

SYNERGISTIC EFFECT OF WATER AND CO-SOLVENTS ON THE HYDROTHERMAL LIQUEFACTION OF AGRICULTURAL BIOMASS TO PRODUCE HEAVY OIL

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Hydrothermal liquefaction was performed on Alberta, Canada's agricultural biomass, corn stover and wheat straw, at an operating temperature of 300°C, initial reactor pressure of 600 psi and zero min retention time. Effects of adding co-solvents (methanol, ethanol, and 2-propanol) on yield and quality of heavy oil has been studied. 2-propanol exhibited to be a promising co-solvent that has improved the quality of heavy oil. Hydrothermal liquefaction of corn stover using a water–2-propanol mixture produced heavy oil having oxygen content of 18.8 wt.%, higher heating value of 32.17 MJ/kg, and total acid number value of 81.74 mg KOH/g oil. Hydrothermal liquefaction of wheat straw using water–2-propanol mixture produced heavy oil showing an oxygen content of 17.99 wt.% and higher heating value of 32.94 MJ/kg.

KEY WORDS: *corn stover, wheat straw, hydrothermal liquefaction, co-solvent, water-co-solvent mixtures, heavy oil*

1. INTRODUCTION

Canada has embarked on a low carbon future, with the aim of utilizing its abundant biomass resources as renewable fuels that can potentially reduce the greenhouse gas (GHG) emissions produced mainly by its transportation of oil and gas sectors. Field crop production was estimated to be 99 million tonnes in 2020 (Agriculture and Agri-Food Canada, 2018), thereby generating agricultural residues that could potentially be used as feedstock for biofuel production. Canadian inventory studies have estimated the lignocellulosic biomass supply to range from 64 to 561 million dry tonnes (Gronowska et al., 2009). There have been underutilized agricultural biomasses that were set aside and neglected in the past, especially through the practice of burning these leftover residues that quickly release carbon to the environment, which could have been used to replace dependency on fossil fuels (DeKay, 2020). It was estimated that Alberta produces

15.8 million tonnes of straws as residues obtained from crop farming (Bailey-Stamler et al., 2007). Despite various hydrothermal liquefaction (HTL) studies conducted on algal biomass that have shown promising yields of heavy oil, Chernova et al. (2017) indicated that the high innate N-content of microalgae (resulting in high N-content of heavy oil) could be reduced by algae strain isolation or providing appropriate cultivating conditions. Such challenges are fairly resolved when lignocellulosic biomasses (having lower innate N-content) were used as biomass feedstock for HTL conversion process. Therefore, with the abundant supply of agricultural biomasses that are less likely to be used for farming purposes, this provides an opportunity for local bioenergy industries to tap into these lignocellulosic biomasses and improve the rural economy of Alberta.

Lignocellulosic biomass is primarily composed of cellulose, hemicellulose, and lignin, along with small amounts of extractives and inorganic materials. Cellulose, a linear polymer present in cell walls of plants, is structurally designed to have highly ordered crystalline zones and less ordered noncrystalline zones (Wertz et al., 2017). Less ordered (amorphous) sections of cellulose are susceptible towards enzymatic degradation. However, because it is present in lower amounts as compared to highly ordered crystalline parts in cellulose, it poses a challenge for complete degradation of this macromolecule (Bajpai, 2016). Hemicellulose is composed of different types of sugars and generally constitutes 20%–50% of the lignocellulosic biomass (Bajpai, 2016; Wertz et al., 2017). The degree of polymerization of hemicellulose is about 50–300, which is very low as compared to that of cellulose (~ 10,000) (Patel and Parsania, 2018). With fewer polymeric compounds present in hemicellulose, this component can prove to be easily degraded as compared to cellulose.

Lignin, which is the third most prevalent polymer present in lignocellulosic biomass, has a complex structure composed of cross-linked polymers of phenolic monomers that provide the plant cell wall with structural strength, rigidity, and hydrophobicity (Bajpai, 2016; Wertz et al., 2017). The polymer presents high resistance towards both mechanical disruption and microbial degradation, making it recalcitrant for various biomass conversion processes (Bernardi et al., 2016; Wertz et al., 2017). Extractives present in lignocellulosic biomass are composed of fatty acids, resin acids, fatty alcohols, stearyl esters, triglycerides, waxes, sterols, and various other phenolic compounds (Tajmirriahi et al., 2021). Inorganic elements present in lignocellulosic biomass are mainly sodium, potassium, calcium, magnesium, sulfur, chlorine, and silicon, that can have both catalytic and inhibiting effects on reactions occurring during thermochemical conversion processes (Hognon et al., 2014). Therefore, estimating the composition of lignocellulosic biomass is vital for understanding the reaction mechanisms that would dictate the distribution of HTL-products.

