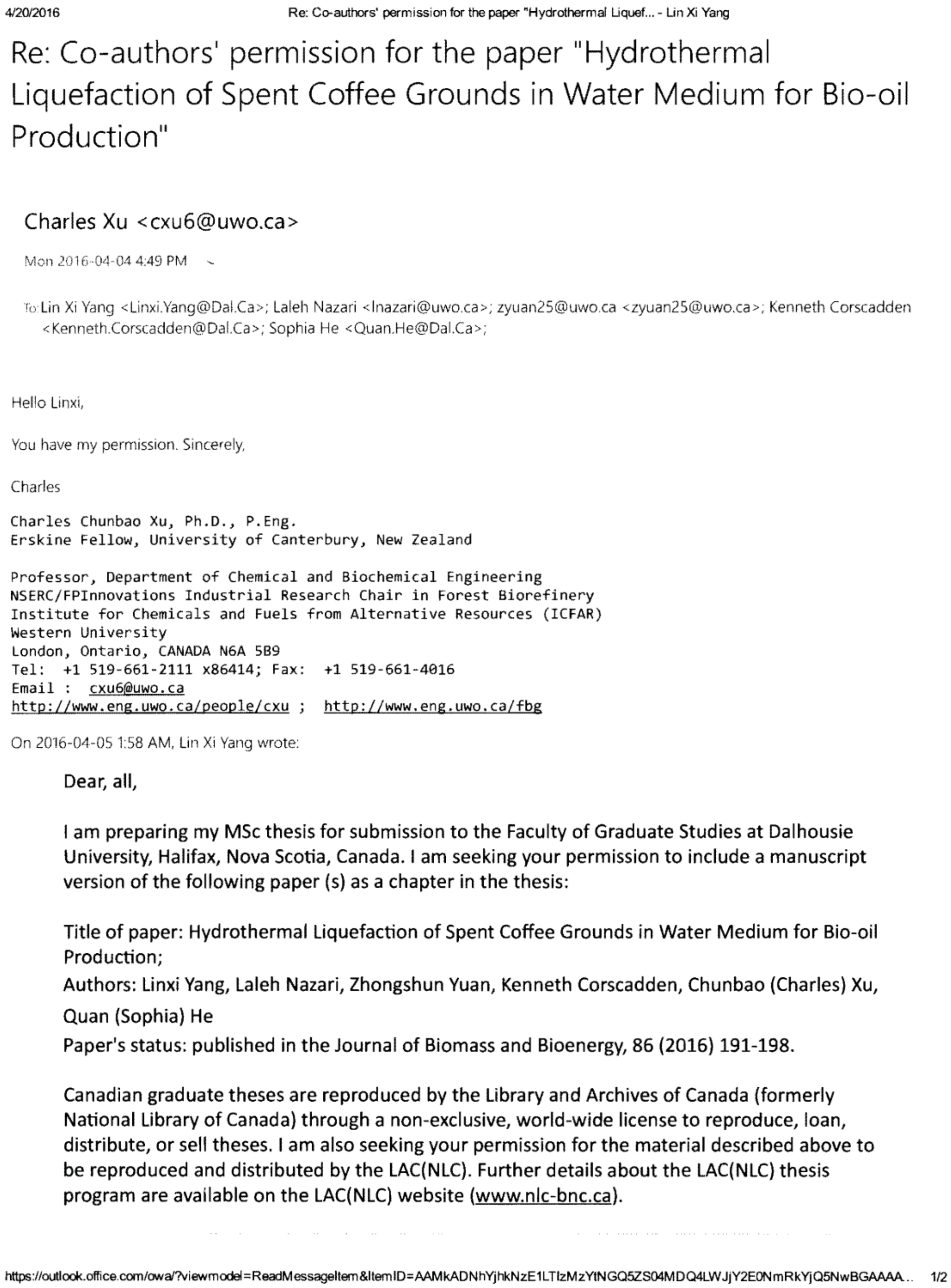

Re: Co-authors' permission for the paper "Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production"

Charles Xu <cxu6@uwo.ca>

Mon 2016-04-04 4:49 PM

To: Lin Xi Yang <Linxi.Yang@Dal.Ca>; Laleh Nazari <lnazari@uwo.ca>; zyuan25@uwo.ca <zyuan25@uwo.ca>; Kenneth Corscadden <Kenneth.Corscadden@Dal.Ca>; Sophia He <Quan.He@Dal.Ca>;

Hello Linxi,

You have my permission. Sincerely,

Charles

Charles Chunbao Xu, Ph.D., P.Eng.
Erskine Fellow, University of Canterbury, New Zealand

Professor, Department of Chemical and Biochemical Engineering
NSERC/FPInnovations Industrial Research Chair in Forest Biorefinery
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On 2016-04-05 1:58 AM, Lin Xi Yang wrote:

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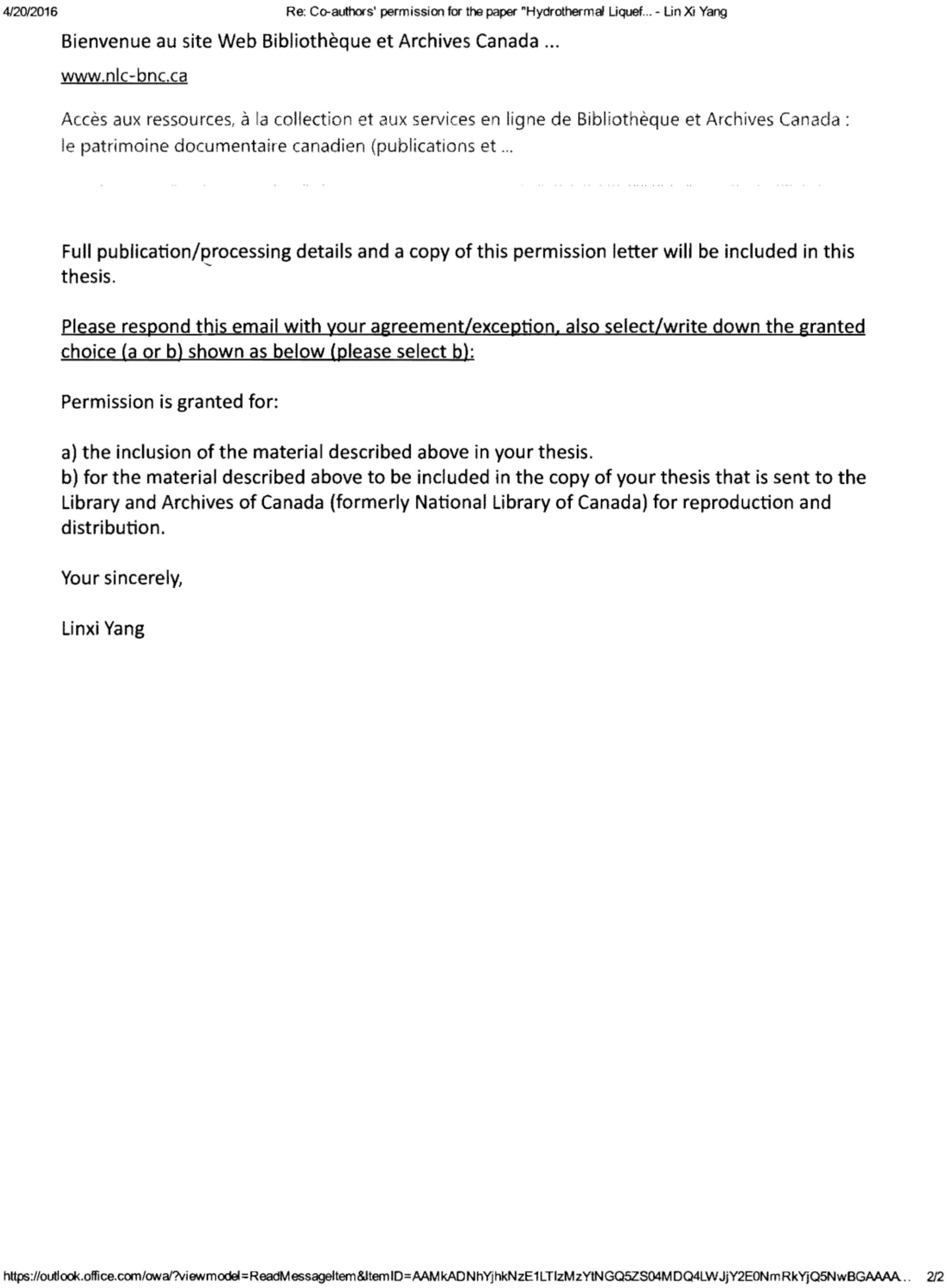

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Re: Co-authors' permission for the paper "Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production"

Zhongshun Yuan <zyuan25@uwo.ca>

Mon 2016-04-04 4:09 PM

To: Lin Xi Yang <Linxi.Yang@Dal.Ca>;

Hi Linxi Yang:

You have my permission.

