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Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems

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Abstract

Lignocellulosic model compounds and aspen wood are processed at supercritical hydrothermal conditions to study and understand feedstock impact on biocrude formation and characteristics. Glucose and xylose demonstrate similar yield of biocrude and biochar, similar biocrude characteristics, and it is hypothesized that reaction mechanisms for the two model compounds are indistinguishable. Glucose and xylose are main sources of substituted cyclopentenones and substantial contributors to oxygenated aromatics mainly in the range of C_6-C_9 number of carbon atoms, and potential, sustainable biogasoline candidates. Lignin yields predominantly aromatic biocrudes having similar C_6-C_9 number of carbon atoms. Model mixtures show good predictability in the distribution of substituted cyclopentenones and oxygenated aromatics, but aspen wood-derived biocrude is more aromatic than predicted by model mixtures. The work extends previous work on the understanding of the chemical mechanisms of lignocellulose liquefaction and the biocrude formation. Potential applications for the biocrudes are identified, where significant sustainability issues for the transport sector can be addressed.

Keywords: Biofuel, Biocrude, Wood liquefaction, Model compounds, Hydrothermal liquefaction, Reaction mechanism

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1. Introduction

Hydrothermal processing of biomass in near-critical water is a viable, scalable and renewable chemical pathway, utilizing the unique properties of hot-compressed water (HCW), to break down the original macromolecules in biomass and convert their fragments into green synthetic liquid (hydrothermal liquefaction, HTL) [1–4] or gaseous fuels (super critical water gasification, SCWG) [5, 6]. The processing technology has been identified as a promising en-

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ergy efficient and sustainable carbon-neutral platform for valorisation of biomasses through bio-fuel production [7]. Hydrothermal processing has successfully been demonstrated to convert a broad range of biomasses into four easily separated phases; a gas phase rich in carbon dioxide and combustible gases (*e.g.* H_2 and CH_4), a combustible biochar solid phase, a distinct water-soluble organic phase suitable for fine chemical extraction or synthetic gas production, and a bulk, water-insoluble and oxygen-lean fraction commonly termed biocrude, all which comprise an ideal no waste discharge system. The biocrude is a blend of numerous intermediate chemical compounds spanning a broad range from *e.g.* oxygenated aromatics, heterocyclic compounds to long chain aliphatic backbones mostly dependent on the feedstock composition. The feasibility of the conversion step of various biomasses into biocrudes has already been proven mostly in batch and less so in continuous processing systems [7], and techno-economic assessments recognize HTL as a profitable process for marketable sustainable liquid fuels, even when followed by a subsequent hydrotreatment step to meet hydrocarbon specs for drop-in applications [8–10]. Several studies have shown that the specific composition of the different types of biomass (wood, grass, vegetable oils, algae etc.) has a major influence on the chemical profile of the biocrude [11–19].

Predictability between feedstock composition and biocrude characteristics is still a topic that needs attention [13, 20]. General trends have been observed, such as microalgae resulting mostly in aliphatic structures, mainly due to the high lipid contents, and lignocelluloses resulting in alkylated cyclopentenones and aromatic structures, the latter expected to originate mainly from lignin conversion. The numerous compounds found in the biocrude and the lack of predictability are considered a significant challenge for technology commercialization. Recently, Carrier et al. investigated the conversion of holocellulose, lignin and α-cellulose extracted from fronds (*Pteris vittata L.*) at sub- and supercritical water conditions, and found that the resulting compounds can be grouped into two main compound pools; one consisting of oxygenated and substituted 5-membered ring structures, such as ketonic cyclopentanes and cyclopentenes (CPs), and one consisting of oxygenated and substituted aromatics (OA) [12, 13]. This is a significant simplification of a highly complex pool of compounds, which further simplifies the identification of downstream applications of the resulting liquids, as these can be characterized by compound families or pools rather than individual compounds.

It was further found that the first group of 5-membered derivative compounds originated from the carbohydrates and that the aromatic derivatives originated both from the carbohydrates and lignin. The compounds obtained consisted mainly of oxygenated paraffins, olefins and aromatics and ranged primarily from the C_5 to C_{10} number of carbon atoms, and had been identified as promising drop-in gasoline candidates [21]. It was also found that the distribution of 5-membered compounds and aromatics was almost invariant to reaction time but sensitive to reaction temperature and feedstock composition, as mentioned above.

Although these observations are indicators of expected product compounds, it is of particular interest to investigate if the distribution of the two primary compound pools can be predicted and produced selectively based on varying the feedstock composition. If this is the case, it provides an opportunity to tailor biocrude composition to the intended downstream purpose by manipulating the feedstock composition.

To the best of our knowledge, a comprehensive study investigating lignocellulosics from a single model compound and model mixtures point of view does not exist. The main objective of this study is thus a novel contribution to the understanding of the chemistry of biocrude formation and the quality of such biocrudes from a model compound viewpoint. It is generally accepted that alkaline conditions and high process severity leads to higher quality biocrude, which justifies processing at supercritical conditions compared to subcritical conditions [7]. Glucose, xylose and alkali lignin as model compounds for cellulose, hemicellulose and lignin, respectively, and their mixtures are processed in an alkaline supercritical water environment to obtain original information on the formation of green fuel range chemicals. It is envisioned that by studying and understanding the biocrude formation of the individual lignocellulose constituents, unique knowledge can be gained towards understanding the relationship between macro-structures (carbohydrates vs. lignin) on the biocrude formation from real biomass feedstock. In this work, an experimental campaign is carried out to investigate:

1. The formation and characterization of the water-insoluble compounds obtained when processing aspen wood under alkaline supercritical water conditions.
2. The formation of biocrude from individual model compounds; glucose, xylose and lignin along with the characterization of the individual biocrudes.
3. The behavior of sugar derived model compounds to understand the biocrude composi-

tion to the chemical properties of the input feed.

2. Materials and Methods

2.1. Materials

Glucose, xylose, lignin (alkali, low sulfonate), sorbitol, xylitol and ethylene glycol (EG) were all purchased from Sigma-Aldrich (≥98 %). Glycerol (99.5 %) was purchased from Brenntag Nordic A/S. Properties of the aspen wood used are listed in Table 1.

