Climate Leading Process Industry: Project 4.2.4 Catalytic hydrodeoxygenation of lignin

An open summary report

Authors: RISE/Anneli Sundman, Marie-Louise Wallberg, Tomas Gustafsson, Jonas Markusson, Jonas Fahrni, Ann-Christine Johansson and Martin Hedberg; Chalmers Tekniska Högskola/Derek Creaser, Abdenour Achour and Louise Olsson; Preem AB/Olov Öhrman; Borealis AB/Lars Pettersson and Tuomas Ouni

TABLE OF CONTENTS

1.   Short summary of the report

The sugar platform is one of the more relevant bio-based raw material platforms for the transition from a fossil-based industry to a bio-based counterpart. Saccharification of lignocellulose being the starting point for 2nd generation sugar platform chemistry, generates large volumes of hydrolysis lignin as a residual stream, in particular when lignin-rich forest raw materials are utilized as starting materials. Hydrolysis lignin is so far not well studied and there is potential for new valorization routes. This report comprises the results from a small pre-study where three different upgrading routes; catalytic direct hydrogenation, hydrothermal liquefication, fast pyrolysis followed by co-hydrotreatment, were studied for prima hydrolysis lignin towards applications such as biofuels, base oils, chemicals or as starting materials for steam cracking to simple olefines. The three routes were briefly investigated in laboratory scale and a technoeconomic analysis was subsequently conducted. In brief, direct upgrading of hydrolysis lignin using slurry hydrotreatment was identified as the most promising route based on the investigated conditions, whereas pretreatment of hydrolysis lignin via hydrothermal liquefaction or fast pyrolysis prior to upgrading by slurry hydrotreatment did not have obvious benefits. However, those pretreatment steps, of which some were conducted at laboratory scale which may be different from continuous or full-scale trials, may be important under other conditions, e.g. liquefication can significantly facilitate the feeding to the hydrotreatment which can be advantageous in large scale processes. The obtained results are promising, but also highlight the need for future studies. Two key questions to address in any future efforts are 1) conversion times in the reactors since they comprise the largest contribution to the production costs and reducing these would strengthen the economic viability of the process and 2) liquid co-feeds to be used for co-upgrading with the hydrolysis lignin should be chosen in a way which makes it possible to a) recirculate the product as co-feed repetitively in subsequent rounds of the process and b) fractionate the product by distillation to provide different product components like a synthetic gasoline/naphtha fraction, a diesel/ kerosene boiling point range fraction and a heavier base oil component fraction from the same crude hydrotreatment product being produced in continuous mode of operation for the slurry hydrotreatment.

2.   Introduction

Enzymatic hydrolysis lignin (HL) is a primary byproduct of the enzymatic hydrolysis step from second generation bioethanol production in which HL is produced in massive quantity and considered as a biowaste [1,2]. Due to the activation during enzymatic hydrolysis and mild enzyme catalytic condition, hydrolysis lignin is more active and cleaner (lower ash and sulfur contents) than the lignin materials obtained from other chemical processes [3]. Despite its good quality, hydrolysis lignin is presently used as a low-grade fuel and therefore efficient strategies to convert it into high-quality fuels and value added chemicals are urgently required [3,4]. Compared to kraft lignin, there has been limited research on valorization of the hydrolysis lignin, as its investigation has only started since 2008 and not exceeded 20 published papers. Homogeneous and heterogenous catalytic conversions are in this case considered.

Aqueous alkaline depolymerization of technical hydrolysis was carried out with a 5% NaOH solution at a temperature of 180 °C for 6 hours, the ratio between the hydrolysis lignin and depolymerizing agent being 1:8 [5]. The major compounds identified were phenolics due to low temperature

extraction [5]. Hydrolytic depolymerization of hydrolysis lignin was further investigated in water and water–ethanol co-solvent at 250 °C for 1 h with 20% (w/v) hydrolysis lignin substrate concentration with or without presence of homogenous catalyst (H_2SO_4/NaOH) [6]. In view of the utilization of lignin for the preparation of polyurethane foams/resins, depolymerization of hydrolysis lignin in water–ethanol mixture without catalyst (H_2SO_4/NaOH) appeared as the best route, producing 70.5 wt.% yield (Mw 1000 g/mole) and a suitable aliphatic (227.1 mg KOH/g) and phenolic (215 mg KOH/g) hydroxyl numbers [6]. Another study reported using alkaline at various temperatures to liquify enzymatic hydrolysis lignin [7]. The degree of depolymerization during hydrothermal liquefication was temperature dependent. The yields of 128 monomeric products quantified (GCMS) were up to 15.4 wt % of dry matter [7].

Direct hydrolysis lignin conversion into valuable chemicals has been investigated using a semicontinuous tubular reactor in the presence of a sulfided solid catalyst [8]. In this study, the studied parameters significantly affected the basic product distribution. The highest severity of the reaction conditions has resulted in more deeply upgraded products. Typically, the yield of naphthenes and paraffins have increased at the expense of aromatics and oxygenates [8]. Wang et al [9] used 5 wt.% Ni/AC catalyst to depolymerize biorefinery corncob hydrolysis lignin at 240 °C for 4 h with 30 bar H_2 [9]. Under optimal conditions, it showed high activity towards reductive fragmentation of hydroxycinnamic esters and β-O-4 linkages and produced 31% selectivity towards unsaturated substituents containing coumarate and ferulate derivatives, which afforded mono-aromatic phenols (up to 12.1 wt%) derived from hydroxycinnamic acid moieties (8.1 wt%) and β-O-4 units (2.7 wt%), respectively [9]. In another study, a corncob enzymatic hydrolysis lignin was depolymerized to aromatic compounds over a NiMo/Al alloy catalyst. After reaction, a considerable solid residue was observed, which indicates that the lignin was not fully liquified [10]. The highest overall aromatic of 255.4 mg/g of lignin with 57.9 wt.% alkylphenols were achieved at 320 ºC and 27.6 bar H_2 for 7.5h in supercritical ethanol, suggesting that $Mo_{1.24}Ni_{0.76}$ is an important active species in the reaction [10]. The same hydrolysis lignin from corncob has been used over an unsupported Ni catalyst in supercritical ethanol [11]. A complete liquefaction of lignin was observed with the highest monomer yield of 28.5% at 280 ºC and 20 bar H_2 for 6h over Ni (220H) catalyst [11].

Tymchyshyn et al. [12] used MoRu/AC catalyst to depolymerize hydrolysis lignin in acetone solvent and obtained high yields around 85 wt.% at 340 °C with 50 bar H2 for 1h [12]. The MoRu/AC catalyst produced a bio-oil with a substantially increased H/C ratio, 1.5 times of that in the feed, and <2 wt.% solid residue, suggesting an excellent hydrogenation/hydrodeoxygenation activity of the MoRu/AC compared to Ru/C [12]. Recently, a selective conversion of enzymatic hydrolysis lignin in supercritical ethanol has been performed over a WO_3/γ-Al_2O_3 catalyst at 320 °C and 0 bar N_2 pressure for 8 h [13]. The enzymatic hydrolysis lignin is completely dissolved and converted into aliphatic and aromatic compounds with a total yield of 363.4 mg/g lignin at 320 °C for 8 h. The yield of aromatic compounds is 315.8 mg/g lignin, accounting for 86.9% of the total yield of the products, and the overall selectivity of alkylphenols reaches 67.5% [13]. More recently, direct conversion of hydrolysis lignin into cyclohexane over NiMo/γ-Al_2O_3 catalyst in a single step [14]. Under initial 30 bar hydrogen at 320 °C for 7.5 h, the highest overall cycloalkane yield of 104.4 mg/g enzymatic hydrolysis lignin with 44.4 wt% selectivity of ethyl-cyclohexane was obtained. The H/C ratio and heating value of the

cycloalkane products increased by 51.9% and 97.2%, respectively, compared to those of the enzymatic hydrolysis lignin feedstock [14].

The overall aim of this pre-study project was to investigate different routes for upgrading of hydrolysis lignin, which may contribute to an improvement of the overall economics of the sugar platform. The project is considered to be a starting point for necessary more extensive efforts investigating the potential for converting hydrolysis lignin to hydrocarbon transportation fuel, base oils, chemicals or starting materials for cracking to simple olefins.

