HYDROTHERMAL LIQUEFACTION OF BLACK LIQUOR

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ABSTRACT: Black liquor, which is produced in large quantities in the pulp & paper industry as a by-product in the Kraft process is an interesting feedstock for hydrothermal liquefaction (HTL). HTL is a thermochemical process to convert organic matter into biocrude for fuel applications or the production of useful chemical compounds and is especially useful for wet biomass. Main organic matter in Black liquor is lignin which is dissolved in an aqueous solution together with the cooking chemicals from pulping. Desired products in HTL of lignin are aromatic compounds. Until now, most research was done with extracted lignin. This work explores the approach to liquefy the lignin directly in the black liquor via HTL as a part of the “Black Liquor to Fuels (BL2F)” project.

In order to investigate the feasibility of direct HTL of black liquor, we performed parameter studies in batch experiments using micro autoclaves. The product phases were separated and analyzed using different analytical methods. Our study shows that the typical depolymerization products of lignin are found dependent on temperatures and residence times. Catechol and its derivates are the aromatic monomer products in the organic phase. The SEC analysis of the biocrude gives a good indication of the depolymerization of the lignin with increasing reaction temperature and holding time. Overall, it can be said that the direct use of black liquor in an HTL process works, which reduces process steps in advance for example extracting the lignin.

Keywords: hydrothermal liquefaction, lignin, thermochemical conversion, biorefinery

1 INTRODUCTION

Lignin is generated in huge amounts of about 50 Mio t from wood pulping as by-product, therefore it is one of the most promising renewable raw materials today. It is a natural marcro molecule (see **Figure 1**) built op from three different phenyl propanoids.

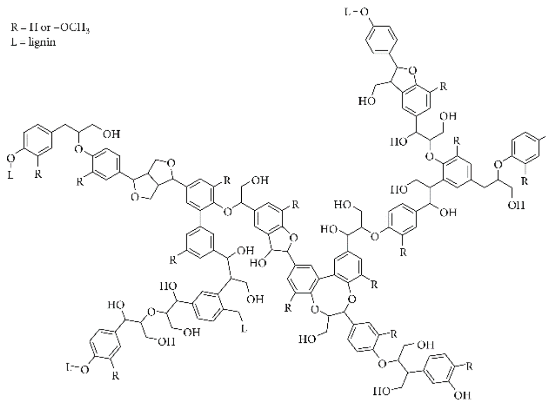

Figure 1: Possible structure of a lignin macro molecule [1]

It has the potential to act both as a base for fuels and as a feedstock for various important platform chemicals, especially aromatic compounds. However, today most of the lignin produced in the paper industry is used for energy production only. Due to the strong price fluctuations in the energy sector, this is problematic from an economic point of view. Furthermore, the potential of lignin in terms of possible raw material for fuels or important platform chemicals is being wasted. For this reason, enormous efforts in research were made on a material utilization of lignin. In the Kraft process, by far the most frequently used pulping process in the paper industry, black liquor is produced as a by-product, in which lignin is dissolved in water together with the pulping chemicals such as sodium sulfide (Na_2S) and sodium hydroxide (NaOH) and other wood components.

While many approaches in lignin recovery from black liquor apply extraction of lignin, drying and further processing, the EU Horizon 2020 project "BL2F" (Black Liquor to Fuels) focus on the direct hydrothermal liquefaction (HTL) of black liquor with the challenge that all the pulping chemicals are present. HTL uses the special properties of water under near-critical conditions (critical point of water: 374 °C, 221 bar) to depolymerize lignin into a biocrude, containing many phenolic components such as catechol. The goal of the BL2F project is to integrate a continuous HTL plant with subsequent upgrading into a paper mill to produce drop-in fuels for shipping and aviation.

To create a successful production of bio fuels from black liquor, it is important to evaluate the process of HTL of black liquor. Therefore, batch experiments are performed to understand the behavior of lignin during the HTL, in presence of the cooking salts.

