Hydrothermal liquefaction of lignocellulosic biomass using water and hydrogen-donor solvent mixtures to produce energy-dense heavy oil

by

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ABSTRACT

Energy transition from non-renewable to renewable energy is required to confront rising levels of greenhouse gas emissions responsible for increasing global temperatures and disrupting weather patterns. Switching to renewable energy sources for energy generation also resolves the issues related to depletion of fossil fuels and promises sustainable growth of the country. Lignocellulosic biomass are renewable sources of energy that can be converted into fuels and platform chemicals, proving to be effective alternative sources of energy generation. Agricultural and forest wastes that are underutilized and abundant in Canada, are carbon-rich sources of energy that have the potential to be used as feedstock in bio-industries. Thermochemical conversion technologies can convert these carbon-rich lignocellulosic biomass into valuable transportation fuels.

Hydrothermal liquefaction (HTL) is a thermochemical conversion technology that allows high-moisture content lignocellulosic biomass feedstocks to be converted into energy-dense heavy oil, along with hydrochar, aqueous phase fraction and gases as by-products. Present study involves the use of corn stover, wheat straw and hardwood as biomass feedstock for HTL conversion process operated at 300°C, final pressure range 2200 psi to 2450 psi, and zero min retention time. HTL experiments will focus on selecting biomass of varying composition of polymers and inorganic content and their effect on yield and quality of heavy oil and hydrochar. Experiments will also extend towards the study of addition of alcoholic Co-solvents to water on heavy oil and hydrochar yield and quality, as a means of initial upgrading step necessary for HTL operation.

HTL experiments were conducted in a 250 mL, T316-T high pressure-high temperature autoclave bench top reactor, with reactions taking place in nitrogen gas environment. Product separation and recovery was conducted through detailed procedure provided in later chapter, heavy oil and

hydrochar was obtained separately for analysis. Characterization tests on heavy oil such as CHNS, GC-MS, TAN and TGA, and for hydrochar CHNS and SEM analysis were conducted.

Among agricultural and forest biomass, highest heavy oil yield obtained was 42.0 wt.% and hydrochar content of 14.6 wt.% when hardwood was the feedstock for HTL experiment, at reactor temperature of 300°C, final pressure of 2200 psi and 0 min retention time. HTL experiments performed on agricultural feedstocks, have shown relatively lesser yield and quality of heavy oil as compared to that obtained by using forest biomass as feedstock, and present HTL experiments using water and Co-solvent mixtures have been conducted on primarily corn stover and wheat straw. Heavy oil derived from wheat straw showed the highest energy content of 32.86 MJ/kg, lowest oxygen content of 17.99 wt.%, highest light naphtha fraction of 20.66 % and lowest middle distillate fraction of 22.56 %, using water-2-propanol mixture. Therefore, addition of alcoholic Co-solvent with water eases the conversion of biomass polymers to valuable chemicals and produces heavy oil resembling gasoline or diesel. Further work is required to understand the interaction of Co-solvents with small constituents of biomass such as extractives and inorganic matter, which would determine the selectivity of certain compounds necessary for producing useful chemicals and fuels. Also, the effect of adding alkali catalyst with water-Co-solvent mixture needs to be explored, in order to understand their performance on heavy oil yield and quality.

PREFACE

This thesis is an original work conducted by the author, Snehlata Das, at the University of Alberta, Edmonton, Canada. Majority of the experiments and characterization tests were conducted at the Department of Chemical and Materials Engineering, with elemental and chemical analysis conducted at the Department of Chemistry and surface morphology tests carried out at the Department of Earth and Atmospheric Sciences, University of Alberta.

Dr. Rajender Gupta was the principal advisor for this project and guided me with the project's experimental plan and documentation review.

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I would like to thank my friends at the University of Alberta – Himanshi, Akanksha, Gustavo, Jim, Omnath, Yang Wu, Shruthi and Manika, for being supportive and creating fun-loving memories with me.

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LIST OF ACRONYMS

GHG – Greenhouse Gas

CO_2 – Carbon dioxide

N_2 – Nitrogen

O_2 - Oxygen

CO – Carbon monoxide

MSW – Municipal Solid Waste

HTL – Hydrothermal liquefaction

HTL-water – Hydrothermal liquefaction conducted in water environment

HTL-products – Products obtained after HTL operation

T – Temperature

P – Pressure

RT – Retention time

RPM – Revolutions per minute

HO – Heavy oil

AO – Aqueous oil

WSH – Water-soluble hydrocarbons

HC – Hydrochar

AP2 – Aqueous phase 2

HO-CS-W – Heavy oil obtained from HTL of corn stover using water as solvent

HO-WS-W – Heavy obtained from HTL of wheat straw using water as solvent

HO-HW-W – Heavy obtained from HTL of hardwood using water as solvent

HO-CS-W2P – Heavy obtained from HTL of corn stover using water and 2-propanol mixture

HO-WS-W2P – Heavy obtained from HTL of wheat straw using water and 2-propanol mixture

HTL-CS-W – HTL experiment performed on corn stover using water as liquefying medium

HTL-WS-WM – HTL experiment performed on wheat straw using water and methanol mixture

HTL-WS-WE – HTL experiment performed on wheat straw using water and ethanol mixture

HHV – Higher Heating Value

GC-MS – Gas Chromatography - Mass Spectrometer

SEM – Scanning Electron Microscope

TAN – Total Acid Number

Chapter 1: Introduction

1.1 Background

The global population is expected to surge from 7.7 billion in 2019 to about 9.2 billion by 2040, increasing the world energy demand by 19% [1, 2]. Canada has observed an increase in energy consumption by 30% between 1990 and 2017 [3]. In 2017, the industrial and transportation sectors of Canada consumed about 52% and 23% of total energy demand, respectively [4]. The largest source of emissions in Canada arises from the oil and gas sectors, produced mainly from extraction and upgrading processes, heavy duty transportation and utilization of process heat [5]. GHG emissions produced from oil sands in-situ extraction process, increased from 157 Mt in 2000 to 194 Mt in 2018 [3]. Passenger and freight transportations have indicated the highest CO_2 emissions in 2018 [3], which is one of the reasons that has led Canada to transition towards a low carbon future and utilize biomass as a renewable option that can potentially reduce the transportation GHG emissions of the country. Biomass is made up of organic materials derived from plants or animals and is a renewable source of carbon that can be converted into transportation fuel, chemicals, heat, or electricity. Canadian inventory studies have estimated lignocellulosic biomass supply to range from 64 to 561 million dry tonnes [6]. Therefore, to address global climate changes and maintain the performance of Canadian economy, Canada aims to utilize biomass as a clean and sustainable technology for energy production.

Liquid fuels derived from biomass are referred to as biofuels and are alternatives to conventional transportation fuels. Biofuels are categorized into first-, second- and third-generation based on the origin of the biomass source. Biofuel production provides energy security, creates jobs, and boosts the economy, and the fuel itself produces relatively fewer amounts of GHG

emissions as compared to conventional fossil fuels. The selection of biomass feedstock is essential for producing biofuels that would not interrupt food-crop demands or is harmful to the process but at the same time meets the standards of commercial fuels.

It was estimated that Alberta produces approximately 15.8 million tonnes of straws annually, with about 3 million tonnes of milling residues produced from select crops grown between 1996-2005 [7]. Nearly half of Canada's surface area is occupied by forests, and Alberta alone owns about 33 million Ha of forestland, out of which about 4.2 million tonnes of logging and mill processing residues are generated annually [8, 9]. These statistics illustrate that Alberta can utilize its vast agricultural and forest residues as biomass feedstocks using various biomass conversion technologies to produce energy-dense fuels and ease residue management issues.

Hydrothermal liquefaction (HTL) is a promising thermochemical conversion technology that can convert high-moisture content biomass feedstocks into energy-dense heavy oil, along with gas, aqueous phase fraction, and solid char as by-products. This conversion process utilizes water primarily as liquefying medium, at sub- and super-critical conditions, to react with the major polymers of biomass, dissolve these macromolecules and produce heavy oil that is often viscous and requires high upgrading. Water as a liquefying medium also generates a higher amount of undesirable aqueous phase fraction that usually contains the highest oxygen content and calls for expensive upgrading if chosen to be converted into useful chemicals. Many researchers have used alcohols as solvents for hydrothermal liquefaction of various biomass. They have found that the hydrogen-donating ability of alcohols improves the quality of heavy oil such as viscosity, oxygen content, energy content, density, and acid content. However, water being inexpensive as compared to alcohols, it becomes difficult to consider alcohol as a suitable liquefying medium for HTL process. Therefore, instead of using only alcohol as a sole solvent, mixing ratios of water and

alcohol can be introduced as an alternative liquefying medium, that could reduce the cost associated with solvent and energy consumption, and produce high-quality heavy oil resembling chemical characteristics similar to gasoline or diesel. The present research project aims to study the potential of using alcohols as Co-solvents to improve the yield and quality of heavy oil and hydrochar.

1.2 Research objectives

The objective of this study focuses on:

- Understanding the effect of utilizing different biomass feedstocks for hydrothermal liquefaction, on yield and quality of heavy oil and hydrochar.
- Understanding the effect of using water-Co-solvent mixtures on the yield and quality of heavy oil and hydrochar.
- Determining the physicochemical properties of heavy oil and hydrochar by conducting characterization tests such as elemental analysis, compositional analysis, TAN, TGA and SEM.

1.3 Thesis organization

This thesis is organized into 5 chapters:

Chapter 1: Introducing the significance of switching from non-renewable to renewable source of energy, biomass selection for producing low-carbon emission biofuels, hydrothermal liquefaction of lignocellulosic biomass and the need for utilizing alcohols with water as an initial upgrading step to produce high-quality heavy oil.

Chapter 2: Section which explains about the composition of carbon-rich lignocellulosic biomass, various biomass conversion technologies that have converted second-generation biomass into useful chemicals and power, various parameters that affect the performance of hydrothermal liquefaction, role of water and alcohols as liquefying medium and reaction pathways taken by these solvents for converting biomass into energy-dense heavy oil. Lastly, a summary of results obtained by researchers who have studied the synergistic effect of water and Co-solvents on heavy oil yield and quality has been presented in this section.

Chapter 3: Experimental section which explains about the hydrothermal liquefaction procedure, separation and recovery of products, and characterization tests conducted on heavy oil and hydrochar.

Chapter 4: Section that provides the quantitative and qualitative analysis of heavy oil and hydrochar, that can allow us to understand effect of biomass composition and role of Co-solvents in improving yield and quality of heavy oil.

Chapter 5: Provides the conclusion of the research objectives and outlines possible areas of research that can be considered for future work.

Chapter 2: Literature Review

2.1 Hydrothermal liquefaction of biomass

2.1.1 Utilization of biomass in conversion technologies

All renewable organic material that is derived from plants and animals is termed as Biomass [10]. Biomass is broadly classified in two ways, that is based on: (i) how they exist in nature (i.e., their place of origin in the environment or the type of vegetation) and (ii) their application as feedstock [11].
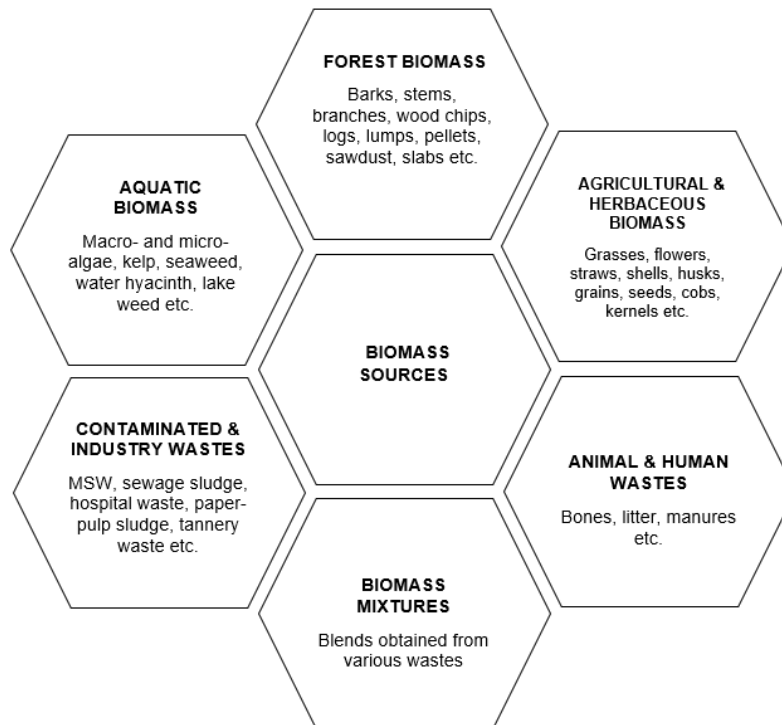
Figure 1: Classification of biomass based on their origin in the environment [12].

Classification of biofuels as first-, second-, and third-generation is primarily based on the origin of biomass used for conversion. First-generation fuels, bioethanol and biodiesel are produced from sugarcane, corn, whey, barley, potato wastes, and vegetable oils such as soybean

and canola oil [13]. Production of first-generation biofuels has received many criticisms, one of them being the utilization of food crops such as sugarcane, where an increase in sugar prices directed the market to favor the production of raw sugar instead of bioethanol [13]. A drawback that arises during the production of biodiesel is when the raw materials are plant seeds, from where oil must be extracted, which can make the process for biodiesel production expensive [13]. Over the years, scientists have improved biodiesel production technology by choosing less expensive sources of oil such as animal fat, recycled cooking oil, and jatropha seeds. Although bioethanol and biodiesel are commercially available and are currently used in transportation fuels, other transportation biofuels have been produced by biofuels industry as well, such as methanol, biocrude, and methane [14].

Second-generation biofuels are produced from non-edible biomass such as lignocellulosic biomass and MSW, which are considered to be more popular biomass feedstocks since they are generally residues obtained from forest harvest operations, wood-based production, agricultural crop production, institutional and household activities.

Third-generation biofuels are produced from algae, usually obtained from sewage sludge, oceans, or lakes. Although algae have produced high energy density oils and have the potential to mitigate CO_2 emissions, the algae biofuel production chain is facing several hurdles, such as strain isolation, nutrient availability, and production management, to name a few [15]. Therefore, lignocellulosic biomass can fairly resolve expenditures related to raw material selection, procurement, pre-treatment, and land usage, thus serving the biofuels industry to produce more second-generation biofuels.

Biomass conversion processes can be categorized mainly into three routes: Thermochemical, Biochemical, and Oil extraction. Thermochemical conversion process includes

combustion, gasification, pyrolysis, and hydrothermal liquefaction. Biochemical conversion process encompasses microbic digestion and alcoholic fermentation. Oil extraction from plant seeds can be categorized into three main methods: mechanical extraction, chemical or solvent extraction, and enzymatic extraction[16]. Thermochemical conversion process employs heat and catalysts, whereas biochemical conversion utilizes enzymes and micro-organisms to transform biomass into fuels, chemicals, or electric power [17]. Thermochemical conversion process provides several advantages over biochemical conversion such as, the ability to produce a diverse range of fuels and chemicals, drastically shorter reaction times, lower catalyst costs, catalyst recycling, and less requirement for sterilization procedures [17]. Oil extraction methods have exhibited various disadvantages such as high infrastructure and operation cost, time-intensive feed preparation process (i.e., separating seeds from fruits, removing kernels from seeds and drying the kernels till optimum moisture content of 15% is attained before extraction process) and long extraction times [18]. Roughly all biomass are heterogeneous by nature and have different qualities even among similar species, therefore not all biomass are suitable for all conversion processes [19]. Li et al. [20] emphasized that biomass quality can influence conversion performance and process economics. In their work, the biomass selection process was categorized into three different scales which are macroscale (physical attributes), microscale (structural attributes) and molecular scale (compositional attributes). Therefore, the importance of biomass selection has to be considered before proceeding with the appropriate conversion process.
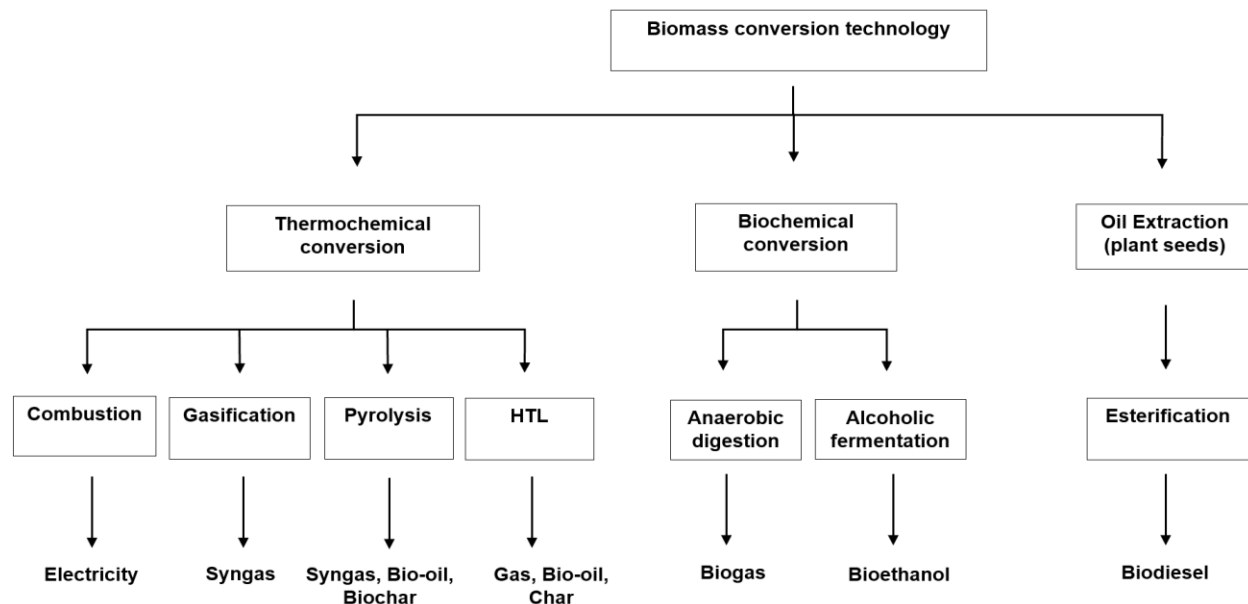
Figure 2: Major conversion pathways for converting second-generation lignocellulosic biomass into power, useful fuels and chemicals [21].

Recognition of biomass as one of the potential renewable sources of energy arises due to the declining supply of affordable fossil fuels and growing concerns of GHG emissions associated with these non-renewable sources. Lignocellulosic biomass represents one of the most abundant fixed carbon containing resource that can decrease CO_2 emissions and air pollution. Sources of lignocellulosic biomass are mostly agricultural wastes, forest residues, MSW, wastepaper, and herbaceous energy crops [22]. MSW, commercial and industrial wastes require extensive processing before being used as feedstocks for conversion. Therefore, agricultural and forest biomass have been considered major renewable resources readily available for energy production [23]. Canada produces millions of tonnes of agricultural biomass each year and can be utilized as feedstocks in local bioenergy industries and improve the rural economy [24]. Farmers consume a portion of crop residues to enhance soil fertility, serve as animal bedding and/or to be used as fodder. Forest biomass comes from harvest residues, low quality trees, materials from forest

thinning, trees that have been damaged due to fire, diseases or insects, trees from "energy plantations" [25]. Underutilized agricultural and forest biomass have been often neglected in the past, especially through the practice of burning these left-over residues that easily release carbon to the environment, which could have been used to offset fossil fuels [25, 26]. With Canada currently transitioning towards bioeconomy, Alberta aims to utilize agricultural and forest biomass to its fullest extent to produce bioenergy and a range of bioproducts [27, 28].