2.1. Project Participants

The following partners worked within this project: RISE/Anneli Sundman, Marie-Louise Wallberg, Tomas Gustafsson, Jonas Markusson, Jonas Fahrni, Ann-Christine Johansson, Jimmy Narvesjö, Mirva Niinipuu, Ann-Charlotte Hällgren and Martin Hedberg; Chalmers Tekniska Högskola/Derek Creaser, Abdenour Achour and Louise Olsson; Preem AB/Olov Öhrman; Borealis AB/Lars Pettersson and Tuomas Ouni. The roles of Preem and Borealis were as speaking partners, but Borealis also conducted some simulations. The other partners conducted most of the laboratory work. This work has been coordinated by RISE and project managers Marie-Louise Wallberg and Anneli Sundman.

2.2. Project structure and report outline

The project was divided into four work packages, each with specific goals. Literature studies were combined with laboratory work and simulations.

WP1 – Prior art

WP2 – Upgrading and characterization

WP3 – Applicability of raw and upgraded hydrolysis lignin

WP4 – Summary including technoeconomic evaluation

Results from the above work packages are reported in chapters 3-6, as well as in confidential reports available for the project members only. Subsequently, chapter 7 provides suggestions for future work, while chapters 8 and 9 provide acknowledgments and references respectively.

3. Prior art

Upgrading of hydrolysis lignin is not as well researched as e.g. Kraft lignin. There are a few research articles on the subject, e.g. [15], but several of them rather focus on lignin in general rather than hydrolysis lignin alone. These may be of relevance for how hydrolysis lignin may be treated and the key parameter is the resemblance between the hydrolysis lignin and the lignin in focus. In contrast, there are several patents available on hydrolysis lignin applications. One such example is Patentnr SU198906A1SU1 which describes the possibility of producing low molecular phenols via hydrogenation in an alkaline water solution. Patentnr CN101348558A, 2008 and Patentnr CN1966545A, 2006 provide insight about how epoxiharts may be developed. There are also patents describing how the properties of hydrolysis lignin may be modified, e.g. via alkaline solutions

followed by hydrothermal treatment with subsequent washing and drying to obtain an activated hydrolysis lignin (Patentnr CN103483597A, 2013). Several patents cover optimized processes for production of carbon from hydrolysis lignin utilizing various heat treatments, e.g. pyrolysis (Patentnr SU994548A1, 1980), (Patentnr SU1663009A1, 1988). Finally, production of liquid and gas from hydrolysis lignin utilizing subcritical conditions, i.e. 250-350°C in various solvents like methanol, ethanol or butanol in the presence of a catalysator is described in (Patentnr RU2409539C1, 2009).

4.   Upgrading and characterization of hydrolysis lignin

The hydrolysis lignin samples used in this study were kindly provided by SEKAB. Proximate and ultimate analysis of the hydrolysis lignin can be found in Table 1. The oxygen content was calculated by difference based on the three analyzed elements. The calculated oxygen content of the starting material, hydrolysis lignin, was 37% which is significantly higher than in *e g* kraft lignin, which typically have oxygen contents around 25%. The nitrogen content was relatively low. Trace element contents were also analyzed, confirming that the alkali metal and silicon contents are quite low, which is positive. The sulfur, present at levels around 1900 ppm, contributes positively to maintaining the activity of the sulfided metal catalysts used during catalytic hydrodeoxygenation with necessary sulfur to avoid sulfur depletion (see below). Consequently, the high sulfur content is considered to be an asset rather than a problem in relation to the chosen upgrading strategy.

Table 1. Proximate and ultimate analysis of hydrolysis lignin.

	Unit	Hydrolysis
Proximate		
Moisture	wt%	43.2
Ash (525°C)	wt%	0.12
Volatiles	wt%, db	75
Ultimate		
C	wt %, db	56.5
H	wt %, db	6.4
N	wt %, db	0.38
S	wt %, db	0.18
O	wt %, db	36.5
Major ash		
Si	mg kg^{-1}, db	19
Al	mg kg^{-1}, db	9
Ca	mg kg^{-1}, db	250
Cu	mg kg^{-1}, db	100
Fe	mg kg^{-1}, db	17
K	mg kg^{-1}, db	110
Mg	mg kg^{-1}, db	30
Mn	mg kg^{-1}, db	24
Na	mg kg^{-1}, db	40
P	mg kg^{-1}, db	30
Ti	mg kg^{-1}, db	0.7
Zn	mg kg^{-1}, db	8

4.1.   Direct catalytic hydrogenation

Direct catalytic hydrogenation is a technique where hydrogen and catalysts are used to convert oxygenated macromolecules (e.g., lignin, see Figure 1) into high-quality fuels and value added chemicals. In this study, performed at Chemical Engineering, Chalmers, the hydrogenation of two types of lignin using metal-based catalysts was investigated with the aim to obtain upgradeable bio-oil products in conventional refinery processes.

4.1.1.   Method

The hydro-conversion of Kraft and hydrolysis lignin was carried out in a closed batch stainless-steel Parr reactor (Process setup, Figure 1). In a typical experiment, the reactor was loaded with a slurry composed of lignin, and catalyst in a solvent (hexadecane) as a co-processing. Thereafter, the reactor was pressurized and heated up to a designated temperature while stirring. The effect of reaction parameters, including temperatures, pressures, residence time, and catalyst/lignin ratios, were investigated. After each experiment, different fractions of lignin products were recovered and analyzed. The typical products are gas, liquid bio-oil, unconverted lignin and bio-char (see Products, Figure 1. These products were analyzed using various analytical techniques such as elemental analysis (CHONS), Nuclear Magnetic Resonance (NMR), Gas Chromatography TCD (GC-TCD), two-dimensional Gas Chromatography (GC×GC-MS/FID) and Karl Fischer (KF). The structural and surface characterization of the catalysts were also performed using other techniques.
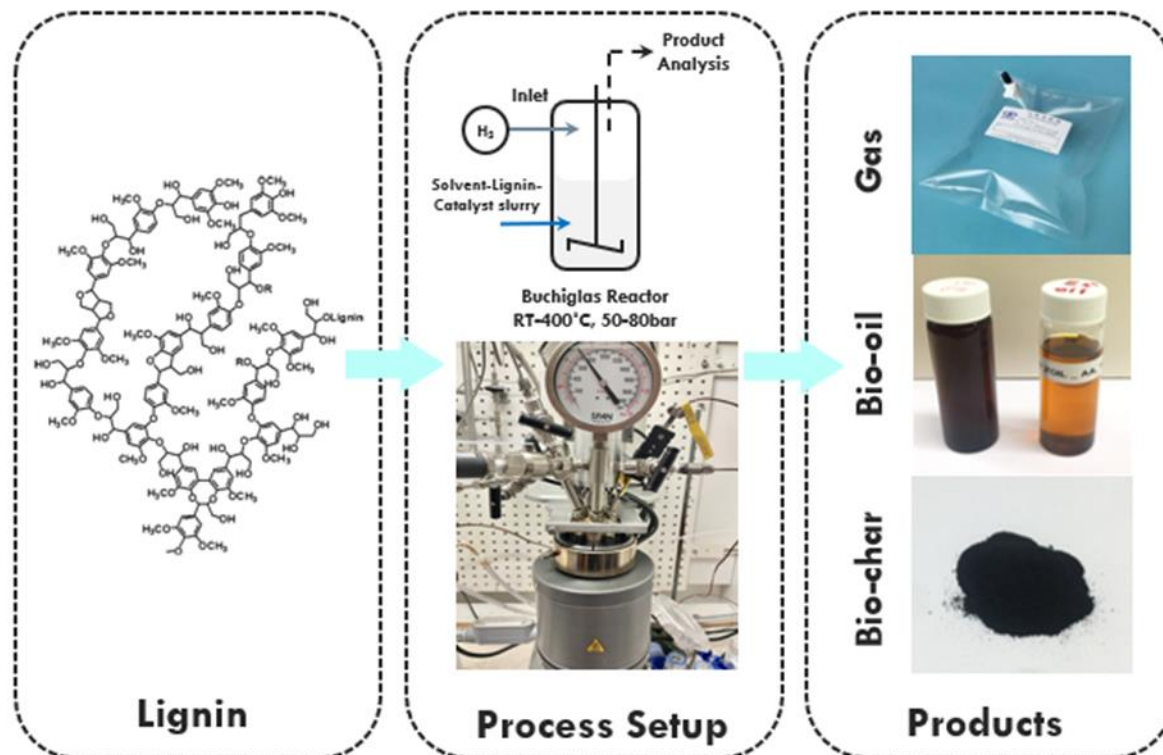

Figure 1. Guidelines for performing lignin-direct catalytic hydrogenation to biorefining process.