Hydrothermal liquefaction (HTL) is a thermochemical conversion process that is distinguished from other processes by its low temperature–high pressure operation, that converts biomass feedstocks into mainly energy-dense bio-oil, with water generally used as the liquefying medium. HTL operation has been carried out at temperature ranges of 200°–400°C and pressure ranges of 4–25 MPa (Toor et al., 2011;

Watson et al., 2020). HTL is preferred to be an ideal thermochemical conversion as compared to pyrolysis, primarily because of its ability to convert biomass feedstocks with high moisture content into energy-dense heavy oil, with higher quantity (Dimitriadis and Bezerigianni, 2017). Products from HTL operation are mainly bio-oil, aqueous phase, gas, and char (Déniel et al., 2016). Mathanker et al. (2020) performed HTL experiments on corn stover, where HTL-products have been recognized as dark-colored highly viscous heavy oil, aqueous phase which can be separated into light oil and water-soluble hydrocarbons, hydrochar as solid residue, and gas. Both sub- and super-critical water have been utilized as liquefying medium for HTL operation. Sub-critical water with temperature near 374°C and pressure near 3200 psi, has exhibited a low dielectric constant, similar to organic solvents, allowing more non-polar molecules to be dissolved in it (Carr et al., 2011). HTL operations conducted using super-critical water have reported severe damages to the reactor as compared to that conducted in sub-critical water medium (Möller et al., 2011). Super-critical conditions induce an uncontrollable number of free-radical reactions, increasing the number of unwanted side-reactions, where intermediate compounds undergo thermal cracking and polymerization reactions to produce more gaseous and char products (Zhu et al., 2014).

Therefore, utilizing water near its critical temperatures and pressures during HTL increases the quantity of liquid products and reduces the yield of solid residues. Given that sub-critical water can provide attractive liquefying properties towards HTL conversion process, there are operating parameters that must be considered for HTL operation, namely temperature, pressure, retention time, heating rate, and biomass composition (Akhtar and Amin, 2011).

Although water has been widely considered as an effective liquefying medium for HTL operation, heavy oil obtained from these experiments were found to be highly viscous and have increased the yield of water-soluble liquid products (showing lower energy density) and oxygen content of heavy oil (Ogi and Yokoyama, 1993; Chumpoo and Prasassarakich, 2010). Solubilizing complex polymers of lignocellulosic biomass were found to be effective on using sub-critical water. However, the HTL process needs to operate at high severities in order to achieve maximum conversion of biomass to liquid products. Co-solvents such as methanol, ethanol, or 2-propanol, show critical temperatures and pressures much less than water, that tend to reduce the overall severity of the HTL operation and produce heavy oil containing much lower oxygen content and higher heating values (HHVs), and thus they are being currently viewed as an alternative liquefying medium (Yuan et al., 2007; Chumpoo and Prasassarakich, 2010; Feng et al., 2014). Super-critical alcohols present gas-like diffusivity and liquid-like density providing single-phase reaction environments and exhibit lower dielectric constants than water, thus enhancing the solubility of higher molecular weight materials produced during decomposition of the three complex polymers (Cheng et al., 2010; Liu et al., 2013). Methanol, ethanol, and 2-propanol are hydrogen-donor solvents, that stabilize unwanted free-radical reactions and easily react with acidic components to form esters (Ogi and Yokoyama, 1993; Cui et al., 2020).

Zhu et al. (2014) conducted HTL experiments on cornstalk using water-methanol mixture and observed that a mixture ratio of 50:50 v/v led to the highest heavy oil yield, where water and methanol participated in hydrolysis and esterification reactions, respectively. Feng et al. (2018) reported that water-ethanol (50:50 v/v) was highly effective in converting biomass into heavy oil as compared to using only water or ethanol. During this liquefaction, water supported the hydrolysis reactions of cellulose and hemicellulose, whereas ethanol promoted efficient degradation of lignin (Feng et al., 2018). Therefore, present HTL experiments will utilize water-co-solvent mixtures and determine the yield and quality of heavy oil.