2.1.2 Structural and Chemical composition of Lignocellulosic biomass

Lignocellulosic biomass consists of varying amounts of three major polymers: cellulose, hemicellulose, and lignin, along with small amounts of acetyl groups, mineral constituents, and phenolic compounds [29]. Cellulose polymeric chains, group together to form microfibrils, and these cellulose microfibrils are wrapped around by hemicellulose, with lignin binding these two polymers in the matrix [31,41]. Figure 3 depicts the structural organization of cellulose, hemicellulose, and lignin in a typical plant cell wall of lignocellulosic biomass such as corn stover, wheat straw, or hardwood. Distribution of the three major polymers in lignocellulosic biomass commonly used as feedstocks for hydrothermal liquefaction is given in Table 1.
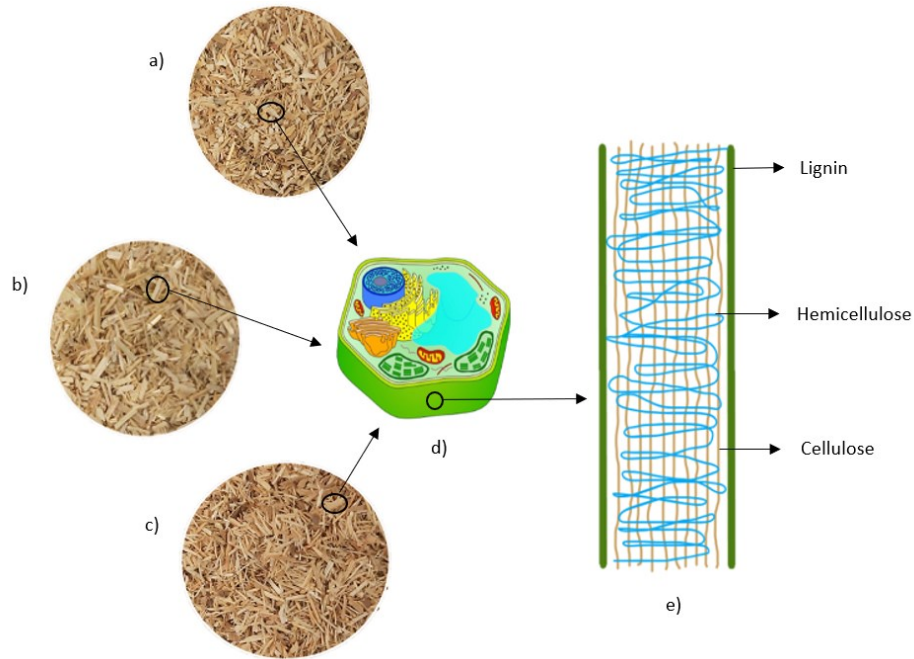
Figure 3: a) Corn stover, b) Wheat straw, c) Hardwood, d) Plant cell [30], e) Polymer matrix of plant cell wall [31].

Table 1: Distribution of major polymers present in various lignocellulosic biomass.

Biomass type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref.
Hardwood	45-55	24-40	18-25	[32]
Softwood	45-50	25-35	25-35	[32]
Corn cob	38.8 ± 2.5	44.4 ± 5.2	11.9 ± 2.3	[33]
Corn stover	38.1	25.3	20.2	[34]
Rice straw	32	24	13	[35]
Sugarcane bagasse	35.2 ± 0.9	24.5 ± 0.6	22.2 ± 0.1	[36]
Wheat straw	37.4	35.6	20.4	[37]
Rice husk	35-40	15-20	20-25	[38]

2.1.2.1 Cellulose

Cellulose is the main macromolecule present in cell walls of higher plants [39]. This macromolecule is a linear polymer composed of D-anhydroglucopyranose units linked with β-1,4-glucosidic bonds and because of this linking, cellulose is also known as β-1,4-D-glucan [39]. As shown in figure 4, a typical monomeric structure of cellulose comprises of: a carbon atom at 1 attached to two oxygen atoms, carbon atoms at 2 and 3 attached to hydroxyl units, a carbon atom at 4 attached to one oxygen atom and a carbon atom at 5 attached to one hydroxymethyl unit [39]. Cellulose has non-uniform distribution of highly ordered crystalline and less ordered non-crystalline (amorphous) zones and the amount of crystalline polymer varies widely with the biomass, with native celluloses containing higher amounts of crystalline polymers as compared to man-made celluloses (e.g., viscose) [39]. The chemical composition, structural conformation of cellulose chains, and the hydrogen bonding networks mostly dictate the degree of crystalline aggregates formation [39]. Amorphous parts of cellulose are more susceptible towards enzymatic degradation; however, highly ordered crystalline parts constitute most of the cellulose composition, making it difficult for complete cellulose degradation [41].
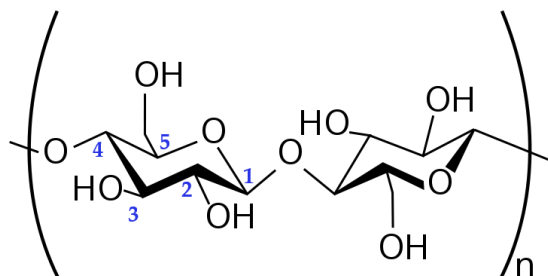
Figure 4: Structure of cellulose polymer chain [40, 39].

2.1.2.2 Hemicellulose

Hemicellulose is composed of a diverse group of carbohydrate polymers and varies between 20-50% of lignocellulosic biomass [39, 41]. Unlike cellulose which contains mostly D-glucose, hemicellulose is composed of different types of sugars such as pentoses (xylose and arabinose), hexoses (glucose, mannose, galactose, rhamnose and fucose), along with D-galacturonic acid and D-glucuronic acid [39]. Hemicellulose forms a complex network of hydrogen bonds that links cellulose microfibrils and lignin, and this polymer is also referred to as "cross linking glucans" [42]. There are four major types of hemicelluloses: xyloglucans, xylans, mannans and β-(1→3, 1→4)-glucans [39]. Xylan hemicellulose is mostly present in hardwood and agricultural biomass, whereas softwood contains mainly glucomannan hemicellulose [29, 41]. The degree of polymerization of hemicellulose is about 50-300, which is very low compared to that of cellulose (~10,000) [43]. Hemicellulose determines the moisture absorption, biodegradation, and thermal degradation of the biomass fiber because it shows the least resistance compared to cellulose and lignin [43]. Figure 5 shows the structures of various types of hemicellulose, where it can be observed that unlike, cellulose which is a linear polymer, hemicellulose has a certain degree of chain branching.

a)

b)

c)
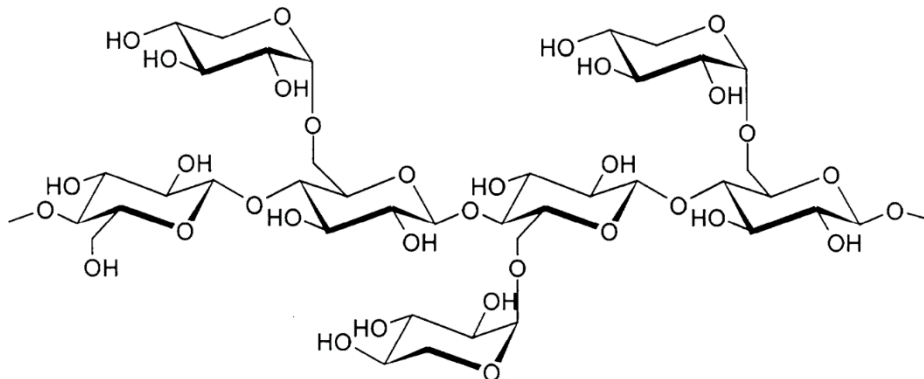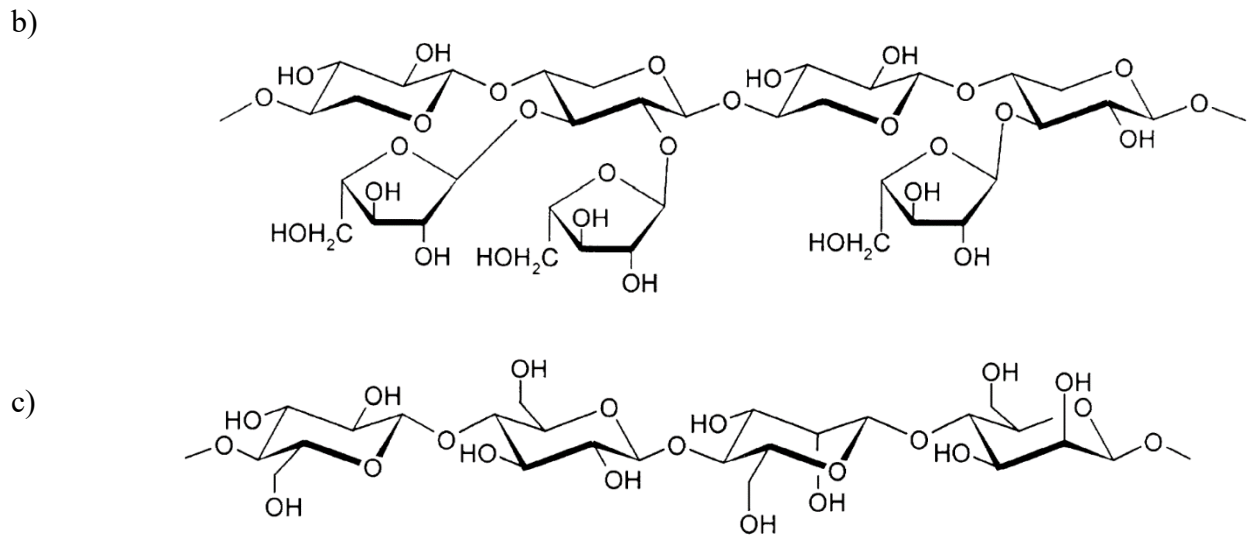
Figure 5: Structures of major hemicelluloses present in plant cell wall: a) Xyloglucan [44], b) example of xylan (arabinoxylan) [44], and c) example of mannan (glucomannan) [44].

2.1.2.3 Lignin

Lignin is a complex molecular structure composed of cross-linked polymers of phenolic monomers that provides structural strength, rigidity, and hydrophobicity to the plant cell wall [39,41]. Lignin shows high resistance towards both mechanical disruption and microbial degradation that makes it recalcitrant towards various biomass conversion processes [39, 45]. The three main phenyl propanoic alcohols present as monomers in lignin are: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [41, 46]. The proportions of these three monolignols in the lignin polymer of plant cell wall varies across different lignocellulosic biomass, with *p*-coumaryl alcohol mainly present in annual plants, coniferyl alcohol mainly present in softwood, and equal amounts of coniferyl and sinaply alcohol present in hardwood [47]. Figure 6 shows the structure of the three monolignols that form lignin. The amount of each of these three units varies across species, age, type of cell and type of tissue [48]. Lignin is formed by the irregular biosynthesis formed by p-hydroxyphenyl (H-units), guaiacyl (G-units), and syringyl (S-units), derived from *p*-

coumaryl, coniferyl, and sinapyl alcohols respectively [49]. H-units could lead to a decrease in molecular weight of lignin, eventually reducing the recalcitrance behaviour of biomass [50]. The ratio between H-, G- and S-units, the actual molecular weight of lignin, and amount of lignin vary across different lignocellulosic biomass, making it difficult to produce relationship with the recalcitrance behaviour of biomass [51, 52, 53]. Therefore, extensive research is required to understand the relationship between these parameters and biomass recalcitrance that could eventually dictate the kind of biofuels and chemicals derived from a particular type of biomass.
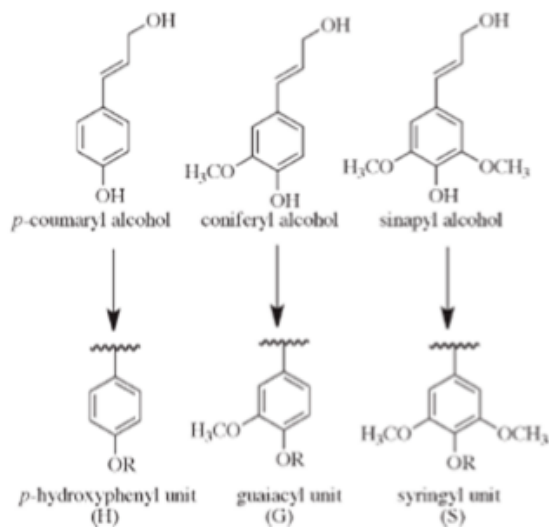
Figure 6: Formation of H-, G- and S-units from the three phenyl propanoic alcohols, to form lignin polymer [54].

2.1.2.4 Minor components present in lignocellulosic biomass

Extractive content is present in small quantities in lignocellulosic biomass and is composed of fatty acids, resin acids, fatty alcohols, stearyl esters, triglycerides, waxes, sterols, and various other phenolic compounds [55]. Inorganic elements present in lignocellulosic biomass are mainly composed of sodium, potassium, calcium, magnesium, sulphur, chlorine, and silicon, that can have

both catalytic and inhibiting effect on reactions occurring during thermochemical conversion processes [56].

2.1.3 Hydrothermal Liquefaction: Process description and Reaction pathways

2.1.3.1 Description of Hydrothermal liquefaction process

Hydrothermal liquefaction (HTL) is a low temperature-high pressure thermochemical conversion technology, that converts biomass feedstock into mainly energy-dense liquid product i.e., bio-oil, utilizing water as the liquefying medium. Hydrothermal liquefaction has been carried out at an operating temperature ranging between 200-400°C, with operating pressure ranging between 4-25 MPa [57, 58, 59]. Among the various existing thermochemical conversion technologies, pyrolysis and hydrothermal liquefaction are predominantly known for producing a dark-coloured, viscous, smoke-like smelling bio-crude or bio-oil [60, 61]. Although a large portion (by mass fraction) of products from HTL is mainly bio-oil or heavy oil, there are gas, char or hydrochar and aqueous phase fractions (containing water-soluble hydrocarbons and light oil) produced in relatively smaller quantities from HTL process [62, 63]. On comparing the two biomass conversion processes, HTL is considered to be the ideal conversion technology to produce bio-oils, shown by its higher energy performance and feedstock flexibility than pyrolysis [64]. Pyrolysis requires drying of biomass feedstock (moisture content should be less than 10% mass fraction), whereas HTL can convert biomass with high moisture content (greater than 50% mass fraction), that reduces the cost for energy consumption needed for drying, since water is the liquefying medium utilized in HTL process [65, 66, 67]. Bio-oils produced from HTL exhibited higher yields, higher energy

contents, lower oxygen contents and higher energy recoveries [65, 68]. Therefore, with a great potential to convert biomass into energy dense bio-oil or heavy oil, a vast number of HTL studies have been conducted on various biomass types, a few studies are listed as shown in Table 2.

Table 2: HTL experiments conducted on various biomass types with varying operating parameters.

Biomass category	Biomass	Liquefying medium	Reactor type	Catalyst	Operating conditions	Results	Ref.
	Rice straw	Water	Autoclave batch reactor, 500mL	None	T: 280, 300, 320°C, RT: 15min, P: 6-9 MPa (N_2, O_2, CO_2)	i) Heavy oil obtained was the highest in N_2 environment and lowest in O_2 environment. ii) O_2 reaction environment provided higher yields of water-soluble products as compared to using N_2 and CO_2.	[69]
Agricultural biomass	Rice straw (4g)	Water (60 mL)	Autoclave batch stainless steel GSH-0.25 reactor, 250 mL	NiO nano catalyst	T: 200, 230, 260, 280, 300°C, RT: 120 min	i) NiO catalyst increased heavy oil yield by 8% at 300°C. ii) NiO catalyst had little effect to improve calorific values of heavy oils at 300°C compared to that of non-catalyzed HTL process.	[70]

Wheat straw (3-5g)	Water & water-alcohol mixtures (0.5-1 mL/min)	Stainless steel tubular reactor	Ru/H-Beta (5wt%)	T:150-350°C, RT: 0 min	i) High-temperature operation resulted in higher HHV of heavy oil due to more effective deoxygenation that took place during conversion. ii) High-pressure operation resulted in higher amounts of oxygen removal from heavy oil. iii) Ru/H-Beta catalyst proved to be effective in increasing the bio-oil yield only in the presence of H_2 reaction environment.	[71]
Corn stover (5g)	Water (30 mL)	Autoclave batch T-316 SS reactor, 250 mL	None	T:250, 300, 350, 375°C, RT: 0, 15, 30, 60 min	i)Highest yield of heavy oil was 29.25 wt.% with conversion of 82.63 wt.%, obtained at 300°C, 2200 psi and 0 min. ii) Heavy oil obtained at 300°C resulted in high fatty acid and fatty acid alkyl ester content and these components were absent at temperatures greater than 300°C and retention time greater than 0 min.	[63]

Corn stalk (10g)	Water (100 mL)	Autoclave batch stainless steel reactor, 1000 mL	None	T:180-300°C, RT: 0-40 min	i) Complete degradation of cellulose was achieved at 280°C. ii) High temperature and reaction time increased gas and volatile organic product yields.	[72]
Barley straw (60g)	Water (400g)	Batch reactor, 1L	K_2CO_3 (10wt%)	T:280-400°C, RT: 15 min	i) Highest bio-crude yield of 35.24 wt.% was obtained at 300°C and lowest heavy oil of 20.35 wt.% was obtained at 400°C. ii) Bio-crude showed higher phenolic content as compared to pyrolysis-derived biocrude, that suggested more lignin decomposition took place in HTL as compared to pyrolysis.	[73]

| Forest biomass | Eucalyptus tree branch (5g) | Water (50 mL) | Batch steel reactor, inner coating with Hastelloy, 300 mL | NaOH, KOH, Pd/C | T:260, 300°C, RT: 30 min | i) Heavy oil yield increased at lower temperatures with the aid of alkali catalyst NaOH.
ii) Addition of the alkali catalysts did not improve the HHVs of heavy oil product.
iii) Heavy oil obtained at 300°C using NaOH showed great reduction in carboxylic acid content as compared to that obtained using KOH. | [74] |
| | Poplar (10g) | Water (100 mL) | Autoclave batch stainless steel reactor, 1L | None | T: 220, 240, 260, 280°C, RT: 30 min | i) HTL conducted at low reaction temperature of 220°C resulted in highest solid residue yield with lowest light and heavy oil yield.
ii) Oxygen content in heavy oil decreased on increasing the reaction temperature from 220 to 280°C, indicating that deoxygenation was significant at higher reaction temperature. | [75] |

					iii) pH levels of light oils varied between 2.35-3.62 and that of heavy oil was between 5.33-5.73, indicating that corrosive power of light oil was higher than heavy oil.
Waste furniture sawdust (10g)	Water (60 mL)	Autoclave batch stainless steel reactor, 600 mL	None	T:180-300°C, RT: 0-60 min, P: 1 MPa N_2	i) Highest heavy oil of 12.7 wt.% was obtained at 280°C, initial pressure of 1 MPa N_2 and retention time of 15min. ii) Carboxylic acid content in heavy oil was the highest at 300°C. iii) Yield of gaseous product increased from 15.7 to 21.9 wt.% when HTL was conducted at 280°C and 1 MPa N_2 initial pressure. [76]

Food/Fruit wastes	Cornelian cherry seeds (10g)	Water (100 mL)	Autoclave batch stainless steel reactor, 500 mL	None	T: 200, 250, 300°C, RT: 0, 15, 30 min	i) Lower reaction temperature of 200°C was not effective in producing high yields of heavy oil. ii) At temperatures above 250°C, shorter retention time, i.e., 0 min, resulted in higher yields of heavy oil. iii) Major compounds identified in heavy oil are furfurals, phenols, and fatty acids.	[77]
	Blackcurrant pomace	Water	Parr batch stainless steel (type 316) reactor, 0.6L	NaOH	T:290-335°C, RT:0-240 min	i) Mass ratio of dry biomass to water of 0.14 showed the highest bio-oil yield and lowest char yield. ii) Addition of 2 wt.% NaOH increased the bio-oil yield from 26 wt.% (with no NaOH) to 31 wt.% . iii) 43% mass fraction of components in bio-oil (obtained at 300°C and holding time of 60 min) fall in medium naphtha region.	[78]

| Aquatic biomass | *Sargassum tenerrimum* algae (5-10mg) | Water, Methanol, Ethanol | Autoclave Parr batch reactor with Hastelloy coating, 100 mL | None | T:260, 280, 300°C, RT: 15 min | i) Bio-oil yield using alcoholic solvents was higher than using water, with maximum yield of 23.8 wt.% obtained using ethanol at 280°C. ii) Solid content increased, and gas yield decreased on using alcoholic solvents for HTL of present algae. iii) Ester content increased in bio-oils derived from HTL using alcohols as solvents. | [79] |
| Animal & Human wastes | Cattle manure | Water | Parr stainless steel reactor HT/HP 4572, 1.8L | NaOH (0.5mol) | T:270-350°C, RT: 0-40 min, P: 0-100 psi of Air, N_2, H_2 and CO | i) Highest bio-oil yield of 48.48 wt.% was attained at reaction temperature of 310°C, with CO reaction environment. ii) Presence of toluene, ethyl benzene and xylene in bio-oil and absence of compound groups C_4-C_{15} alkanes indicated that bio-oil resembles more of crude oil than gasoline or diesel. | [80] |

With the investigations conducted on HTL-products to assess the energy content and fuel properties, it has been found that bio-oil is the most desirable product as compared to the three by-products, where the bio-oil could be upgraded to be used as light fuels such as gasoline and diesel, adhesives and phenol resins; bio-char could be used for power generation, metal and dye adsorption, pollutant reduction in wastewater treatment facilities, soil remediation and biogas catalyst; aqueous phase could be used for recirculation to increase bio-oil yield, source of nutrient for microalgae growth; the potential applications for gaseous products has not been deeply explored till date, owing to its low yield obtained from HTL laboratory-scale processes [81, 82]. Light oil or Aqueous oil fraction has been another by-product from HTL process that has not been studied further for its application.