4.1.2.   Results and discussion

In this study, we studied both feedstocks, hydrolysis lignin (provided by SEKAB) and Kraft lignin (Sigma-Aldrich) from the waste liquors produced during the pulping process. Measurements were

performed to compare both raw lignin materials, such as elemental analysis, thermogravimetric analysis, and chemical structure. The results in this study showed that the hydrolysis lignin displayed lower ash and sulfur contents than the Kraft lignin. However, the oxygen content of hydrolysis lignin is higher due to presence of cellulosic units. These differences may be due to the influence of the lignin-type and their extraction chemical process (enzymatic vs. physical isolation) and can thereby influence the products yields and selectivity.

Under identical operating conditions in the reactor, hydrolysis lignin displays the highest bio-oil product and lowest char formation relatively to Kraft lignin. This implies that one of the keys factors to improve the product yields and selectivity is the chemical structure of the lignin-type. These results provide a clear trend in the context of improving the extent of deoxygenation with higher carbon recovery in the biooil product, despite the fact that higher initial oxygen content was found in the hydrolysis lignin feedstock. Thus, both lignin-types and the reaction conditions influenced the quantity and quality of the bio-oil obtained. Moreover, the bio-oil from the hydrolysis lignin showed lower oxygen content, which would facilitate the upgrading. Furthermore, the presence of hydrogen and catalyst resulted in a reduction of the sulfur content in the lignin-oils (<0.02 wt.%), showing the efficiency of the catalyst in hydrodesulfurization (HDS) reaction.

The quantity of monomers (aromatics/naphthenes, phenolics, alkanes/cycloalkanes, ketones, alcohols) in the lignin-oils is of high interest to indicate the target product classes in this study. Therefore, all lignin-oils were subjected to GCxGC analysis to determine these monomers. A higher bio-oil yield (> 80 wt.%), containing > 50 wt.% of monomers, was obtained for hydrolysis lignin at 400 ºC, 80 bar of hydrogen, during 5 h reaction using 10 wt.% of catalyst loading. This significant result was accompanied with a low amount of char (< 10 wt.%). In comparison with Kraft lignin-oil at identical conditions, the total oil yield was higher than 60 wt.% with monomer yield between 40-47 wt.%. It is noteworthy to mention that the solid char could be further reduced by adjusting the hydrogen pressure, residence time and/or catalyst concentration (5 to 10 wt.%), leading to significantly increase in the amount of lignin-oil and monomers yields. Increasing the catalyst concentration would increase the turnover and therefore, probably reduce the residence time. In addition, an evaluation of the volatility of the produced lignin-oil showed that the hydrolysis lignin oil contained products that are less thermally stable, which started to decompose in the range 110-205°C. However, higher temperatures are required to completely volatize the produced Kraft lignin oil. A journal paper will be submitted during the year based on these results.

4.2. Hydrothermal liquefaction of hydrolysis lignin

Hydrothermal liquefaction (HTL) is a technique where high temperature and pressure is utilized to convert biomass into a mostly liquid state. A number of demo and pilot plants exist, e.g. at Aalborg University in Denmark, in Tofte in Norway and Licella's plant in Australia. Target products comprise e.g. fuels, aromatic chemicals and resins.

4.2.1. Method

HTL bio-oil was produced in an HTL reactor. A suspension comprising 10% hydrolysis lignin, 10% tall oil pitch, a residue from distillation of tall oil for biodiesel production, and 80% water was produced. The tall oil pitch, is a low value component containing rosin acids, fatty acids, sitosterols and esters, and likely some undefined polymerized material. The tall oil pitch was added to increase the oil phase of the reaction since this may support the oil production. Furthermore, it leads to a clearer

spontaneous phase separation after the reaction. The reaction was run at 300 °C and 120 bar. The reaction duration was set to 13 min and excluded the 5 min heating time and 3 min cooling time.

The crude product from the reactor was cooled down from 70 °C to room temperature. Then the suspension was homogenized via dispersing with a T25 ULTRA-TURRAX before being filtered over a pressure filter at 5 bar (Filterpaper 22 μm pore size). The filter cake was split to two compositionally similar parts. Half of the filter cake formed the sample *Char & oil blend* where the oil and the char fractions were blended. The other half of the filter cake was suspended in 2-Methyl-Tetrahydrofuran to separate the oil and char fractions. The suspension was stirred and sonicated, then filtered. The filter cake was dried at 80 °C to form the *Char* sample and the filtrate, i.e. oil, was concentrated via evaporation (40 °C, 30 mbar, 1 h). Solid material was formed in this concentrated oil fraction. Hence, the precipitated solids formed the sample *Solid* and the soluble part of the oil formed the sample *Liquid*. The workup process is illustrated in Figure 2 below.
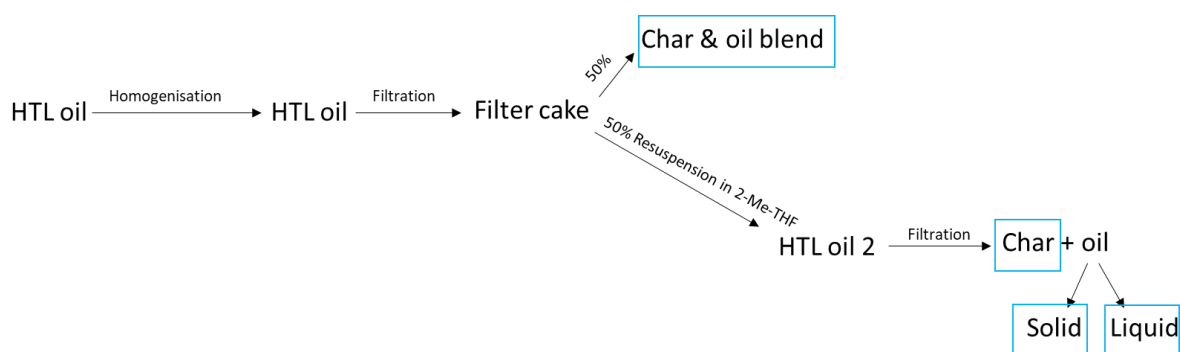

Figure 2. Work-up process for the different fractions of the HTL-oil. The four collected samples are shown in blue boxes.

The starting materials and products were analyzed with respect to elemental composition for carbon, hydrogen and nitrogen. Oxygen was assumed to be the remaining fraction. Where possible, water content was determined via Karl-Fischer titration. Energy values were calculated by using formula (1) below without taking the Ash term in consideration [16]. The energy contents of oils were measured using a bomb calorimeter. When water values were available, the raw elemental values were divided by the dry matter content (DMC) of the sample.

$$E = 0.3491*C + 1.17383*H - 0.1005*O - 0.0151*N - 0.0211*Ash \quad (1)$$

4.2.2. Results and discussion

In total, four different samples resulted from the produced HTL bio-oil. They comprised of one blended char and oil sample and three samples resulting from the separation of the char fraction from the oil fraction of the HTL oil. Please revisit Figure 2 above for more details. The elemental compositions of these phases are presented in Table 2.

Table 2. Analytical results of each starting material and isolated fractions. Energy values "E*" were determined by equation (1) [11]. Energy values "E+" were determined by bomb-calorimeter.

Fraction	O/C	H/C	C / %	E* / MJ·kg⁻¹	E+ / MJ·kg⁻¹	H₂O / %
Starting materials						
H-Lignin	0,70	0,11	55,1	22,6		N/A
Tall oil	0,42	0,10	65,8	27,8	40,3	2,5
Isolated fractions						
Char	0,28	0,09	72,5	30,8		N/A
Liquid (oil)	0,61	0,08	59,2	22,6	38,8	3,3
Solid (oil)	0,23	0,12	73,9	34,1		N/A
Oil Char blend	0,32	0,13	68,7	32,2	32,8	

In line with previous studies, the HTL-oils exhibit higher oxygen content than their fossil crude oil counterparts as well as compared to diesel or biodiesel [17, 18]. However, compared to the more technically mature pyrolysis process, the HTL resulted in oils containing less oxygen and having characteristics more in common with fossil crude oil than pyrolysis oils. HTL oils should therefore be easier to upgrade in refineries which today are adapted to fossil crude oil [19]. Hydrodeoxygenation is one route of upgrading the HTL oils and making them more suitable for e.g. transportation fuel applications since this reduces the oxygen content as well as the molecular weight [17].