Table 1: [a]Ultimate analysis was carried out in a Perkin Elmer 2400 Series II CHNS/O system. [b]Fibre composition was determined by the Van Soest method in a FOSS 121 Fibertec unit. [c]Ash content measured by heating a sample to 850 °C and hold isothermally for 2 hours. daf = dry,ash-free. N.D. = Not Detected

[a]Ultimate analysis (wt. %, daf.)	
C	50.39 (0.86)
H	6.19 (0.08)
N	0.19 (0.02)
S	N.D.
O (by difference)	43.23 (0.08)
[b]Fibre Composition (wt. %, db.)	
Cellulose	63.59 (0.86)
Hemicellulose	7.65 (0.11)
Lignin	22.13 (0.17)
Extractives (by difference)	6.63 (0.01)
[c]Ash	0.46 (0.02)

2.2. Experimental procedure

All experiments were carried out in rapidly heated, 10 mL batch micro-reactors. For each run, the reactor was loaded with 5 g of pre-mixed solutions reaching an estimated final autogenous reaction pressure of circa 300 bars. All mixtures consisted of 20 wt. % input bio-feedstock, for all combinations of model compounds, mixtures hereof or real biomass mixed in demineralized water. K_2CO_3 was added as an alkaline catalyst amounting to 10 wt. % of the input bio-feedstock (pH 11.5). The reactor was purged with nitrogen before heating, and then heated to 400 °C in a pre-heated fluidised sand bath (Techne SBL-2D) for 15 minutes (including the heating period) and finally quenched in water. Typical heating and cooling rates for the micro-reactors are 250-450 K/min. and >1000 K/min., respectively, conclusively eliminating any heating and cooling rate effects compared to the time spent at final reaction conditions.

Five mixtures (Mix1-5) of glucose, xylose and lignin were investigated to study qualitative effects on the biocrudes from different compositions. The compositions of the five mixtures were chosen in order to frame the composition of a variety of lignocellulosic feedstock obtained from Demirbas et al. [22]. The compositions of the five mixtures are displayed in Table 2.

Table 2: Composition of the five model compound mixtures investigated. The five mixtures are arranged as four corner and one center point, framing the variety of cellulose, hemicellulose and lignin compositions of lignocellulosic biomass [22].

	Mix1	Mix2	Mix3	Mix4	Mix5
Cellulose/Lignin	1/3	1/3	3	3	8/3
Hemicellulose/Lignin	1/3	3	3	1/3	8/3

2.3. Recovery and analysis of biocrude

After the reactor was cooled to room temperature any overpressure was vented through a top valve. No further attention was given to the gas phase in this work. As in most comparable work with micro-reactors, extraction and separation of products from the micro-reactor was found challenging as some products remained partially emulsified in the aqueous phase and had to be extracted by an appropriate water-insoluble solvent to obtain stable and reproducible results. In the adopted procedure, the aqueous phase and easily removable products were poured out of the reactors and filtered to remove any solids. The emulsified aqueous phase was then extracted using diethyl ether (DEE) which led to a phase separation.

The phase separation lead to two identifiable phases: A top DEE with solubles fraction, and a bottom aqueous phase. The DEE with solubles fraction was decanted and evaporated to recover the DEE-solubles. The reactor was then rinsed with acetone and the obtained material filtered. After filtration of the solid phase, the acetone fraction was evaporated (556 mbar, 40 °C) to remove the acetone. The leftover product, a mixture of biocrude and residual water, was extracted using DEE and finally the DEE with solubles fraction was evaporated (990 mbar, 40 °C) to recover the biocrude. The total amount of solids was dried overnight before weighing. All experiments were performed in triplicates.

Qualitative analyses of all biocrude samples were carried out on a Thermo Scientific Trace 1300 ISQ GC-MS system, (Length: 15 m., i.d.: 0.25 mm., film: 0.25 μm film, TG-SQC column). Prior to analysis, all samples were diluted in DEE and subjected to the following oven temperature profile; 40 °C was held for 3 minutes, then ramped to 325 °C at 8 °C/min and finally kept at this temperature for 4 minutes. Injector and ion source temperatures were 280 °C, split ratio was 1:20, and flow rate of the carrier gas (helium) was 1.0 mL/min. Compounds were identified by mass spectra comparison with the NIST mass spectral data library. Selectivities of compounds were calculated by peak areas.

For the most abundant compounds, an index of hydrogen deficiency, Ω, was calculated according to Equation 1, expressing the sum of rings and double bonds, such as C=C and C=O, contained within the chemical structures.

$$\Omega = \frac{2 + 2C - H}{2} \tag{1}$$

For single ring structures, which have mostly been observed in the biocrudes, Ω-1 then gives the number of hydrogen molecules needed to be added to that structure in order to obtain the corresponding saturated oxygenated hydrocarbons. This does not necessarily correspond to the number of hydrogen molecules needed to obtain the corresponding alkanes, since the carbonyl groups (C=O), for instance, only represents one double bond but two hydrogen molecules are needed to remove the oxygen. Moreover, an effective hydrogen-to-carbon ratio, $\mathrm{H/C_{eff}}$, was calculated as a quality measure for each compound according to Equation 2.

$$\mathrm{H/C_{eff}} = \frac{H - 2\mathrm{O}}{C} \tag{2}$$

Finally, the boiling point (BP) and the density for each compound are given. For those compounds, of which the boiling points and densities could not be obtained from literature, the Yamamoto-Molecular Break (Y-MB) method is used. The Y-MB method estimates physico-chemical properties by breaking the specific compound SMILES (Simplified Molecular Input Line Entry Syntax) notations into corresponding functional groups.

Functional group identification was done by IR spectroscopy, carried out at room temperature on a Thermo Scientific Nicolet 380. Spectrum resolution was 1 cm^{-1} and recorded in the range of 4000-700 cm^{-1}. Elemental composition was measured using a Perkin Elmer 2400 Series II CHNS/O system. Due to a combination of small sample sizes, sample sulphur and nitrogen contents close to the detection limit of the equipment and slightly inhomogeneous samples (giving rise to large standard deviations), it was not possible to measure neither sulphur nor nitrogen in any of the resulting biocrudes. However, as expected for lignocellulose and indicated in Table 1, these can be neglected.

3. Results and Discussion

3.1. Characterization of water-insoluble compounds obtained from aspen wood

Aspen wood was processed in order to investigate and characterize obtained water-insoluble chemical compounds. Figure 1 shows that approximately 42 % of the aspen wood is converted into a water-insoluble but ether-soluble biocrude, consisting of numerous chemical compounds. The solid yield amounted to approximately 18 %.

GC-MS analysis was carried out to study the chemical compounds contained within the biocrude in order to investigate the origin of the compounds presented in Table 3.