2 EXPERIMENTAL

2.1 Materials

The pulp mill (The Navigator Company in Portugal) provided the black liquor, as well as extracted lignin. This is the unprocessed by-product of the Kraft process. A typical black liquor contains the lignin, the hemicellulose, other wood residues and the cooking chemicals from the Kraft process. The feedstock is eucalyptus wood, which belongs to the hardwood category. The feedstock was stored in a refrigerator at 5 °C to slow down possible oxidation processes. Freezing was not an option due to phase separation as well as mechanical destruction of the lignin molecules. The batch experiments were carried out in micro autoclaves made at the institute with a volume V = 25 mL, consisting of a stainless steel with the material number 1.4571 (see **Fig. 2**). Nitrogen was used as inert gas. We used a custom-built station for closing and opening the micro autoclaves (see **Fig. 3**), which also allows us to take gas samples. The other chemicals used in this study are ethyl acetate, dimethyl sulfoxide (DMSO).

Figure 2: Micro autoclaves used for the batch experiments

Figure 3: Micro autoclave station: a) Container for autoclaves; b) pressure measurement; c) septum for taking gas samples

2.2 Feedstock characterization

Fig. 4 shows the black liquor. Various analytical methods were used for characterization. To measure the density ρ_{BL} a densitometer of Anton Paar, model DMA 4500M was used. To determine the dry mass m_{tr} 15 mL of the black liquor was dried at 105 °C for 24 h. The resulting solid was crushed with a mortar and again placed in the oven at the same conditions for 24 h to remove as much residual moisture as possible. The residue was then weighed and the dry mass fraction w_{tr} was determined.

$$w_{tr} = \frac{m_{tr}}{m_{total}} \tag{1}$$

The mass m_{total} describes the total mass of the black liquor before drying. For the mass of the ash $m_{ash,815\,°C}$, the dry mass was heated to 815 °C in a crucible furnace (Leco TGA-701). From this, the ash-free and water-free dry mass $m_{tr.waf}$ could be determined.

$$m_{tr,waf} = m_{total} * w_{tr} * \left(1 - \frac{m_{ash,815\,°C}}{m_{tr}}\right) \tag{2}$$

This value is also used for yield calculations since it covers most of the biomass in the black liquor and lignin is the major part of it. To analyze the chemical composition we used elemental analysis for C, H, N, S (EA, vario EL cube, Elementar Analysensysteme GmbH) and an inductively coupled plasma – atomic emission spectroscopy for other elements (ICP-AES, Agilent 725 ICP-OES spectrometer, Agilent). Both samples, the dry matter from black liquor and the extracted lignin, were analyzed with these two analysis systems.

Figure 4: Pristine black liquor

2.3 Batch experiments and analytics

At the beginning of the batch experiments, the black liquor is filled into the micro autoclaves described in chapter 2.1. The volume of black liquor is dependent on the reaction temperature T_R in order to keep the pressure at the same level under equilibrium hydrothermal conditions. The respective volumes of black liquor together with the reaction temperature T_R are listed in **Table 1**.

Table 1: Volumina of BL V_{BL} in micro autoclave at different reaction temperature T_R