Based on mass, 24% of the product ended up in the char fraction and 64 % ended up in the oil fraction. The corresponding numbers based on carbon yield are 29% and 62-78%, respectively. The liquid oil was further analyzed via ^{1}H-NMR. In brief, the solid precipitate from the fractionated biooil contains most of the aromatics originating from the lignin and is also enriched regarding aliphatic ethers and alcohols. The liquid contained less carboxylic acid, less aldehydes, less aliphatic esters or alcohols, but more aliphatic H compared with the solid phase. Based on ^{31}P-NMR spectroscopy following hydroxyl group derivatization, it was concluded that the depolymerized lignin is mostly found in the solid HTL-oil as indicated by the higher overall oxygen content and the significantly higher content of aliphatic alcohols and phenols. Average molecular weight based on gel permeation chromatography was 696 g mol⁻¹ for the liquid biooil and 766 g mol⁻¹ for the solid precipitate of the biooil. Depolymerization occurred but was not complete and the overall molecular weight distribution was still much too large for the molecules in the mixture to be of any significant use as starting materials replacing current small molecule bulk and fine chemicals. Hence, as expected, HTL alone is not sufficient for production of starting materials for small molecule bulk or fine chemicals. Further process steps are required, but HTL lowers the oxygen content and thereby reduces hydrogen consumption in subsequent steps and it transforms the solid hydrolysis lignin into a pumpable form, which may be a requirement for future integration in current refinery infrastructure.

4.3. Fast pyrolysis of hydrolysis lignin

Fast pyrolysis is a thermochemical process where biomass is thermally decomposed in the absence of oxygen into primarily a liquid, pyrolysis oil, but also non-condensable gas and solid residue. The oil can be used as renewable heating oil replacing petroleum oils and gas, upgraded to produce drop-in fuels, recovery of sugar-derived components as platform chemicals and use of pyrolytic lignin as a phenol replacement in resins. Fast pyrolysis is proven at commercial scale and worldwide capacity is expanding. In Sweden Pyrocell recently announced that they have commissioned Sweden's first production unit and also started their production [20].

4.3.1. Method

A bench scale set up based on a drop tube furnace was used for the continuous fast pyrolysis experiment. The experimental setup is presented schematically in Figure 3. Dried, 100%, hydrolysis lignin was continuously added (1 g/min) together with nitrogen gas to the pyrolysis reactor in a drop tube furnace. In the reactor pyrolysis of the lignin was carried out at atmospheric pressures at 500°C. After the reactor the solid residue was separated and the pyrolysis vapors were further condensed in two steps. Cold nitrogen was added to the pyrolysis vapors in the first step which decreased the temperature to ~100°C. In the second cooling step, the liquid products were collected by passing the gas flow through glass bottles which were immersed in a glycerol cooling bath at -15°C. The last bottle was equipped with a glass filter to collect formed aerosols. The temperature of the gas leaving the cooling bath was about 10 °C. After passing through a glass wool filter the non-condensable gas were continuously analyzed for CO, CO_2, H_2, N_2, O_2, CH_4 and C_2H_4 using a Varian 490 micro gas chromatograph equipped with a flame ionization detector (FID) and water and formaldehyde using a FTIR Multigas HS 2030. In addition, every 30 minutes, the gas products were collected in gas sampling bags for analysis of higher hydrocarbons and alcohols using a Varian CP-3800 gas chromatograph equipped with a FID. The product yields were determined gravimetrically, i.e. by weighing the starting material as well as the products, together with the produced non-condensable gas. The pyrolysis oil was analyzed by means of water via Karl Fischer and volatile compounds via gas chromatography on a Shimadzu GCMS QP2010.
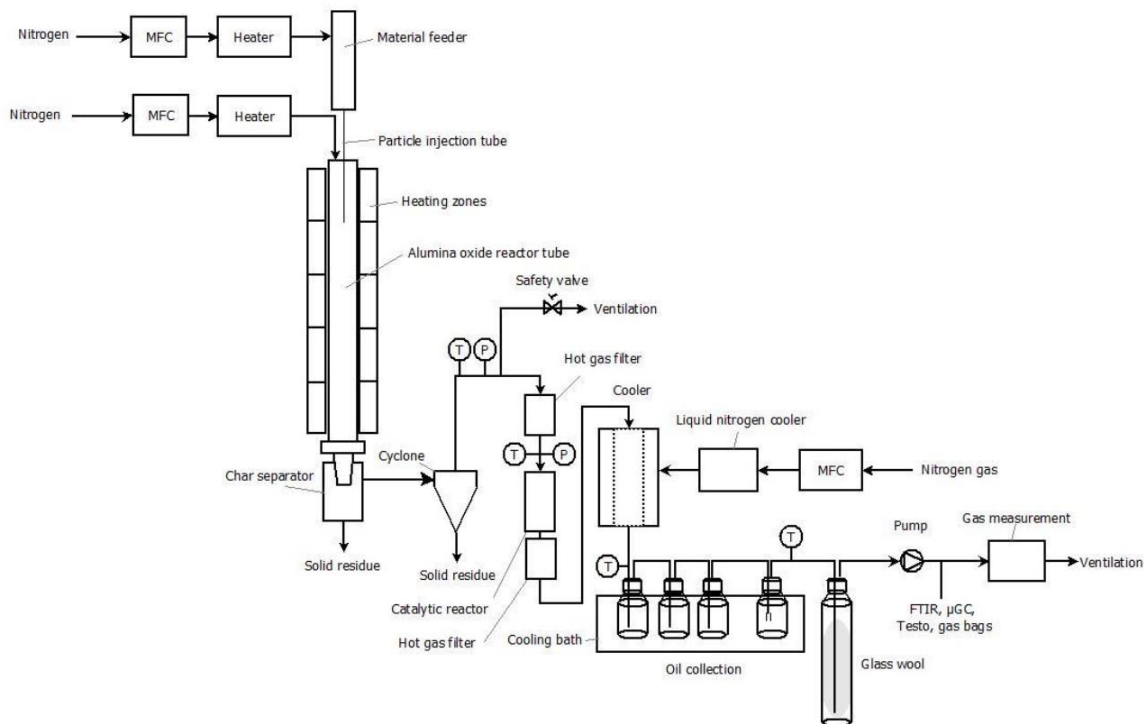
Figure 3. Schematic experimental set up of the pyro drop tube furnace.

4.3.2.　Results and discussion

Hydrolysis lignin was successfully pyrolyzed in the bench scale system for two hours. The hydrolysis lignin powder was fed smoothly without interruptions and this resulted in quite even gas concentrations over time, see Figure 4. The main components in the non-condensable pyrolysis gas were CO_2, CO, H_2, CH_4 and traces of C2, C3, methanol and formaldehyde.
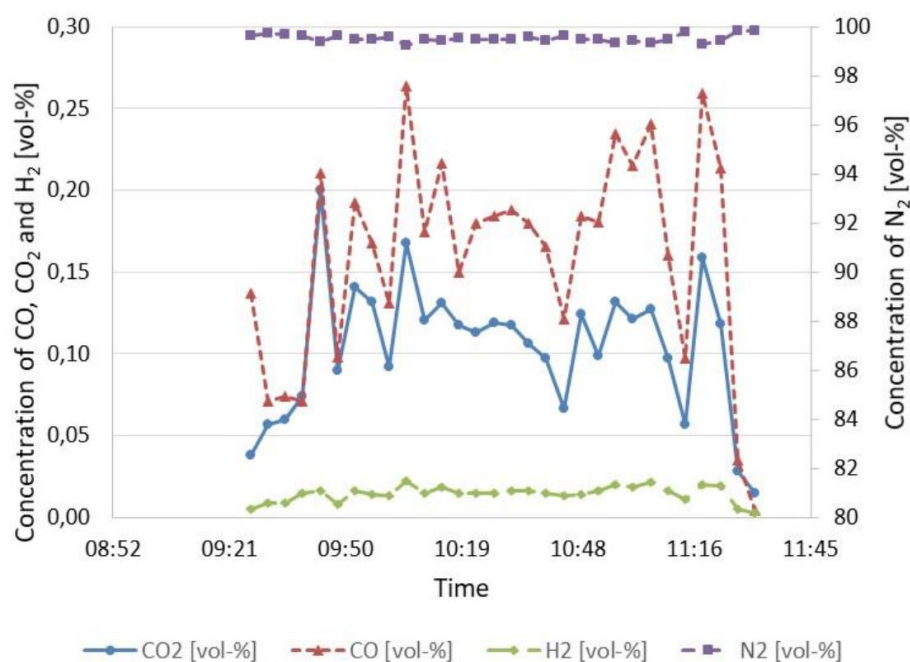
Figure 4. Main gas concentrations, CO_2, CO, H_2 and N_2, measured on the microGC during the pyrolysis experiment. Note the different scales.