Thank you!

Sincerely,

Dr. Zhongshun (Sean) Yuan
Institute for Chemicals & Fuels from Alternative Resources (ICFAR)
University of Western Ontario
22312 Wonderland Rd. N RR#3
Ilderton, ON N0M 2A0
Phone: 519-661-2111 X 86723 (day)
email: zyuan25@uwo.ca

On 04/04/16, **Lin Xi Yang** <Linxi.Yang@dal.ca> wrote:

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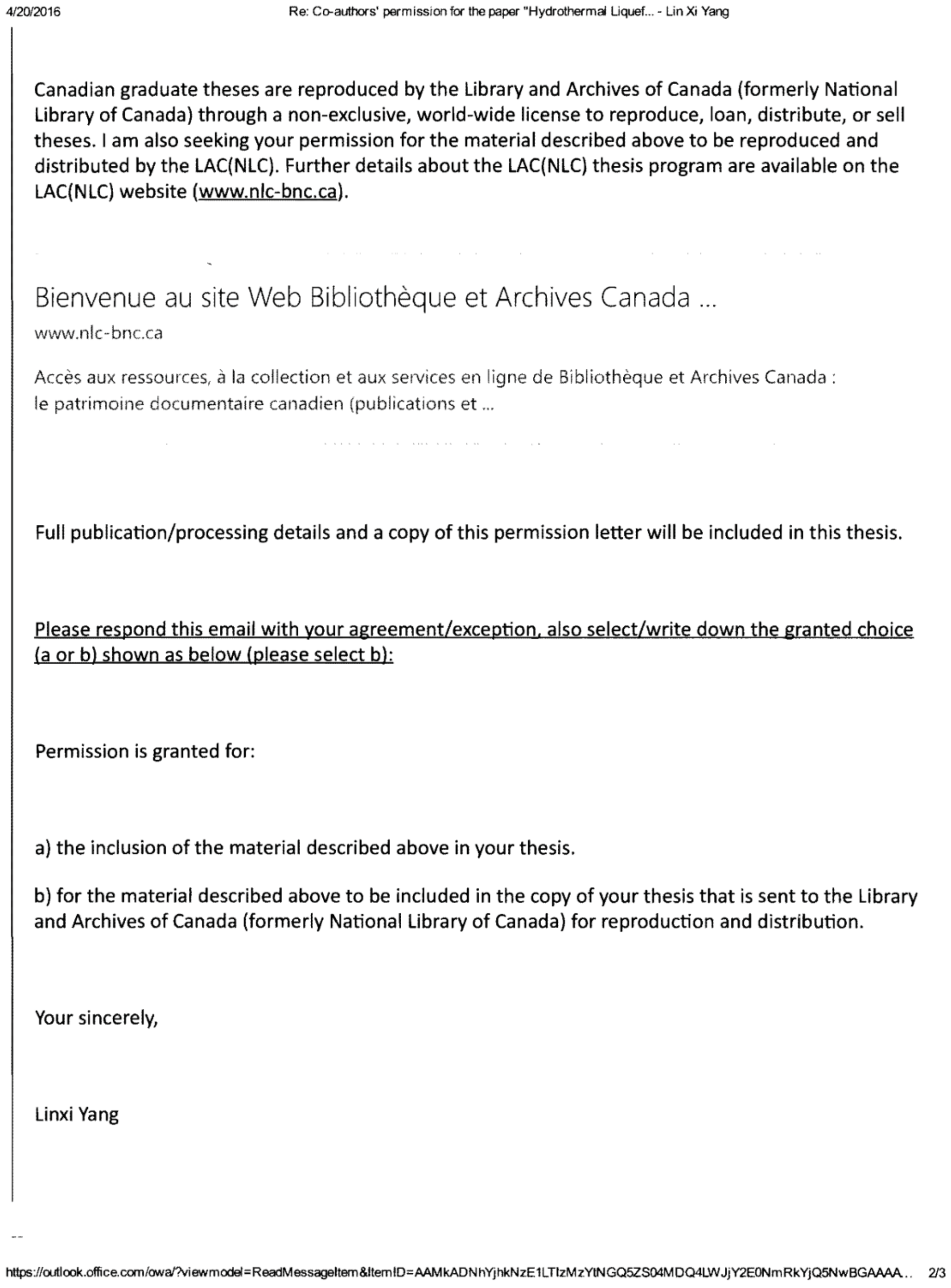

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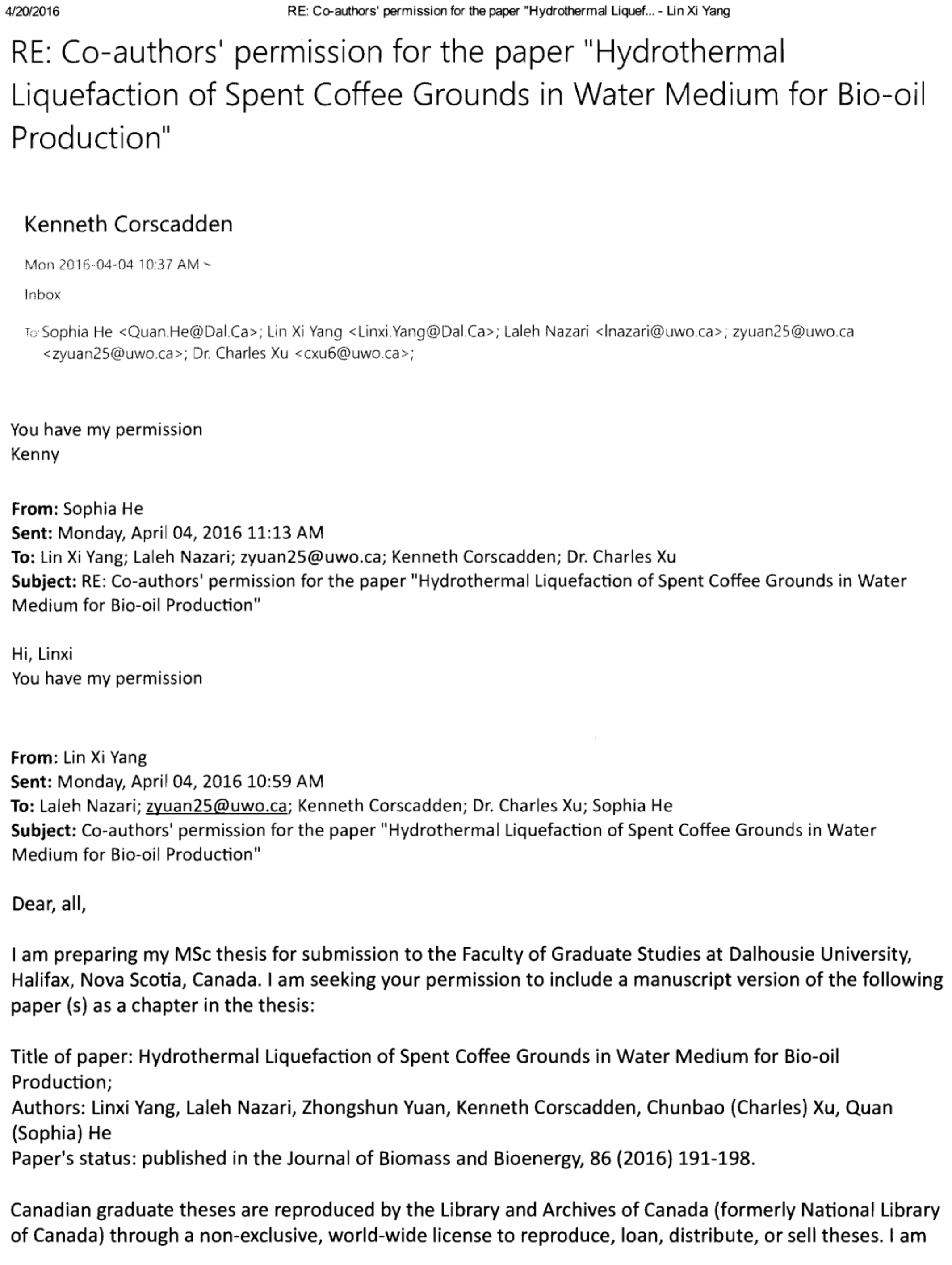