T_R	250 – 275 °C	300 – 350 °C	375 °C	400 °C
V_{BL}	17.5 mL	15 mL	12.5 mL	5 mL

The reactors are weighed both before filling and afterwards. They are then placed in the autoclave station and purged with nitrogen to ensure an inert atmosphere. After repeated rinsing, a pressure of approx. 10 bar is built up and the reactor is tightly sealed. The built-up pressure seals the reactor from the inside. Weighing again provides the mass of nitrogen in the system. To set the reaction temperature T_R we use a sand bath. From preliminary experiments with water, it is known that after a heating time of t_H = 10 min, the final reaction temperature T_R is reached in any case inside the investigated temperature range. In the further course, we will discuss the holding time t_R, which represents the time after t_H. After the holding time t_R has elapsed, the reactors are taken out of the sand bath and immediately cooled in a water bath. We performed experiments at different reaction conditions from 250 – 400 °C with t_R = 20 min and from 0 – 30 min with T_R = 375 °C. All the experiments were done at least in triplicates, and the resulting values show their average and standard deviation (error bars in figures). After that, the dried and cleaned micro autoclaves and again mounted in the autoclave station. The lines are purged with nitrogen and then the reactor is opened. The gas is fed into the gas trap and can be extracted using a gas-tight syringe. Afterwards it is injected into a GC 6890 Hewlett Packard gas chromatograph loaded with a thermal conductivity detector and a flame ionization detector (GC-TCD/FID). The GC-TCD/FID is equipped with a Molsieve 5 A and a column Hayesep Q (both Restek).

To determine the carbon content in the gas, the volume fractions φ_i of CO, CO_2 and alkanes to iso-butane as well as the olefins ethene and propene are measured. Due to the unavoidable air content in the sample, the volume fractions still have to be corrected.

$$\varphi_{i,corr} = \frac{100 * \varphi_i}{100 - \varphi_{O_2} - (\varphi_{O_2} * \frac{78}{22})} \tag{3}$$

φ_{O_2} is the measured volume fraction of oxygen and the ratio 78/22 describes the surrounding air (ratio N_2/O_2). The pressure p displayed on the manometer at the autoclave station must also be corrected, as this describes the pressure in the entire system. The pressure in the closed reactor can be calculated with the following correlation.

$$p_{corr} = \frac{p}{0.082} \tag{4}$$

The correlation was previously determined by autoclaves filled with different pressures. The ideal gas law is used to determine the amount of substance of the individual gases n_i.

$$n_i = \frac{p_{corr} * V * \frac{\varphi_{i,corr}}{100}}{R * T_{room}} \tag{5}$$

V is the free volume of the microautoclave. The room temperature is assumed to be $T_{room} = 296{,}15\ K$ and R represents the universal gas constant. Finally, to calculate the total mass of carbon in the gas $m_{C,g}$ the individual masses are added together. It is important to note that for molecules with multiple carbon atoms, the number of these is taken into account. With the number of carbon atoms in the molecule v_i and M_C as the molecular weight of carbon, the equation is then given by

$$m_{c,g} = \left(\sum n_i * v_i\right) * M_C \tag{6}$$

After taking the gas sample, the reactor is fully opened and vacuum filtration with a nylon filter (diameter: 45µm, Whatman) is used to separate the solid from the liquid. The residue in the reactor was declared as loss. Due to the low mass loss (see carbon mass balance later), we decided not to wash the residue from the reactor with a solvent. The solid residue is dried at 105 °C. It is then pulverized and analyzed by EA and ICP to identify both the carbon content and possible precipitated salts.

An aliquot of the filtrate is analyzed for carbon content using a Dimatoc 2100 (Dimatec Analysentechnik GmbH). The sample is diluted with ultrapure water (1:100). The instrument determines the total (TC) as well as the inorganic carbon content (TIC) of the liquid. The organic carbon content (TOC) is then determined by difference. Another aliquot is used to determine and quantify aromatic monomers with a gas chromatograph. For the determination of individual unknown components, Agilent's GC 6890N equipped with a non-polar capillary column (Rxi-5Sil, Restek) and an Agilent 5973 MSD mass spectrometry detector is used (GC-MS). The underlying database originates from the National Institute of Standards and Technology (NIST). For the quantification of some aromatic monomers, the Agilent GC 7820A with an FID and the same type of column is used (GC-FID). The procedure for sample preparation is based on the method used by Forchheim et al [2]. For this, the sample must first be placed in the appropriate matrix to obtain the best possible results later. The first step is to acidify the sample to a pH of 3-4 with concentrated hydrochloric acid (20 wt. %, ca. 6M). The acidified liquid phase is then re-filtered with a syringe filter (pore size 0.22 µm) to remove precipitated components. Next, 1.3 mL of the sample is mixed with 0.52 mL of extractant, ethyl acetate, in a 2.5:1 ratio. The internal standard (ISTD), which will be needed later for quantification, is also dissolved in the extraction solvent. This is pentadecane. The sample vessel is shaken for one minute and then allowed to stand for one hour. After the standing time has elapsed, a clear phase separation is visible, in which the organic phase is the upper one. Part of the organic phase is diluted with ethyl acetate (1:3 dilution) and analyzed with the gas chromatographs. A total of ten different aromatic compounds could be clearly determined and quantified. A distribution coefficient K_i in an ethyl acetate/water was determined for each of these components. The following table (see **Table 2**) lists the components and the respective coefficient