This oil fraction, derived from aqueous phase during separation, contains high oxygen content due to a greater number of phenolic compounds present than that found in heavy oil, resulting in low HHV and making it undesirable for upgrading [76, 78, 83]. Therefore, there are primarily four product streams, i.e., bio-oil or heavy oil, bio-char or hydrochar, aqueous phase, and gas, that have been investigated for their future applications to a certain extent, depending on their yield obtained from the HTL process. It is necessary to understand the effect of various parameters involved during the conversion of biomass through HTL pathway since the yields of HTL-products have been reported to be dependent on the process- and feed-related parameters.

2.1.3.2 Role of Sub- and Super-critical water in HTL conversion process

Hydrothermal liquefaction has been conducted in both sub- and super-critical conditions. Water in sub-critical regions, i.e., near 374°C and 3200 psi, exhibits a lower dielectric constant, similar to that of organic solvents, increasing the solvation power to dissolve non-polar molecules, and this property of water is gaining attention to be used as extraction fluid [84]. On a molecular level of understanding the hydrogen bond interactions in high-temperature water, thermal agitation reduces the strength of each hydrogen bond, causing a drastic reduction in dielectric strength and therefore water tends to become more non-polar, easily dissolving more non-polar hydrocarbons in it [84]. Referring to figure 7, the dissociation constant (Kw) of water near its critical point is nearly three orders of magnitude higher than that at room temperature, resulting in increased H^+ ion and OH^- ion concentrations provide acid- or base-catalysed reactions, that can aid in biomass hydrolysis reactions [85]. Water at super-critical conditions, i.e., greater than 374°C and 3200 psi, provides a single-phase reaction environment where reactions can proceed with ease since there is no interphase mass transport that can hinder reaction rates [Sava. However, corrosion effects on reactor's interior have been reported to be higher in super-critical water medium as compared to the liquefaction conducted in sub-critical water medium [87]. Therefore, with various advantages that sub-critical water can provide for HTL process and reactions occurring during the biomass conversion process, it is necessary to regulate process-related parameters such as operating temperature, operating pressure, retention time, and heating rate. There are also feed-related parameters such as biomass composition, biomass-to-solvent ratio, gas supplied for HTL-reactions and catalyst that have influenced the yield of HTL-products and bio-oil properties.
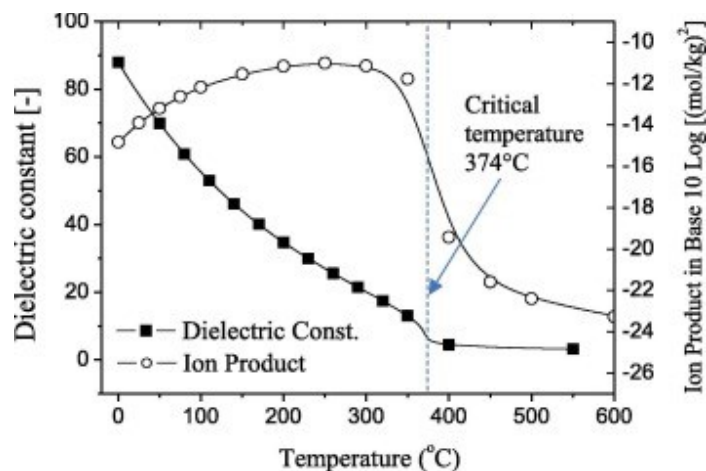
Figure 7: Dielectric constant and dissociation constant of water at sub-critical and super-critical conditions [88].

2.1.3.3 Process- and Feed-related parameters that affect yield of HTL-products

HTL conducted using only water as the solvent has resulted in a trend where heavy oil yield has been observed to increase with increase in operating temperature to a certain temperature and then decrease on further increasing the operating temperature, with the highest yield often obtained between 280-300°C [72, 73, 75, 76, 77, 79]. Usually at this temperature range the yield of solid residue is the lowest, and as reaction temperature increases above 375°C, both light and heavy oil undergo high-temperature cracking reactions to produce more gaseous products, and repolymerization and condensation reactions occur to produce solid residue products [76, 63, 73]. Temperature majorly influences the initial reactions occurring in HTL: dehydration, decarboxylation, and hydrolysis, that are dominant in sub-critical operations, and once super-critical conditions are reached, compounds rearrange themselves through condensation, cyclization and repolymerization [58, 89]. Complete decomposition of cellulose was achieved at 250°C, and at reaction temperatures above 285°C, heavy oil fraction decreased [90, 91]. Hemicellulose decomposition took place in a reaction temperature range between 150-210°C and

lignin component required high severity conditions for degradation and was reported to be physically and chemically stable till 350°C [92, 93]. Increasing the operating temperature increases the reaction rate and changes the reaction mechanism, where ionic reactions are promoted at temperatures below the sub-critical water, whereas at temperatures near super-critical water region, homolytic bond breakage was promoted that led to free-radical formation [87]. High pressure operation is crucial to prevent vaporization of water and it was reported that yield of heavy oil did not significantly increase on increasing final pressure above 3200 psi, indicating that HTL operation is effective in liquid phase conditions rather than vapor phase conditions [94, 95]. The reduced efficiency of HTL conversion at super-critical conditions was also reported by Chan et al. [96], where for HTL conducted at 390°C, increasing the final reaction pressure from 25 MPa to 35 MPa, resulted in decreasing the heavy oil yield. When HTL was conducted at operating temperatures ranging between 250-300°C, both aqueous phase and heavy oil yield increased on increasing the pressure from 300 psi to 600 psi, and bio-char content decreased for operating temperatures ranging between 250-375°C [63]. The variation of product yields can be explained according to the severity of HTL-operating conditions where, solid residue content increases at milder operating conditions (T: 100-200°C, P < 2 MPa) and gaseous products increases at high severity operating conditions (T: 350-750°C, P: 20-42.5 MPa) [86, 91, 92]. Yin et al. [80] reported that when HTL of cattle manure was conducted in any of the process gases i.e., CO or N_2, heavy oil yield decreased with increase in retention time and that the highest yield of heavy oil was obtained at 310°C with 0 min retention time. Solid residue content at 0 min was the lowest, i.e., ranging between 2-8 wt.% under CO and N_2 atmosphere, among all other retention times ranging between 0-40 min. Mathanker et al. [63] reported that on increasing the retention time from 0 min to 15 min, heavy oil, aqueous oil and gas fractions decreased whereas hydrochar content increased

owing to the carbonization reactions taking place in the oil fractions. Increasing the retention time

to beyond 15 min resulted in decreasing the hydrochar content and increasing the gas content [63].

Wang et al. [97] observed similar trend, where solid residue content showed a gradual decrease

from 15.3 wt.% at 30 min to nearly 13 wt.% at 120 min, and gaseous products increased from

nearly 17.6 wt.% at 30 min to 25.6 wt.% at 120 min. Longer retention times may have promoted

secondary reactions (thermal cracking and repolymerization reactions) occurring in liquid and

solid products to form more gaseous products [63, 98]. Variation of heating rates have significantly

changed the yield of liquid products, however, no change in chemical composition was detected

during the GC-MS analysis of liquid products [99]. Zhang et al. [99] conducted HTL on corn stover

at 350°C, final pressure 20 MPa and retention time of 10 min and reported that on increasing the

heating rate from 5-140°C/min, the yield of liquid products increased from 51 wt.% to 71 wt.%,

gaseous products decreased from 29 wt.% to 21 wt.% and solid residue content decreased from 20

wt.% to 9 wt.%. Brand et al. [100] similarly reported that a slower heating rate of 2°C/min, slightly

increased the heavy oil yield from 8 wt.% to 15 wt.%, whereas when heating rate was increased to

20°C/min, heavy oil yield drastically increased from 5 wt.% to 27 wt.%, when HTL was conducted

on pine sawdust in water at operating conditions of 250-350°C and retention time of 1 min. Faster

heating rates have strongly influenced the yield of heavy oil, with possible explanations being: i)

degradation reactions in biomass feedstock are enhanced, ii) unwanted side reactions are reduced,

iii) easier breakage of plant cell walls, releasing cell contents into reaction medium and iv) prevents

repolymerization reactions eventually reducing solid residue formation [101]. Elemental

composition of solid residue has also been affected by varying heating rates as reported by Brand

et al. [100], where for a slow heating rate of 2°C/min, the H/C and O/C ratio decreased leading to

higher HHVs as compared to that obtained from a higher heating rate of 20°C/min. Thus, HTL

conducted at slower heating rates, longer retention times and higher temperatures can lead to formation of high energy dense solid residue and can possibly explain the lower yields and lower HHVs of heavy oil fraction.

Although the effect of various process-related parameters discussed so far have been studied extensively, where researchers have concluded that these parameters have strongly influenced the HTL-product yield distributions, there have been only a countable number of HTL-related studies conducted to investigate the effects of varying biomass composition on HTL-product yield and quality. Tian et al. [102] conducted HTL on corn straw, peanut straw, soybean straw and rice straw at an operating temperature of 320°C and retention time of 60 min and reported that maximum heavy oil yield of 15.8 ± 0.8 wt.% was obtained from soybean straw as compared to the rest of the biomass. Soybean straw having the highest cellulose content of 42.39 wt.% and cellulose:hemicellulose (wt.%) of 1.92, proved that biomass containing high amounts of cellulose can produce higher yields of heavy oil from HTL conversion process. Demirbaş [103] conducted HTL on domestic biomass wastes such as beech wood, spruce wood, hazelnut shell and tea waste, at operating temperatures between 277-377°C and retention time of 25 min and reported that the highest heavy oil yield attained was 28 wt.% at 377°C with beech wood as the biomass feedstock. Increase of hemicellulose content in biomass also resulted in higher heavy oil content, following similar trend as that obtained from the studies conducted on the effect of cellulose content on heavy oil yield. Presence of high amounts of lignin fraction in biomass has shown decline in heavy oil yield, when HTL was conducted without using catalyst, and has exhibited higher yield of char formed during HTL process [104, 105]. Singh et al. [69] conducted HTL on rice straw in N_2, O_2 and CO_2 environment, and reported that highest heavy oil yield of 17 wt.% and conversion of 78% was achieved in N_2 gas environment at a reaction temperature of 280°C.

O_2 environment during HTL produced more oxygenated compounds, increasing the water-soluble fractions and phenol content of bio-oil. Increasing biomass concentration in biomass and solvent mixture, decreased the heavy oil yield and increased the char content. Déniel et al. [78] explained that having higher biomass concentrations could possibly produce higher amounts of unstable intermediates from liquid products, that would repolymerize and lead to increase in char formation. Present HTL experiments in this project with take biomass-to-solvent ratio of 1:6, since increasing biomass loading beyond this ratio will cause mechanical issues to the stirrer and increasing solvent quantity beyond the ratio would exceed the final pressure limit that was designed for the reactor. Lastly, catalyst participation in biomass conversion through HTL process determines the yield and quality of heavy oil. Alkali catalysts have reportedly improved bio-oil yield and suppressed char formation [74]. Wu et al. [74] observed maximum heavy oil of 61.2 wt.% and 57.7 wt.% using NaOH and KOH, respectively. Both Zhu et al. [73] and Wu et al. [74] have reached a conclusion that performance of alkali catalysts for biomass conversion is better at milder operating conditions. However, higher heating values of heavy oil have not significantly improved on using catalyst for HTL [70, 73, 74]. Therefore, with an understanding of both process- and feed-related parameters that affect the yield of HTL-products and quality of heavy oil, next section will briefly describe the possible reactions taking place in biomass during HTL operation.

2.1.3.4 Reaction pathways for conversion of biomass through HTL process

Lignocellulosic biomass is heterogeneous in composition and constructed from an intricate network of polymers, which leads to complex chemistry when these components of biomass interact with each other. Interaction of cellulose, hemicellulose, and lignin with water under thermal treatment enables hydrolysis reaction, where these macromolecules are hydrolyzed to form monomers and phenolic compounds [106]. Hydrolysis and dehydration reactions are rapid in

the presence of acids, which can be substituted by using sub-critical water that possesses high ion product, where the high concentrations of H^+ and OH^- ions allow to catalyze these reactions, which is not supported when conversion is carried out in water at ambient conditions [107]. In sub-critical HTL operation, both hydrolysis and dehydration follow ionic reactions, however, when HTL is conducted at super-critical conditions, dehydration reactions may proceed with free-radical mechanism [107]. C-C bond cleavage also proceeds by free-radical mechanism via aldol splitting and utilizing alkali salts have improved the C-C bond cleavage rate [107]. HTL conducted at low temperatures and shorter retention times, have generated phenolic monomers and dimers, obtained by cleavage of ether and C-C bonds [108]. As the reaction temperature increases, these phenolic intermediates undergo demethoxylation, alkylation and condensation reactions to form various alkyl phenols and aromatic oligomers [108]. Figure 8 shows the manner in which cellulose, hemicellulose and lignin participate in various decomposition reactions that take place during HTL.
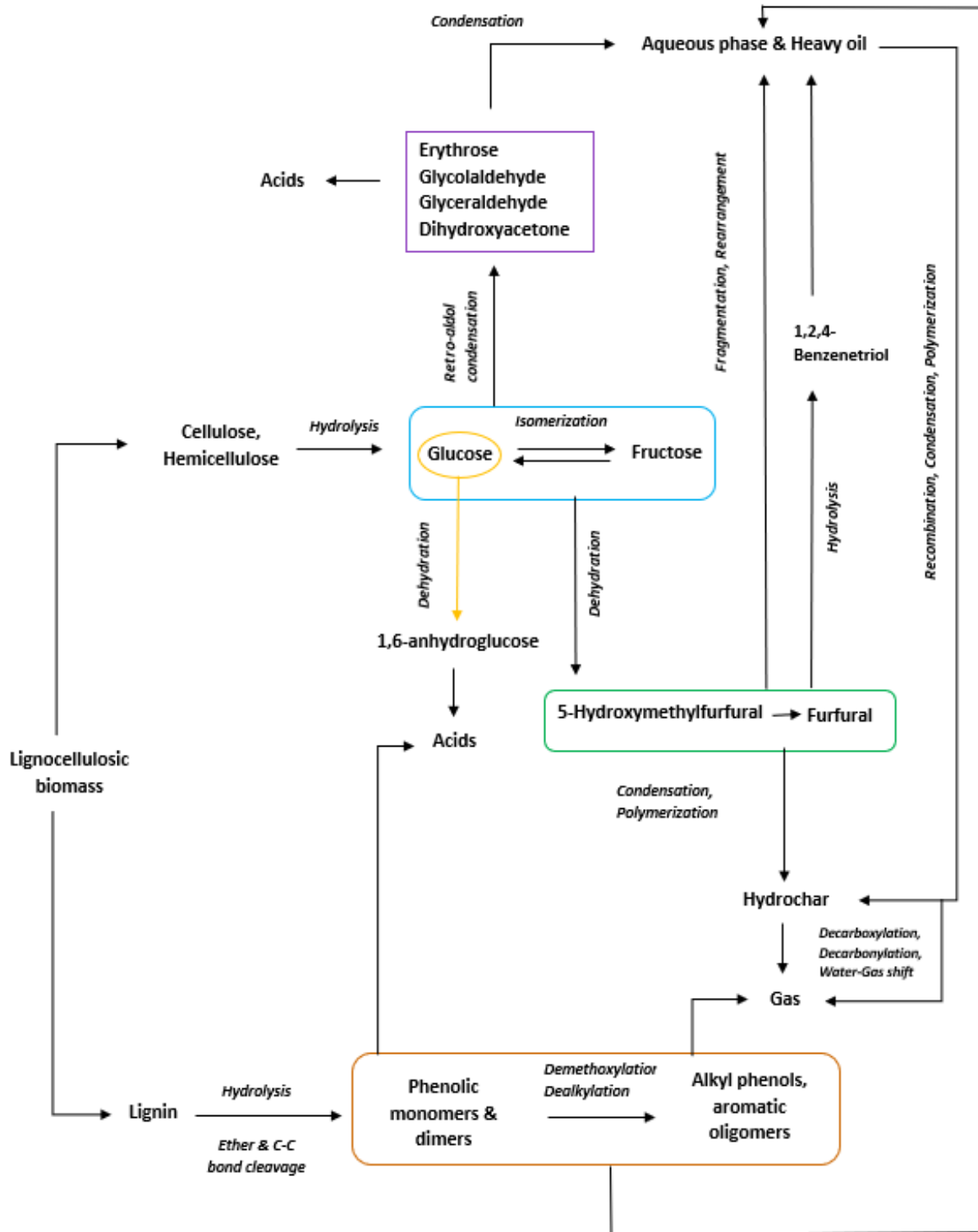
Figure 8: Reaction pathways occurring during biomass conversion through HTL, adapted from [107, 108, 109, 110].

2.2 Hydrothermal liquefaction using alcohols and water-Co-solvent mixtures

2.2.1 Parameters for assessing the quality of heavy oil produced from HTL process

As discussed in previous sections, HTL-factors such as process- and feed-related parameters have played a major role in HTL-product yield distribution. Interestingly, even the physical and chemical properties of heavy oil are highly dependent on these factors. Physical properties of heavy oil can be determined by studying viscosity, density, TAN, energy content, boiling point range and chemical properties can be determined by studying the elemental distribution (CHNS-O) and molecular composition of heavy oil [61, 111]. Physical and chemical properties of heavy oil obtained from thermochemical conversion technologies are often compared to commercial fuels such as gasoline and diesel [111]. Table 3 focuses on the earlier mentioned physical and chemical properties that are exhibited by gasoline, diesel, and heavy oil.