The mass balance for the pyrolysis of hydrolysis lignin can be found in Figure 5. The pyrolysis oil was phase separated into an oily fraction and an aqueous fraction. The liquid yield was around 47 wt.%, of which 37 wt.% corresponds to the oily fraction and the rest, 10 wt.%, corresponds to the aqueous fraction. Expressed in organic liquid the yield was 42 wt.%, which corresponds to organic liquid without water. Approximately 29 wt.% was collected as solid residue and 19 wt% as gas. These numbers are in good agreements with the literature, for example in Pienihäkkinen et al. 2021 ([15]) hydrolysis lignin was pyrolyzed with an organic liquid yield varying between 32-51 wt.%, solid residue between 24-43 wt.% and gas yield from 5-21 wt.%

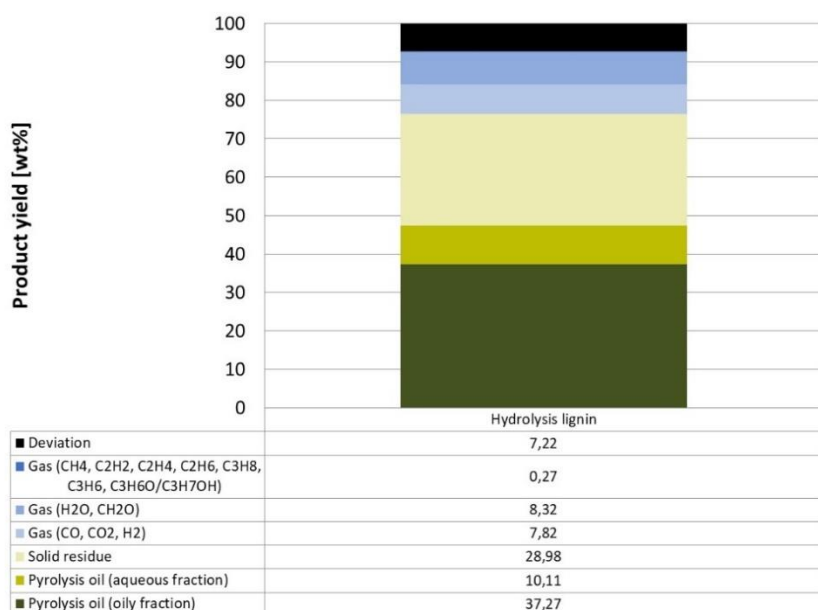|	Hydrolysis lignin
■ Deviation	7,22
■ Gas (CH4, C2H2, C2H4, C2H6, C3H8, C3H6, C3H6O/C3H7OH)	0,27
■ Gas (H2O, CH2O)	8,32
■ Gas (CO, CO2, H2)	7,82
Solid residue	28,98
■ Pyrolysis oil (aqueous fraction)	10,11
■ Pyrolysis oil (oily fraction)	37,27

Figure 5. Mass balance for the fast pyrolysis experiment conducted with hydrolysis lignin.

GC-MS analysis of the organic and aqueous fractions of the pyrolysis oil showed high amounts of sugars and lignin monomers. Levoglucosane was the main sugar component and highly abundant in both organic and aqueous fractions. This is an expected results from an experiment where pyrolysis has been conducted on a lignocellulosic material. Phenols and guaiacols were detected especially in the organic fraction.

^{1}H NMR of the pyrolysis oil showed high concentrations of aromatics, olefin and oxygenates. The overall composition was very different from that of HTL oil, e.g. the aliphatic:aromatic ratio was 71:29 for the pyrolysis oil and 97,3:2,7 for the liquid biooil sample. From the ^{31}P-NMR analysis, it was clear that the pyrolysis oil was completely dominated by aliphatic alcohols and phenols. The average molecular weight was 319 g mol^{-1} and it was concluded that pyrolysis is efficient in depolymerizing hydrolysis lignin. The resulting molecules have relevant sizes for chemical industry applications, though one challenge is the complexity of the mixture.

4.4.   Hydrodeoxygenation of hydrolysis lignin

Hydrodeoxygenation (HDO) is a process conducted at elevated temperature and pressure where hydrogen reacts with oxygen, in the sample, in the presence of a catalyst and forms water. Rejection of the oxygenated compound results in the formation of a saturated carbon-carbon bond. Different types of catalysts exist, e.g. molybdenum, cobalt and nickel-based ones. HDO is described as a promising route to remove oxygen from various streams. The technology has been used within the petrochemical refineries since several years, but has more recently been applied to streams based on biomass, e.g. pyrolysis oils produced from lignocellulosic material.

4.4.1. Method

Upgrading of the hydrolysis lignin via hydrotreatment was conducted with two different co-feeds: a light fossil co-feed from the oil industry and a much heavier one with a considerably higher boiling point range. Experiments were conducted for all three upgrading routes (direct slurry upgrading, co-feeding of pyrolysis oil from hydrolysis lignin and co-feeding of HTL-oil from hydrolysis lignin). The hydrodeoxygenation step was performed in a high temperature and high-pressure Büchi batch reactor. In a typical experiment, the lignin component (10% w/w) was mixed with either light fossil co-feed or heavier fossil co-feed (90% w/w), (pre-) catalyst in the form of molybdenum ethylhexanoate and dimethyl disulfide were added to the reactor. A hydrogen atmosphere was established at room temperature before increasing the pressure to 105-121 bar. The hydrodeoxygenation was then performed at a reaction temperature of 340-425 °C. After reaction, the reaction mixture was decanted from the reactor into a 50 mL Falcon tube and centrifuged at 4000 rpm for 15 minutes. The product was decanted, and the solid residue and reactor were rinsed with 50 mL of pentane followed by rinsing with 50 mL tetrahydrofuran (THF) to dissolve any unconverted more polar components. The hydrodeoxygenated products were analyzed using ^{1}H-NMR and ^{31}P-NMR (hydroxyl number determination). Furthermore, the hydrodeoxygenation products were analyzed via thermogravimetric analysis to determine their boiling point ranges (TGA-Simdist). For selected samples, the content of aromatic hydrocarbons was characterized using High Pressure Liquid chromatography with refractive index detection (LC-RI). The latter analysis quantifies amounts (w/w) of mono-, di-, tri- and polyaromatic hydrocarbons in the hydrodeoxygenated product mixtures.

4.4.2. Results and discussion

Upgrading of hydrolysis lignin, HTL oil and pyrolysis oil using naphtha as a co-feed, resulted in moderate to good yields of liquid hydrocarbon product. The hydrodeoxygenation experiments with the light co-feed gave low yields due to the partial decomposition of the light co-feed into gaseous components under all reaction conditions investigated. Oxygen contents were low in all liquid hydrocarbon products obtained. A higher amount of coke was observed for the direct hydrotreatment of hydrolysis lignin in light and heavy co-feeds. As for the heavier co-feed upgraded samples, the yields were higher, 80-85%. However, all samples contained oxygen (0,08-1,5%) as well as coke (1-2.6%). To summarize, the results showed that using light co-feeds in terms of boiling point ranges, was not beneficial whereas heavy co-feed co-upgrading gives a better yield and better overall quality of the liquid hydrocarbon mixture. Future work should focus on using liquid co-feeds as starting oils, where experiments are then made to evaluate recirculation of parts of the liquid product as co-feed in the next round of reactions in a repetitive fashion, rapidly reaching a point where just new lignin is added making the product fully renewable.

^{1}H-NMR-spectra did not show any presence of oxygenates, e.g. aliphatic alcohols and/or ethers or phenols, or olefins. Furthermore, ^{31}P-NMR-data showed that there are no significant levels of aliphatic alcohols or carboxylic acids in the products, which also have a low phenol content. Hence, the hydrodeoxygenation of the various hydrolysis lignin fractions were successful.

Analysis of the amount of mono-, di and tri/polyaromatic hydrocarbons revealed that overall, the products consist mostly of aliphatic hydrocarbons with a higher aromatics-content for the experiments to which hydrolysis lignin or thermochemically treated hydrolysis lignin has been added. The only product mixtures which contain significant amounts of remaining phenols as a result of non-complete hydrodeoxygenation is the product of hydrodeoxygenated hydrolysis lignin in heavier co-

feed. According to LC-RI-data aliphatic hydrocarbons dominates in the products, especially where naphtha was utilized as co-feed. There is however some increase in monoaromatics content resulting from lignin, HTL- or pyrolysis oil addition to the starting mixture for hydrotreatment in the case of using the lighter co-feed. As for the heavier co-feed, the aromatics content appears almost unaffected by lignin, HTL or pyrolysis oil additions.