Table 2: Distribution coefficient K_i for all quantified compounds with GC-FID in an ethylacetate - water mixture

Component name	**Distribution coefficient K_i**
Phenol	0,95
Guaiacol	0,92
Catechol	0,82
3-Methoxycatechol	0,7
3-Methylcatechol	0,83
4-Methylcatechol	0,7
Syringol	0,75
4-Ethylcatechol	0,87
Syringaldehyde	0,67
Acetosyringon	0,65

Together with the dilution factor a, the extraction volume factor b, the ISTD factor c and the raw data $\beta_{i,raw}$ of the GC-FID analysis following equation is given to determine the mass concentration of the compounds in the original samples.

$$\beta_i = \frac{\beta_{i,raw} * a * b * c}{K_i} \tag{7}$$

The dilution factor a describes the overall dilution of the original sample, the extraction volume factor b takes the ratio between the volume of the sample and the extractant into account and the ISTD factor c considers the ratio between the concentration of ISTD in the analyzed sample and the original ISTD concentration in the extractant.

To calculate the yields of the species $Y_{i,BM}$ to increase the comparability between processes, we need the mass of the feedstock m_{feed} in the reactor before processing and the mass of the collected liquid product phase $m_{liq,prod}$ as well as $m_{tr,waf}$ and m_{total}.

$$Y_{i,BM} = \frac{\frac{\beta_i}{\rho} * m_{liq,prod}}{\frac{m_{tr,waf}}{m_{total}} * m_{feed}} \tag{8}$$

In the last step, the average molecular weight of the biocrude is determined. The procedure is the same as for the sample preparation of the GC analysis. The difference is that the extracting agent is evaporated to finally have only the organic matter left. A spatula tip of this is then dissolved in 2 - 3 mL DMSO and analyzed by size exclusion chromatography (SEC). From the chromatograms obtained, the average molecular weight within the calibration limit can be determined. During the analysis, this was between 250 and 10000 g/mol. We use a Hitachi LaChrom diode array detector DAD L-2455 with a Viscotek A2500 column.

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3 RESULTS AND DISCUSSION

3.1 Results of Feedstock Characterization

The black liquor that we received from our project partners is a dark, low-viscosity liquid with little to no solid residue. Even filtration of the untreated black liquor does not change this. The following tables list all relevant data from the various analyses. The density is close to water.

Table 3: Results of feedstock characterization

$\boldsymbol{w_{tr}}$	$\boldsymbol{w_{ash,815\,°C}}$	$\boldsymbol{w_{tr,waf}}$	$\boldsymbol{\rho_{BL}}$	$\boldsymbol{pH}$
14.5 wt. %	6.5 wt. %	8.4 wt. %	1.0725 kg*l^{-1}	> 12.5

All the mass fractions are related on m_{total}. It is clearly visible that most of the black liquor consists of water.