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RE: Co-authors' permission for the paper "Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production"

Kenneth Corscadden

Mon 2016-04-04 10:37 AM

Inbox

To: Sophia He <Quan.He@Dal.Ca>; Lin Xi Yang <Linxi.Yang@Dal.Ca>; Laleh Nazari <lnazari@uwo.ca>; zyuan25@uwo.ca <zyuan25@uwo.ca>; Dr. Charles Xu <cxu6@uwo.ca>;

You have my permission
Kenny

From: Sophia He
Sent: Monday, April 04, 2016 11:13 AM
To: Lin Xi Yang; Laleh Nazari; zyuan25@uwo.ca; Kenneth Corscadden; Dr. Charles Xu
Subject: RE: Co-authors' permission for the paper "Hydrothermal Liquefaction of Spent Coffee Grounds in Water Medium for Bio-oil Production"

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To: Laleh Nazari; zyuan25@uwo.ca; Kenneth Corscadden; Dr. Charles Xu; Sophia He
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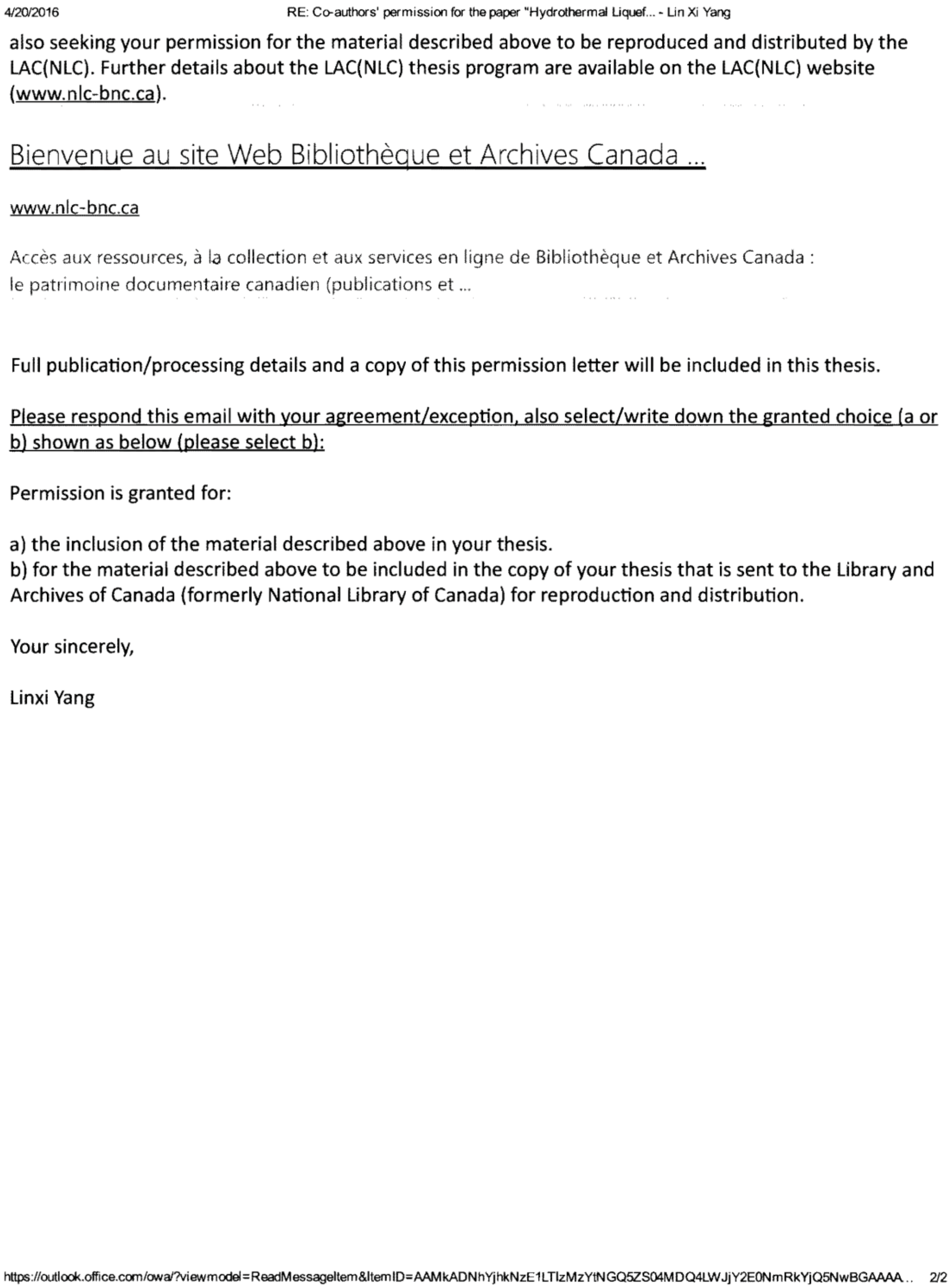

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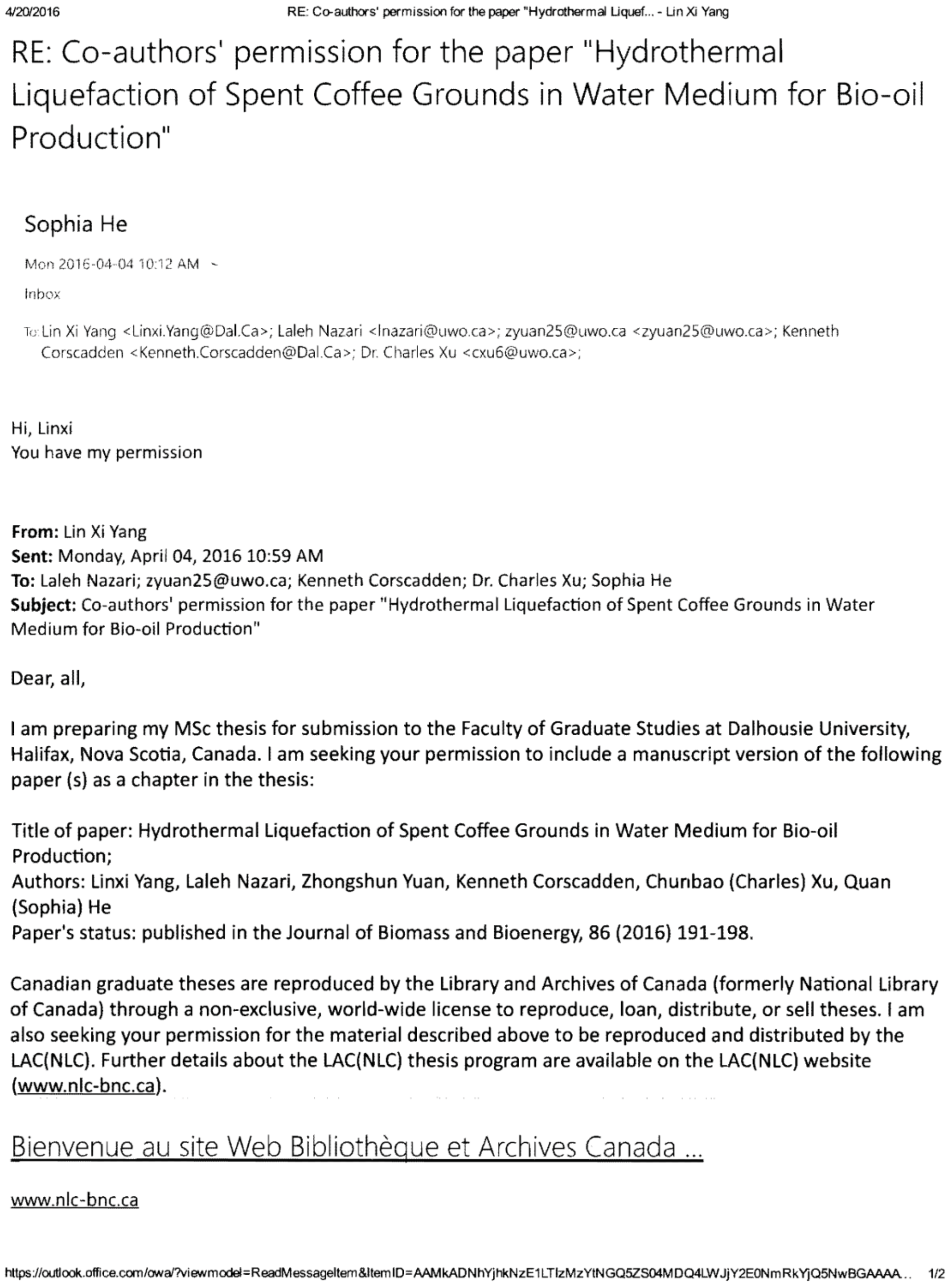