Table 3. Selected NMR data for the hydrodeoxygenation products.

Lignin component	Fossil co-feed	OH (mmol/g)	Aliphatic vs Aromatic-H
Starting material			
Lighter co-feed	_	_	98 : 2
Heavier co-feed	-	-	97:3
Products			
Hydrolysis lignin	Lighter	0,129	97 : 3
HTL-oil	Lighter	0	98 : 2
Pyrolysis oil	Lighter	0,114	97 : 3
Hydrolysis lignin	Heavier	0,92	96 : 4
HTL-oil	Heavier	0,053	96 : 4
Pyrolysis oil	Heavier	0,068	96 : 4

All TGA-Simdist curves for samples containing hydrolysis lignin indicate that those products contain significantly higher amounts of heavier more high-boiling components. Interestingly, the product boiling point curve for the direct slurry hydrotreatment of hydrolysis lignin in the lighter co-feed provides a product profile more in line with the co-feed itself with larger heavy residues for the HTL and pyrolysis oil products, which display higher boiling point curves already from 80% weight loss and onwards.

Corresponding TGA Simdist curves for samples using the heavier co-feed suggest that the hydrotreated products are very similar to the hydrotreated heavier co-feed itself. The physicochemical properties of the pyrolysis and HTL bio-oils make them immiscible with the hydrocarbon co-feeds used in this study and the overall process is therefore the same for the bio-oils as for the solid particle slurry obtained when using the untreated hydrolysis lignin as starting material. The currently used slurry catalyst does not display any clear signs of deactivation during the reactions. Further work is however needed to characterize the degree of catalyst inhibition occurring for the different raw materials.

5. Applicability of upgraded hydrolysis lignin

This small project has shown that hydrolysis lignin can serve as a source of renewable carbon for producing relevant hydrocarbon mixtures in slurry hydrotreatment processes, giving lower amounts of less useful byproducts like coke than the structurally different kraft lignin. Provided that investments are made in adapted multiphase slurry hydrotreatment equipment, a type of upgrading equipment which is today not existing in oil refineries in Sweden but is available elsewhere [21-23], it may in the future be possible to use hydrolysis lignin and other types of lignin for the production of hydrocarbon mixtures which can be integrated as starting materials in already existing oil refinery infrastructure, producing renewable alternatives to basic transport fuels, chemicals, solvents and base oils produced today in very large volumes.

Fossil naphtha used today for steam cracking to olefins like ethylene, propene etc, is a side product from the oil refinery obtained by distillation of crude oil and further treatment steps like desulfurization to remove sulfur. On a molecular level, naphtha is a mixture of mainly saturated substituted acyclic and monocyclic hydrocarbons having between four to eleven carbon atoms. This means that the carbon chains and rings of naphtha correspond well to the length and structure of the carbon chains found in the native lignin structure (nine carbon chains dominate the lignin structure e.g. coniferyl and sinapyl alcohol lignin monomers [24, 25]). In particular kraft lignin but to some extent also hydrolysis lignin however deviates structurally from native lignin in the plant or tree and have longer carbon chains and condensed ring structures, which form during the Kraft process and the saccharification of lignocellulose respectively. This likely explains the small but significant increased content of heavier molecules observed in the product when adding lignins to for instance vacuum gas oil (VGO) before hydrotreatment.

The results obtained in this project confirm that hydrolysis lignin is likely not suitable for producing only naphtha range hydrocarbons alone but is instead useful for co-upgrading with heavier feedstocks, producing a mixture of hydrocarbons from which naphtha-like hydrocarbon mixtures can be distilled off as a separate lower-boiling fraction. Heavier fractions like diesel-range and base oil-range (lubricants, extender oils, transformer oils and other industrially used heavier oil components) fractions are also obtained and can be separated from the relatively small amounts of non-volatile residue present. Hydrocracking would further increase the fraction of lighter hydrocarbons. Sustainable Air Fuel could be one interesting product A small but significant effect of lignin-addition on the hydrotreatment co-upgrading product is observed, causing slightly different proportions between paraffins, iso-paraffins, olefins, naphthenes and aromatics compared with upgrading pure fossil feedstocks.

Future work will need to focus on decreasing the use of fossil liquid co-feeds e.g. by instead using heavier parts of the slurry hydrotreatment product repetitively as co-feed in subsequent slurry hydrotreatment reactions repetitively, in the presence of the same recycled catalyst portion just adding more lignin component for every round. If applied, the latter would rapidly lead to a 100% renewable product for refinery integration. This kind of process, which is conceptually similar to the Bergius process for lignite (brown coal) liquefaction [26], may constitute an interesting option for scale up to full production scale where lignin is one carbon source contributing to the production of crude hydrocarbons which can be used as renewable analogues of already established petrochemical starting materials and thereby products in the future.

6. Technoeconomic evaluation of upgrading routes for hydrolysis lignin

A rough estimation of the techno-economic performance of the investigated processes for converting hydrolysis lignin into a renewable oil was conducted for the three upgrading routes described in chapter 4. Hydrodeoxygenation was part of all three routes and conducted in a slurry hydro cracker (SHC). The three routes comprised: a) pyrolysis + SHC, b) HTL + SHC and c) SHC. The evaluation was based on mass and energy efficiency, a rough production cost estimation (capital expenditure (CAPEX) + operating expenditure (OPEX)), as well as a rough estimation of environmental performance. Hence, these estimations should be seen as relative numbers, rather than absolute quantitative numbers. Some of the key input data are summarized in Table 4 below. The overall aim was to make an initial comparison of the different processes for converting hydrolysis lignin into renewable oil product.

Table 4. Input data utilized in the technoeconomic evaluation.

Item	Cost in SEK/MWh or carbon footprint in CO_2 eq/MJ[1]
Hydrolysis lignin	510
H_2 via electrolysis	750
H_2 via natural gas via steam methane reforming	420
Carbon footprints for the hydrolysis lignin	1,6
Carbon footprints for H_2 via electrolysis	18,7
Carbon footprints for H_2 via natural gas SMR	91,4

[1]Estimations

Based on experimental data, e.g. oil yield and oxygen content, process balances were set up. All H_2 consumption was assumed to be caused by conversion of O into H_2O, as well as by saturation of cleaved C-O bonds. For the process cost estimations, it was assumed that the lignin upgrading would be connected to an upstream ethanol plant and thereby benefit from integrated heat and power, shared infrastructure costs, as well as reduced transportation costs. The ethanol plant was assumed to be in the scale of 100 ktonne ethanol year[-1] resulting in 150 ktonne lignin year[-1] with a corresponding energy value of 130 MW. The costs for the conversion reactors were based on operational pressure, residence time in the reactor and reactor material.

In brief, the highest mass yield as well as energy yield relative the lignin raw material was calculated for the direct slurry hydrocracking. Considering energy yield in terms of oil product in relation to the starting materials lignin and H_2, HTL had a slightly higher value than the SHC. For all three conversion routes the SHC only route resulted in the largest cost, which was directly related to the size of the SHC, i.e. highest investment cost for the direct conversion route and lowest investment cost for the pyrolysis route, see Figure 6 below.
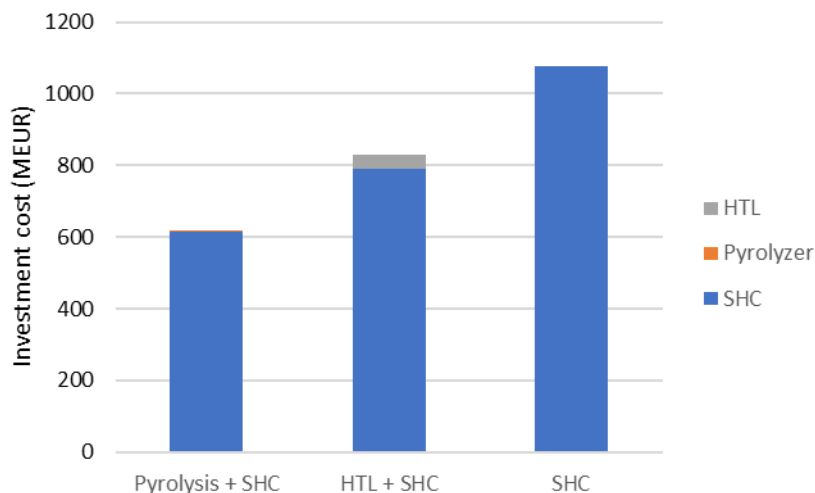
Figure 6. Qualitative comparison of investment costs for the three investigated hydrolysis lignin upgrading routes.