In this present study, HTL operation will be performed on two different kinds of agricultural biomass feedstocks, corn stover and wheat straw, at an operating temperature of 300°C, starting pressure of 600 psi, and retention time of 0 min. Methanol, ethanol, and 2-propanol will be added as co-solvents to water, and HTL operation will be performed in the same operating conditions as mentioned earlier. Through these HTL experiments, it is necessary to understand whether water-co-solvent mixtures are effective for different types of biomasses and the quality of heavy oil obtained will be assessed by its oxygen content, HHV, acidic content, chemical composition, and boiling point distribution.

2. MATERIALS AND METHODS

2.1 Materials

Corn stover and wheat straw were chosen as the lignocellulosic biomass feedstocks for present HTL experiments. Corn stover and wheat straw were obtained from northern and southern farms of Alberta, Canada, and were received at the large-scale fluid laboratory, located at the Department of Mechanical Engineering, University of Alberta (Vaezi et al., 2013). The three feedstocks were ground and sieved to particle size range of 0.425–1 mm for the present HTL experiments; this particle size range was found to be suitable for HTL operation conducted in previous studies (Mathanker, 2020). Moisture content, volatile matter, ash content, fixed carbon content, and elemental composition of biomass feedstocks are provided in Table 1. Deionized water was obtained from Millipore Milli-Q® Gradient instrument. Reagent-grade chemicals: acetone (≥ 99.5% purity), methanol (≥ 99.8% purity) and 2-propanol (≥ 99.5% purity) were purchased from Fisher Scientific International Inc., and ethanol (90.25% purity) was purchased from LabChem Inc.

$$\text{\%O content (wt.\%)} = 100 - [\text{C (wt.\%)} + \text{H (wt.\%)} + \text{N (wt.\%)} + \text{S (wt.\%)}]$$

$$\text{\%HHV(MJ/kg)} = (0.196 \times \text{Fixed Carbon}) + 14.119$$

TABLE 1: Proximate analysis and elemental composition of the two agricultural feedstocks

Biomass	Moisture content	Volatile matter	Ash content	Fixed carbon	C (wt.%)	H (wt.%)	N (wt.%)	O^s (wt.%)	HHV^{ss} (MJ/kg)
Corn stover	6.07	72.42	5.80	15.71	42.73	5.46	1.03	50.78	17.20
Wheat straw	5.87	71.39	5.78	16.96	42.81	5.47	0.51	51.21	17.44

2.2 Liquefaction Procedure

Hydrothermal liquefaction experiments on agricultural 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. In a typical HTL experiment, 5 g of corn stover (CS) or wheat straw (WS) was 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 organic solvents (methanol, ethanol, or 2-propanol) were considered as co-solvents. The reactor was sealed with flexible graphite gaskets, clamped onto the fixed head, then stirrer was set to 75 revolutions per minute to mix solid and liquid parts well before purging the reactor three times with 232 psi (16 bar) of N₂ gas. The reactor was heated to a target temperature of 300°C, with a starting pressure of 600 psi and reaction was held for 0 min (cooling water was started as soon as reactor temperature reached 300°C).

2.3 HTL-Products Recovery Procedure

After the reactor was cooled down to room temperature, the reactor was depressurized, and gas product was vented without further analysis. Then the reactor vessel was detached from the fixed head, and separation techniques such as filtration, rotary evaporation and drying, were conducted on the slurry mixture to recover mainly aqueous phase (AP), heavy oil (HO), and hydrochar (HC). The aqueous phase fraction was not analyzed in the present study. In order to separate product fractions from water-insoluble phase, acetone was rinsed down the walls of reactor, surfaces of stirrer blades and cooling coil, to recover maximum amount of the phase. For HTL experiments conducted in water, the aqueous phase (AP) was separated out from the slurry mixture before acetone was used for washing the water-insoluble phase. However, for HTL experiments utilizing water–co-solvent mixtures, the entire slurry mixture was washed with acetone. The water-insoluble phase was separated into two fractions: acetone-soluble and acetone-insoluble phases. 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 (HC). Rotary evaporation was conducted on acetone-soluble phase, to remove acetone and small amounts of water-soluble products (at 50°C and 90°C, respectively under reduced pressure), to recover the dark-colored heavy oil (HO). Figure 1 depicts the recovery procedure used for HTL experiments that involved water-co-solvent mixture as liquefying medium.