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Sophia He

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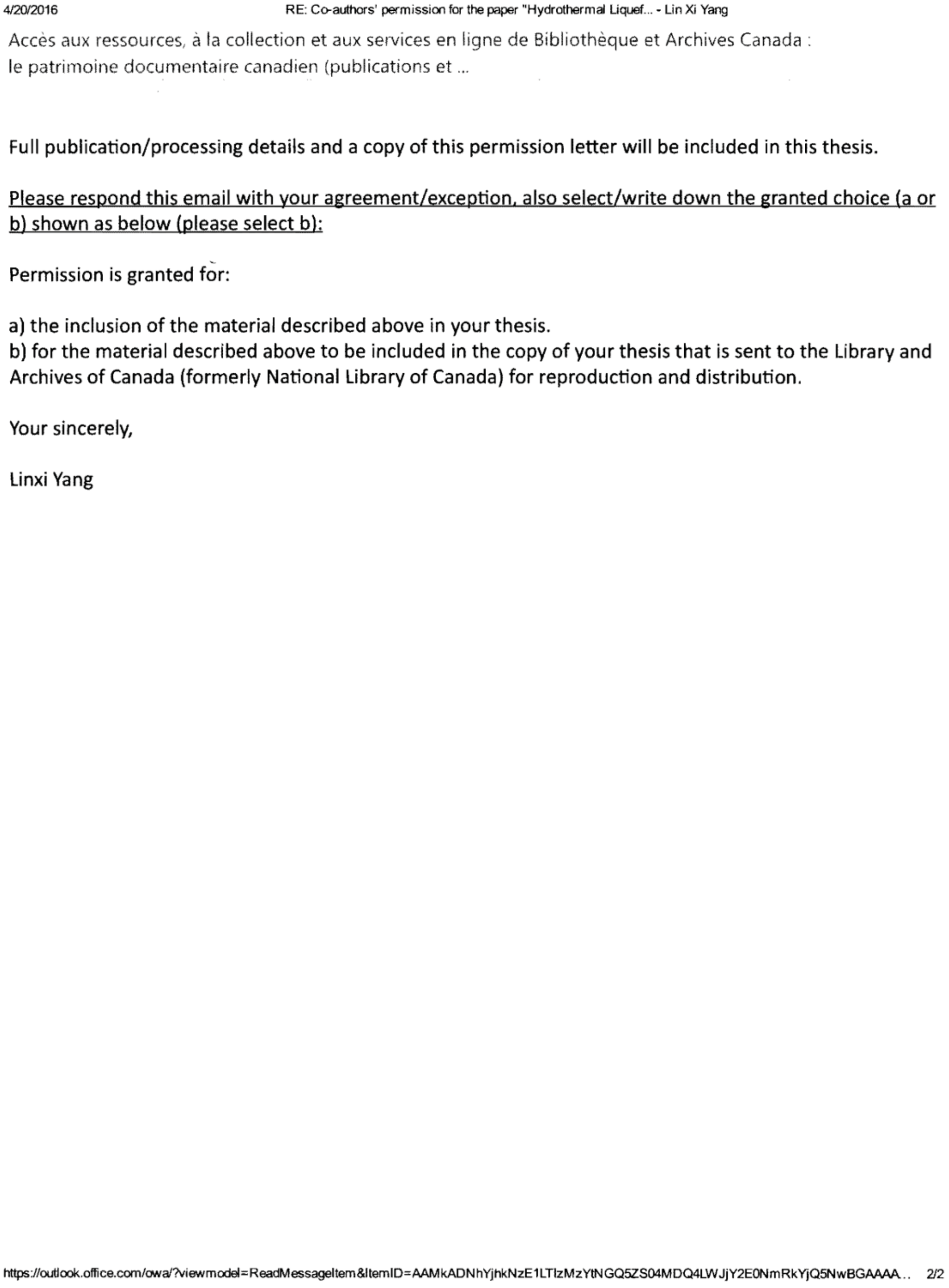

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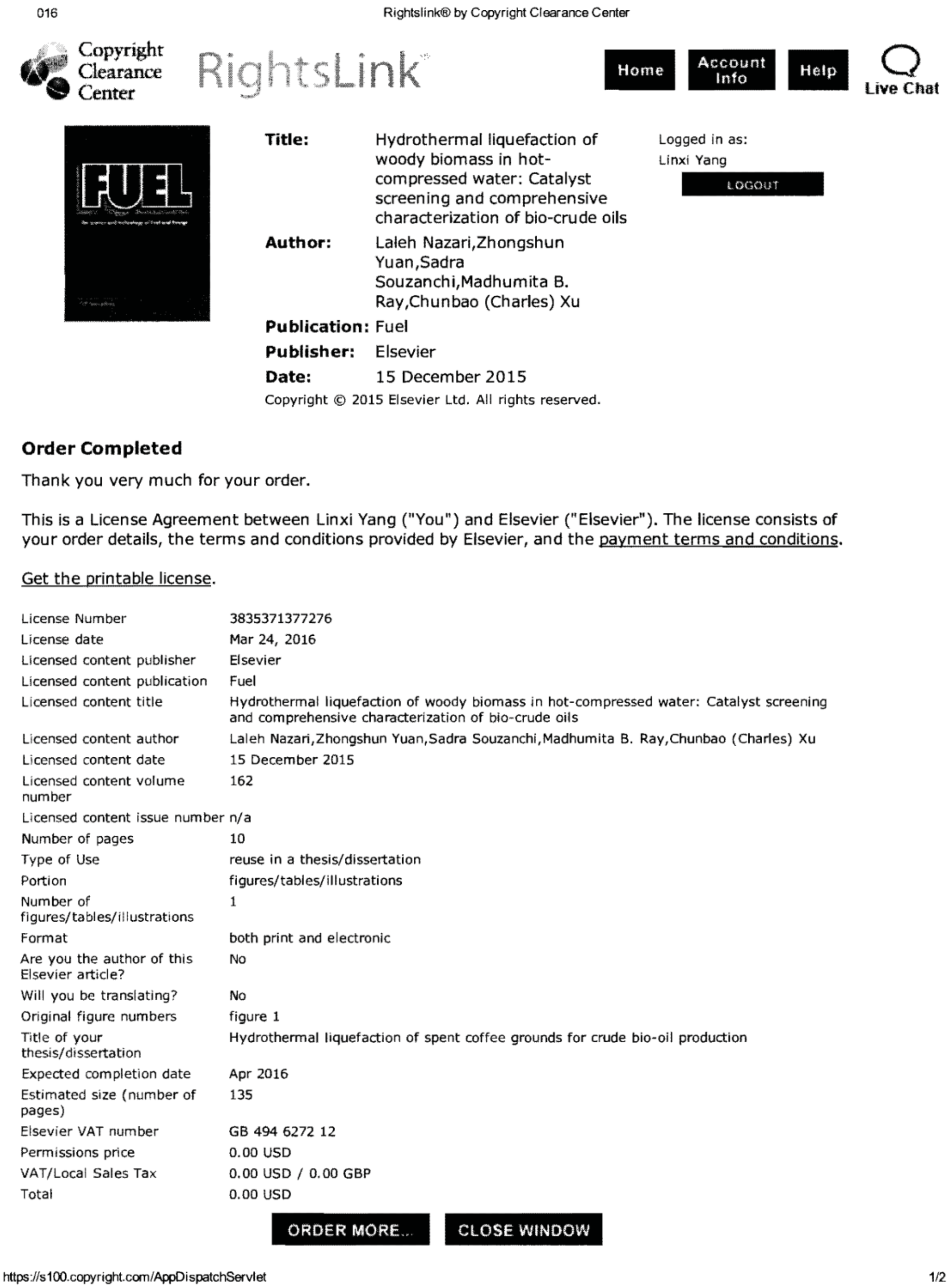