Firstly, it is observed that for aspen wood the chemical compounds can be grouped into two main groups, cyclopentenones (CP) and oxygenated aromatics (OA), as it was found from processing fronds [12, 13]. Moreover, it is observed that the majority of compounds range from C_5-C_9, typical for gasoline range hydrocarbons. In order to characterize the different compounds their H/C_{eff} ratios have been plotted against the total chromatogram in Figure 2. It is noted that the CPs generally show higher H/C_{eff} ratios than the OAs, which is consistent with the hydrogen deficiency, Ω, observed in Table 3. The CPs exhibit Ω of 2 or

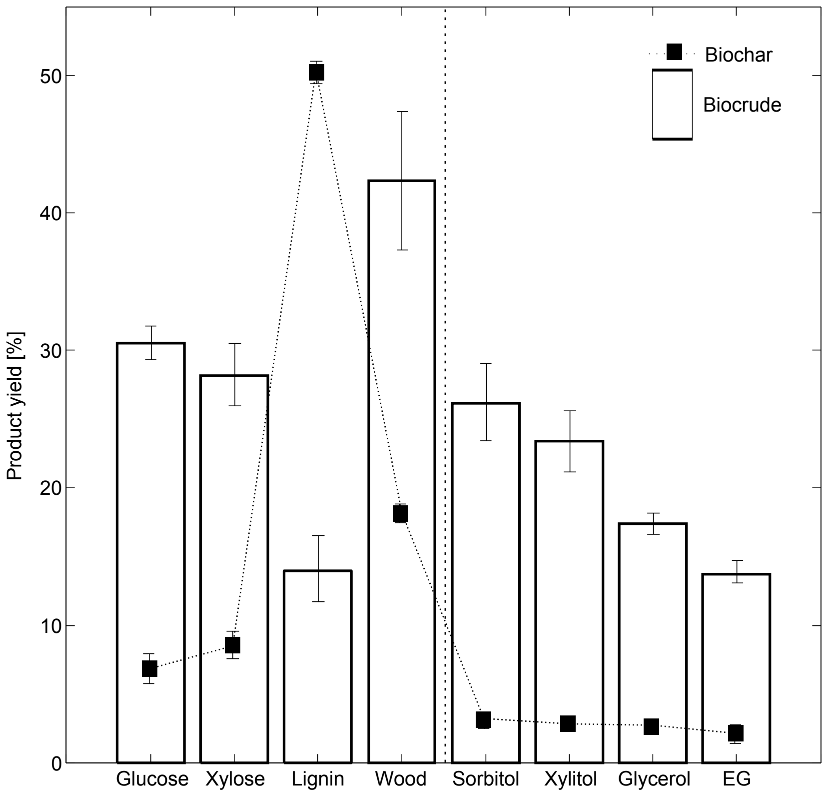

Figure 1: Biocrude and biochar yields for aspen wood, lignocellulosic model compounds and polyols when processed at alkaline conditions at 400 °C and 15 min. EG = Ethylene glycol

Table 3: Main product compounds (by GC-area) obtained when processing aspen wood at alkaline supercritical water conditions. Terminology: (CP), Cyclopentene/pentane derivatives, (OA), Oxygenated aromatics, (HC), Hydrocarbons, (O) Others.

	TR (min)	Compounds	Formula	Ω [-]	H/C$_{\mathrm{eff}}$ [-]	BP [°C]	Density [kg/m^3]
1	1.71	Furan, tetrahydro-2,2,5,5-tetramethyl- (O)	$C_8H_{16}O$	1	1.75	112	811
2	2.06	Cyclopentanone (CP)	C_5H_8O	2	1.2	130.6	950
3	2.81	Furan, 2-methyl- (O)	C_5H_6O	3	0.8	63	927
4	2.94	Cyclopentanone, 2-methyl- (CP)	$C_6H_{10}O$	2	1.35	139	917
5	2.99	Diacetone alcohol (CP)	$C_6H_{12}O_2$	1	1.34	166	938
6	4.46	2-Cyclopenten-1-one, 2-methyl- (CP)	C_6H_8O	3	1.01	154.4	980
7	5.21	1,3-Dimethyl-1-cyclohexene (HC)	C_8H_{14}	0	1.75	128.2	812
8	5.79	2-Cyclopenten-1-one, 3-methyl- (CP)	C_6H_8O	3	1.01	154.4	980
9	6.32	Phenol (OA)	C_6H_6O	4	0.67	181.7	1070
10	6.44	2-Cyclopenten-1-one, 3,4-dimethyl- (CP)	$C_7H_{10}O$	3	1.15	167.1	952
11	7.39	2-Cyclopenten-1-one, 2,3-dimethyl- (CP)	$C_7H_{10}O$	3	1.15	186.9	965
12	7.84	O-Cresol (OA)	C_7H_8O	4	0.86	191	1047
13	7.92	2-Cyclopenten-1-one, 3,4,4-trimethyl- (CP)	$C_8H_{12}O$	3	1.25	182.1	938
14	8.27	p-Cresol (OA)	C_7H_8O	4	0.86	201.8	1035
15	8.46	Guaiacol (OA)	$C_7H_8O_2$	4	0.56	205	1129
16	8.72	2-Cyclopenten-1-one, 3-(1-methylethyl)- (CP)	$C_8H_{12}O$	3	1.25	188.5	934
17	9.66	3,5-Xylenol (OA)	$C_8H_{10}O$	4	1	222	981
18	10.5	5-Hydroxy-2,2-dimethylhexan-3-one (O)	$C_8H_{16}O_2$	1	1.5	203	946
19	10.64	Catechol (OA)	$C_6H_6O_2$	4	0.34	245.5	1344
20	11.31	m-Cresol, 5-ethyl- (OA)	$C_9H_{12}O$	4	1.11	224	964
21	11.7	p-Cresol, 2-ethyl- (OA)	$C_7H_8O_2$	4	0.56	224	964
22	11.79	Phenol, 2,4,6-trimethyl- (OA)	$C_9H_{12}O$	4	1.11	221	984
23	12	4-Ethylguaiacol (OA)	$C_9H_{12}O_2$	4	0.89	235	1041
24	12.22	4-Methylcatechol (OA)	$C_7H_8O_2$	4	0.56	251	1123
25	13.25	1,3-Benzenediol, 4,5-dimethyl- (OA)	$C_8H_{10}O_2$	4	0.75	284.1	1162
26	13.77	4-Ethylcatechol (OA)	$C_8H_{10}O_2$	4	0.75	272.7	1086
27	14.13	1,4-Benzenediol, 2,5-dimethyl- (OA)	$C_8H_{10}O_2$	4	0.75	278.3	1108
28	14.54	1,4-Benzenediol, 2,3,5-trimethyl- (OA)	$C_9H_{12}O_2$	4	0.89	293.8	1100
29	14.72	4-Ethylguaiacol (OA)	$C_9H_{12}O_2$	4	0.89	235	1041
30	15.2	1,3-Benzenediol, 4-propyl- (OA)	$C_9H_{12}O_2$	4	0.89	286	1055
31	15.46	Benzene, 3-ethyl-1,2,4,5-tetramethyl- (HC)	$C_{12}H_{18}$	4	1.5	231.3	889
32	15.68	Hydroquinone, trimethyl- (OA)	$C_9H_{12}O_2$	4	0.89	293.8	1100
33	16.07	p-Propylguaiacol (OA)	$C_{10}H_{14}O_2$	4	1	262.5	1018
34	24.54	Retene (HC)	$C_{18}H_{18}$	10	1	379.6	1062

3 corresponding to the ketone double bond (Ω=2) and whether the ring is saturated (Ω=0) or unsaturated (Ω=1), respectively. All the OAs display Ωs of 4, which correspond to the single benzene rings.