Yield of products obtained from all HTL experiments were calculated as follows:

$$\text{Heavy oil, HO (wt.\%)} = \frac{\text{Weight of Heavy oil}}{\text{Weight of Biomass feedstock}} \times 100 \quad (1)$$

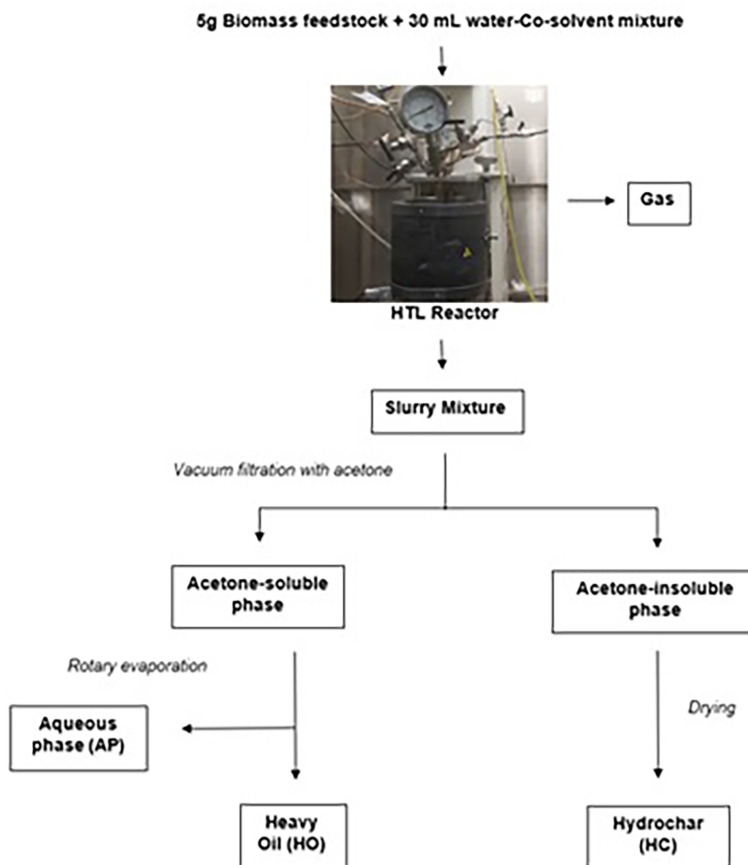


FIG. 1: HTL-products recovery for HTL experiments using 50:50 v/v water-co-solvent mixture as liquefying medium

$$\text{Hydrochar, HC (wt.\%)} = \frac{\text{Weight of Hydrochar}}{\text{Weight of Biomass feedstock}} \times 100 \quad (2)$$

$$\text{Gas (wt.\%)} = \frac{(W_f - W_r)}{W_f} \times 100 \quad (3)$$

where W_f refers to the weight of biomass feedstock and deionized water loaded into reactor, and W_r refers to weight of the fraction recovered after HTL operation. Aqueous phase (AP) fraction was calculated by difference.

2.4 Characterization Methods

2.4.1 Proximate Analysis of Biomass Feedstock

Corn stover and wheat straw feedstock were studied in LECO TGA 701, for their moisture content, volatile matter, ash content, and fixed carbon content, using the ASTM D7582 method.

2.4.2 Elemental Composition of Biomass Feedstock and Heavy Oil

Elemental composition (CHNS) of the agricultural feedstocks and heavy oil were performed on Thermo Fisher Flash 2000 Organic Elemental Analyzer (Department of Chemistry, University of Alberta).

2.4.3 Chemical Composition of Heavy Oil

Chemical composition of heavy oil was determined using gas chromatography–mass spectrometer (GC-MS) obtained from Agilent Technologies (7890 GC system – 5975C VL MSD). Highly probable compounds were identified by comparing mass spectra obtained from NIST library (MS search 2.3).

2.4.4 Total Acid Number Analysis of Heavy Oil

The total acid number (TAN) analysis of heavy oil was conducted using Mettler Toledo T50 apparatus, and ASTM D664 method was applied for analysis.

2.4.5 Boiling Point Distribution of Heavy Oil

Distribution of various boiling point materials present in heavy oil, was determined by using thermogravimetric analyzer (TGA), which was performed on SDT Q 600 (TA Instruments).