Title: Hydrothermal liquefaction of woody biomass in hot-compressed water: Catalyst screening and comprehensive characterization of bio-crude oils

Author: Laleh Nazari,Zhongshun Yuan,Sadra Souzanchi,Madhumita B. Ray,Chunbao (Charles) Xu

Publication: Fuel

Publisher: Elsevier

Date: 15 December 2015

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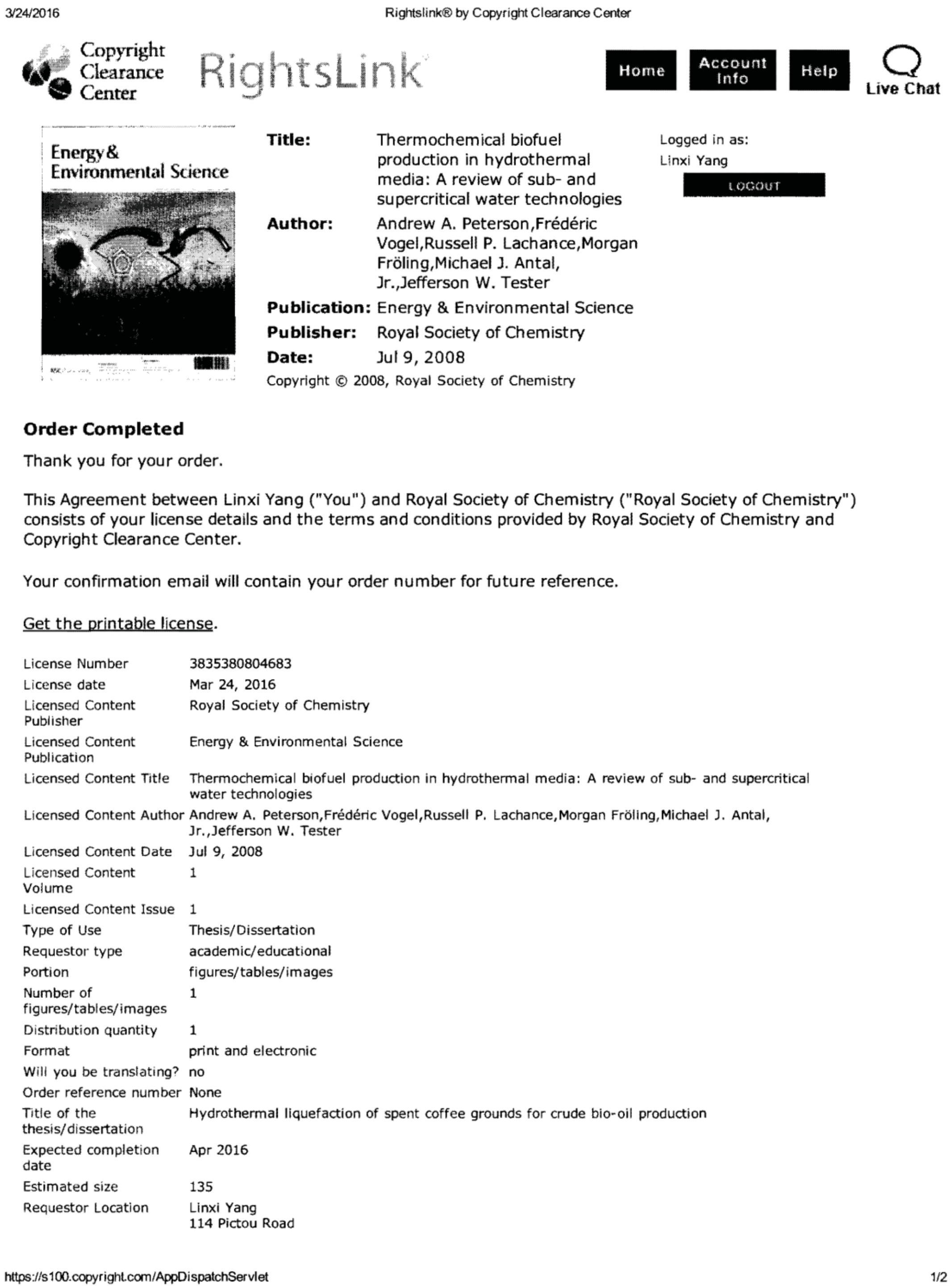

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Author: Andrew A. Peterson,Frédéric Vogel,Russell P. Lachance,Morgan Fröling,Michael J. Antal, Jr.,Jefferson W. Tester

Publication: Energy & Environmental Science

Publisher: Royal Society of Chemistry

Date: Jul 9, 2008

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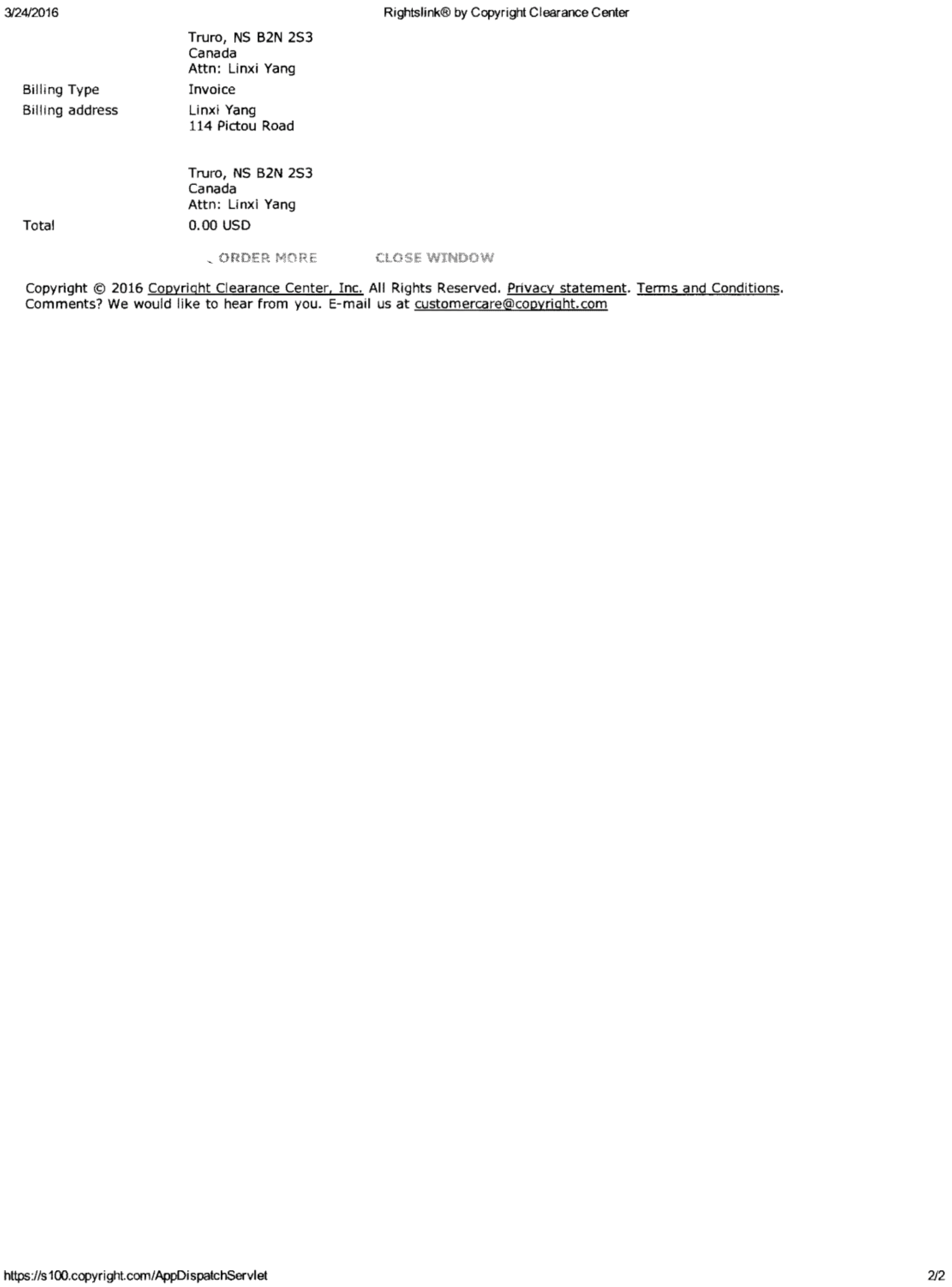