Table 4: Elemental analysis and ICP results for dry mass from BL; Oxygen calculated by difference

Element symbol	**Mass fraction in dry mass / wt. %**
C (EA)	34
H (EA)	3.4
N (EA)	< 0.1
S (EA)	4.7
O (Diff.)	38.8
Na (ICP)	17.7
K (ICP)	1.3

It is clear from **Table 4** that a larger proportion of the dry matter consists of inorganic material. It is very likely that these components are the cooking chemicals used in the Kraft process in the paper industry [3]. They are predominantly alkali metal salts, more precisely NaOH and Na_2S. This explains, among other things, the high mass fraction of sodium in the dry mass. Potassium compounds are possibly added in smaller quantities as additives. In addition, the added Na_2S also explains the increased sulfur content. Other compounds such as chlorine, calcium or silicon were found only in traces and are not listed here. This will be dealt with in subsequent papers. It is also interesting to note that almost no nitrogen is present. This fact was taken into account in the identification of components by excluding nitrogen compounds as possible products from the outset. Overall it can be said, that our feedstock has the typical properties of hardwood black liquor. Comparison with literature confirms this [4]. Furthermore, we also analyzed the extracted lignin for the same elements to confirm that the alkali metals and a large part of the sulfur are mainly inorganic substances (see **Table 5**)

Table 5: Elemental analysis and ICP results for extracted lignin from BL; Oxygen calculated by difference

Element symbol	**Mass fraction in dry mass / wt. %**
C (EA)	60.3
H (EA)	5.7
N (EA)	< 0.1
S (EA)	2.6
O (Diff.)	31
Na (ICP)	0.4
K (ICP)	< 1

3.2 Results of HTL of Black Liquor

The results of the batch experiments are presented below. The first part focuses on the carbon mass balance, the second part covers the production of aromatic monomers and the last part deals with the depolymerization of the lignin with respect to the molecular weight.

In general, the HTL products looked all quite similar. We got a black solid powder and a brownish liquid phase without any phase separation. At higher temperatures and longer holding times, the liquid became clearer and slightly reddish.

Carbon mass balance

Figure 5 shows the carbon mass balance for the series of experiments at the reaction temperature T_R of 250 – 400 °C with a holding time of t_R = 20 min. The carbon content in the solid, in the liquid phase, divided into organic and inorganic, in the gas phase and the deficit are shown. Overall, 75 - 95 wt. % of carbon was found in the product phases in all experiments. The residue in the reactor as well as escaping gas can explain the remaining loss. The carbon content in the gas phase is not relevant at the lower temperatures. It only becomes clearly visible from T_R = 375 °C. The large part of the carbon is due to the production of CO_2, which mainly results from decarboxylation. A small part of carbon is bound in short-chain alkanes and olefins, mainly methane as well as ethane. Carbon monoxide was not detected. The carbon dioxide produced is probably also responsible for the increase in inorganic carbon with increasing temperature. We assume that this is CO_2 dissolved in the liquid phase. Some of this dissolved CO_2 may also contribute to carbonate formation. The most important part of the mass balance concerns the last two areas. It is clear to see that the organic carbon content in the liquid phase decreases sharply with higher reaction temperature. Instead, the carbon content in the solid phase increases dramatically. At a reaction temperature of T_R = 400 °C, almost half of the carbon is bound in the solid. This is counterproductive, since it is primarily from the organic liquid phase. One possible explanation for this result is to be found on the process side. Due to our batch reactors sufficient mixing could not be achieved all time. This in turn leads to increased crosslinking reactions between the formed aromatic products and the unreacted educts and therefore, carbonization takes place especially with longer holding times. The lignin molecule with its high aromatic structure also contributes to this, as aromatics have an increased tendency to char forming reactions [5]. It is also important to note that although large amounts of organic carbon are present at lower temperatures, this is due to incomplete depolymerization of the lignin. With increasing reaction temperature the carbon content in the solid residue rises (see **Table 6**).