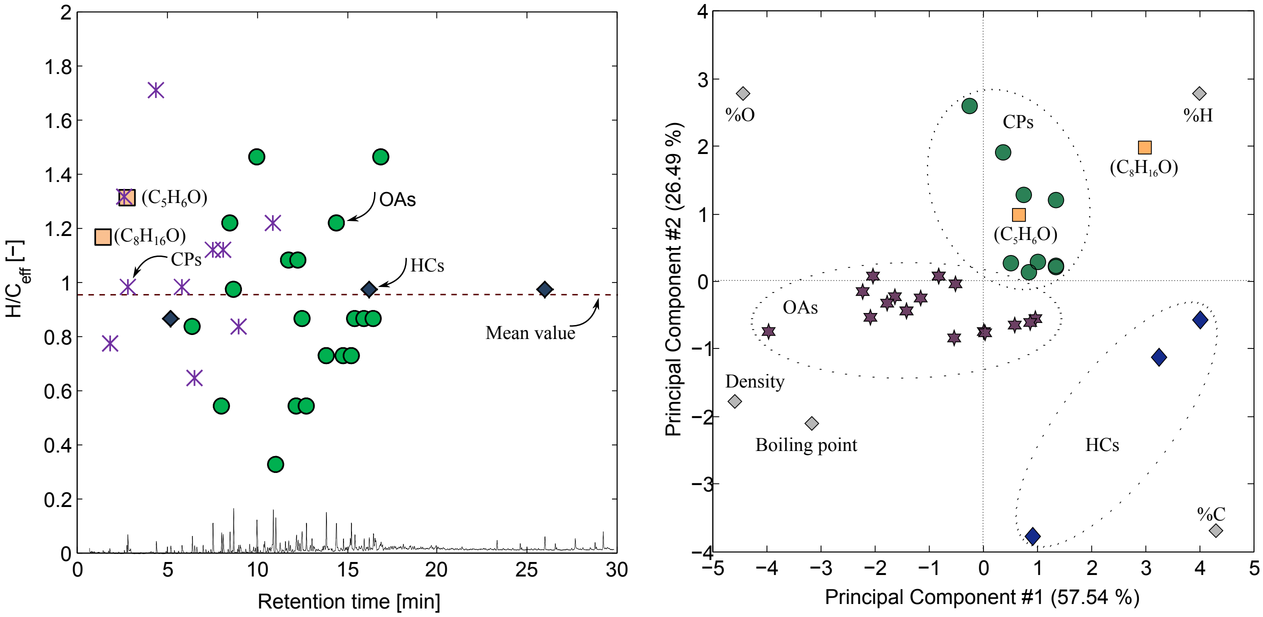

Figure 2: Left: H/C$_{eff}$ for the compounds identified from the aspen wood-derived biocrude. Mean value represented the measured H/C$_{eff}$ of the bulk biocrude from aspen wood. Terminology: *(CP)*, Cyclopentene/pentane derivatives, (OA), Oxygenated aromatics, (HC), Hydrocarbons, (O) Others. Right: Biplot of the PCA model for the compounds identified in the aspen wood-derived biocrude.

A principal component analysis (PCA) was further compiled to investigate if the CPs and the OAs could be further classified based on other parameters than the H/C$_{eff}$ ratio. In Figure 2 the CPs and the OAs are observed to cluster in two distinct areas indicating similar characteristics within the clusters but dissimilar characteristics between the two clusters. Based on the PCA, the CPs generally showed higher hydrogen content and lower oxygen content than the OAs, which corresponded to the H/C$_{eff}$ ratios. Furthermore, it was recognized that the OAs showed mostly higher densities and higher boiling points than the CPs. From an application point of view it is an important fact that the biocrude can be characterized by two main compound groups with distinct properties, as aromatics and cyclo-olefins/paraffins are common constituents of transport fuels. As discussed previously, it is of particular interest to investigate if the distribution of the two primary compound pools (OAs and CPs) can be predicted a priori based on the feedstock composition, and subsequently selectively produced according to a specific end use. Therefore, model compound studies were carried out to investigate the formation of biocrude from the individual model compounds (glucose, xylose, and lignin) along with the characterization of the individual biocrudes.

3.2. Characterization of glucose, xylose and lignin derived biocrudes

The conversion of the individual constituents of lignocelloluse was investigated at alkaline supercritical water conditions. Glucose was selected as an appropriate cellulose model compound, since cellulose readily depolymerises to glucose monomers under the present conditions [23]. Xylose was selected as a hemicellulose model compound, since xylan is generally the main constituent for hardwood hemicellulose [24]. As with cellulose, xylan readily depolymerises to xylose monomers at the given conditions. Alkali lignin (Sigma Aldrich) was chosen as the lignin representative.

Figure 1 shows that lignin produced a significantly amount of biochar, around 50 wt. %, and less biocrude, around 15 wt. %, than is the case of glucose and xylose, which is consistent with previous studies [11, 25]. Although it appears that glucose produces slightly more biocrude than xylose (30.6 vs. 28.2 wt. %, respectively), and slightly less biochar (6.9 vs. 8.6 wt. %, respectively), taking experimental variations into account, the yield distribution (biocrude and biochar) from glucose and xylose are statistically indifferent based on the Student's t-test. Hence, from the present observations it can be objectively concluded that glucose and xylose give similar yields under the investigated conditions. It also appears, that all model compounds produced less biocrude than that obtained from aspen wood, indicating that synergetic reactions must occur enhancing the biocrude formation. Assuming that the yield can be estimated by a weighted sum of the model compounds, the calculated biocrude mass yield of aspen wood should be approximately 26 %, but 42 % is obtained experimentally. Calculated biochar yield of aspen wood is around 16 %, based on model compounds, compared to the 18 % obtained experimentally.