Table 3: Physical and chemical properties of gasoline, diesel, and heavy oil [a-112, b-113, c-114, d-115, e-116, f-117, g-111, h-118].

Properties	Gasoline	Diesel	Heavy oil
Dynamic viscosity (mPa s)	0.292 (@ 20°C)[a]	799.4 (@ 20°C)[a]	67,000 (@ 40°C)[f]
Density (kg/m^3)	680 (@ 20°C)[a]	888 (@ 20°C)[a]	1.14 (@ 15°C)[f]
TAN (mg KOH/g oil)	-	1.70[b]	108-159[g]
Energy content (MJ/kg)	44-46[c]	42-46[c]	27-38[f,g]
Boiling point range (°C)	32-184[d]	307-352[e]	< 149[h] – Gases and light naphtha 149-566[h] – Kerosene to Heavy Vacuum Gas Oil > 566[h] – Residue

Heavy oil obtained from HTL process has got significant negative attributes such as high viscosity, corrosiveness, reduced heating value, high instability issues that makes it undesirable to be directly used as transportation oils such as diesel engine oils [119]. Viscosity property determines the ease of pumping oil to the injection system, as well as atomization and combustion quality of the oil [120]. Presence of aromatic hydrocarbons, alcohol or acidic compounds has led to the formation of highly viscous heavy oil [80, 61]. The corrosive characteristic of heavy oil is mainly responsible for instability conditions occurring during storage operations, where with time, carboxylic acids in heavy oil undergo esterification reaction to form esters and water [121]. Aqueous phase obtained from HTL of lignocellulosic biomass are mostly comprised of oxygenated compounds with high amounts of organic acids and alcohols [122, 123]. Zhu et al. [124] conducted HTL operation on barley straw with three recycles of aqueous phase operation, where it was reported that both heavy oil and solid residue yield increased significantly as compared to HTL conducted using fresh water, indicating that organic acids present in aqueous phase accelerated the decomposition rate to form more heavy oil and solid residue fraction. Although organic acids have been observed to improve heavy oil formation, aqueous phase should contain higher organic acid content than heavy oil, which could be beneficial to obtain higher heavy oil yields when aqueous phase recirculation is utilized during HTL of biomass. With an impressive increase in yield of heavy oil with recirculation experiments, however, the elemental composition and atomic ratio of heavy oil did not improve significantly as compared to HTL experiment conducted using fresh water, and the authors suggested further upgrading steps are required for deoxygenation of heavy oil. Higher heating value (HHV) of heavy oil is much lower than commercial fuels, such as gasoline and diesel, owing to its high oxygen content [125], thus, improving the HHV of heavy oil is necessary to be compatible with current engine designs. Stability of heavy oil can be estimated by factors

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such as viscosity, water content, acid content (pH value/Total acid number) [126]. Reactions that occur during storage of heavy oils are: esterication of alcohols with carboxylic acid compounds, polymerization and condensation of olefins to form polyolefins and acetalization of alcohols and aldehydes/ketones, produce water as by-product [121], thereby increasing the water-content of heavy oil. HTL operation using only water as sole solvent has produced lower yield of heavy oil, along with high oxygen content, low HHV and high viscosity [127]. Therefore, it is necessary to upgrade HTL operation to produce high yield of heavy oil and improve the quality of heavy oil to meet similar properties compared to commercial transportation fuels such as those mentioned in Table 3.

2.2.2 Role of alcohols as sole solvents on the yield and quality of heavy oil

Selection of liquefying medium or solvent determines the yield and quality of products obtained from HTL operation. Participation of solvent during HTL involves transporting heat to biomass feedstock, becoming miscible in biomass polymers, dissolving large complex macromolecules in it, and changing thermodynamic environment in favor of facilitating certain chemical reactions [128]. Alcohols such as methanol (T_C = 239.4°C, P_C = 1069.8 psi), ethanol (T_C = 240.7°C, P_C = 891.49 psi) and 2-propanol (T_C = 235.1°C, P_C = 690.4 psi) (all critical temperatures and pressures have been calculated using Aspen Hysys V9), have critical temperatures and pressures much lesser than that of water, resulting in milder HTL operations [129] and weaker hydrogen bonding than that in water [133].Super-critical alcohols can exhibit lower dielectric constants than sub-critical water, where dielectric constant of methanol at 253°C is about 7, of ethanol at 246.2°C is about 4.1, much lower than water at 300°C showing dielectric constant of 21 [130, 131, 85]. Solvents with lower dielectric constant, can dissolve numerous non-polar organic compounds such as high-molecular weight materials produced from

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decomposition of cellulose, hemicellulose, and lignin [94]. Utilizing super-critical alcohols as liquefying medium for HTL operation offers many advantages such as: (i) ease of product separation, where single-phase liquid product is obtained when using alcohols as solvents as compared to double-phase liquid products (can be split into water-soluble and water-insoluble fraction) is obtained from using only water, (ii) Corrosion is a matter of great concern when HTL is conducted using sub-critical water, whereas super-critical alcohols result in no corrosion issues, and (iii) Acts as hydrogen-donor agents, where hydrogen donated from these alcohols depolymerize the biomass, remove oxygen from biomass in the form of water and act as free-radical inhibiting agent, reducing the rate of repolymerization and formation of solid residue [132]. Major reactions that take place between the complex polymers of biomass and super-critical alcohols are esterification, alkylation, hydroxyalkylation and deoxygenation, effectively increasing the heavy oil yield [134]. Warabi et al. [135] studied the rate of reaction for trans-esterification and alkyl-esterification reaction on rapeseed oil and free fatty acid samples (Palmitic, Stearic, Oleic and Linoleic acid), where alkyl-transesterification experiments were carried out on fatty acid samples using super-critical methanol. The group concluded that trans-esterification of triglycerides in rapeseed oil is much slower than that of alkyl-esterification conducted on fatty acids. Another conclusion that can be drawn from this study is that all biomass have certain fractions of triglycerides and free fatty acids content, and with the rate of trans-esterification slower, many of the free fatty acids remain unconverted. Therefore, super-critical alcohols are required to convert these free fatty acids into alkyl esters and increase the overall ester content of heavy oil obtained from HTL operation. Alkylation of phenols produces alkylphenols, that are important chemical intermediates used in resin manufacturing and agrochemicals industry, along with production of antioxidants [136]. Hydroxyalkylation reactions reduced C=O to CH−OH and

C=C to CH−CH, and this reaction was more efficient in super-critical alcohol medium rather than sub-critical water [137]. Deoxygenation reactions are enhanced at reaction temperature of 400°C when super-critical water is used, where heavy oil obtained from HTL using super-critical water, showed an oxygen content of 13.4 wt.% [132]. However, at a high reaction temperature of 310°C, heavy oil showed much higher oxygen content of 42.0 wt.%, when super-critical alcohols were used as liquefying solvents [132]. Figure 9 shows possible reactions and probable products obtained when super-critical alcohols are used as liquefying medium in HTL process.
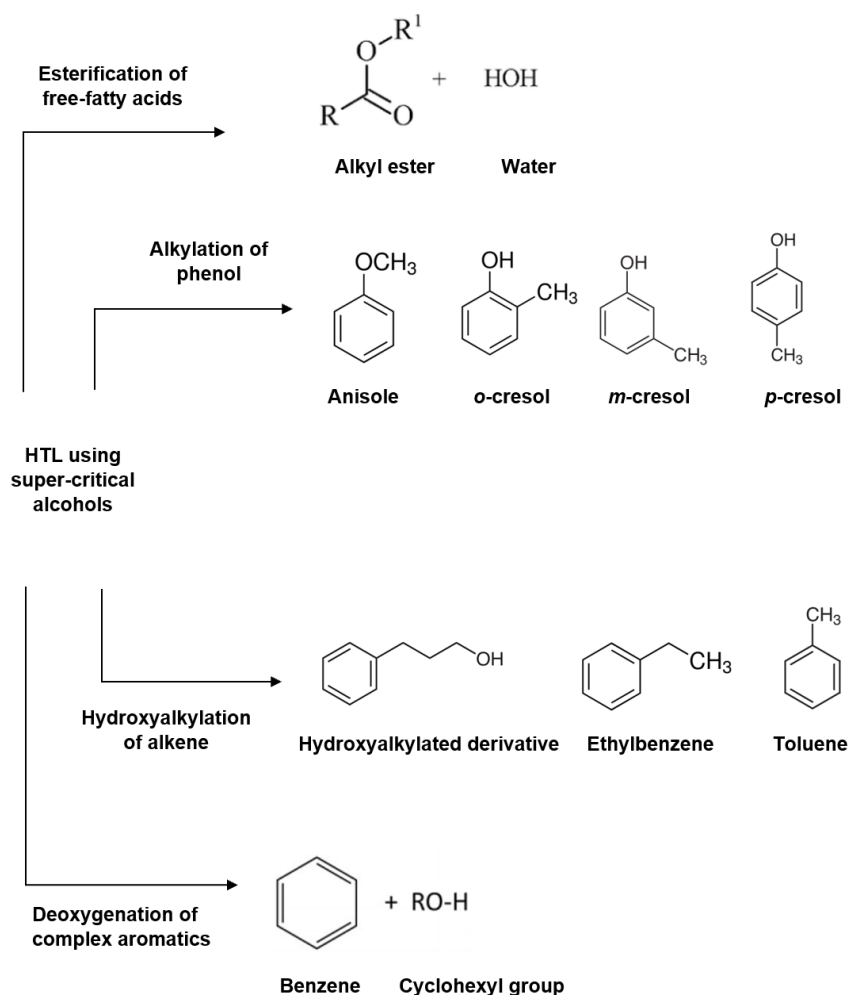
Figure 9: Possible chemical reactions occurring when super-critical alcohols are utilized for HTL conversion process, adapted from [138, 139, 144, 147] and structures obtained from [140, 141, 142, 143,145, 146].

On understanding the reaction scheme shown in figure 9, heavy oil produced from using alcohols as sole solvents for HTL operations may contain large amounts of low-molecular weight compounds [132]. Energy requirement would be higher when deoxygenation is carried out in super-critical water, which could be mitigated by using super-critical alcohols. Sohani [148] considered viscosity and acid content as major properties that determine the quality of heavy oil, and both these properties decreased with decrease in oxygenated compounds present in heavy oil. Hence, super-critical alcohols are promising liquefying mediums that can produce heavy oils with lower oxygen content and improve its quality in terms of energy content, density, viscosity, and acid content. Subsequent section will summarize the results obtained by various researchers on their study of involving super-critical alcohols as Co-solvents for HTL operation, which has affected the yield and quality of heavy oil.

2.2.3 Role of water-Co-solvent mixtures on the yield and quality of heavy oil

This section will concentrate on the application of alcohols, methanol, ethanol, and 2-propanol, as Co-solvents in HTL operations conducted on different lignocellulosic biomass by various researchers. Table 4 shows the findings obtained by various researchers that have utilized water and Co-solvent mixtures, with varying mixing ratios of both these solvents, and their effect on heavy oil yield, HHV and elemental composition.

Table 4: Results obtained by various researchers when water-Co-solvent mixtures were utilized for HTL of various agricultural and forest biomass.

Biomass	Operating condition	Co-solvents	Oil yield (wt.%)	HHV (MJ/kg)	C (wt.%)	H (wt.%)	O (wt.%)	Results	Ref.
Rice straw	T: 300 °C RT: 3 min	Ethanol/water (5:5) 2-propanol/water (5:5) ml	38.35 39.70	29.66 30.75	- 63.81	- 7.10	- 27.29	i) Bio-oil yield increased with alcohol-water ratio range from 0:10 to 5:5 and decreased from 6:4 to 10:0. ii) Solid residue content was higher when ethanol-water was used, as compared to 2-propanol-water mixture.	[127]
Pinewood	T: 300 °C RT: 15 min	100 wt.% water	39.13	-	-	-	-	i) Presence of 50 wt.% methanol or ethanol in solvent-water mixture resulted in >95 wt.% conversion of biomass and yield of bio-oil was >65 wt.% at 300°C	[149]
		50 wt.% ethanol	65.74	-	-	-	-		
		100 wt.% ethanol	25.92	-	-	-	-		
		50wt.% methanol	64.45	-	-	-	-		

		100 wt.% methanol	23.54	-	-	-	-	and retention time of 15 min, compared to the runs using sole solvents.	
Rice husk	T: 260 °C RT: 20 min	100 vol% water 50vol% ethanol 100 vol% ethanol	13.16 21.07 18.44	25.03 27.04 27.56	60.55 64.88 63.63	6.93 6.78 7.46	30.24 25.99 26.23	i) Optimum ratio of 5:5 ethanol-water mixture provided relatively higher yield of heavy oil with low oxygen content. ii) ii) Ethanol provided decomposition of macromolecules such as cellulose, hemicellulose and lignin, at milder operating conditions.	[150]
Pinewood	T: 300 °C RT: 15 min	100 vol% methanol 20 vol% methanol 50 vol% methanol 80 vol% methanol 100 vol% water	24.25 40.02 54.65 27.79 29.96	- - - - -	- - - - -	- - - - -	- - - - -	i) 50 vol% water content enhanced solvolytic liquefaction of pinewood. ii) Mixture of methanol and water promoted more decomposition of some plant tissue in pine as compared to using purely methanol or water.	[151]
Wheat straw	T: 300 °C RT: 120 min	100 vol% water 25 vol% ethanol 50 vol% ethanol 75 vol% ethanol 100 vol% ethanol	15.1 15.5 27.8 22.4 23.7	20.5 25.5 27.8 28.5 28.2	- - - - -	- - - - -	- - - - -	i) Optimum water-ethanol mixture ratio of 50:50 (v/v) was found to be effective in producing high yield of heavy oil and HHV at 300°C and nearly 1450 psi.	[71]
Cornstalk	T: 300 °C RT: 30 min	100 vol% water 20 vol% methanol 40 vol% methanol 50 vol% methanol 80 vol% methanol 100 vol% methanol	45.15 45.71 48.07 52.40 43.92 28.10	- - - - - -	- - - - - -	- - - - - -	- - - - - -	i) Equal ratio of methanol and water mixture showed best synergistic effect on degradation of lignin.	[152]

Feedstock	Conditions	Solvent						Remarks	Ref
Poplar	T: 300 °C RT: 15 min	100 vol% water	28.8	-	-	-	-	i) More amounts of ketone, aldehyde and carboxylic acid were found in heavy oil liquefied with 70:30 (v/v) water-methanol mixture. ii) Yield of esters decreased with increase in water content in solvent mixture.	[153]
		20 vol% methanol	36.2	-	-	-	-		
		30 vol% methanol	38.9	-	-	-	-		
		40 vol% methanol	37.3	-	-	-	-		
		60 vol% methanol	31.8	-	-	-	-		
		80 vol% methanol	32.8	-	-	-	-		
		100 vol% methanol	23.2	-	-	-	-		
White birch bark	T: 300 °C RT: 15 min	50 vol% Ethanol (ml)	58.81	30.59	68.36	8.08	22.69	i) Major compounds: ester derivatives, aromatics, ketones, butanoic acid, propanoic acid.	[154]
Camphor tree sawdust (CTS)	T: 280 °C RT: 30 min	50:50 (v/v) water-ethanol	61.5	24.6	61.6	6.5	31.6	i) Conversion of biomass was highest when equal ratio of water-ethanol was used as liquefying medium, as compared to those obtained by using only water or ethanol as solvents.	[155]
Bamboo	T: 260°C RT: 0 min	100 vol% water	14.63	26.04	67.21	5.67	27.03	i) Ethanol favoured deoxygenation reactions, whereas water facilitated dehydration reactions and produced heavy oil with high H/C ratio.	[156]
		20 vol% ethanol	15.31	27.00	67.77	6.08	26.05		
		40 vol% ethanol	5.14	26.11	67.82	5.51	26.53		
		60 vol% ethanol	2.97	25.73	66.64	5.65	27.54		
		80 vol% ethanol	2.86	26.34	67.36	5.80	26.68		
		100 vol% ethanol	1.94	22.14	59.35	5.77	34.70		
Pinewood sawdust	T: 300 °C RT: 30 min	50 wt.% ethanol	47.63 ± 0.09	25.89	65.60	6.13	28.24	i) Middle distillates (343-538°C) were the highest in heavy oil, obtained from equal ratio ethanol-water mixture, than using only water as solvent.	[157]
Rice straw	T: 300 °C RT: 60 min	100 vol% water	12.3	35.3	-	-	-	i) Using KOH as catalyst with 50:50 water-methanol mixture as liquefying medium, resulted in maximum bio-crude yield of 39.9 wt.%.	[158]
		25 vol% methanol	14.3	32.1	71.5	7.7	19.2		
		50 vol% methanol	31.1	32.8	72.7	7.8	17.8		
		75 vol% methanol	16.3	31.2	69.1	7.7	20.9		

2.2.3.1 Effect of water and Co-solvent mixture ratio on the yield of HTL-products

From Table 4, it was observed that addition of hydrogen-donor alcohols to water during HTL of lignocellulosic biomass had led to higher yields of heavy oil, higher HHV and better degradation of macromolecules to produce high yields of low-boiling point materials. The ratio of water to alcohol was crucial in determining the distribution of HTL-products. Yuan et al. [127] investigated the effect of water and Co-solvent ratio on the yield of heavy oil and hydrochar content using rice straw as biomass, at a reaction temperature of 300°C and retention time of 3 min. Water-ethanol and water-2-propanol ratio mixtures were varied from 0-100 vol% Co-solvent concentration. The group reported that 50:50 v/v ratio of water-ethanol and water-2-propanol produced the highest heavy oil yield of 38.35 wt.% and 39.70 wt.%, and hydrochar content was 19.21 wt.% and 19.66 wt.%, respectively. Liu et al. [150] reported that HTL experiments conducted at different temperatures of 260, 300, and 340°C, and different water-ethanol ratios (0, 50, and 100 vol% ethanol), highest heavy oil yield of 21.11 wt.% was obtained by using 50:50 v/v ratio of water and Co-solvent. Similarly, Zhao et al. [151] obtained highest heavy oil yield of 54.65 wt.% using 50:50 v/v water-methanol mixture, as compared to yields of 24.25 wt.% (only methanol), 40.02 wt.% (20 vol% methanol), 27.79 wt.% (80 vol% methanol), and 29.96 wt.% (only water). Therefore, considering 50:50 v/v water and Co-solvent mixture as the optimum ratio that will produce higher heavy oil yields, it is necessary to understand whether this heavy oil obtained by using this ratio is affected by varying reaction temperature, as will be discussed in section 2.2.3.2.

2.2.3.2 Effect of reaction temperature on HTL-product yield using water-Co-solvent mixture

Cheng et al. [149] performed HTL experiments on pinewood using 50:50 v/v ratio of water-ethanol, with operating temperature range between 200-350°C and a retention time of 15 min. The group reported that heavy oil yield increased from 25 to 66 wt.% and hydrochar reduced from 70 to 5 wt.% on raising the reaction temperature from 200 to 300°C. Above 300°C, hydrochar, gas, and aqueous phase fractions increased, and heavy oil yield decreased, owing to thermal cracking and condensation reactions that are dominant at these temperature regions. With pinewood as biomass, Zhao et al. [151] performed HTL experiments with a reaction temperature range of 240-320°C, retention time of 15 min, with 50:50 v/v ratio of water-methanol mixture. Heavy oil increased from ~ 40.5 to 63.2 wt.%, hydrochar decreased from ~ 46.2 to 12.5 wt.%, and gas increased from ~13 to 24.5 wt.%, when temperature rose from 240 to 280°C. Varying reaction temperature during HTL of rice husk using 50:50 v/v water-ethanol mixtures have been studied by Liu et al. [150], where HTL experiments were conducted on three temperatures (260, 300, and 340°C), with retention time of 20 min. With 50:50 v/v ratio of water-ethanol as liquefying medium, highest heavy oil yield of 21.11 wt.% was obtained at 260°C, with yields of 18.85 wt.% and 10.04 wt.% obtained at 300°C and 340°C, respectively. Although gas and aqueous phase fraction increased from 53.48 to 67.21 wt.% on increasing the temperature from 260 to 340°C, minimum yield of hydrochar of 21.52 wt.% was obtained at 300°C. Pan et al. [155] reported that the heavy oil and hydrochar yield trend had varied drastically on using 50:50 v/v water-ethanol mixture, when reaction temperature was increased from 240 to 320°C, using camphor tree sawdust as biomass feedstock and maintaining a retention time of 30 min. Heavy oil yield increased from 45.58 to 61.38 wt.% on increasing the temperature from 240 to 280°C and then decreased to 27.9 wt.% at 320°C. Hydrochar showed a

similar downward trend that previous researchers have found, where the yield was 37.37 wt.% at 240°C, yield dropped to a minimum of 17.93 wt.% at 280°C, and then rose to 29.89 wt.% at 320°C. On observing the trend from earlier mentioned results, it is evident that a temperature region between 260-300°C provided the highest heavy oil yield and lowest hydrochar yield on using equal ratios of water-Co-solvent mixtures.