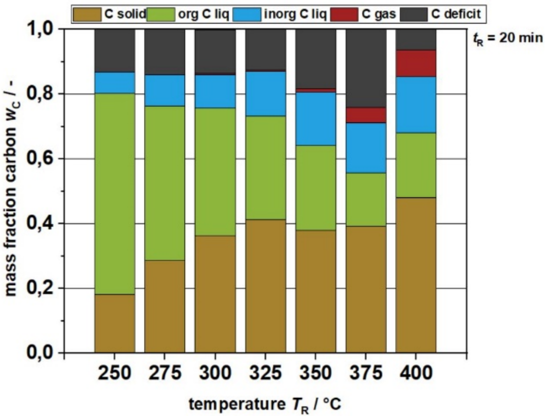

Figure 5: Carbon mass balance; $T_R = 250 - 400$ °C; $t_R = 20$ min

Table 6: Mass fractions of different elements in solid phase at different reaction temperatures; same procedures as in feedstock characterization

	Mass fraction in solid / wt. %						
T_R	C	H	N	S	O	Na	K
250	53	4.8	0.1	2	32.22	7.28	0.61
275	54.2	4.1	0.2	2.2	31.4	7.28	0.63
300	59	3.9	0.2	1.0	27.93	6.53	0.54
325	66.5	4.4	0.2	1.5	22.74	4.67	< 0.5
350	72.6	5.1	0.2	1.5	17.75	2.85	< 0.5
375	77.8	5.3	0.2	1.3	13.89	1.52	< 0.5
400	79.2	5.1	0.2	1.1	14.4	2.19	< 0.5

To counteract this, we looked at the holding times of $t_R = 0 - 30$ min minutes at a reaction temperature of $T_R = 375$ °C in the next series of experiments (see **Figure 6**). In general, it can be said that the influence of the holding time in the investigated frame is significantly lower than temperature range. For the short holding times up to $t_R = 5$ min, a doubling of the organic phase is possible. In total, up to 25 wt. % organic carbon is present in the liquid phase. Regarding the loss, it still has to be said that a sticky mass was formed during the longer holding times, which was somewhat more difficult to remove from the reactor. Therefore, the losses are higher in this area.

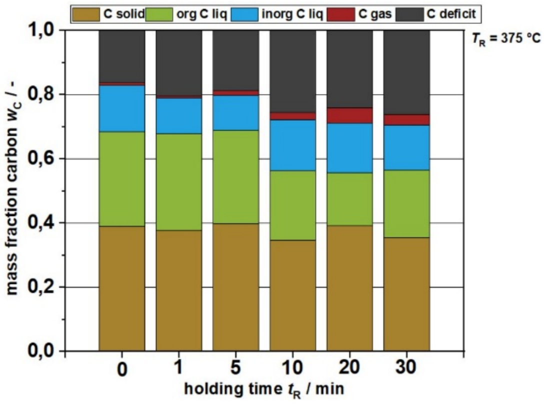

Figure 6: Carbon mass balance; $t_R = 0 - 30$ min; $T_R = 375$ °C

Aromatic monomer yields

To get more details about the organic part of the liquid phase, we extracted the organic phase and analyzed it by GC-MS. We were able to identify several typical aromatic components. For the quantification, we limited ourselves to the components, which were interesting in our eyes or present in large peaks (see **Table 2**). It can be said that the different aromatic compounds found reflect the typical products of HTL of lignin [6]. This indicates that the HTL process also works with the direct use of black liquor as feedstock and that depolymerization of lignin takes place. We could also see the typical degradation products of hemicelullose such as cyclopentenones or various carboxylic acids. These will not be discussed in detail here, since the aromatics are the main focus here. **Figure 7** shows the yields of the selected aromatic compounds versus the reaction temperature T_R. Catechol as well as its derivatives are clearly the main products in this observation. While 3-Methoxycatechol (blue) has the highest yield at T_R = 250 °C, catechol (green) as well as 4-Methylcatechol (pink) are highest at 300 °C. Phenol, which is repeatedly mentioned as the main product in other works around HTL of lignin [7], hardly plays a role in our work. Derivatives such as cresols or xylenols could also be identified, but their yields were very low and are therefore not listed here. What is also clearly visible is the separation between intermediates and secondary products. Especially the change from functional groups like carboxyl (-COOH), methoxy ($-OCH_3$) or aldehyde groups (-CHO) to hydroxy (-OH) and methyl groups becomes obvious ($-CH_3$). Interestingly, this already happens at the lower temperatures. At T_R = 300 °C the catechol already reaches its maximum. With increasing temperature, all further yields decrease until at T_R = 400 °C hardly anything can be detected. This is also consistent with the observations from the carbon mass balance. The low proportion of organic carbon in the liquid phase is also reflected here. We assume that the aromatics coke or react further into the gas phase.