Infrared spectroscopy of the biocrudes was carried out to investigate chemical functionalities. It is important to keep in mind, that such "qualification" is severely hampered by the complex crude mixtures containing plentiful chemical substances. Therefore, results from

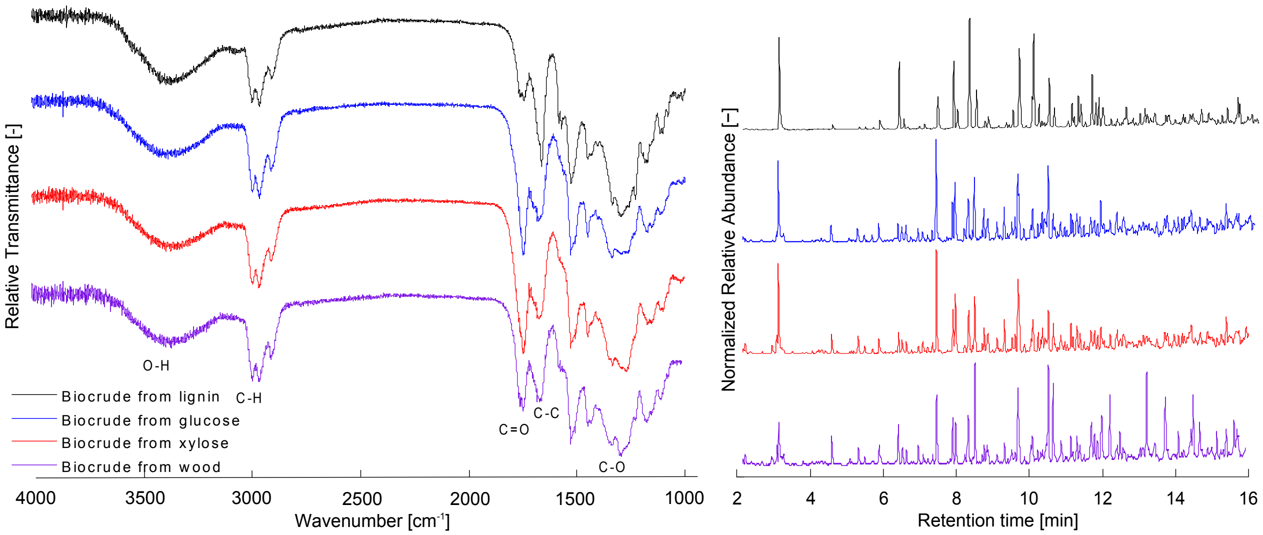

Figure 3: Left: IR spectra of the biocrudes obtained from glucose, xylose, lignin and aspen wood, and Right: Normalized gas chromatography/mass spectroscopy chromatograms.

such analysis may not be conclusive but rather used to qualify similarities/differences and hence distinguish biocrudes obtained from different model compounds and mixtures. In Figure 3 IR spectra from the glucose, xylose, lignin and aspen wood experiments are shown. First of all, it is observed that the four biocrudes display similar IR absorption spectra, which indicates analogous chemical structures. All spectra exhibit pronounced absorptions in the vicinity of 3650-3100 cm^{-1}, typical for the -OH functional group. Unavoidably, this absorption is contributed by residual water that is still bound in the biocrude phase, even though DEE was applied for extraction. Unfortunately, it was not possible to quantify the amount of residual water by *e.g.* Karl Fisher titration due to small sample sizes. As detected by the mass spectrometry of the biocrude obtained from wood, the -OH absorption contribution is most likely to be present due to aromatic -OH stretching as phenolic compounds were detected in all biocrudes. The region between 3000-2800 cm^{-1}, typical for C-H bond absorptions, are observed on all spectra. These absorption contributions are ascribed to the majority of the cycloalkenes/alkane (CPs) and the aromatic structures (OA and HC) represented, but also to a minor extent alkyl groups present. The absorptions between 1780 and 1680 cm^{-1} is attributed to C=O bond stretching and is observed to be more intense for biocrudes obtained from carbohydrates and aspen wood than for the lignin-derived biocrude.

This observation is consistent with the observation of cyclic ketones in the biocrude from carbohydrate containing feedstock, which only presents a minor fraction in the lignin-derived biocrude. The region from 1600-1585 cm^{-1}, together with the band in the vicinity of 1500-1400 cm^{-1} and the strong absorption below 900 cm^{-1} in the fingerprint region indicate in-ring C-C bond stretch, interpreted as substituted aromatics. Not surprisingly due to the inherent aromatic origin, the absorptions in this region are more intense for the lignin-derived biocrude, than for carbohydrates derived biocrudes. But it is noticeable that, by IR interpretation, in terms of aromatic structure, biocrudes obtained from carbohydrates exhibit a similar aromatic structure to that from lignin. In previous studies carbohydrates have only been attributed as a minor source of aromatic structures [26, 27], but present results show a more equalized contribution among the wood constituents. Observed from mass spectrometry, the C=C peaks are interpreted to be contributed by oxygenated aromatics and by ketonic cyclopentene/pentane structures. The broad band at 1400-1100 cm^{-1} is attributed to C-O functionalities such as the alcohols, phenols, ethers, and esters observed in all biocrudes. Based on IR interpretation the aspen wood biocrude exhibits more C=O functionalities than the lignin-derived biocrude, and slightly less than the glucose and xylose derived biocrudes. It was observed that IR spectra of biocrudes obtained from any of mixtures (Mix1-5) show similar properties. In fact, by comparing any of the biocrudes from the three model compounds and mixtures hereof with the aspen wood or real lignocellulosic biomasses from other studies, it is remarkable how similar the biocrudes are in terms of IR spectroscopy [26, 28]. This is further supported by observing the GC-MS spectra of the four biocrudes from the three model compounds and the aspen wood in Figure 3. Although the relative abundances vary for the individual compounds, significant similarities can be identified. It is readily observed that the majority of chemical compounds from both biocrudes are alike, which was also suggested by the IR spectra. In fact, all the compounds identified from the model compound biocrudes were traced in the aspen wood-derived biocrude.

In addition to small organic compounds like propionic acid, propylene glycol and multiple ring compounds, the majority of ether-soluble compounds (>70 %, by GC-area) was found to be CPs and OAs in the C_6-C_9 carbon chain range for the model compound biocrudes,