2.2.3.3 Effect of retention time on HTL-product yield using water-Co-solvent mixture

Duration of retention time affects the yield of HTL-products, where Zhao et al. [151] conducted HTL experiments using 50:50 v/v ratio of water-methanol at reaction temperature of 300°C, at different retention times ranging from 0-25 min. Highest heavy oil yield of 54.65 wt.%, lowest hydrochar and gas yield of 10.75 wt.% and 34.5 wt.%, respectively, were obtained at 15 min retention time. Similarly, Zhu et al. [152] obtained highest heavy oil yield of 52.40 wt.%, lowest hydrochar and gas yield of 11.80 wt.% and 33.64 wt.%, at 30 min retention time. On observing the results from the previous authors, hydrochar and gas yields were found to dip anywhere between 15-30 min, resulting in slightly higher heavy oil yield.
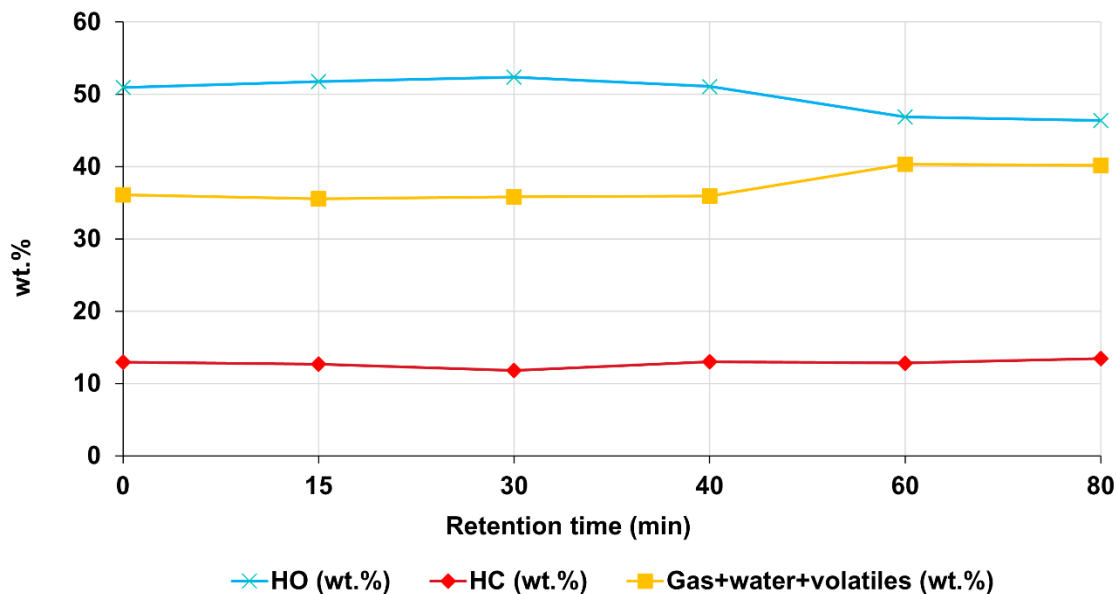
Figure 10: HTL-product yield distribution with varying retention time, with HTL conducted on cornstalk at 300°C, using 50:50 v/v water-methanol mixture, adapted from Zhu et al. [152].

Therefore, for HTL experiments conducted using 50:50 v/v ratio of water and Co-solvent mixture, a temperature range between 260-300°C and retention time range between 15-30 min may favour higher heavy oil yields, lower yields of hydrochar, aqueous phase and gas fractions. However, present HTL experiments will be conducted at same operating conditions as previously conducted by Mathanker et al. [63], where reaction temperature will be set at 300°C, biomass-to-solvent ratio of 1:6, initial reactor pressure of 600 psi and 0 min retention time will be maintained throughout. Similar operating conditions were maintained in order to understand whether these operating conditions are also favourable for HTL experiments using 50:50 v/v water-Co-solvent mixture, in improving the yield and quality of heavy oil.

Chapter 3: Experimental Procedure

3.1 Biomass feed preparation and Chemicals utilized for HTL process

Corn stover, wheat straw, and hardwood were selected as the lignocellulosic biomass feedstocks for present HTL studies. Corn stover and wheat straw were obtained from Northern and Southern farms, and Aspen woodchips were obtained from a wood processing facility in Alberta, Canada [159, 160]. These feedstocks were received at the large-scale fluid laboratory, located at the Department of Mechanical Engineering, University of Alberta, where the particle size was prepared to a range between ~3.2-19.22 mm for both corn stover and wheat straw, and 6-10 mm for Aspen woodchips [149, 150]. The three feedstocks were then ground and sieved to particle size range of 0.425-1 mm for present HTL experiments. Chosen particle size range has been found to be suitable for HTL operation conducted in previous studies [63]. Corn stover (Cellulose: 38.1 wt.%, Hemicellulose: 25.3 wt.%, Lignin: 20.2 wt.%), wheat straw (Cellulose: 37.4 wt.%, Hemicellulose: 35.6 wt.%, Lignin: 20.4 wt.%), and hardwood (Cellulose: 45-55 wt.%, Hemicellulose: 24-40 wt.%, Lignin: 18-25 wt.%), data from table 1 have been assumed as biomass feedstock composition for present HTL experiments. Deionized water was obtained from Millipore Milli-Q® Gradient instrument. Reagent-grade chemicals: Acetone ($\geq$ 99.5% purity), Methanol ($\geq$ 99.8% purity) and 2-Propanol ($\geq$ 99.5% purity) were purchased from Fisher Scientific International Inc., and Ethanol (90.25% purity) was purchased from LabChem Inc.
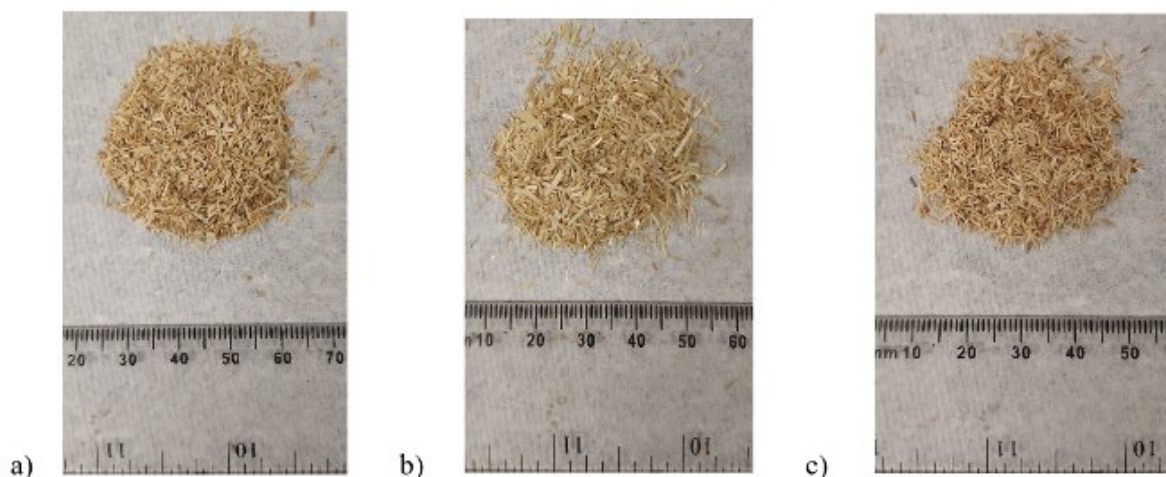
Figure 11: a) Corn stover, b) Wheat straw and c) Hardwood, all with particle size of 0.425-1 mm

3.2 HTL procedure and separation of HTL-products

Hydrothermal liquefaction experiments on agricultural and forest biomass were conducted in a 250 mL, T316-T Stainless Steel (Parr 4843) autoclave bench top reactor, which can operate up to a maximum operating pressure of 5000 psi (345 bar) and operating temperature of 500°C. The bench top reactor was designed to have a magnetic stirrer (4-blade, impeller 1.38" dia.) attached to a stirrer motor. The reactor (moveable vessel) had an inside diameter of 2.5 inches and an inside depth of 3.2 inches. Water flows through a single-loop cooling coil designed inside the reactor. There are 2 split rings, 8 compression bolts, and 2 safety latches, to attach the moveable vessel to the fixed head. Figure 12 depicts the lab-scale reactor arrangement, along with other external instruments that complete the reactor operation.
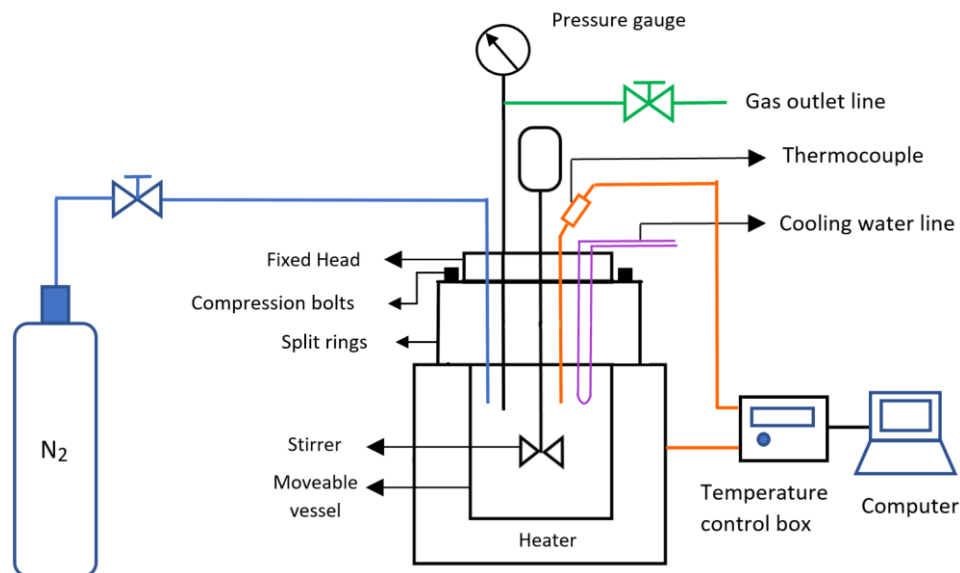
Figure 12: Schematic diagram for bench top reactor arrangement.

In a typical HTL experiment, 5g of corn stover (CS), wheat straw (WS), or hardwood (HW) was weighed and loaded with 30 mL deionized water or water-Co-solvent mixture (50:50 v/v) into the reactor vessel. When HTL was performed using water-Co-solvent mixture, water was considered as the primary solvent and alcohols (Methanol, Ethanol, 2-Propanol) were considered as Co-solvents. The reactor was sealed with gasket (Parr Flexible graphite, 2-1/2" ID) and clamped onto the fixed head, then stirrer was set to 75 RPM to mix solid and liquid parts well before purging the reactor 3 times with 16 bar of N_2 gas, to remove any contaminants stuck on interior surfaces of reactor vessel. Initial pressure inside the reactor was set to 600 psi; however, the final pressure varied between 2200 psi to 2450 psi, depending on liquefying medium used during HTL operation. The reactor was heated to a target temperature of 300°C, with a starting pressure of 600 psi. The reaction was held for 0 min, i.e., cooling water cycle was immediately started once the reactor reached the target temperature. Heating and cooling cycles have been maintained to be similar for all biomass feedstocks utilized for HTL, as depicted in figure 13.
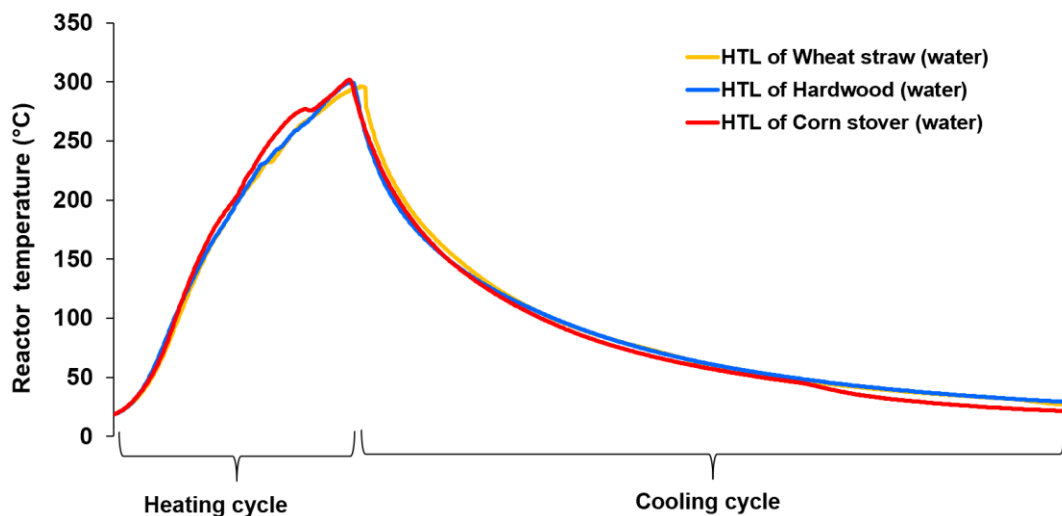
Figure 13: Heating and Cooling cycle for HTL operation of agricultural and forest biomass.

Once the reactor temperature dropped down to room temperature, the reactor was depressurized, and gas product was released. Then, the reactor vessel was opened, and separation techniques such as filtration, rotary evaporation and drying, were conducted on the slurry mixture to recover mainly Aqueous phase (AP1, AP2), Heavy oil (HO) and Hydrochar (HC). Primary filtration step separated the slurry mixture into aqueous phase and water-insoluble phase for HTL-water experiments, and acetone-soluble phase and acetone-insoluble phase for HTL-water-Co-solvent experiments. Filtration was conducted using Whatman No. 2 filter papers (70 mm Ø), Büchner funnel and suction flask. For HTL conducted with only water, Aqueous oil (AO) and Water-soluble hydrocarbons (WSH) were recovered through rotary evaporation of AP1 fraction. Since aqueous phase fraction contain mainly oxygenated compounds, have high acid content and low HHV, AO and WSH from AP1 were not analyzed in the present study. Acetone was selected as an extraction solvent for vacuum filtration for recovering heavy oil obtained from both HTL-water and HTL-water-Co-solvent process. The solvent was rinsed down the walls of reactor,