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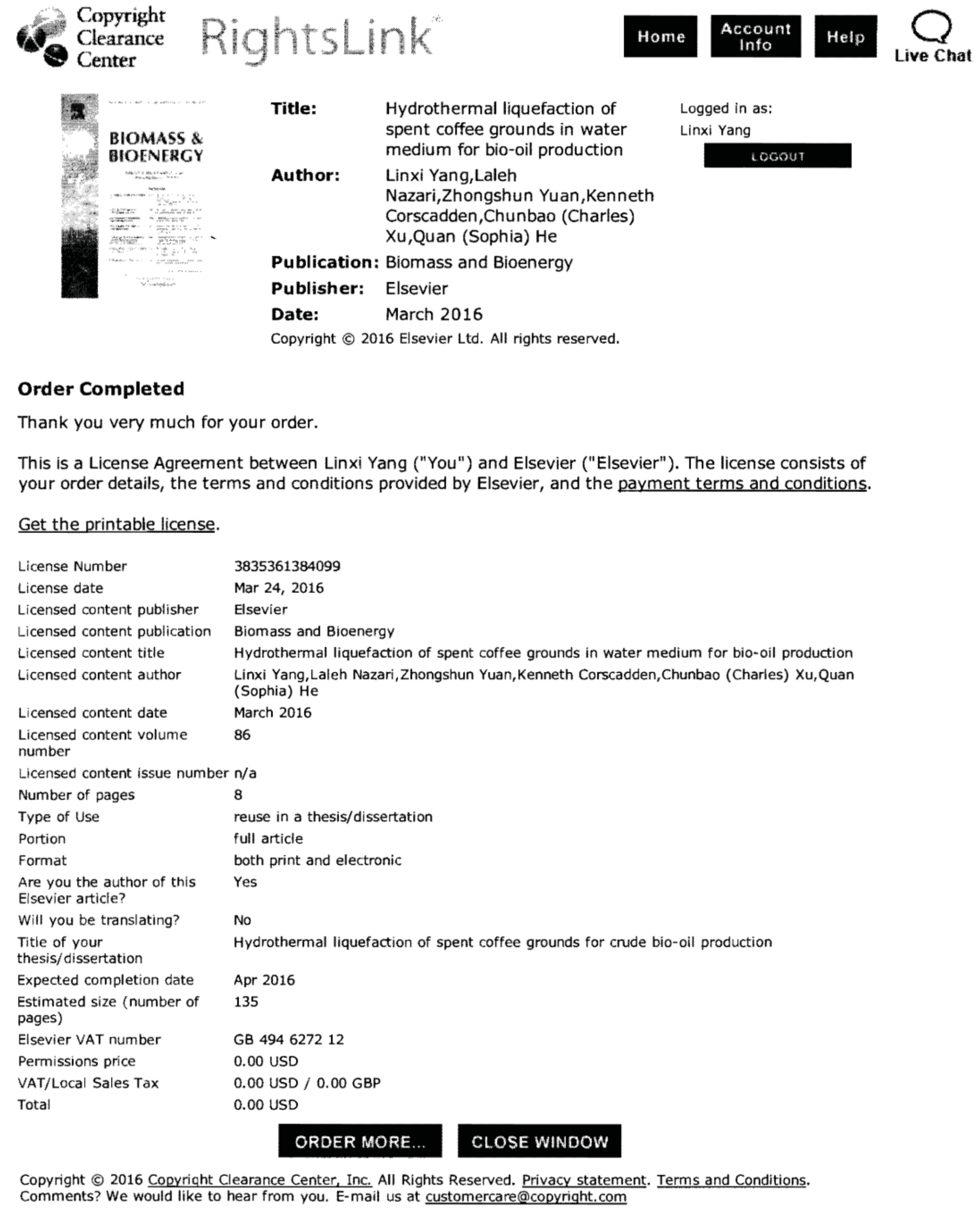

Title: Hydrothermal liquefaction of spent coffee grounds in water medium for bio-oil production

Author: Linxi Yang,Laleh Nazari,Zhongshun Yuan,Kenneth Corscadden,Chunbao (Charles) Xu,Quan (Sophia) He

Publication: Biomass and Bioenergy

Publisher: Elsevier

Date: March 2016

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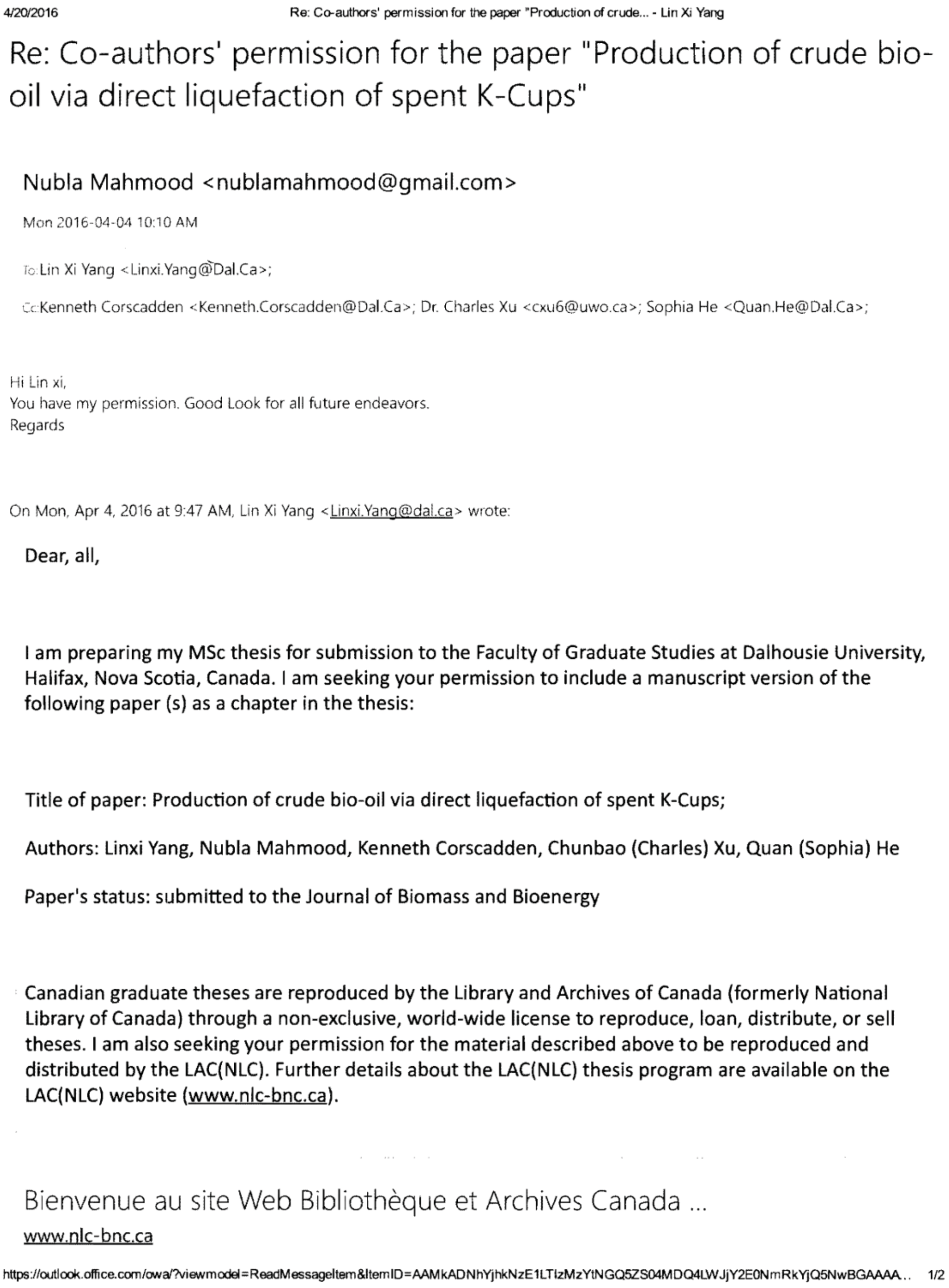