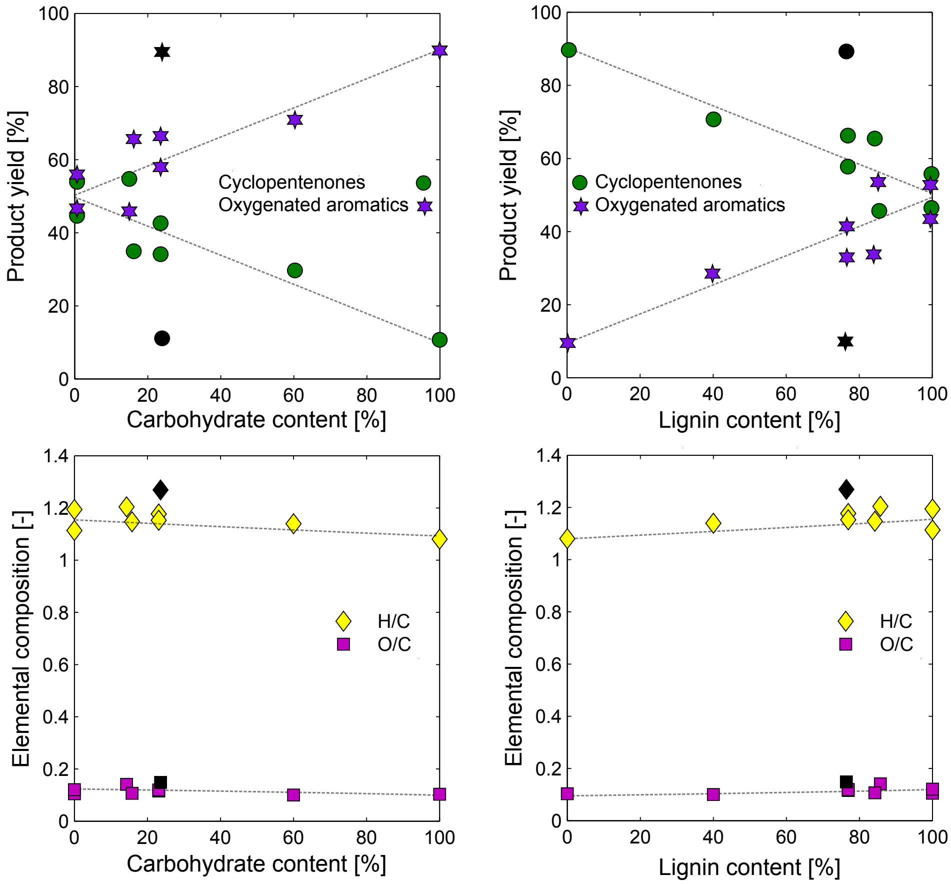

Figure 4: Normalized relative distributions of cyclopentenones (CPs) and oxygenated aromatics (OAs) in the biocrudes, and atomic H/C and O/C ratios as functions of the carbohydrate and lignin content in the model mixtures. Black markers represent the aspen wood-derived biocrude.

similar to the observation of the aspen wood-derived biocrude. In order to investigate the effect of feed composition, *i.e.* the relative amount of glucose, xylose and lignin, on the biocrudes composition, Figure 4 shows the normalised distribution of cyclopentenones (CPs) and oxygenated aromatics (OAs) as a function of carbohydrate and lignin content of the model mixtures. It was found that the relative content of aromatics increases according to the sequence: lignin $>$ xylose $\approx$ glucose. Linear trends were found between of amount of CPs and OAs in the biocrudes to the amount of carbohydrates and lignin in the model mixtures. Diverging from this trend is the aspen wood-derived biocrude. In structural composition, Mix4 mimics the aspen wood but it clearly appears that the wood biocrude displays a more distinct aromatic nature and deviating from the linear trends. This fact identifies a potential challenge when model compound mixtures are compared to real biomasses. A plausible explanation for the observed discrepancy between model compound mixtures and the aspen wood may be found the fundamental chemical differences. The alkali lignin used as lignin model compound was found slightly alkaline, when slurried in water (pH 9 in a 20 % dry matter slurry). Conversely, it was found that when slurrying aspen wood in water, acidic conditions were observed (pH 4 in a 20 % dry matter slurry). The pH has a significant influence on the chemical pathway, where alkaline conditions favour Retro-Aldol reactions, whereas acidic conditions favour dehydration of carbohydrates and hence aromatics formation. Furthermore, from a structural point of view it has previously been found that the type of lignin and the crystallinity of cellulose are influential factors on the product distribution [18, 29, 30]. Further investigation on such factors have to be carried out to conclude if this may influence the compound distribution between real biomass and model mixtures.

Elemental analyses of the biocrudes, presented by atomic H/C and O/C ratios, as a function of carbohydrates and lignin content in the feed are shown in Figure 4. Similarity among the obtained biocrudes was previously revealed from the IR measurements, supported by GC-MS identification of structurally identical compounds and is further manifested by the elemental analyses. Interestingly, it was observed that the atomic ratios of the glucose, xylose and lignin-derived biocrudes were equal, which is in agreement with earlier findings [25, 31]. Hence, the H/C and O/C ratios were found almost invariant to the feed composition represented by the zero slope trends in Figure 4. A common denominator for all experiments was that the oxygen contents of all biocrudes were significantly lower than that of the corresponding starting materials. For glucose and xylose, which are of equal initial H/C and O/C ratios, it was observed that both the H/C and O/C ratios decreased when comparing to the biocrudes, supporting the hypothesis that biocrude compounds were initially formed along a dehydration pathway. The oxygen contents decreased from approximately 53 wt. % to 11.3 (±0.35) and 12.8 (±0.42) wt. % for glucose and xylose, respectively. Alkali lignin was also observed to proceed along a similar trajectory, along which both the H/C and O/C ratios decreased, but less pronounced than observed for glucose and xylose. As opposed to glucose and xylose, lignin did not dehydrate but likely liberated oxygen by decarboxylation and/or decarbonylation. The decrease in H/C ratio may also be explained by loss of methyl- and methoxy-groups or due to the fact that alkali lignin probably contained residual polysaccharides, giving rise to a dehydration pathway which was then superimposed on the actually lignin trajectory.

TGA-simulated distillation was performed to estimate the relative distribution of compounds based on boiling points. According to Duan et al. the method resembles a miniature distillation evaluating the boiling range of biocrude, although it is likely that some degradation at elevated temperatures occur [32]. Hence, the method does not truly yield a true boiling point distribution but enables evaluation of the different biocrudes relatively to each other. Results are presented in Figure 5, which also presents distillation data on commercial fuels and general cuts. Again, it is noted that the biocrudes from glucose and xylose showed identical trends. It was previously mentioned, that the compounds identified in the biocrudes are potential gasoline compounds, showing high octane ratings and good solubility in gasoline [21]. However, from Figure 5 it can be observed that less than 20 % of the total biocrude masses distilled under the boiling point range of marketable gasoline (EN 228). Slightly less than 40 % distilled under the boiling range of diesel (EN 590) and roughly 80 % of the biocrude masses distilled under boiling range of gas oil. Like for the CP/OA distributions, the aspen wood and lignin-derived biocrudes showed comparable TGA curves. Slightly higher than for the glucose and xylose biocrudes, the lignin and aspen wood biocrudes displayed over 60 % of cumulative fractions under the boiling point of common diesel (EN 590). The cumulative fractions under the boiling point of gas oil are comparable to the glucose and xylose derived biocrudes. Figure 5 also illustrates the different volatile compounds identified by GC-MS according to their boiling point reported in Table 3.