3. RESULTS AND DISCUSSION

3.1 Effect of Addition of Co-Solvent on the Yield of HTL-Products

Figures 2 and 3 provide a comparison of yield of HTL-products obtained from HTL conducted with only water and that by using 50:50 v/v water–co-solvent mixtures. Relatively high yields of heavy oil were obtained when HTL was conducted on corn stover using water–methanol and water–2-propanol mixtures as compared to that when only water was used as sole solvent. With water as sole solvent (HTL–CS–W), heavy oil yield obtained was 36 wt.%. However, using water–methanol (HTL–CS–WM) and water–2-propanol (HTL–CS–W2P) for HTL, produced a higher heavy oil yield of 42 wt.%

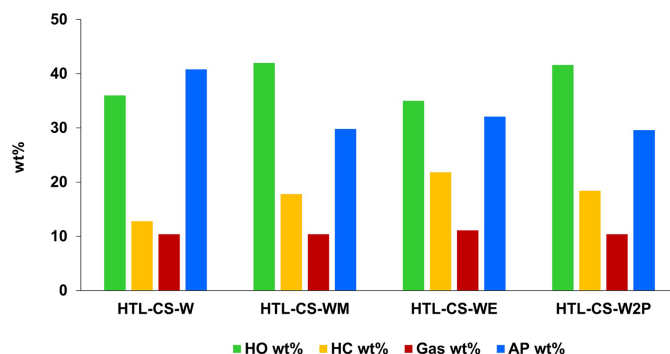


FIG. 2: Distribution of products obtained from HTL of corn stover (CS) using only water and 50:50 v/v water-co-solvent mixtures

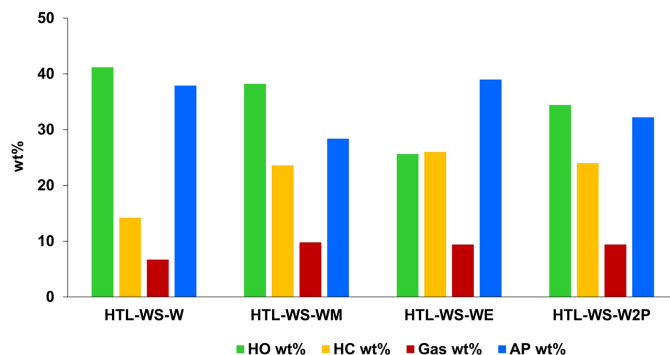


FIG. 3: Distribution of products obtained from HTL of wheat straw (WS) using only water and 50:50 v/v water-co-solvent mixtures

and 41.6 wt.%, respectively. When wheat straw was the biomass feedstock, HTL-water experiment (HTL-WS-W) produced a heavy oil yield of 41.2 wt.%, whereas that obtained by using water-methanol (HTL-WS-WM) and water-2-propanol (HTL-WS-W2P) produced heavy oil yield of 38.2 wt.% and 34.4 wt.%, respectively. HTL using water-ethanol as liquefying medium either decreased the yield of heavy oil (when wheat straw was used as feedstock, HTL-WS-WE, yield of HO was 25.6 wt.%) or has not significantly changed the yield of heavy oil (when corn stover was used as feedstock, HTL-CS-WE, yield of HO was 35.0 wt.%). Interestingly, the yields of heavy oil obtained from present HTL operating conditions range from 34.4 wt.% to 42.0 wt.%, which are much higher than those obtained by Okekunle et al. (2021) through fast pyrolysis of another lignocellulosic biomass. The yield of gaseous products did not change for either of the two biomass feedstocks, when HTL experiments have been conducted with water or water-co-solvent mixtures at present operating conditions. Aqueous phase products have decreased on adding co-solvents with water. Among the various reactions that take place during HTL, dehydration reactions could result in aqueous phase formation and

therefore, with HTL–water experiments show higher aqueous phase products than those experiments involving water–co-solvent mixtures. Conversions for HTL–water experiments were 87.20 wt.% (corn stover as feedstock) and 85.80 wt.% (wheat straw as feedstock). For HTL experiments using water–co-solvent mixtures as liquefying medium, conversions were 82.20 wt.% (HTL–CS–WM), 78.20 wt.% (HTL–CS–WE), 81.60 wt.% (HTL–CS–W2P), 76.40 wt.% (HTL–WS–WM), 74.0 wt.% (HTL–WS–WE), and 76.0 wt.% (HTL–WS–W2P).