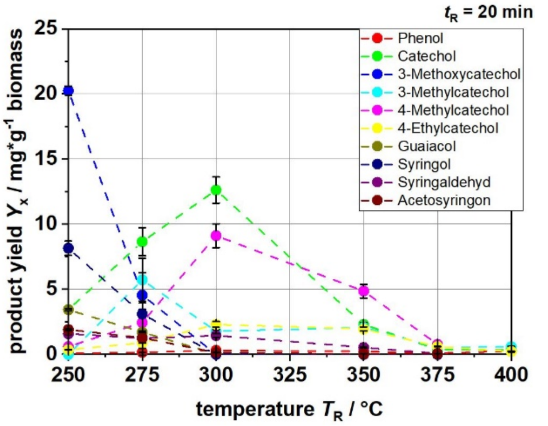

Figure 7: Product yields of aromatic compounds after HTL of black liquor; $T_R = 250 - 400$ °C; $t_R = 20$ min

As before in the case of the carbon mass balance, we have also investigated the influence of the holding time t_R. The results are shown in **Figure 8**. The experiment at a holding time $t_R = 0$ min could not be evaluated due to lack of product. The same products as in the previous experiments were found at low holding times. The maximum is at the shortest holding time $t_R = 1$ min. From there on, the yields of all aromatics decrease continuously. Interestingly, the yields of the catechols, which have alkyl chains as substituents, are significantly higher than at lower temperatures with longer holding times. It can be concluded that higher reaction temperatures favor alkylation. The reason for this may be the formation of alkyl radicals during HTL. These are formed mainly at higher reaction temperatures [6]. It can also be said that the yields of the various aromatics are significantly increased at lower holding times, which is typical for primary products in the batch mode. This, together with the previous result, suggests that a holding time of $t_R = 20$ min is clearly too high.

We took a closer look at the aromatics that could be extracted from the product phase. From the results, we derived a simple reaction scheme (see **Figure 9**). This can serve as a basis for a possible reaction kinetic model in the future. Starting from lignin as the starting material, intermediates such as syringol and its derivatives, but also guaiacol or 3-methoxycatechol are formed. These then react further at longer holding times or higher reaction temperatures to form the actual products, the catechols. As mentioned before, we assume that the aromatics formed continue to react in the gas phase to CO_2, H_2 and hydrocarbons, but at the same time also settle in the solid phase by coking.

What is striking is the difference of hardwood compared to softwood. Earlier works by Schuler et al. [6, 8] discusses HTL from extracted lignin, specifically Indulin AT. This comes exclusively from softwood. In contrast to that work, this yields significantly more guaiacol and phenol instead of syringol. This can probably be attributed to the fact that Softwood consists almost exclusively of a phenylpropanoid, coniferyl alcohol. Hardwood, on the other hand, consists of a mixture of coniferyl and sinapyl alcohol (see **Figure 10**). The degradation of sinapyl alcohol must be worked out in more detail in future experiments.