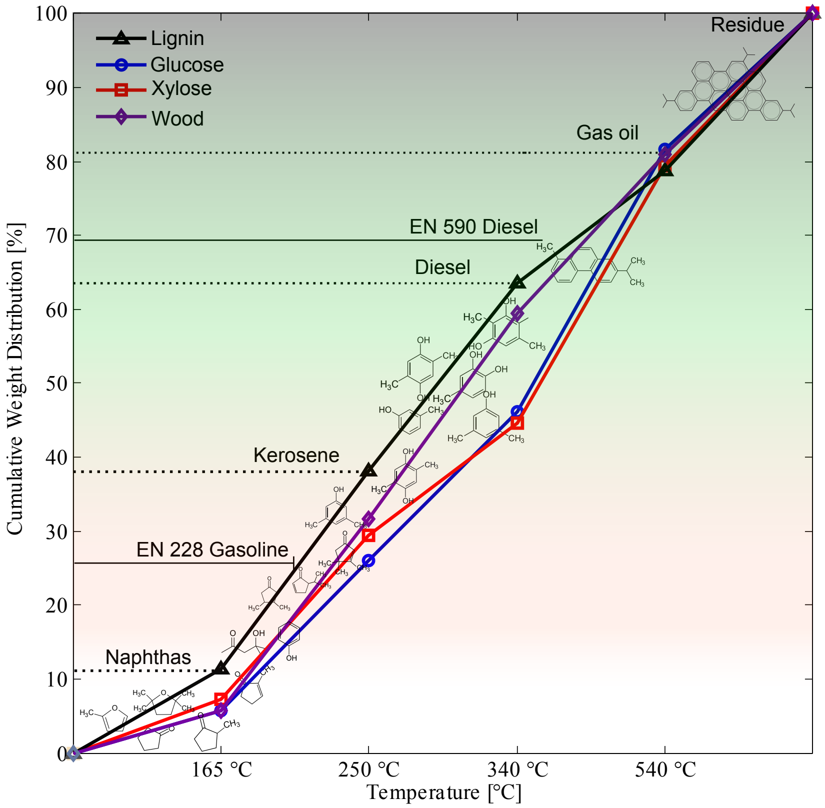

Figure 5: TGA-simulated distillation of the glucose, xylose, lignin and aspen wood-derived biocrudes. True distillation data of commercial fuels and crude oil cuts are included. A pseudo compound is illustrated in the residue temperature range.

The reaction mechanism is complex and consists of multiple chemical reactions. The apparent similarities between the glucose and xylose biocrudes both in terms of yield, composition and the chemical analyses performed, suggest that the chemical mechanism is identical for the two model compounds. This fact significantly reduces the mechanism complexity, and it is hypothesized that all carbohydrates performed equally and that lignocellulose, in general, then can be modeled as only carbohydrates and lignin, without considering the distribution of cellulose and hemicellulose macrostructures.

Carbohydrates are known to degrade along two main pathways in hot-compressed water; dehydration and Retro-Aldol condensation. As previously noticed in other studies, the product compounds observed in the biocrudes, suggest that glucose and xylose follow the dehydration pathway, leading to cyclization of the C_5 (xylose) and C_6 (glucose) structures such as furfural and 5-HMF [4, 19]. At severe conditions furfurals undergo decarbonylation losing oxygen and carbon causing a decrease in carbon chain number, or dehydration leading ultimately to the formation of aromatic compounds (OAs) [33]. Furthermore, the increase in carbon chain numbers to mainly C_5-C_9 compounds then suggests substitution and condensation reactions like Friedel-Crafts, Aldol or Diels-Adler reactions with short chained (C_1-C_4) compounds resulting in ketonization. Retro-Aldol reactions of sugars are known for the production of such short chained compounds and often found the in water phase, mainly in the form of aldehydes, alcohols and ketones, and greatly promoted by high alkalinity [34].

Table 4 shows the time dependent total carbon content (TOC) and the pH of the water phase when processing glucose, which manifests, that acidic compounds were initially formed, most likely alongside dehydration reactions. The pH was observed to decrease drastically from an initially strong alkaline solution to acidic conditions. The pH then slightly increased, indicating consumption of acidic compounds probably through condensation reactions. Carboxylic acids have been observed to form ketones under the given conditions, which explains the pH decrease and observation of ketones in the biocrude. The observation was accompanied by TOC measurements of the water phase. Initially, the TOC decreased explaining the consumption of short chained C_1-C_4 acidic compounds. The pH and TOC were observed to stabilize with increasing reaction time. Hence, it is hypothesized that glucose and xylose degraded into a pool of identical short chained intermediates, which then further recombined and condensed internally or with compounds formed along a dehydration pathway. These reactions, combined with decarboxylation and decarbonylation, are plausible explanations for the increasing carbon chain number and decreasing oxygen content.

From the GC-MS spectra in Figure 3 it is noted that the first distinct peak, identified to be diacetone alcohol, was far more pronounced for the model compound biocrudes than for the aspen wood biocrude. It is hypothesized that diacetone alcohol formed *via* condensation of two acetone molecules; acetone, which was known to form from acetic acid condensation.

Table 4: Time course of pH and total organic carbon (TOC) of the water phase during processing of glucose.

	Initial	1 min.	3 min.	5 min.
pH	11.5	4.01	5.05	5.25
TOC [mg/L]	100	53.3	35.3	37.9

Acetic acid is known to form *via* Retro-Aldol reactions of carbohydrates, including glucose and xylose, catalysed by alkaline and supercritical conditions. Again, it must be also kept in mind that residual polysaccharides are likely to be found it the alkali lignin due to a non-ideal fractionation, which may explain the presence of diacetone alcohol formed from carbohydrates. The formation of cyclopentene and cyclopentane derivatives (CPs) is a more complex mechanism, but it is here proposed that diacetone alcohol cyclization is a plausible reaction for the formation of the cyclopentane backbone. Substitution and condensation reactions, hydrogen-transfer reactions etc. may then assist in increasing the number of carbon atoms of the resulting compounds.

Lignin is believed to degrade primarily through cleavage reactions or by hydrolysis of ether-bonds forming mainly OAs. Decarbonylation or decarboxylation alongside losses of methyl- and methoxy-groups are plausible side reactions explaining the decrease in observed H/C ratio. Despite the fact that the chemical pathway to biocrude compounds varies among lignin and carbohydrates, the elemental composition of the lignin-derived biocrude was found alike to those obtained from glucose and xylose, but far more aromatic in structure. However, based only on bulk properties like elemental composition, heating value etc., one will observe that the properties of biocrudes are practically invariant in terms of the cellulose, hemicellulose and lignin ratios in the feed. On a more molecular level, one will however observe that chemical functionalities of the biocrudes change due its origin; more ketones are formed from glucose and xylose while aromatic compounds like phenols and catechols etc. are formed from lignin.