surfaces of stirrer blades and cooling coil, to recover maximum amount of the water-insoluble phase or slurry mixture for both HTL procedures. On filtering the acetone-washed water-insoluble phase, two fractions were obtained: acetone-soluble phase and acetone-insoluble phase. The acetone-insoluble phase was collected on the filter paper and then placed inside an oven for drying overnight at 105°C. The product obtained after drying operation was termed as Hydrochar. Rotary evaporation was conducted on acetone-soluble phase, to remove acetone (at 50°C under reduced pressure), to recover dark, viscous Heavy oil. For HTL conducted with water and Co-solvent mixtures, the entire slurry mixture is filtered using acetone, to separate acetone-soluble and acetone-insoluble phase. Hydrochar is recovered in the similar manner as mentioned earlier, however, for rotary evaporation conducted on acetone-soluble phase, acetone and AP2 were removed under reduced pressure (at 50°C and 90°C respectively) to produce dark, relatively less-viscous Heavy oil. All filtrations were conducted under vacuum conditions. Water recovery from aqueous phase caused difficulty because of similar boiling point materials present in aqueous phase, and thus separation of water was not conducted on either AP1 or AP2. HTL utilizing water and Co-solvent mixtures was conducted only on corn stover and wheat straw. HTL experiments using only water have been conducted on all the three biomass. Figure 13 and 14 depicts the separation procedure utilized for all HTL experiments as mentioned earlier.
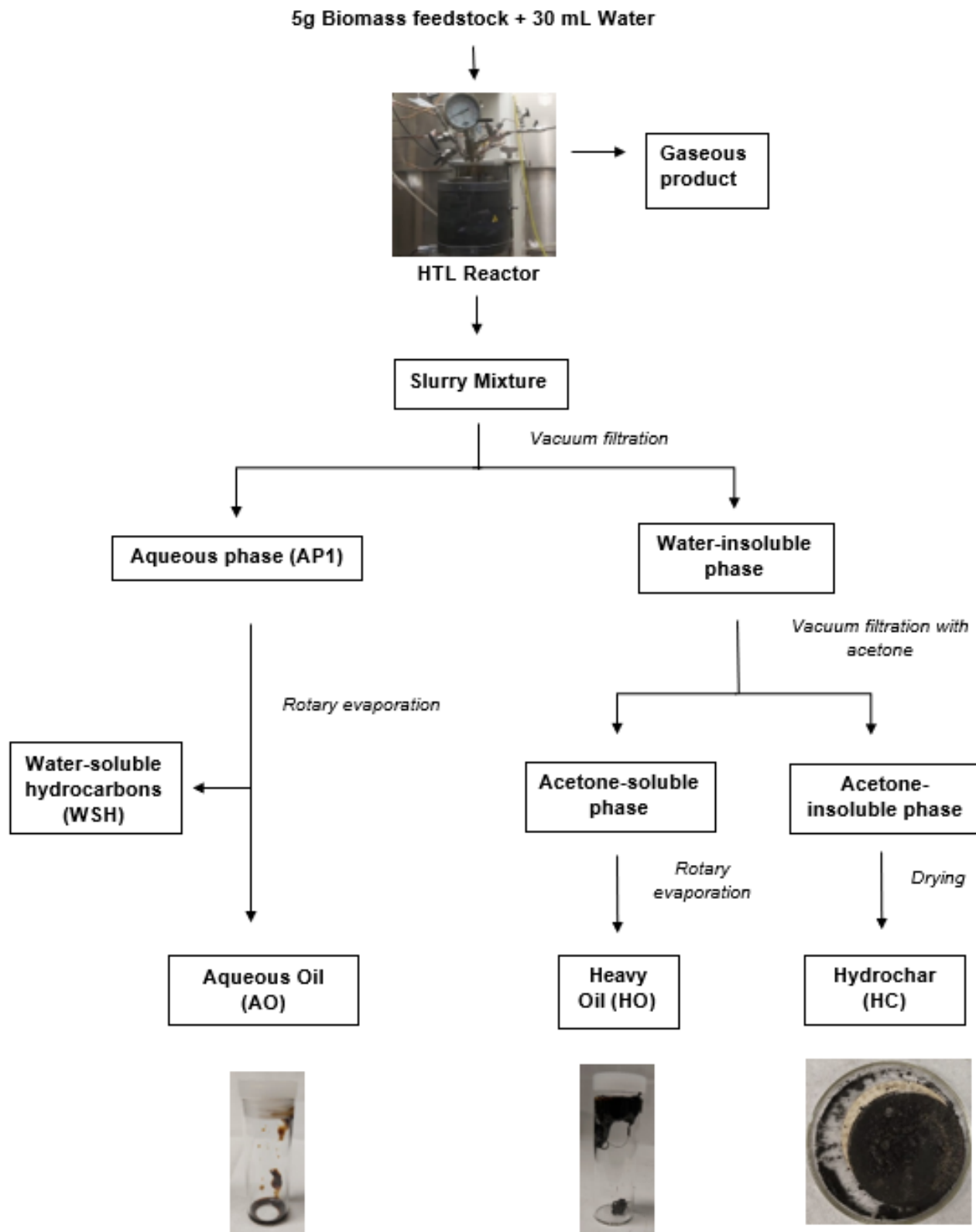
Figure 14 : Separation procedure conducted for HTL experiments using water as sole solvent.
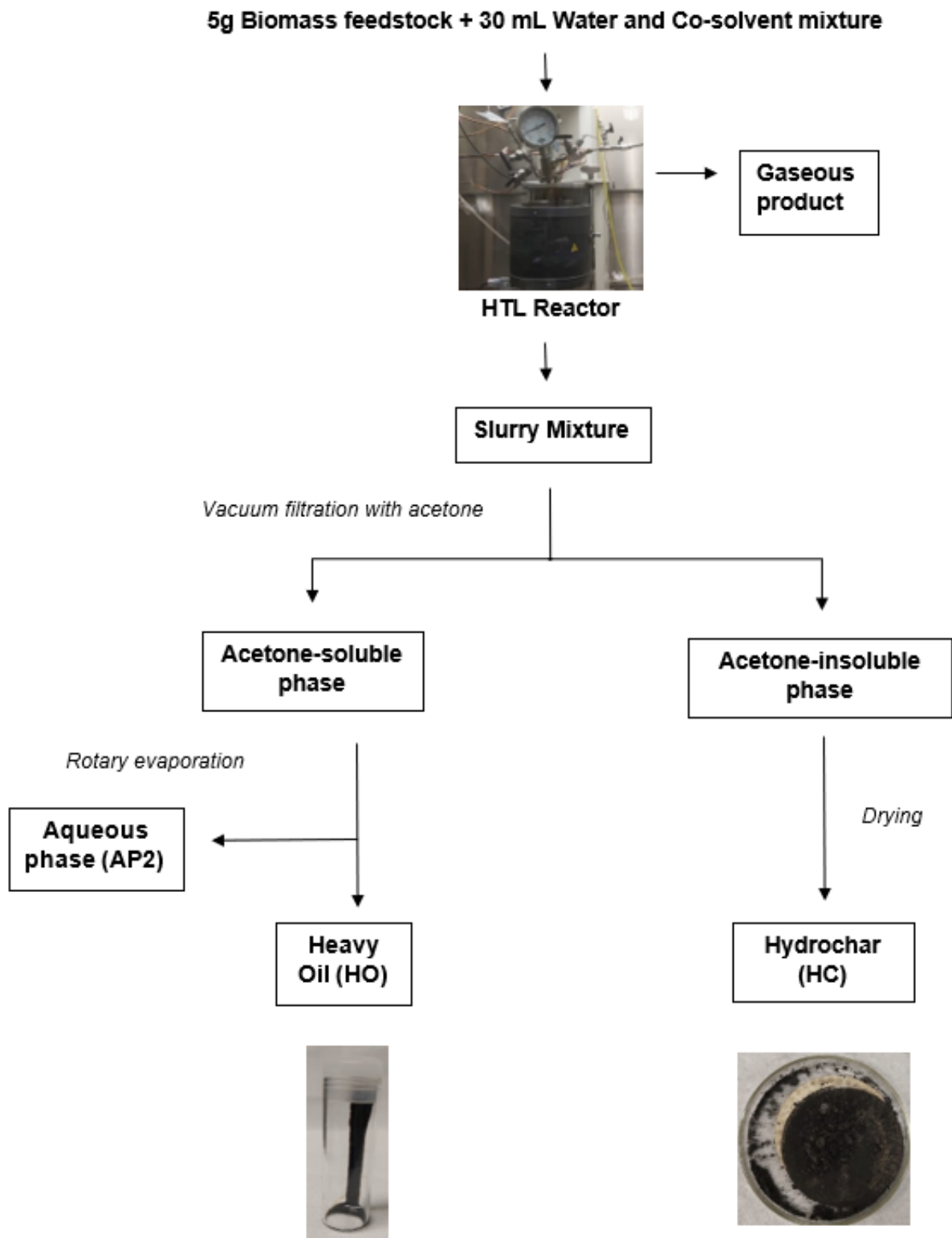
Figure 15: Separation procedure conducted for HTL experiments using water and Co-solvent mixture.

3.3 Characterization of biomass feedstock and products obtained from HTL process

3.3.1 Proximate analysis

Corn stover, wheat straw and hardwood feedstock were studied in LECO TGA 701, for their moisture content, volatile matter, ash content and fixed carbon content, using ASTM D7582 method. Feedstock samples were weighed to approximately 1g, collected in ceramic crucibles and placed inside the crucible holder slots of the instrument for analysis. Using N_2 as carrier gas, moisture content analysis was conducted by heating each sample from 25 to 107°C at a heating rate of 6°C/min with hold time of 15 min, followed by heating the samples from 107 to 950°C at a heating rate of 50°C/min with hold time of 7 min to determine the volatile matter and fixed carbon content. Analysis of ash content was conducted in O_2 environment, where temperature was lowered to 600°C and then heated to 750°C at a heating rate of 6°C/min.

Figure 16: LECO TGA 701 used for Proximate analysis of Corn stover, Wheat straw and Hardwood.

3.3.2 Elemental composition

Elemental composition (CHNS) of the biomass feedstocks, heavy oil and hydrochar were performed on Thermo Fisher Flash 2000 Organic Elemental Analyzer (Department of Chemistry, University of Alberta). Sample was placed in tin cup and dropped into a vertical quartz tube (combustion chamber maintained at 1000°C) with Helium gas used in the environment. Once sample entered the combustion chamber, a fixed volume of oxygen was added to the Helium gas, which burnt the sample and the tin container. C, H, N and S of sample was detected in CO_2, H_2O, NO_x and SO_2, respectively. These gases were then detected in a thermal-conductivity detector, which was analyzed by Eager Xperience software and generated the area count data showing the percentage of C, H, N and S present in the sample.

Figure 17: Thermo Fisher Flash 2000 Organic Elemental Analyzer used for CHNS analysis.

3.3.3 Chemical composition

Chemical composition of heavy oil was determined using Gas Chromatography – Mass Spectrometer (GC-MS) obtained from Agilent technologies (7890 GC system – 5975C VL MSD). The GC-MS instrument used for analysis was present in the Mass Spectrometry lab located at the Department of Chemistry, University of Alberta. This instrument is equipped with a HP-5ms capillary column (5% phenyl-methylpolysiloxane phase) with dimensions of 30 m × 0.25 mm ×0.25 μm. Before the heavy oil sample was injected into the GC-MS, a small amount of the heavy oil was dissolved in dicholoromethane (DCM), filtered using 0.2 μm PTFE filter, then separated top heavy oil layer from water using microcentrifuge. After sample preparation, 1μL of this heavy oil sample was injected into GC with a split ratio of 50:1 and Helium as the carrier gas. The column temperature of GC was programmed to start at 40°C with a hold time of 3 min, raising the temperature to 180°C and held for 1 min, then heating proceeded to 280°C with a hold time of 5 min and ultimately reaching a final temperature of 290°C and held at 1.4 min. The temperature of the transfer line between the GC and MS system was maintained at 280°C. Highly probable compounds were identified by comparing mass spectra obtained from NIST library (MS search 2.3).

Figure 18: Agilent Technologies (GC 7890A – MS 5975C) used for GC-MS analysis of Heavy oil.

3.3.4 Boiling point distribution

Distribution of various boiling point organic compounds present in heavy oil, was determined by using Thermogravimetric Analyzer (TGA), which was performed on SDT Q 600 (TA Instruments). Approximately, 2.6 mg to 5.6 mg of heavy oil was weighed into an alumina cup (90 µL) and was placed in the cup holder of the TGA. Using N_2 as the carrier gas, the furnace temperature was heated from 25°C to 900°C, at a heating rate of 10°C/min and flow rate of the carrier gas was set to 50 mL/min. Once furnace temperature reached 900°C, the carrier gas was changed to O_2, with a flow rate of 50 mL/min, and the temperature was held for 10 min to combust any remaining heavy oil sample present in the cup.
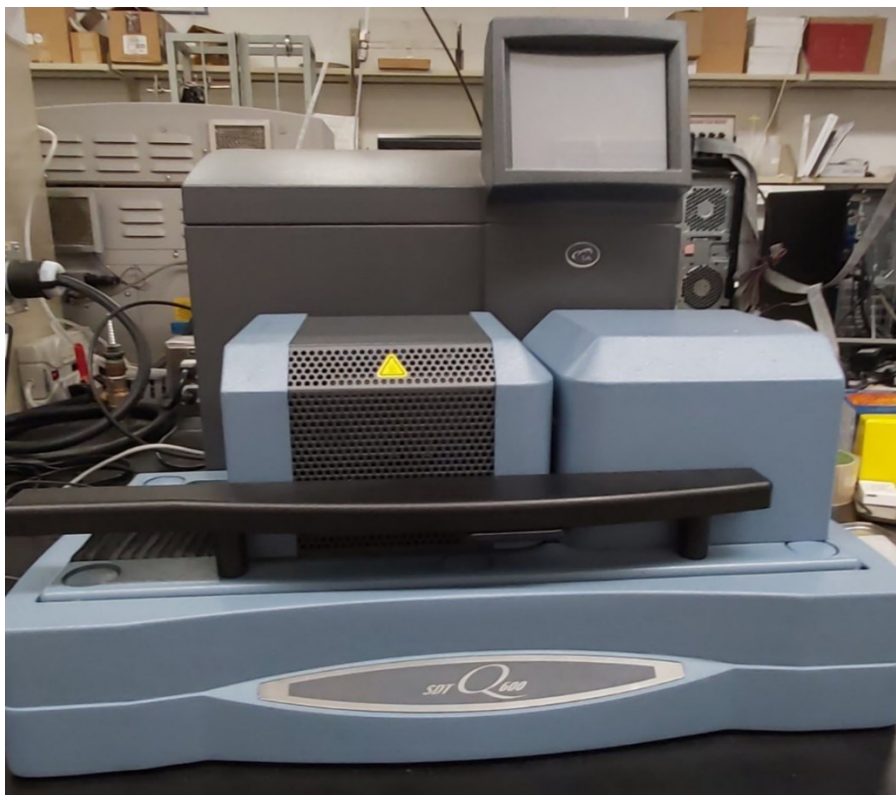
Figure 19: SDT Q 600 (TA Instruments) used to perform TGA analysis on Heavy oil.

3.3.5 Total Acid Number (TAN) analysis

The presence of acidic constituents in heavy oil was determined by measuring the Total Acid Number (TAN) value, which detects the amount of potassium hydroxide (mg) required to neutralize unit gram of the sample oil analyzed. TAN analysis was conducted using Mettler Toledo T50 apparatus and ASTM D664 method was applied for analysis. Approximately between 35-160 mg of heavy oil was weighed, dissolved in 60 mL of titration solvent (mixture of deionized water, isopropyl alcohol, and toluene) and then titrated with 0.1 M KOH solution. Commercial buffer solutions of pH 4, 7 and 11 were used as pH indicators for this analysis.

3.3.6 Surface morphology study

SEM analysis of Hydrochar was conducted using Zeiss Sigma 300 VP-FESEM, present at the Department of Earth and Atmospheric Sciences, University of Alberta. Biomass samples were gold-coated to improve quality of imaging, however hydrochar samples were not coated and a little amount of sample was place under the microscope directly for imaging. All SEM imaging were conducted at an accelerating voltage of 15 kV.
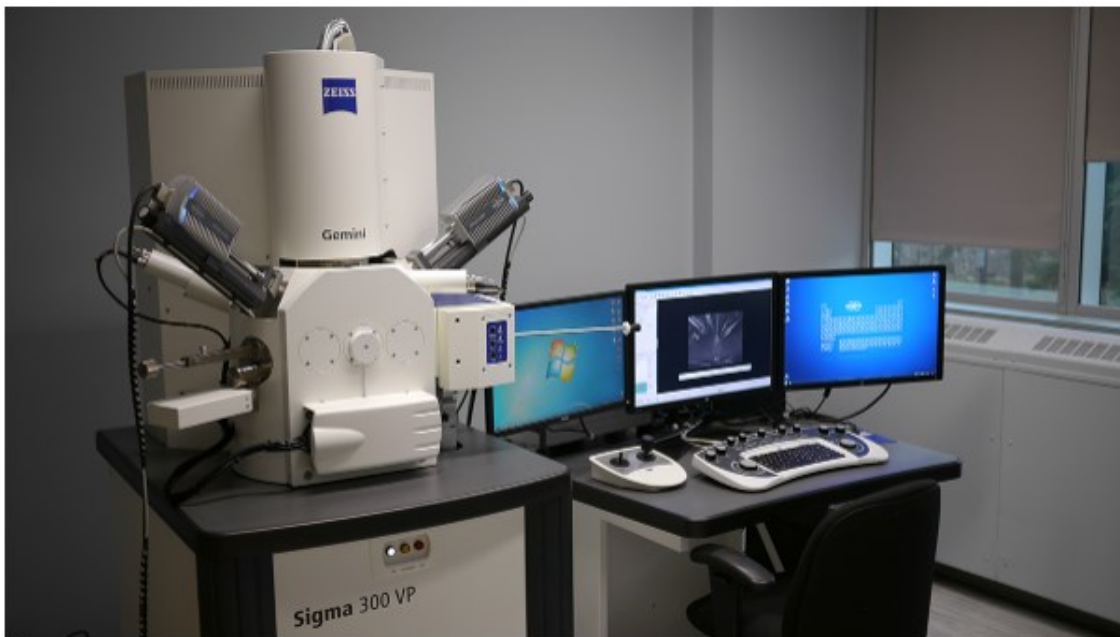
Figure 20: Zeiss Sigma 300 VP-FESEM used to perform SEM analysis on biomass and hydrochar.

Chapter 4: Results and Discussion

4.1 Effect of using varying biomass feedstocks on yield of heavy oil from HTL experiments

On observing the results from Table 5, agricultural feedstocks, corn stover and wheat straw have similar compositional matrix and energy content. Oxygen content is calculated as difference from CHNS composition (S content is assumed to be negligible) and HHV is calculated using Dulong formula. Hardwood used for the present experiments shows the highest innate HHV with the lowest ash content. Yield of HTL-products have been calculated as follows:

$$HO \text{ (wt.\%)} = \frac{W_{HO}}{W_B} \times 100$$

$$AO \text{ (wt.\%)} = \frac{W_{AO}}{W_B} \times 100$$

$$HC \text{ (wt.\%)} = \frac{W_{HC}}{W_B} \times 100$$

$$Gas \text{ (wt.\%)} = \frac{W_f - W_r}{W_f} \times 100$$

$$Conversion \text{ (wt.\%)} = \frac{W_B - W_{HC}}{W_B} \times 100$$

WSH (wt.%) = 100 − [HO (wt.%) + AO (wt.%) + HC (wt.%) + Gas (wt.%)]

AP2 (wt.%) = 100 − [HO (wt.%) + HC (wt.%) + Gas (wt.%)]

where, W_B is the weight of the biomass feedstock used for HTL experiment, W_f is the weight of biomass feedstock and deionized water loaded into reactor, W_r is the weight of recovered fraction obtained after HTL, W_{HO}, W_{AO}, W_{HC}, are the weight of heavy oil, aqueous oil, and hydrochar, respectively. AP2 refers to the aqueous phase fraction obtained from HTL experiments that have used 50:50 v/v water-Co-solvent mixtures as the liquefying medium.

Table 5: Proximate analysis and Elemental distribution of biomass feedstocks.

	Moisture content	Volatile matter	Ash content	Fixed carbon	C (wt.%)	H (wt.%)	N (wt.%)	O[1] (wt.%)	H/C	O/C	N/C	HHV[2] (MJ/kg)
Corn stover	6.07	72.42	5.80	15.71	42.73	5.46	1.03	50.78	1.53	0.89	0.021	13.17
Wheat straw	5.87	71.39	5.78	16.96	42.81	5.47	0.51	51.21	1.53	0.90	0.010	13.14
Hardwood	5.60	80.60	0.49	13.31	46.34	5.88	0.15	47.63	1.52	0.77	0.003	15.56

[1]O content (wt. %) $= 100 - [\, C\ (wt.\%) + H\ (wt.\%) + N\ (wt.\%) + S\ (wt.\%)\,]$

[2]HHV (MJ/kg) $= (0.338 \times C) + 1.428 \times \left(H - \frac{O}{8}\right) + (0.095 \times S)$

Table 6: Product yield distribution for HTL experiments conducted using only water.

Biomass for HTL	HC wt.%	HO wt.%	AO (wt.%)	WSH (wt.%)	Gas (wt.%)	Conversion (wt.%)
Corn stover	12.8	36.0	21.4	19.4	10.4	87.20
Wheat straw	14.2	41.2	16.4	21.5	6.7	85.80
Hardwood	14.6	42.0	16.6	17.2	9.6	85.40

Figure 21 depicts the varying yields of heavy oil obtained by using agricultural and forest

biomass as feedstock for HTL process. Using water as sole solvent, heavy oil obtained from

hardwood (bar HTL-HW-W) shows the highest yield of 42.0 wt.%, followed by using wheat

straw (bar HTL-WS-W) with 41.2 wt.% and lastly by using corn stover (bar HTL-CS-W) with a

yield of 36.0 wt.%. Typical composition of hardwood from Table 1 suggests that the cellulose

and hemicellulose content is much higher than that of wheat straw and corn stover, which may

lead to an increase in heavy oil yield. Lignin composition, referring to Table 1, was the highest in

hardwood, followed by wheat straw and then corn stover, resulting in higher yields of hydrochar.