The composition of present agricultural feedstock used for HTL experiments were assumed as: wheat straw showing 37.4 wt.% cellulose, 35.6 wt.% hemicellulose, and 20.4 wt.% lignin content, and corn stover showing 38.1 wt.% cellulose, 25.3 wt.% cellulose, and 20.2 wt.% lignin content (Bicho and McRae, 2008; Cherubini, 2010). With lower lignin content in corn stover, hydrochar content from HTL of corn stover using water–co-solvent mixture was lower than that obtained from HTL of wheat straw using either water–methanol, water–ethanol, or water–2-propanol mixture. This also indicates that corn stover, having marginally lower hemicellulose and lignin content than wheat straw, had better molecular interaction with water and co-solvents at the same retention time as those experiments performed on wheat straw. However, extractive and inorganic content present in small quantities in lignocellulosic biomass could provide catalytic or inhibiting effects during decomposition reaction and could also alter the yield of HTL-products. Referring to the results obtained from both Zhu et al. (2014) and Zhao et al. (2013), it is possible that a longer retention time (15–30 min) could have slightly improved the heavy oil yield. Therefore, biomass composition determines the interaction between the constituents of the biomass, water and co-solvents. The following section provides analysis to understand the quality of the heavy oils derived from HTL using water–methanol and water–2-propanol experiments.

3.2 Effect of Addition of Co-Solvent on the Quality of Heavy Oil

Oxygen content of heavy oil was calculated as difference from CHNS results (Fig. 4) and HHV of heavy oil was calculated by using the following formula (Channiwala and Parikh, 2002):

$$\begin{aligned} \text{HHV}(\text{MJ/kg}) = & (0.3491 \times C) + (1.1783 \times H) + (0.1005 \times S) - (0.1034 \times O) \\ & - (0.0151 \times N) - (0.0211 \times \text{Ash}) \end{aligned} \quad (4)$$

For evaluating the HHV of heavy oil using Eq. (4), the ash content and sulfur content of heavy oil were considered to be negligible for the present experiments. HHV for present corn stover and wheat straw biomass feedstocks, as mentioned in Table 1, was

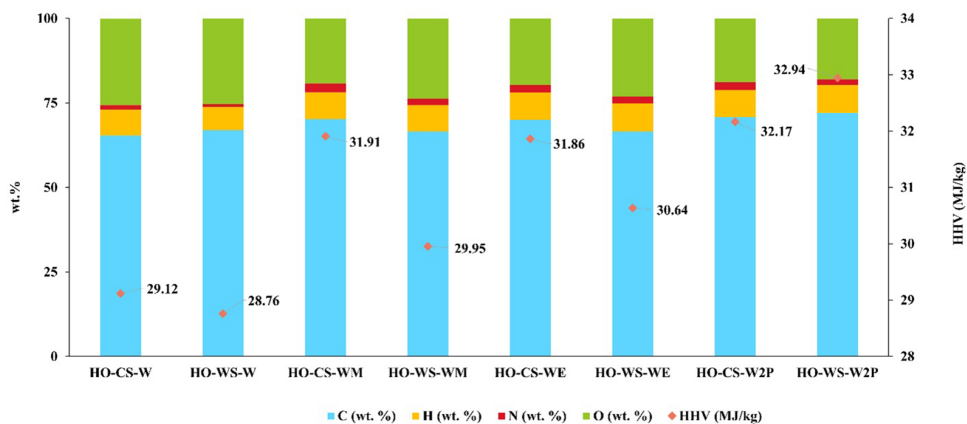


FIG. 4: Elemental distribution and HHVs of heavy oil

calculated using the formula referred by Demirbaş (1997), which was used to calculate the HHV for 16 biomass feedstocks. Heavy oil obtained by using water–2-propanol from HTL of corn stover (HO–CS–W2P) and wheat straw (HO–WS–W2P) exhibited HHVs of 32.17 MJ/kg and 32.94 MJ/kg, respectively. These HHVs are higher than that obtained from using only water, with 29.12 MJ/kg (HO–CS–W) and 28.76 MJ/kg (HO–WS–W) when corn stover and wheat straw were used for HTL experiments, respectively. Lowest oxygen content of heavy oil obtained from HTL of corn stover was 18.8 wt.% and that obtained from wheat straw was 17.99 wt.%, when 2-propanol was the co-solvent.