4/20/2016 Re: Co-authors' permission for the paper "Production of crude... - Lin Xi Yang

Re: Co-authors' permission for the paper "Production of crude bio-oil via direct liquefaction of spent K-Cups"

Nubla Mahmood <nublamahmood@gmail.com>

Mon 2016-04-04 10:10 AM

To:Lin Xi Yang <Linxi.Yang@Dal.Ca>;

Cc:Kenneth Corscadden <Kenneth.Corscadden@Dal.Ca>; Dr. Charles Xu <cxu6@uwo.ca>; Sophia He <Quan.He@Dal.Ca>;

Hi Lin xi,
You have my permission. Good Look for all future endeavors.
Regards

On Mon, Apr 4, 2016 at 9:47 AM, Lin Xi Yang <Linxi.Yang@dal.ca> wrote:

Dear, all,

I am preparing my MSc thesis for submission to the Faculty of Graduate Studies at Dalhousie University, Halifax, Nova Scotia, Canada. I am seeking your permission to include a manuscript version of the following paper (s) as a chapter in the thesis:

Title of paper: Production of crude bio-oil via direct liquefaction of spent K-Cups;

Authors: Linxi Yang, Nubla Mahmood, Kenneth Corscadden, Chunbao (Charles) Xu, Quan (Sophia) He

Paper's status: submitted to the Journal of Biomass and Bioenergy

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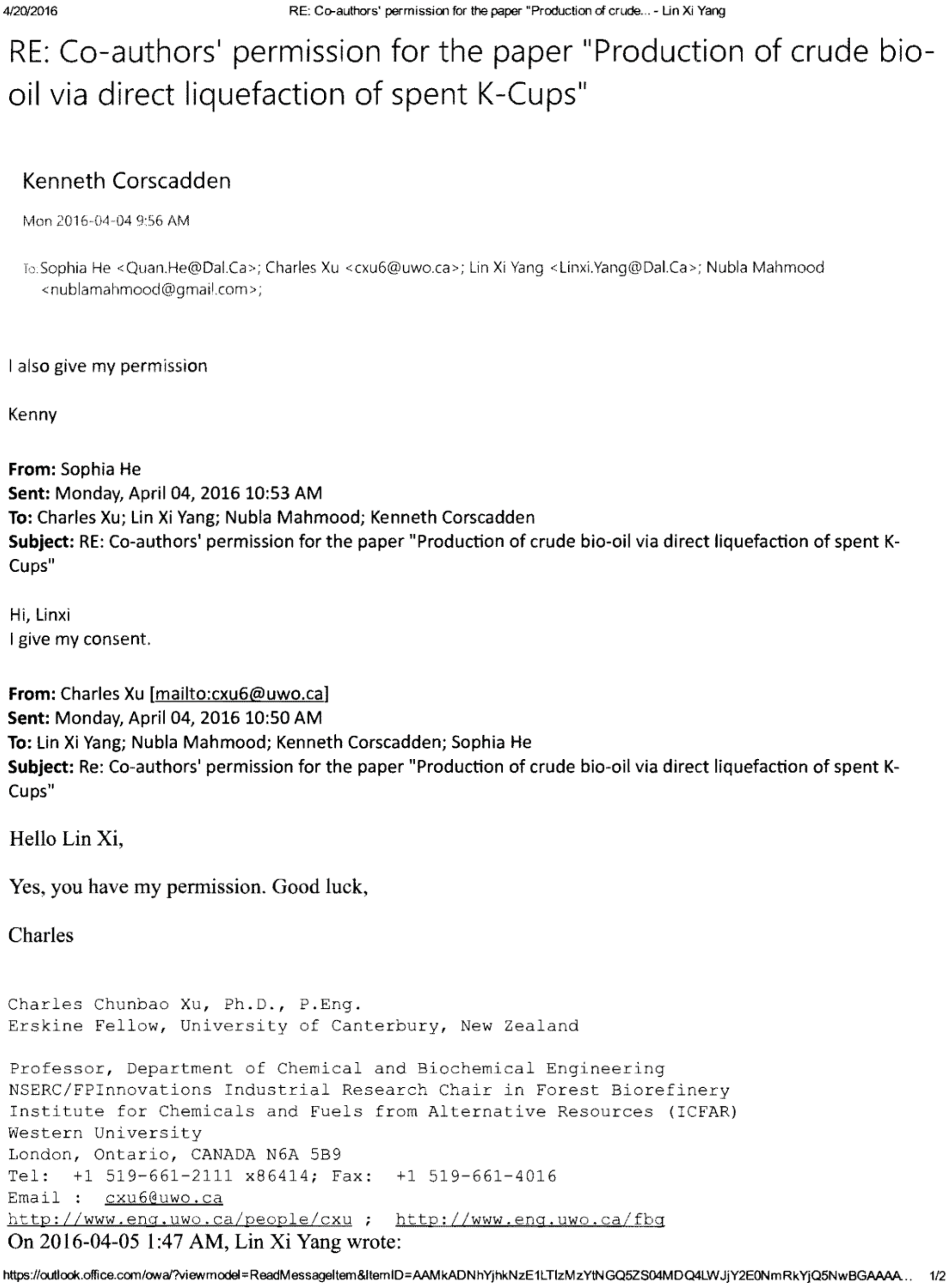
Your sincerely,

Linxi Yang

--
Dr. Nubla Mahmood
Postdoctoral Fellow
Institute for Chemicals and Fuels from Alternate Resources (ICFAR)
Department of Chemical and Biochemical Engineering (CBE)
Western University (UWO)
London, Ontario, Canada
Mobile: +1 519-281-4596



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Kenneth Corscadden

Mon 2016-04-04 9:56 AM

To: Sophia He <Quan.He@Dal.Ca>; Charles Xu <cxu6@uwo.ca>; Lin Xi Yang <Linxi.Yang@Dal.Ca>; Nubla Mahmood <nublamahmood@gmail.com>;

I also give my permission

Kenny

From: Sophia He
Sent: Monday, April 04, 2016 10:53 AM
To: Charles Xu; Lin Xi Yang; Nubla Mahmood; Kenneth Corscadden
Subject: RE: Co-authors' permission for the paper "Production of crude bio-oil via direct liquefaction of spent K-Cups"

Hi, Linxi
I give my consent.