Similar observations were reported by Tian et al. [102]. With temperature as one of the major

parameters for HTL biomass conversion reactions, assuming hemicellulose and cellulose

completely decomposes at temperatures lesser than 300°C, it is possible that intermediates from

these two components have been converted to middle- and slightly higher-boiling point materials

that are present in liquid products. With temperatures much closer to 300°C, free-radical

reactions seem to be more favourable than ionic reactions, leading to more unstable

intermediates, possibly produced by continuing lignin decomposition, which then repolymerize

and condense to form solid residue or hydrochar. Therefore, both hardwood and wheat straw that

show slightly higher lignin content than corn stover, may have more unstable intermediates that

repolymerize and condense to form hydrochar, yield slightly higher than that obtained from corn

stover. Also, biomass containing high ash content can cause damage to the equipment. Among

the three feedstocks used for present HTL studies, typically hardwood shows the highest

cellulose and hemicellulose content, and current proximate analysis shows that it contains the

lowest ash content, which can lead to easier production of heavy oil, without causing fouling to

the equipment. As observed from figure 21, the heavy oil yield obtained from agricultural

feedstocks are visibly lesser than that obtained from forest biomass; therefore, subsequent HTL studies on improving their yield is conducted using water and Co-solvent mixtures, to understand the significance of Co-solvent participation on heavy oil yield at similar operating conditions.
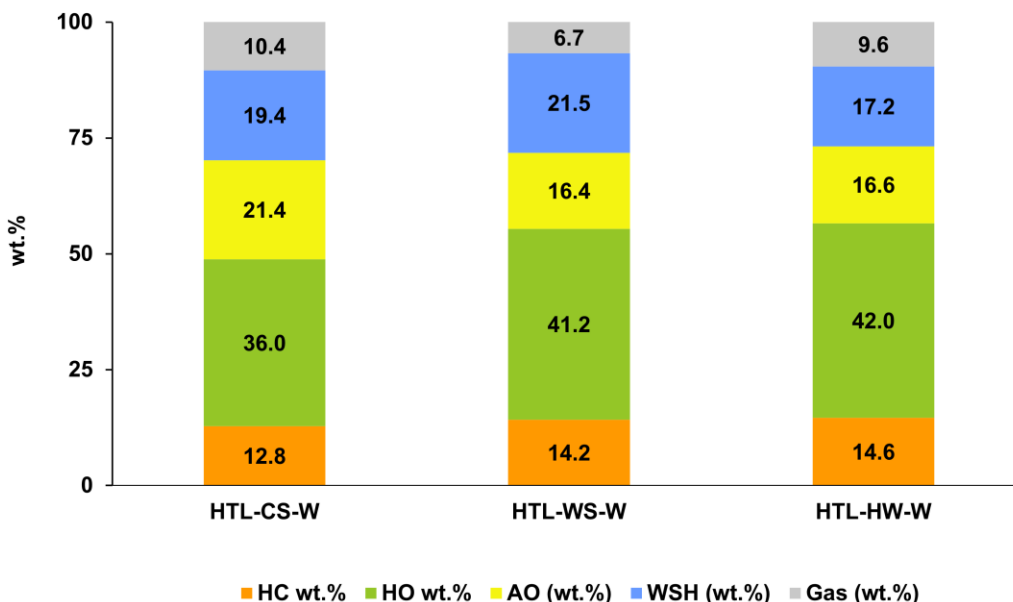
Figure 21: HTL-product yield distribution as a function of varying biomass feedstock, using water as sole solvent.

4.2 Effect of addition of Co-solvent on yield of heavy oil using water-Co-solvent mixture

As verified by various researchers that equal ratio of water and alcohol is optimum for effective liquefaction of various lignocellulosic biomass, following results presented in this section have been obtained from HTL experiments conducted on the two agricultural feedstocks, using 50:50 (v/v) water-methanol, water-ethanol, and water-2-propanol mixture as liquefying medium. Referring to figure 22, highest heavy oil yield of 42.0 wt.% is obtained from HTL experiment performed on corn stover using 50:50 (v/v) water-methanol mixture. A trend that is consistently observed is that heavy oil obtained from corn stover with HTL conducted using water-Co-solvent

mixtures is higher compared to when wheat straw is the feedstock. Another consistent result is the increase in hydrochar content on using water-ethanol mixture, with similar result obtained by Yuan et al. [127]. Conversion of biomass seems to reduce on using water-Co-solvent mixtures, where similar observation was made by Singh et al. [161]. Yield of aqueous phase obtained from HTL-water experiments is much higher than the yield of aqueous phase fraction obtained when water-Co-solvent mixture is used. Improvement of heavy oil yield is similar to results obtained by other researchers, where water-methanol (for both wheat straw and corn stover) and water-2-propanol (only for corn stover) provided higher yields of heavy oil as compared to using only water as sole solvent. Co-solvents here primarily degrade lignin and dissolve high-molecular weight compounds in it for further conversion, whereas cellulose and hemicellulose decomposition are carried out in water. Co-solvents being hydrogen-donor solvents promote esterification, alkylation, hydroxyalkylation, and deoxygenation reactions, converting large macromolecules of biomass to mainly low- and middle-boiling point materials, as will be observed in the TGA curves in section 4.3.3. However, heavy oil obtained from water-ethanol is much lower than that obtained from HTL-water experiments. Similar trend in heavy oil yield was observed by Yuan et al. [127]. This may indicate that biomass composition has a vital role to play that can dictate the interaction between the polymers of biomass with water and Co-solvent, resulting in different yield of products. While present in small quantities in biomass, it is possible that the extractive component of biomass may also alter the yield of products entirely, which requires further studies. It is also possible that a longer retention time (15-30 min) can slightly improve the yield of heavy oil, as suggested in section 2.2.3.3. Although water-methanol mixture has provided higher yields of heavy oil, harmful phenolic raisins are said to be produced from methanol, as reported by Chen et al. [162]. On comparing the yields of heavy oil produced from the three water-Co-solvent mixtures,

water-2-propanol mixture can be considered a better liquefying medium as it also provides an improved quality of heavy oil, as will be discussed in subsequent sections.

Table 7: Product yield distribution for HTL experiments conducted using water and Co-solvent mixture.

Biomass for HTL	Co-solvent	HC wt.%	HO wt.%	AP2 (wt.%)	Gas (wt.%)	Conversion (wt.%)
Corn stover	Methanol	17.8	42.0	29.8	10.4	82.2
	Ethanol	21.8	35.0	32.1	11.1	78.2
	2-Propanol	18.4	41.6	29.6	10.4	81.6
Wheat straw	Methanol	23.6	38.2	28.4	9.8	76.4
	Ethanol	26.0	25.6	39.0	9.4	74.0
	2-Propanol	24.0	34.4	32.2	9.4	76.0
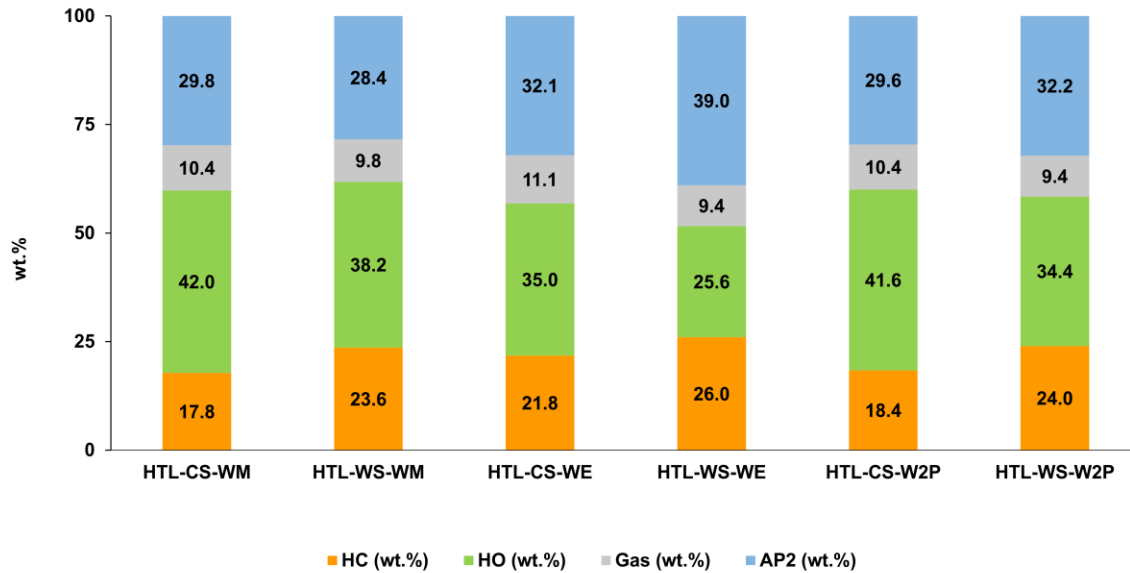
Figure 22: HTL-product yield distribution as a function of varying Co-solvents with water.

4.3 Qualitative analysis of heavy oil and hydrochar products from HTL experiments

4.3.1 Analysis of elemental composition of heavy oil and hydrochar products

By comparing elemental composition results from Table 5 and 8, C-, H-, and N- content have increased for heavy oils as compared to the C-, H-, and N-content of all three biomass. O-content of heavy oils have decreased drastically as compared to the O-Content present in higher amounts in the biomass feedstocks. With HHV directly related to C- and H-content, and inversely related to O-content [163], heavy oil HO-WS-W2P shows high C-content of 72.12 wt.% and H-content of 8.19 wt.%, low O-content of 17.99 wt.%, leading to higher HHV of 32.86 MJ/kg. When corn stover is the feedstock, heavy oil obtained showed a C-content of 70.84 wt.%, H-content of 7.99 wt.%, O-content of 18.8 wt.% and HHV of 32.0 MJ/kg. O-content of hydrochars have increased and that of heavy oil have decreased for HTL experiments using water-Co-solvent mixtures. Decrease of O/C ratios in heavy oils obtained from using water-Co-solvent mixture shows that alcoholic solvents have improved deoxygenation of biomass polymers producing more water-soluble oxygenated compounds that shift towards the aqueous phase. H/C ratio of heavy oil ranges between 1.18-1.39 for HTL experiments conducted using water and between 1.35-1.50 for HTL experiments using water-Co-solvent mixture. H/C ratio of commercial diesel is 1.81 [164], requiring further upgrading of heavy oil obtained from HTL using water-Co-solvent mixture. Comparing the HHV from table 9, most of the hydrochars generated from all experiments are slightly higher than peat (HHV is 23.69 MJ/kg) [165].

Table 8: Elemental distribution, atomic ratio, and energy content of heavy oils derived from HTL experiments using only water and water-Co-solvent mixture.

Heavy oil samples	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	H/C	O/C	N/C	HHV (MJ/kg)
HO-CS-W	65.4	7.59	1.37	25.5	1.39	0.29	0.018	28.41
HO-WS-W	66.97	6.8	0.9	25.33	1.22	0.28	0.012	27.82
HO-HW-W	66.67	6.54	0.17	26.63	1.18	0.3	0.002	27.12
HO-CS-WM	70.2	8.0	2.59	19.21	1.37	0.21	0.032	31.72
HO-WS-WM	66.57	7.81	1.84	23.79	1.41	0.27	0.024	29.4
HO-CS-WE	70.02	8.05	2.26	19.67	1.38	0.21	0.028	31.65
HO-WS-WE	66.59	8.32	2.02	23.06	1.5	0.26	0.026	30.28
HO-CS-W2P	70.84	7.99	2.37	18.8	1.35	0.2	0.029	32.0
HO-WS-W2P	72.12	8.19	1.7	17.99	1.36	0.19	0.02	32.86

Table 9: Elemental distribution, atomic ratio, and energy content of hydrochar derived from HTL experiments using only water and water-Co-solvent mixture.

Hydrochar samples	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	H/C	O/C	N/C	HHV (MJ/kg)
HC-CS-W	60.71	4.28	2.05	32.96	0.85	0.41	0.029	20.75
HC-WS-W	67.25	4.38	1.39	26.97	0.78	0.3	0.018	24.18
HC-HW-W	73.02	4.66	0.26	22.07	0.77	0.23	0.003	27.39
HC-CS-WM	69.3	4.35	2.21	24.14	0.75	0.26	0.027	25.32
HC-WS-WM	66.58	4.15	1.67	27.6	0.75	0.31	0.021	23.5
HC-CS-WE	67.72	4.22	2.14	25.92	0.75	0.29	0.027	24.28
HC-WS-WE	69.01	4.12	1.89	24.97	0.72	0.27	0.024	24.76
HC-CS-W2P	69.58	4.36	2.36	23.7	0.75	0.26	0.029	25.52
HC-WS-W2P	70.96	4.16	1.84	23.04	0.70	0.24	0.022	25.81

4.3.2 Analysis of chemical composition of heavy oil samples

All compounds listed in Table 10 and 11 have an area % greater than 1, with rest of compounds present in small concentrations in heavy oil samples. Full list of compounds is available in Appendix A. Major compounds identified in heavy oil produced from HTL-water experiments are carboxylic acids, aldehydes, alkanes, amides, ethers, ketones, phenols, amines, and aromatics. Formation of carboxylic acid is caused by the decomposition reactions of

extractives, followed by retro-aldol condensation reactions on intermediates formed from decomposition of cellulose and hemicellulose component of biomass [72, 109]. Formation of aldehydes and ketones mainly takes place by retro-aldol condensation of glyceraldehyde and other intermediates obtained during decomposition of cellulose and hemicellulose [166]. Phenolic compounds derived from lignin decomposition, are much higher in heavy oils obtained from HTL-water experiments than that the heavy oils obtained by using water and Co-solvent mixture. This means that HTL using only water as solvents can produce bio-phenolic raisins from its heavy oil. However, the presence of oxygenated compounds such as phenols, alcohols, carboxylic acids, ketones, aldehydes, ethers, in high amount can lead to an increase in oxygen content of heavy oil derived from HTL-water experiments, that would require further upgrading to produce fuel similar to diesel.

Table 10: Chemical composition of heavy oil samples obtained from HTL performed on the three biomass using only water.

Compound class	Area % (HO-CS-W)	Area % (HO-WS-W)	Area % (HO-HW-W)
Acids	3.88	3.03	3.96
Alcohols	-	-	-
Aldehydes	1.23	1.57	8.80
Alkanes	-	-	1.16
Amides	3.95	3.94	3.32
Ethers	1.04	1.96	2.34
Ketones	8.05	10.64	6.33
Phenols	44.92	40.98	39.04
Esters	-	-	-
Amines	-	-	1.31
Aromatics	-	-	1.91
Others	-	1.34	2.62
Total	63.07	63.47	70.78

Major compound classes detected in heavy oils derived from HTL experiments conducted using water-Co-solvent mixtures are mostly alcohols, amides, ketones, phenols, esters, amines, and aromatics. Presence of N-containing compounds such as amides and amines have increased, leading to increase in nitrogen content of heavy oils. The proteins in extractives are degraded into amino acids, following which deamination of amino acids produces ammonia and decarboxylation of amino acids produces organic acids and amines [57]. Since organic acids have not been detected in these heavy oils, it is possible that these are mostly present in the aqueous phase, thereby reducing the acid content of heavy oil. Amide compounds are also formed from amino acids, as by-products, through condensation and cyclization reactions [167]. Presence of ketones, aldehydes and organic acids can undergo esterification and acetalization over time with storage of heavy oil, forming large amounts of water as by-product leading to instability issues of heavy oil. With reduced content of ketones, aldehydes and organic acids, heavy oil obtained from water-Co-solvent mixtures can improve the stability of the heavy oil. Ester content of heavy oil has increased significantly on using Co-solvents, where esterification reactions are highly favoured in the presence of alcoholic Co-solvents. Ester content from heavy oil obtained from HTL of wheat straw conducted in water-ethanol mixture is the highest (54.19 %), followed by that obtained from water-2-propanol mixture (29.14 %). Although water-ethanol mixture shows higher ester content and varied distribution of compounds that can improve the stability of heavy oil, the yield of heavy oil is shown to be compromised. Oxygenated compounds (i.e., sum of alcohols, phenols, carboxylic acids, ketones, aldehydes, and ethers) are highest in HO-CS-W2P with 23.15%, as compared to HO-WS-W2P having 18.21% oxygenated compounds. This is in agreement with the CHNS data from table 8, where O-content of HO-CS-W2P is 18.8 wt.% and that of HO-WS-W2P is 17.99 wt.%.

Considering major N-containing compounds to be amides and amines, N-compounds of HO-CS-W2P is 4.31 % and that of HO-WS-W2P is 3.15 %. Presence of amides and amines increases the nitrogen content of heavy oil, and total amide and amine content of HO-WS-WM is 5.89 %, that of HO-WS-WE is 4.14 % and of HO-WS-W2P is 3.15 %. It is preferable to have more fractions of nitrogenous compounds in aqueous phase than in heavy oil, since nitrogenous compounds are resistant towards upgrading process (i.e., cause catalyst deactivation) required to produce fuel that has diesel-like properties. Therefore, with concerns related to quality of heavy oil affected by ketones, acids, aldehydes, N-containing compounds, water-2-propanol can be an ideal water-Co-solvent mixture that can produce heavy oil with better quality and relatively higher ester content.

Table 11: Chemical composition of heavy oil samples obtained from HTL performed on wheat straw using water and Co-solvent mixture.

Compound class	Area % (HO-WS-WM)	Area % (HO-WS-WE)	Area % (HO-WS-W2P)	Area % (HO-CS-W2P)
Acids	-	-	-	-
Alcohols	1.48	1.63	1.18	-
Aldehydes	-	-	-	-
Alkanes	-	-	-	4.94
Amides	3.22	2.92	1.21	-
Ethers	-	-	-	1.48
Ketones	3.03	1.07	3.33	2.22
Phenols	30.84	6.04	13.70	19.45
Esters	10.54	54.19	29.14	24.86
Amines	2.67	1.22	1.94	4.31
Aromatics	3.83	1.67	3.21	2.81
Others	1.04	3.46	-	2.37
Total	56.65	72.20	53.72	62.44

4.3.3 Analysis of boiling point distribution of compounds present in heavy oil samples

TGA curves have been plotted, as shown in figure 23, for heavy oils obtained from HTL-water experiments using all three biomass feedstocks, and those obtained from agricultural feedstocks using water-2-propanol mixture. Heavy oil obtained from HTL-water experiments shows boiling point curve resembling that of heavy Iraqi crude oil [111], and that obtained from HTL using water-Co-solvent mixture shows boiling point curve resembling that of diesel [111]. Referring to table 12, middle-distillates that include light and heavy vacuum gas oil (VGO) present in heavy oils are as follows: 35.69 % in HO-CS-W, 38.56 % in HO-WS-W, 36.83 % in HO-HW-W, 33.16 % in HO-CS-W2P, and 22.56 % in HO-WS-W2P. This indicates that higher amounts of middle-distillates are found in heavy oil obtained from HTL-water experiments than those obtained from using water-Co-solvent mixture. Heavy oil obtained using water-Co-solvent mixture have distillates resembling gasoline- and kerosene-like fractions. A few of high-boiling point materials present in heavy oil obtained using water mentioned with their boiling point are n-Hexadecanoic acid (347°C), 9-Octadecenamide, (Z)- (430°C), abietic acid (440°C); boiling point temperatures have been referred from NIST Chemistry WebBook SRD 69. Therefore, addition of Co-solvent to water provides an initial upgrading step during HTL, producing fuel similar to gasoline and kerosene.

Table 12: Percentage of various fractions found in heavy oil that resemble the different distillate fractions in crude oil.

Boiling point fractions	% in HO-CS-W	% in HO-WS-W	% in HO-HW-W	% in HO-CS-W2P	% in HO-WS-W2P
Light naphtha (gasoline) (25-149°C)	18.3	11.21	13.29	18.33	20.66
Medium naphtha (kerosene) (149-232°C)	11.29	14.17	10.86	35.4	35.61
Gas oil and Light VGO (232-371°C)	18.58	20.52	20.94	18.84	12.45
Heavy VGO (371-566°C)	17.11	18.04	15.89	14.32	10.11
Residue (>566°C)	34.72	36.06	39.02	13.11	21.17
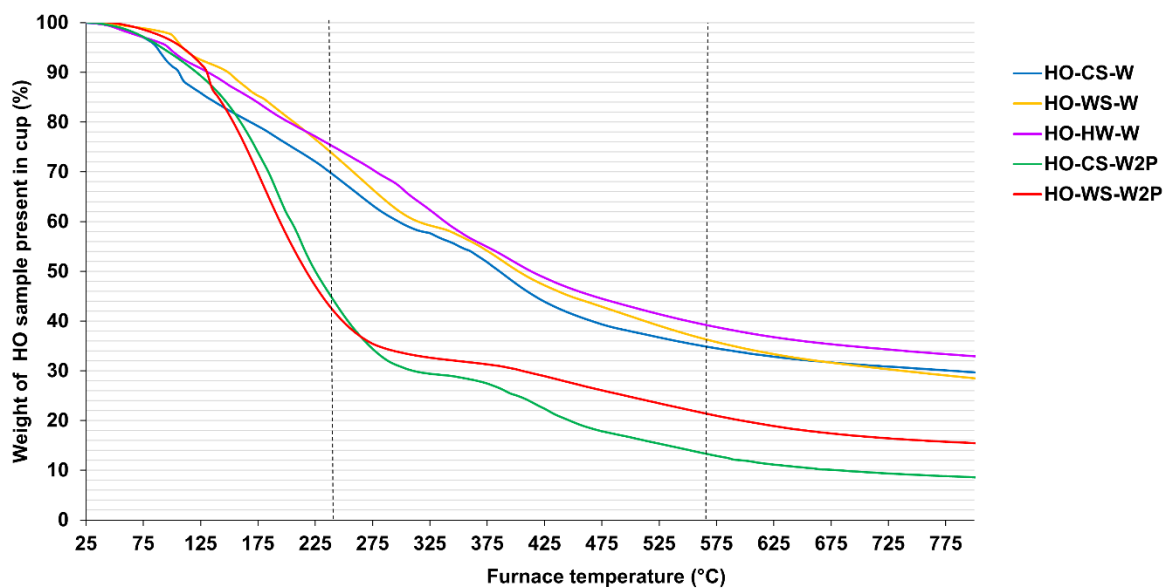
Figure 23: Boiling point distribution of compounds present in heavy oil samples.