The cost for the conversion reactors exerted the largest contribution to the production costs of hydrogenated oil product. It was followed by the cost for hydrolysis lignin. Here, the trend is the opposite compared with the investment cost, i.e. the highest production costs are calculated for the pyrolysis lignin and the lowest ones for the direct conversion using SHC, irrespective of H_2 origin (electrolysis or H_2 from natural gas reforming), see Figure 7. For production costs expressed as SEK/MWh, the costs for HTL followed by SHC are similar to those of SHC, see Figure 8.
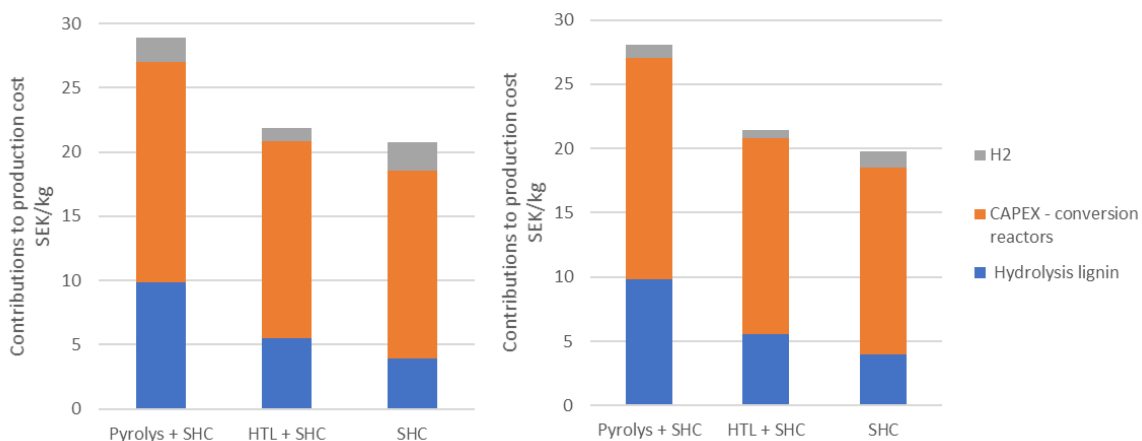

Figure 7. Comparison between the conversion routes using H_2 from electrolysis to the left and H_2 from natural gas reforming to the right. The production cost is per kg hydrogenated oil product.
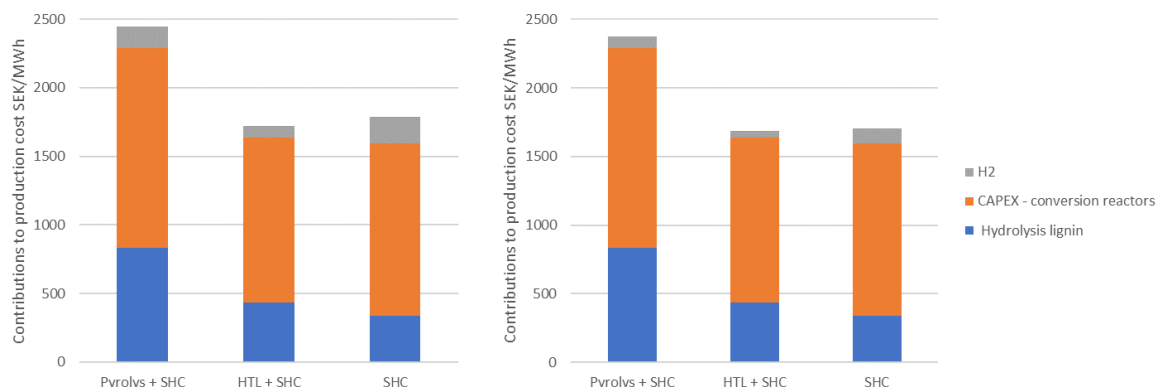
Figure 8. Relative comparison between the conversion routes using H_2 from electrolysis to the left and H_2 from natural gas reforming to the right. The production cost is per MWh hydrogenated oil product.

As stated above, the cost for the conversion reactors exerted the largest contribution to the production costs. Simulations varying the reaction time in the SHC showed that it is possible to decrease of the production cost with something in the range of ca 25% by reducing the reaction time in the SHC with 50%. Hence, optimization of parameters, e.g. reaction time in the SHC, bears a clear potential for improving the overall economics of the process since it accounts for more than half of the production cost for all three conversion routes. The lower oil yield for pyrolysis compared with HTL and direct SHC contributes to the relatively higher contribution of the hydrolysis lignin cost in the overall production cost in Figures 7 and 8 above. Furthermore, comparing pyrolysis and HTL with direct SHC, the two former ones comprise starting materials with lower oxygen content. Therefore, a lower quantity of hydrogen is required in the hydrodeoxygenation step and this is reflected in the H_2-contribution to the production cost for three different routes, see Figures 7 and 8 above.

In terms of contributions to carbon footprint, a clear difference is observed between calculations based on H_2 from electrolysis and those based on H_2 obtained via natural gas reforming. The latter is associated with a significant carbon footprint, therefore it was an expected result that much higher contributions were given by the later one, see Figure 9 below. In both cases, the lowest contribution to the carbon footprint was given by the conversion route utilizing HTL in combination with SHC. This is based on an HTL oil with an oxygen content of 20%, i.e. a typical value for an HTL oil. It is also an expected result given that both HTL and pyrolysis reduces the oxygen content in the biomass and this occurs to a higher extent during HTL compared with pyrolysis.
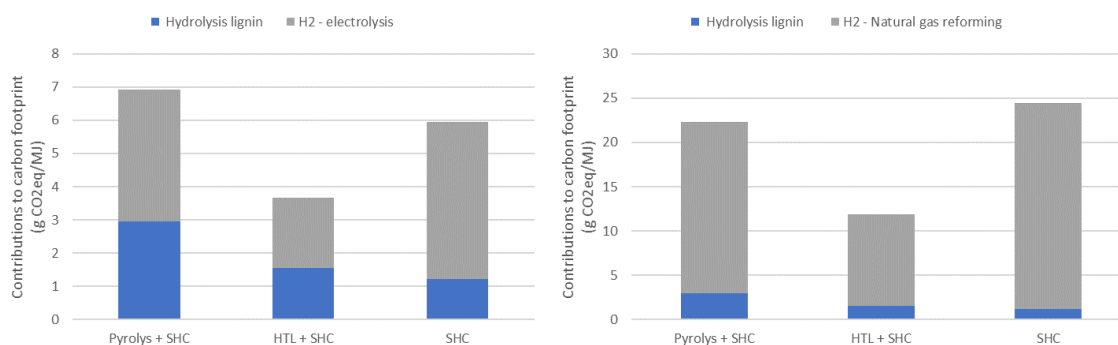
Figure 9. Comparison of the contributions to carbon footprint for the three investigated upgrading routes using H_2 from electrolysis (left) and H_2 from natural gas reforming (right). Please note the different scales.

The derived lignin oils present acceptable levels of carbon footprint (based on assumptions of hydrogen consumption in the project) to be considered as feedstocks for second generation drop-in feeds. The lowest production cost and highest mass & energy efficiency was observed for the SHC/HDO process due to reduced carbon loss from lignin-to-oil. The direct upgrading requires a higher hydrogen consumption to reach similar degree of deoxygenation as for the two-step routes. To produce cost competitive second generation drop-in feedstocks, significant process optimization is required to reduce production costs, e.g. reduced residence time in the conversion reactors.

7.   Conclusions and future work

We have experimentally demonstrated that hydrolysis lignin may be converted via three different routes, followed by hydrotreatment yielding hydrocarbons. The yield varies for the different routes. This prestudy consisted of a very limited amount of laboratory work. Hence, caution should be taken when making conclusions based on such a limited amount of experimental data and as indicated in chapter 6, the technoeconomical evaluation was incomplete in the sense that data for several parameters were missing and assumptions were made instead. Still, important conclusions and future direction, as well as questions to be further addressed can be extracted from the experimental data.

- Process optimization is required to reduce production costs, e.g. reduced residence time in the hydrotreatment reactor and optimal catalyst concentration and catalyst recovery.
- Another aspect which will be considered in future work is to utilize the whole HTL oil rather than just the light fraction, since there are unclear benefits if any with upgrading the light and the heavy HTL-oil fractions separately.
- The use of light co-feed for hydrotreatment in this project was a practical compromise since the budget of the project did not allow studies on distilling off lighter product fractions for instance from hydrotreated and cracked mixtures of lignin or bio-oils with heavier co-feeds, which would be a more natural and relevant way forward. The latter is however proposed to be the subject of subsequent development efforts in the event that further projects are financed that study the upgrading of lignin to naphtha.