3.3. Characterization of biocrudes from carbohydrate derived model compounds

It was elucidated that carbohydrates, glucose and xylose, form biocrude compounds through an initial dehydration pathway parallel to Retro-Aldol reactions forming to distinct pools of intermediates. Followed by reductive condensation reactions within or between the intermediates, the carbon chain numbers were observed to increase from the C_5 and C_6 of the initial compounds. To investigate if these pathways were common for other similar compounds, four different polyols; sorbitol (C_6), xylitol (C_5), glycerol (C_3) and ethylene glycol (C_2) were all processed under identical hydrothermal conditions. All compounds yielded equal O/C ratios (O/C=1) but varying H/C ratios. In Figure 1 it is noticed, that all compounds formed an ether-soluble phase (biocrudes) and a biochar phase, indicating that even shorter chained polyols, such as glycerol and ethylene glycol, are prone to condensation, likely through Retro-Aldol reactions. In fact, it was found that cyclic compounds are formed similar to those found in the glucose and xylose experiments, supporting the hypothesis that biocrudes were formed *via* an intermediate pool of short-chained compounds.

Like for the biocrude elemental composition, it was found that yields were correspondingly affected by the elemental composition of the starting materials. It is realized that for the given model compounds the higher the H/C_{eff} ratio the lower the biocrude and biochar yields. However, the chain number may be a latent factor, since the higher the H/C_{eff} the lower the carbon chain number for the investigated model compounds. Interestingly, the biocrudes obtained from the four polyols showed H/C and O/C ratios equal to those from previous experiments. These observations also support the hypothesis, that biocrude compounds from carbohydrates and their derivatives were formed by initial dehydration reactions, followed by condensation/oligomerization reactions increasing the compound carbon chain number and ultimately causing biochar formation.

Based on the number of carbon atoms observed for the compound majority, the compounds obtained suggest gasoline range applications. It was observed that oxygen atoms were mainly positioned in only two oxygen-containing functional groups; ketones (CPs) and alcohols in phenolic compounds (OAs), which deliver valuable information to downstream processes. Important biofuel parameters such as reactivity, solubility in other liquid fuels, combustion properties, vapor pressure etc. are all affected by the compound structures. Naturally, oxygenated functionalities may also cause undesirable properties, *e.g.* increased densities and boiling points, why a subsequent upgrading-processing step, *e.g.* hydrotreatment, may be required to meet hydrocarbon drop-in specifications and enhance fuel related properties such as heating value and volatility etc. Here, hydrogen consumption and equilibria of hydrogenation may vary depending on the compound structures, *e.g.* ketonic and phenolic [24, 35, 36].

As expressed previously, Ω can be used as an indicator for the hydrogen required to convert oxygenates into their corresponding alkanes. Two sample hydrogenation reactions of two compounds commonly found in the biocrudes are shown in Figure 6. By removing the oxygen heteroatom in the ketone and phenolic groups and hence converting them into the corresponding hydrocarbons by hydrodeoxygenation, their properties in terms of heating value and boiling point are greatly altered. It is observed that by removal of the oxygen heteroatom, BTX (Benzene, Toluene and Xylene) equivalents are obtained with significantly higher calorific values and lower boiling points. Secondly, saturation of the compound ring leads to gasoline equivalents with even higher calorific value and lower boiling point.

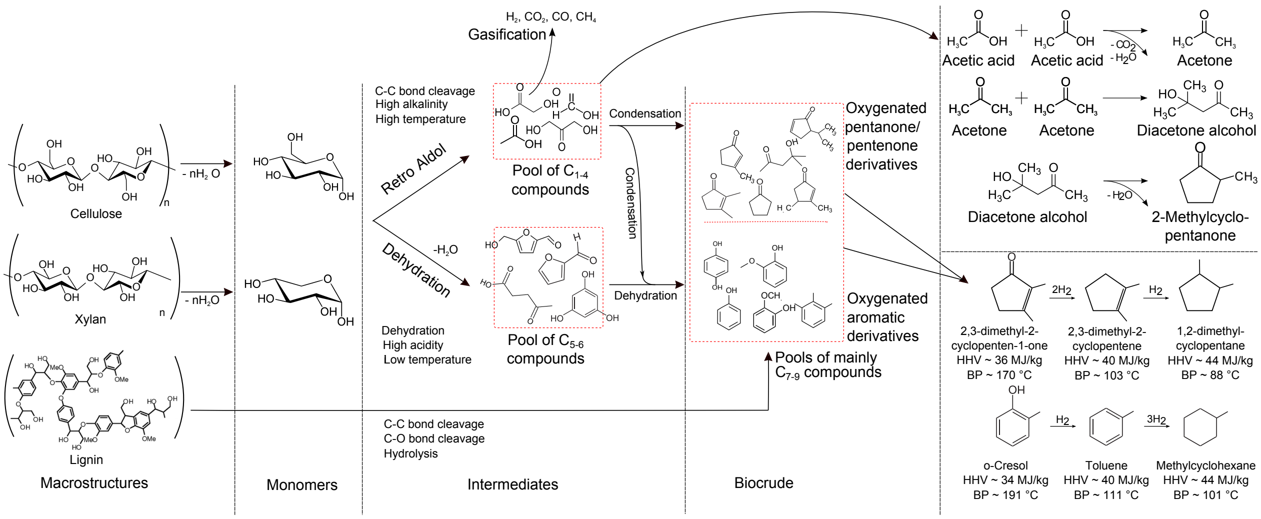

Figure 6: Left: Proposed reaction scheme for the formation of biocrude. Upper right: Proposed reaction for the formation of 2-methylcyclopentanone from acetone. Lower right: Hydrogenation and properties of sample compounds.

In conclusion, the biocrudes obtained are potential sources of sustainable biofuels, of which the properties can be controlled by feedstock composition. However, more work has to be done to understand the lack of predictability between model compounds and real biomasses, and more parametric studies have to be carried out to investigate if the selectivities of cyclopentenones and oxygenated aromatics can be controlled by other process parameters than the feed composition.

4. Conclusions

Compositional effects of lignocellulosic biomass on biocrude formation and characteristics were investigated. The majority of compounds from aspen wood was distributed between two main groups; cyclopentenones and oxygenated aromatics. Based on yields and biocrude characteristics, it was concluded that glucose and xylose underwent identical reaction mechanisms. Elemental compositions of the biocrudes were found almost invariant to the distribution of carbohydrates and lignin. Distribution of cyclopentenones and oxygenated aromatics varied linearly to the carbohydrates and lignin contents. Consistency was displayed when comparing model mixtures, however, aspen wood-derived biocrude displayed an inconsistency, in that the biocrude was more aromatic than expected from its analogous model mixture.

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