4.3.4 Analysis of acid content present in heavy oil samples

From Table 13, heavy oil derived from using hardwood as feedstock for HTL-water experiment (HO-HW-W) shows the highest TAN value as compared to HO-CS-W and HO-WS-W, with similar result observed in table 10. Higher TAN values are associated with higher content of carboxylic acids, generally produced by the decomposition of extractives (amino acid formation), cellulose, hemicellulose, and lignin degradation, mentioned by the reaction pathways depicted in figure 8. Therefore, it is expected that heavy oil obtained from hardwood, that is having comparatively higher cellulose, hemicellulose, and lignin content, should be more acidic as compared to those obtained from corn stover and wheat straw. On observing the GC-MS results given in table 10 and 11, acid content is prevalent in HO-CS-W than that in HO-CS-W2P, with considerably lower acid content detected in HO-CS-W2P. These results match with the TAN results presented in Table 13. Biomass with higher oxygen content, and with water as liquefying medium resulted in producing more oxygenated hydrocarbons, and it is highly possible that excess

carboxylic acid may have transferred to the heavy oil. Lowered TAN results from heavy oil obtained from using water-Co-solvent mixture, proves that addition of Co-solvent has significantly reduced acid content. However, these TAN values are nowhere close to the TAN of diesel which is 1.70 mg KOH/g oil [113], thus suggesting the need for upgrading of present heavy oils.

Table 13: TAN results of heavy oil samples obtained from HTL using only water and that by using water-Co-solvent mixture.

Liquefying medium	Biomass	TAN (mg KOH/g oil)
Pure water	Corn stover	92.78
	Wheat straw	112.95
	Hardwood	187.83
Water-Ethanol	Wheat straw	82.56
Water-2-Propanol	Corn stover	81.74

4.3.5 Analysis of surface morphology of hydrochar samples

Figure 24 shows the surface morphology of the intact structure of the raw biomass and the degraded hydrochar obtained after HTL conversion process. Figure 24 a) and 24 d) shows the initial robust structure with smooth surface of corn stover and wheat straw. Hydrochars in figure 24 b), 24 c), 24 e) and 24 f) show irregular surfaces and different sizes of pores. Several cracks and holes can be observed in HC-CS-W and HC-WS-W as shown in figures 24 b) and 24 e), caused due to evolution of volatile and low-boiling point materials. Hydrochar samples in figure 24 c) and 24 f), show higher degree of destruction of the biomass matrix, with greater number of small, round flake-like structures, as compared to hydrochar obtained from HTL-water experiments.

The white patches observed in figure 24 b) and 24 e) may be inorganic compounds that can cause the microscope to get blurred, suggesting that more inorganic compounds are present in hydrochar obtained using water.

a)   b)   c)

d)   e)   f)
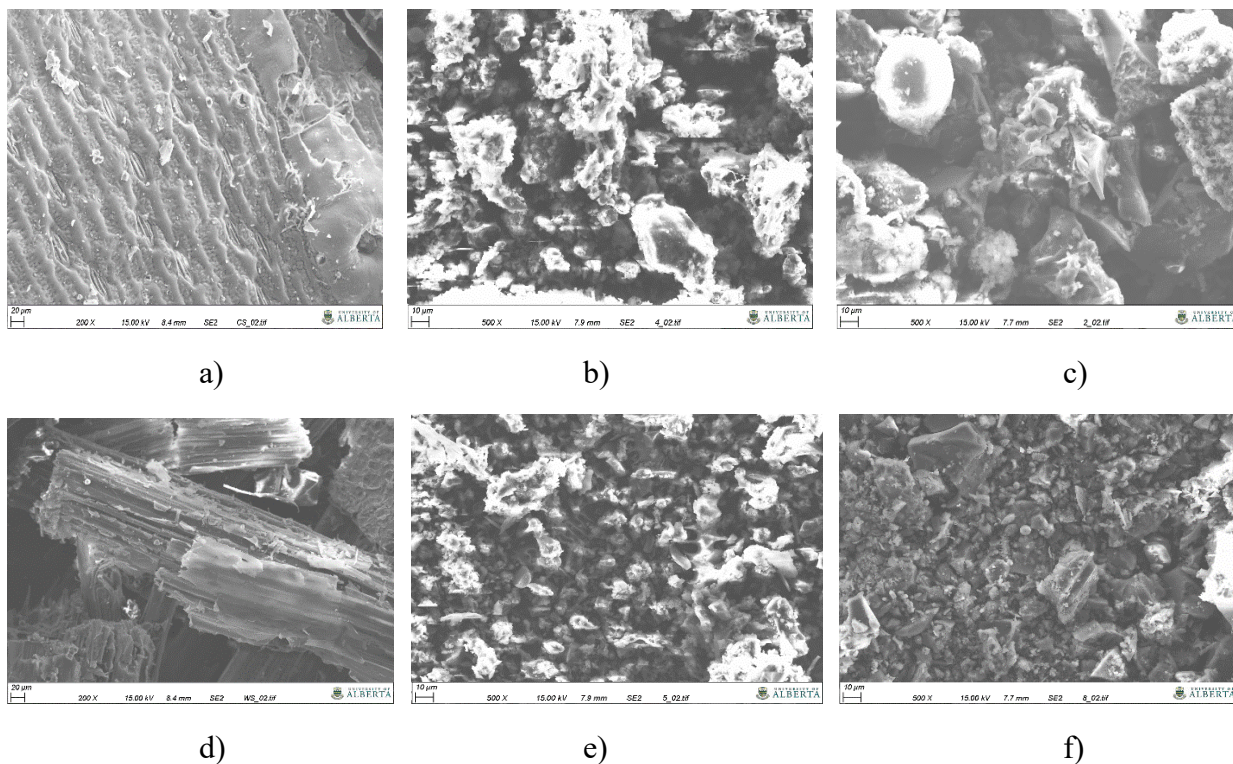
Figure 24: Surface morphology of hydrochar samples: a) Raw corn stover, b) HC-CS-W, c) HC-CS-W2P, d) Raw wheat straw, e) HC-WS-W, f) HC-WS-W2P.

Chapter 5: Conclusion and Future work

5.1 Conclusion

HTL experiments conducted on agricultural and forest biomass produced low-fluidity, high oxygen content, low HHV, high acid content heavy oil. The three biomass feedstocks had varying composition of cellulose, hemicellulose, lignin, extractives, and inorganics, that affected the heavy oil yield. Present HTL operating conditions resulted in negligible to slightly improved heavy oil yields when water-Co-solvent mixtures were utilized as liquefying medium. However, the addition of Co-solvents significantly improved the quality of heavy oil. Alcoholic Co-solvents has assisted water with conversion of the three polymers, because of its favourable thermodynamic conditions at the operating temperature of 300°C and final pressure ranging between 2378-2450 psi. Methanol may produce harmful bio-phenolic resins and ethanol for the present studies had not been beneficial towards increasing heavy oil yield. Extractive and inorganic interactions with ethanol could have affected the heavy oil yield, and further work is required to understand the reaction scheme between ethanol, extractives, and inorganics of biomass. Heavy oil obtained from water-2-propanol had not significantly increased the heavy oil content but had improved the quality of heavy oil, showing lowest oxygen content of 17.99 wt.% and 18.8 wt.%, highest HHV of 32.86 MJ/kg and 32.0 MJ/kg, for wheat straw and corn stover, respectively. Heavy oil also showed lowered acid content (TAN and GC-MS results) and showed relatively high ester content, lower ketones and aldehydes, lower major N-containing compounds such as amides and amines. SEM analysis of hydrochar samples showed that hydrochars obtained from HTL experiments using water-2-propanol mixture successfully destroyed the polymeric structures of raw corn stover and wheat straw, as compared to hydrochars obtained from HTL-water experiments. Therefore,

addition of alcohol such as 2-propanol among the other two alcohols, is an ideal Co-solvent for producing high-quality heavy oil resembling commercial fuels such as gasoline and diesel.

5.2 Future work

- Understanding the role of extractives and inorganics in biomass and their effect on heavy oil and quality.

- Understanding the reaction kinetics of the interaction between Co-solvent, water and biomass polymers that will enable the choice of combining the kinds of biomass with organic solvent.

- Understanding the combination of catalysts and Co-solvents with water and biomass, and their effect on heavy oil yield and quality.

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APPENDIX A

Table A1

GC-MS results of the different heavy oils obtained from HTL experiments using water and water-Co-solvent mixtures (Area % > 1)

RT (min)	Compounds	HO-CS-W	HO-WS-W	HO-HW-W	HO-CS-W2P	HO-WS-W2P	HO-WS-WM	HO-WS-WE
5.03	Furfural	-	-	1.87	-	-	-	-
6.36	2-Cyclopenten-1-one, 2-methyl-	1.61	-	1.06	-	-	-	-
7.36	2-Furancarboxaldehyde, 5-methyl-	-	-	1.67	-	-	-	-
7.65	Phenol	4.07	2.56	5.21	3.72	2.04	1.72	-
8.33	1,2-Cyclopentanedione, 3-methyl-	-	-	1.17	-	-	1.85	-
8.53	2-Cyclopenten-1-one, 2,3-dimethyl-	1.23	1.08	-	-	3.33	-	-
8.53	Cyclopentane, 2-ethylindene-1,1-dimethyl-	-	-	1.16	-	-	-	-
8.76	Phenol, 2-methyl-	1.25	-	-	-	-	-	-
8.76	N-Benzyloxycarbonyl-dl-norleucine	-	-	1.26	-	-	-	-
8.91	3-Cyclohexen-1-carboxaldehyde, 3-methyl-	1.23	-	-	-	-	-	-
9.05	Phenol, 4-methyl-	2.20	2.02	2.51	-	-	-	-

RT	Compound							
9.05	Phenol, 3-methyl-	-	-	-	-	-	2.61	-
9.05	Glycine, N-carboxy-, N-benzyl ester	-	-	-	3.17	-	-	-
9.27	Phenol, 2-methoxy-	6.74	5.77	5.24	-	-	-	-
9.51	Bicyclo[2.2.1]heptane, 2-(2-propenyl)-	-	-	-	3.24	-	-	-
9.51	Bicyclo[3.2.1]oct-3-en-2-one, 4-methyl-	-	-	-	-	-	1.18	-
9.54	3-Pyridinol	-	-	-	-	-	-	2.01
9.76	3-Pyridinol, 2-methyl-	-	-	-	1.25	-	-	1.31
10.28	Phenol, 4-ethyl-	11.57	6.42	-	14.48	7.33	6.07	-
10.29	4-Ethylphenyl acetate	-	-	-	-	-	-	2.25
10.45	Bicyclo[2.2.2]octane, 1-bromo-4methyl-	-	-	-	1.70	-	-	-
10.45	3-Pyridinol, 2,6-dimethyl-	-	-	-	-	-	1.45	-
10.47	2(1H)-Pyridinone, 3,6-dimethyl-	-	-	-	-	-	-	1.07
10.66	Phenol, 2-methoxy-4-methyl-	1.38	1.16	2.20	-	-	-	-
10.7	1,4-Dihydrothujopsene-(l1)	-	-	-	2.81	-	-	-
10.71	1H-Pyrazole,-1-acetonitrile, 4,5-dihydro-3-methyl-α-(2-thienyl)-	-	-	-	-	-	-	1.72
10.72	Isophorone diisocyanate	-	-	-	-	-	1.29	-
11.07	(E)-4-((1R,5S)-2,5,6,6-Tetramethylcyclohex-2-en-1-yl)but-3-en-2-one-rel-	-	-	-	1.09	-	-	-

11.26	1-(3,5,6-Trimethyl-2-pyrazinyl)-3-methyl-1-butanone	-	-	-	1.12	-	-	-
11.26	3-Pyridinol, 2-ethyl-6-methyl-	-	-	-	-	-	1.42	-
11.46	Phenol, 2-ethyl-4-methyl-	-	-	-	-	1.54	-	-
11.53	1,2-Benzenediol, 3-methoxy-	1.94	-	-	-	-	-	-
11.57	Spiro [4.4] non-3-en-2-one, 4-methyl-3-(1H-tetrazol-5-yl)-1-oxa	-	-	-	1.25	-	-	-
11.73	Phenol, 4-ethyl-2-methoxy-	7.90	7.00	2.71	-	-	2.07	-
11.74	2,5-Dimethoxyphenethylamine	-	-	-	3.12	-	-	-
11.74	4-Acetyl-3-hydroxyphenyl acetate	-	-	-	-	2.35	-	-
11.84	3-Methylcatechol, diacetate	-	-	-	1.10	-	-	-
11.84	1,2-Benzenediol, 4-methyl-	-	-	-	-	1.01	2.19	-
11.84	4-Hydroxy-4a,8-dimethyl-3-methylene-3,3a,4,4a,7a,8,9,9a-octahydroazuleno[6,5-b]furan-2,5-dione	-	-	-	-	-	-	1.74
12.1	Isobutyl (5-isopropyl-2-methylphenyl) carbonate	-	-	-	1.12	-	-	-
12.43	1,4-Benzenediol, 2-methyl-	1.00	1.11	1.44	-	-	-	-
12.46	Cyclopropanecarboxamide, 2,2-dimethyl-3-(2-methyl-1-propenyl)-N-(2-phenoxyethyl)-	-	-	-	-	-	-	1.20

12.57	Phenol, 2,6-dimethoxy-	5.74	10.26	14.36	-	-	11.55	-
12.57	2,6-Dimethoxyphenylacetate	-	-	-	6.14	7.29	-	-
12.57	Phenol, 2,6-dimethoxy-, acetate	-	-	-	-	-	-	5.52
12.69	2H-Oxocin-2,8(5H)-dione, 3,4,6,7-tetramethyl-	-	-	-	-	-	1.04	-
12.77	Phenol, 2-methoxy-4-propyl-	-	1.15	-	-	-	1.59	-
12.77	Benzeneacetic acid, α-hydroxy-3-methoxy-, methyl ester	-	-	-	1.04	1.60	-	-
12.92	2-Methoxy-5-methylphenol, 3-methylbutyl ether	-	-	-	1.48	-	-	-
12.92	4-Ethylcatechol	-	-	-	-	1.78	1.59	-
12.92	1,3-Benzenediol, 4-ethyl-	-	-	-	-	-	-	1.30
13.04	3-Buten-2-one, 4-(2,5,6,6-tetramethyl-2-cyclohexen-1-yl)-	-	1.10	-	-	-	-	-
13.13	Vanillin	-	-	1.07	-	-	-	-
13.53	Acetophenone, 4'-hydroxy-	1.41	-	-	-	-	-	-
13.63	Phenol, 2,6-dimethoxy-4-methyl-	-	1.75	2.99	-	-	-	-
13.63	Acetamine, N-(4-methoxy-2-nitrophenyl)-	-	-	-	-	-	1.47	-
13.77	5-Isopropylidene-4, 6-dimethylnona-3,6,8-trien-2-ol	-	-	-	-	1.18	-	-
14.08	p-Cymene-2,5-diol	1.12	-	-	-	-	-	-
14.08	Ethanone, 1-(2-hydroxy-6-methoxyphenyl)-	-	1.18	-	-	-	-	-

14.47	Benzene, 1,2,3-trimethoxy-5-methyl-	1.04	1.96	2.34	-	-	-	-
14.47	Trimethoxyamphetamine, 2,3,5-	-	-	-	1.19	1.94	2.67	1.22
15.36	Homosyringaldehyde	-	1.57	1.63	-	-	-	-
15.37	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester, (Z, Z)-	-	-	-	1.73	-	-	
15.37	Benzene, 1-ethyl-3-(phenylmethyl)-	-	-	-	-	3.21	3.83	-
15.37	4-Methoxy-1,3-benzodioxole-5-carboxylic acid	1.09	-	-	-	-	-	-
15.37	Benzene, 1,1'-propylidenebis-	-	-	-	-	-	-	1.67
15.99	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	-	-	2.55	-	-	-	-
16.22	5-tert-Butylpyrogallol	-	1.77	-	-	-	-	-
16.9	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	3.79	7.28	2.32	-	-	-	-
17.37	Syringylacetone	-	-	1.78	-	-	-	-
18.43	2-(1-Carboxy-1-methylethyl)-3,4,6-trimethylbenzoic acid	-	-	2.06	-	-	-	-
19.19	Hexadecanoic acid, methyl ester	-	-	-	2.47	3.20	4.87	3.90
19.59	n-Hexadecanoic acid	2.79	-	-	-	-	-	-

19.59	2-Bromotetradecanoic acid	-	1.80	-	-	-	-	-
19.6	Estra-1,3,5(10)-trien-17β-ol	-	-	-	-	-	1.48	1.63
19.62	Isopropyl palmitate	-	-	-	6.21	6.06	-	10.82
19.76	8-Amino-6,7-dimethoxy-4-methylquinoline	-	-	1.31	-	-	-	-
20.01	Hexadecanoic acid, ethyl ester	-	-	-	-	1.71	-	7.28
20.38	i-Propyl 14-methyl-pentadecanoate	-	-	-	-	1.13	-	-
21.21	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	-	-	-	-	-	1.05	-
21.28	9-Octadecenoic acid, methyl ester, (E)-	-	-	-	-	1.18	-	-
21.28	6-Octadecenoic acid, methyl ester, (Z)-	-	-	-	-	-	1.88	2.05
21.35	16-Octadecenoic acid, methyl ester	-	-	-	-	-	-	1.02
21.56	Methyl stearate	-	-	-	1.27	1.53	1.44	3.03
21.65	Abietic acid	-	1.23	-	-	-	-	
21.71	10-Octadecenoic acid, methyl ester	-	-	-	-	-	-	2.81
21.94	Hexadecanoic acid, 15-methyl-, methyl ester	-	-	-	1.73	-	-	
21.95	Hexadecanoic acid, 14-methyl-, methyl ester	-	-	-	-	1.38	-	4.11
22.04	Ethyl oleate	-	-	-	-	-	-	3.27
22.11	(E)-9-Octadecenoic acid, ethyl ester	-	-	-	-	-	-	1.68

22.32	Octadecanoic acid, ethyl ester	-	-	-	-	1.73	-	6.45
23.89	3-(6-Hydroxy-3,7-dimethyl-octa-2,7-dienyl)-4-methoxy-phenol	-	-	2.38	-	-	-	-
23.9	L-4-Hydroxy-3-methoxyphenylalanine	-	1.34	-	-	-	-	-
24.13	9-Octadecenamide, (Z)-	3.95	3.94	3.32	-	1.21	1.75	1.72
28.24	(1,6,6-Triphenylhexyl)benzene	-	-	1.91	-	-	-	-
29.51	2β,15β-dihydroxypregn-4-ene-3,20-dione	-	-	1.36	-	-	-	-
29.73	Hyocholic acid	-	-	1.90	-	-	-	-