- Another step forward would be to utilize parts of the product as co-feed in subsequent reaction rounds or even no cofeed slurry hydrotreatment/-cracking, i.e. upgrading of the pure bio-oils from HTL or pyrolysis since they, unlike solid powder from hydrolysis lignin are pumpable also without co-feed. The latter entirely different upgrading strategy for the bio-oils will likely produce liquid hydrocarbon products having a unique and different composition on a molecular level.
- Future work should aim at lowering the co-feed, e.g. to 70% compared with today's 90%.
- Characterization of the degree of catalyst inhibition occurring for the different raw materials should be included in future work.

8. Acknowledgement

9. References

[1]   J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, The Catalytic Valorization of Lignin for the Production of Renewable Chemicals, (2010) 3552–3599.

[2]   V.K. Ponnusamy, D.D. Nguyen, J. Dharmaraja, S. Shobana, J.R. Banu, R.G. Saratale, S.W. Chang, G. Kumar, A review on lignin structure, pretreatments, fermentation reactions and biorefinery potential, Bioresour. Technol. 271 (2019) 462–472. https://doi.org/https://doi.org/10.1016/j.biortech.2018.09.070.

[3]   J.-Y. Kim, H.W. Lee, S.M. Lee, J. Jae, Y.-K. Park, Overview of the recent advances in lignocellulose liquefaction for producing biofuels, bio-based materials and chemicals, Bioresour. Technol. 279 (2019) 373–384. https://doi.org/https://doi.org/10.1016/j.biortech.2019.01.055.

[4]   A. Tribot, G. Amer, M. Abdou Alio, H. de Baynast, C. Delattre, A. Pons, J.-D. Mathias, J.-M. Callois, C. Vial, P. Michaud, C.-G. Dussap, Wood-lignin: Supply, extraction processes and use as bio-based material, Eur. Polym. J. 112 (2019) 228–240. https://doi.org/https://doi.org/10.1016/j.eurpolymj.2019.01.007.

[5]   S. Nenkova, T. Vasileva, K. Stanulov, Production of phenol compounds by alkaline treatment of technical hydrolysis lignin and wood biomass, Chem. Nat. Compd. 44 (2008) 182–185. https://doi.org/10.1007/s10600-008-9009-z.

[6]   N. Mahmood, Z. Yuan, J. Schmidt, C.C. Xu, Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents, Bioresour. Technol. 190 (2015) 416–419.

https://doi.org/10.1016/j.biortech.2015.04.074.

[7]   M.M. Jensen, D.T. Djajadi, C. Torri, H.B. Rasmussen, R.B. Madsen, E. Venturini, I. Vassura, J. Becker, B.B. Iversen, A.S. Meyer, H. Jørgensen, D. Fabbri, M. Glasius, Hydrothermal Liquefaction of Enzymatic Hydrolysis Lignin: Biomass Pretreatment Severity Affects Lignin Valorization, ACS Sustain. Chem. Eng. 6 (2018) 5940–5949. https://doi.org/10.1021/acssuschemeng.7b04338.

[8]   J. Horáček, F. Homola, I. Kubičková, D. Kubička, Lignin to liquids over sulfided catalysts, Catal. Today. 179 (2012) 191–198. https://doi.org/https://doi.org/10.1016/j.cattod.2011.06.031.

[9]   S. Wang, W. Gao, L.-P. Xiao, J. Shi, R.-C. Sun, G. Song, Hydrogenolysis of biorefinery corncob lignin into aromatic phenols over activated carbon-supported nickel, Sustain. Energy Fuels. 3 (2019) 401–408. https://doi.org/10.1039/C8SE00359A.

[10]   Y. Bai, K. Cui, Y. Sang, K. Wu, F. Yan, F. Mai, Z. Ma, Z. Wen, H. Chen, M. Chen, Y. Li, Catalytic Depolymerization of a Lignin-Rich Corncob Residue into Aromatics in Supercritical Ethanol over an Alumina-Supported NiMo Alloy Catalyst, Energy & Fuels. 33 (2019) 8657–8665. https://doi.org/10.1021/acs.energyfuels.9b01457.

[11]   Y. Sang, M. Chen, F. Yan, K. Wu, Y. Bai, Q. Liu, H. Chen, Y. Li, Catalytic Depolymerization of Enzymatic Hydrolysis Lignin into Monomers over an Unsupported Nickel Catalyst in Supercritical Ethanol, Ind. Eng. Chem. Res. 59 (2020) 7466–7474. https://doi.org/10.1021/acs.iecr.0c00812.

[12]   M. Tymchyshyn, A. Rezayan, Z. Yuan, Y. Zhang, C. (Charles) Xu, Reductive hydro-processing of hydrolysis lignin over efficient bimetallic catalyst MoRu/AC, Ind. Eng. Chem. Res. (2020). https://doi.org/10.1021/acs.iecr.0c01151.

[13]   F. Mai, Z. Wen, Y. Bai, Z. Ma, K. Cui, K. Wu, F. Yan, H. Chen, Y. Li, Selective Conversion of Enzymatic Hydrolysis Lignin into Alkylphenols in Supercritical Ethanol over a WO3/γ-Al2O3 Catalyst, Ind. Eng. Chem. Res. 58 (2019) 10255–10263. https://doi.org/10.1021/acs.iecr.9b01593.

[14]   Q. Liu, Y. Bai, H. Chen, M. Chen, Y. Sang, K. Wu, Z. Ma, Y. Ma, Y. Li, Catalytic conversion of enzymatic hydrolysis lignin into cycloalkanes over a gamma-alumina supported nickel molybdenum alloy catalyst, Bioresour. Technol. 323 (2021) 124634. https://doi.org/10.1016/j.biortech.2020.124634.

[15]   E. Pienihäkkinen, C. Lindfors, T. Ohra-aho, J. Lehtonen, T. Granström, M. Yamamoto, A. Oasmaa, Fast Pyrolysis of Hydrolysis Lignin in Fluidized Bed Reactors, *Energy & Fuels* 2021, 35, 18, 14758-14769. https://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.1c01719

[16]   Sheng C., A. J. (2005). Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass and Bioenergy* , pp. 499-507.

[17]   Anheden M., e. a. (2017). *Determination of potential improvements in bio-oil production. Production of transportation fuel components in value chains integrating pulp & paper and oil*

refinery industry. Report No 2017:16. Available at www.f3centre.se: f3 The Swedish Knowledge Centre for Renewable Transportation Fuels, Sweden.

[18]   Ramirez J. A., B. R. (2015). A review of hydrothermal liquefaction bio-crude properties and prospects for upgrading to transportation fuels. *Energies*, pp. 6765-6794.

[19]   Eliott D. (2016). Retrieved from Hydrothermal liquefaction of biomass, revisited. Doug Elliott of Pacific Northwest National Laboratory, USA, revisits his earlier article. In IEA Bioenergy Newsletter 38. October 2016. : http://task34.ieabioenergy.com/wp-content/uploads/2016/10/Pyne-Newsletter-38-FINAL.pdf

[20]   https://news.cision.com/setra-group/r/pyrocell-has-started-production,c3420250

[21]   https://www.eni.com/en-IT/operations/slurry-technology-eni.html

[22]   https://honeywell-uop.azurewebsites.net/?document=uop-uniflex-mc-residuehydrocracking-process-datasheet&download=1)

[23]   R. Prajapati, K. Kohlib, S. K.Maitya. Slurry phase hydrocracking of heavy oil and residue to produce lighter fuels: An experimental review. *Fuel* **2021**, *288*, 119686, https://doi.org/10.1016/j.fuel.2020.119686

[24]   S. Constant, H. L. J. Wienk, A. E. Frissen, P. de Peinder, R. Boelens, D. S. van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosselink, P. C. A. Bruijnincx. *New insights into the structure and composition of technical lignins: a comparative characterisation study. Green Chem.*, **2016**, *18*, 2651-2665, https://doi.org/10.1039/C5GC03043A;

[25]   C. S. Lancefield, H. L. J. Wienk, R. Boelens, B. M. Weckhuysen, P. C. A. Bruijnincx. *Identification of a diagnostic structural motif reveals a new reaction intermediate and condensation pathway in kraft lignin formation. Chem. Sci.*, **2018**, *9*, 6348-6360, https://doi.org/10.1039/C8SC02000K.

[26]   F. Bergius, patent US 1,342,790, **1920** and German patent 301,231, **1913**.