From: Charles Xu [mailto:cxu6@uwo.ca]
Sent: Monday, April 04, 2016 10:50 AM
To: Lin Xi Yang; Nubla Mahmood; Kenneth Corscadden; Sophia He
Subject: Re: Co-authors' permission for the paper "Production of crude bio-oil via direct liquefaction of spent K-Cups"

Hello Lin Xi,

Yes, you have my permission. Good luck,

Charles

Charles Chunbao Xu, Ph.D., P.Eng.
Erskine Fellow, University of Canterbury, New Zealand

Professor, Department of Chemical and Biochemical Engineering
NSERC/FPInnovations Industrial Research Chair in Forest Biorefinery
Institute for Chemicals and Fuels from Alternative Resources (ICFAR)
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Email : cxu6@uwo.ca
http://www.eng.uwo.ca/people/cxu ; http://www.eng.uwo.ca/fbg

On 2016-04-05 1:47 AM, Lin Xi Yang wrote:

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Paper's status: submitted to the Journal of Biomass and Bioenergy

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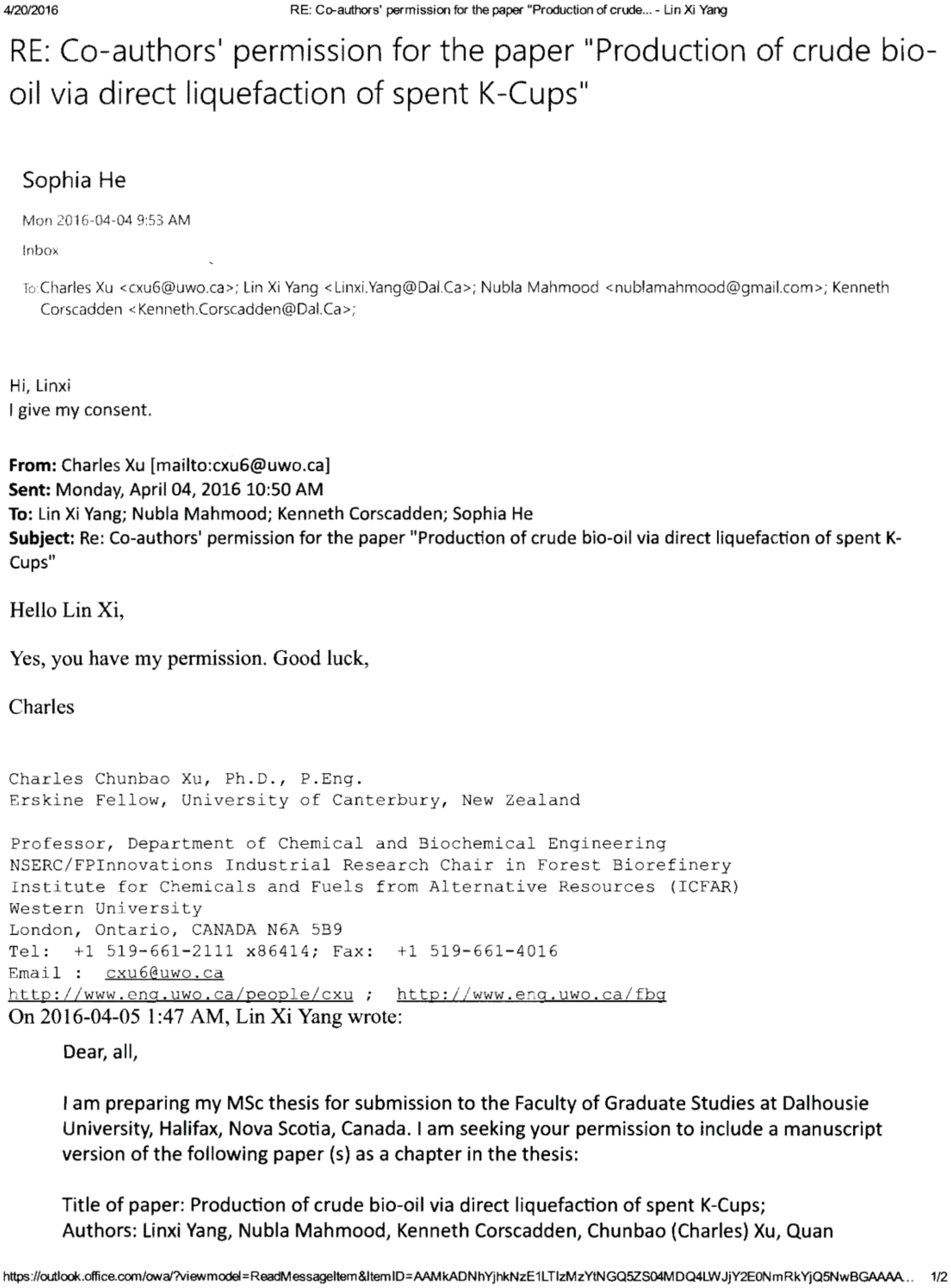

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Sophia He

Mon 2016-04-04 9:53 AM

Inbox

To: Charles Xu <cxu6@uwo.ca>; Lin Xi Yang <Linxi.Yang@Dal.Ca>; Nubla Mahmood <nublamahmood@gmail.com>; Kenneth Corscadden <Kenneth.Corscadden@Dal.Ca>;

Hi, Linxi
I give my consent.

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Erskine Fellow, University of Canterbury, New Zealand

Professor, Department of Chemical and Biochemical Engineering
NSERC/FPInnovations Industrial Research Chair in Forest Biorefinery
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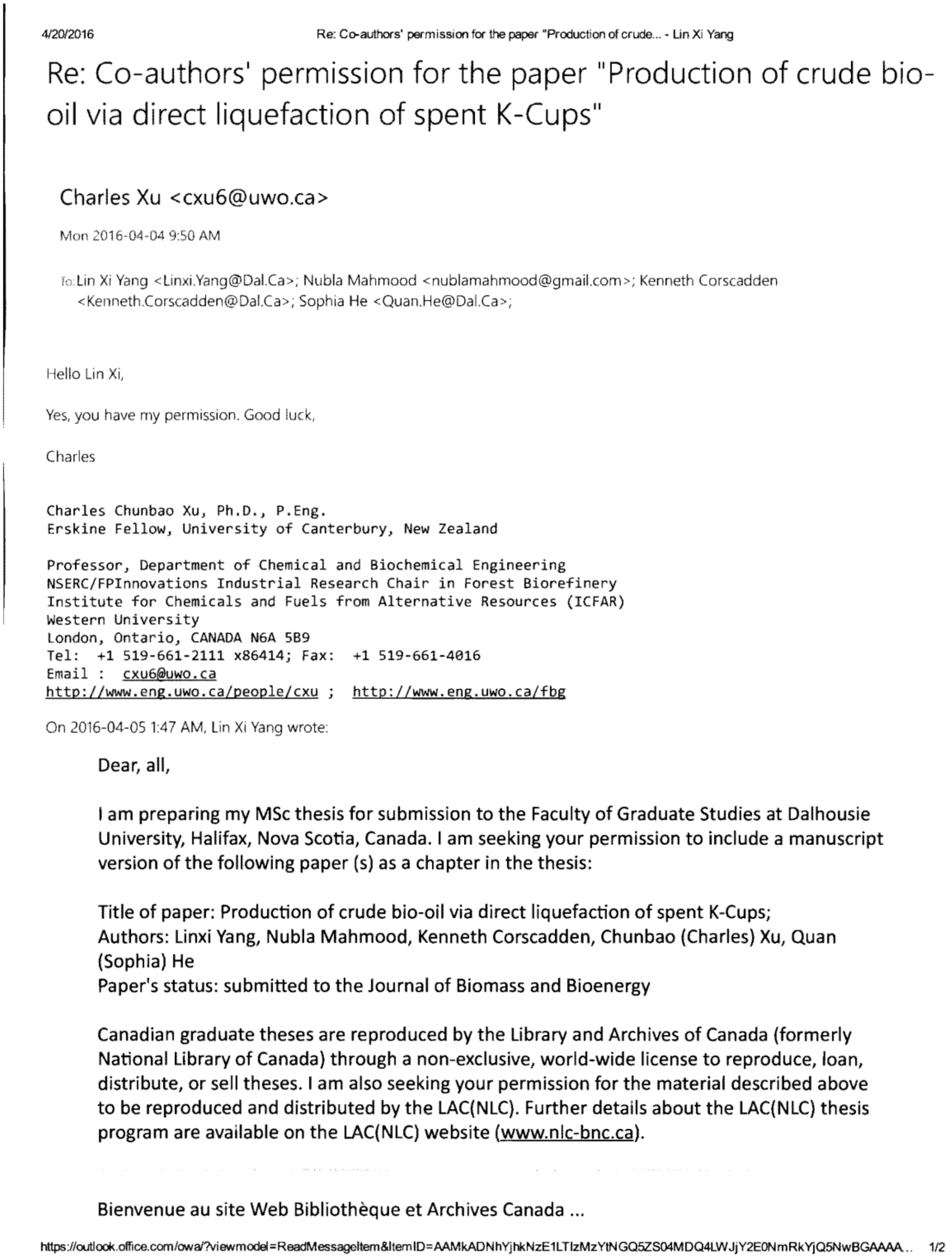

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Professor, Department of Chemical and Biochemical Engineering
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