Table 2 shows that ester (diesel-like compounds) has increased for heavy oils obtained from HTL conducted using water–2-propanol mixtures. The results in Table 2 show the sum of compounds present in each organic class; only compounds having area % > 1 were accounted for this calculation. Presence of acidic components in heavy oil obtained from HTL–water experiments can be also observed by the TAN values. TAN values, as reported in Table 3 show that addition of co-solvents have significantly reduced the acid content, indicating that esterification of fatty acids present in biomass effectively yielded more esters during the conversion process. Total oxygenated compounds (alcohols, phenols, carboxylic acids, ketones, aldehydes, and ethers) are higher in HO–CS–W2P with 23.15% as compared to HO–WS–W2P with 18.21%. This result is consistent with the CHNS data presented in Fig. 4, where O content of HO–CS–W2P is 18.8 wt.% and that of HO–WS–W2P is 17.99 wt.%.

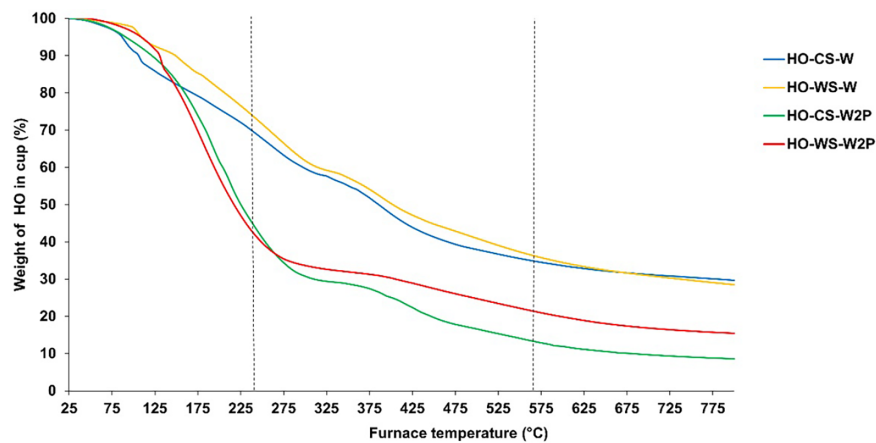
Middle-distillate fractions (232°–566°C) are higher in heavy oils obtained by using water as sole solvent than those heavy oils obtained by using water–co-solvent mixtures (Fig. 5). Middle-distillate fraction present in the four heavy oils (Fig. 5) were: 35.69% in HO–CS–W, 38.56% in HO–WS–W, 33.16% in HO–CS–W2P, and 22.56% in HO–WS–W2P. On comparing the present boiling point curves with those obtained from Anouti et al. (2016), HO–CS–W2P and HO–WS–W2P follow curves similar to that of diesel, and HO–CS–W and HO–WS–W show curves that resemble heavy Iraqi crude oil.

TABLE 2: Distribution of compounds present in heavy oil obtained from water and water–2-propanol HTL experiments

Compound class	Area % (HO-CS-W)	Area % (HO-WS-W)	Area % (HO-CS-W2P)	Area % (HO-WS-W2P)
Acids	3.88	3.03	—	—
Alcohols	—	—	—	1.18
Aldehydes	1.23	1.57	—	—
Alkanes	—	—	4.94	—
Amides	3.95	3.94	—	1.21
Ethers	1.04	1.96	1.48	—
Ketones	8.05	10.64	2.22	3.33
Phenols	44.92	40.98	19.45	13.70
Esters	—	—	24.86	29.14
Amines	—	—	4.31	1.94
Aromatics	—	—	—	3.21
Others	—	1.34	—	—

TABLE 3: TAN analysis of heavy oil obtained from HTL-water and HTL-water-2-propanol experiments

Heavy oil	TAN (mg KOH/g oil)
HO-CS-W	92.78
HO-WS-W	112.95
HO-CS-W2P	81.74
HO-WS-W2P	82.56

**FIG. 5:** TGA curves for different heavy oils obtained from HTL experiments

4. CONCLUSIONS

HTL operations conducted using 50:50 v/v water–co-solvent mixtures have mainly influenced the quality more than the yield of heavy oil for the present operating conditions. Biomass with varying composition of cellulose, hemicellulose, lignin, extractives, and inorganic content have affected the yield of heavy oil. On comparing the liquefaction performance of the three water–co-solvent mixtures, water–2-propanol mixture has improved the quality of heavy oil, with lowest oxygen content, highest HHV, lower TAN value, and having compounds similar to diesel (in terms of GC-MS and TGA results). Future work in this project may involve the participation of catalysts with water–co-solvent mixtures, in order to explore the potential of enhancing both the yield and quality of heavy oil.

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