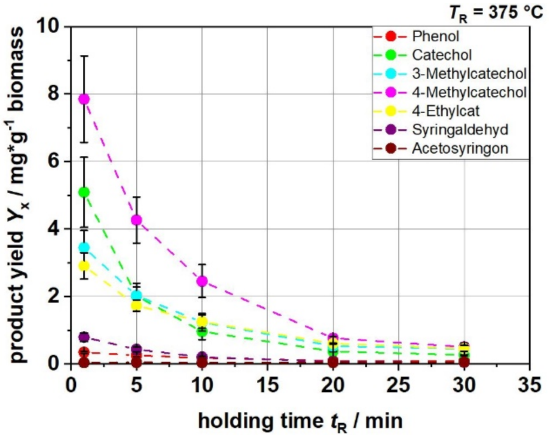

Figure 8: Product yields of aromatic compounds after HTL of black liquor; $t_R = 1 - 30$ min; $T_R = 375$ °C

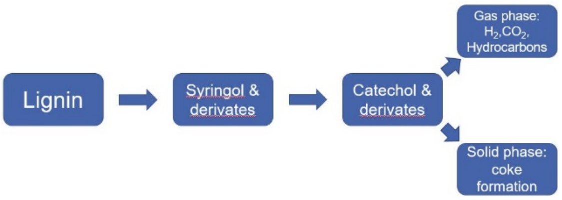

Figure 9: simple reaction pathway based on our obvservations

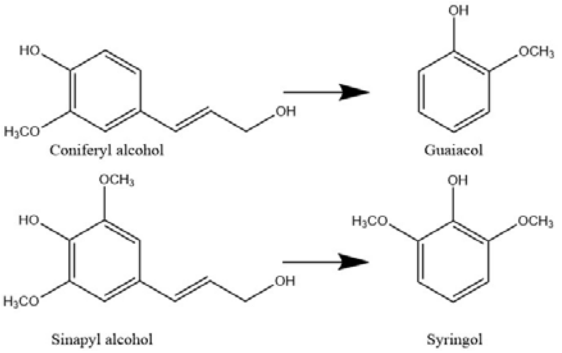

Figure 10: The two main phenylpropanoids (left) and their monomer compound as intermediate in the product (right)

Average molecular weight analysis

What is also important is to look on the first reaction step. We assume, oligomers with more than one aromatic ring will break from the lignin structure first before breaking down even more to form the aromatic monomers (see **Figure 11**).

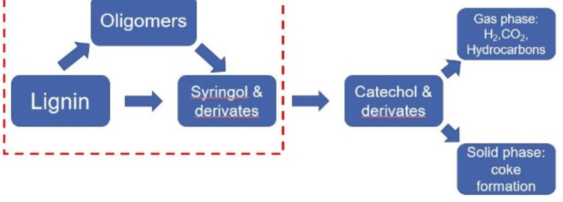

Figure 11: Reaction pathway from Figure 10 including the oligomer step

To investigate this assumption, we looked at the molecular weight of the organic phase after evaporation of the extraction solvent, the so-called biocrude. The SEC serves as the analysis method for this purpose. We chose DMSO as the solvent for sample preparation. The reason for this is the ability of DMSO to dissolve both polar and non-polar substances. In our case, we have exactly such components with the lignin and its depolymerization products, especially the larger ones. There are also studies in the literature that prove this [9]. The value we get as a result describes the average molar mass over the whole chromatogram within the calibration limits. The extracted lignin has an average molecular weight $M_{W,Lig} \approx 4200$ g/mol. **Figure 12** shows the change in molecular weight with increasing reaction temperature T_R. Already at 250 °C the molecular weight is below 4000 g/mol. Up to T_R = 325 °C, only a slight decrease can be observed. After that, a rapid reduction in molecular weight sets in. At T_R = 375 °C, an average molar mass of $M_W \approx 2100$ g/mol is reached. At T_R = 400 °C, we could no longer extract enough organic product phase. It is striking that even at the lowest measured molecular weight the molecules are still very large. However, since we can see the production of aromatic compounds at the same time, we assume that, on the one hand, direct cleavage of aromatic monomers also takes place. At the same time, we assume that the lignin molecule as a whole is not completely broken down, but that smaller and smaller fragments are separated at the outer ends of the molecule. To confirm these assumptions, subsequent research will need to look at these oligomers in more detail.

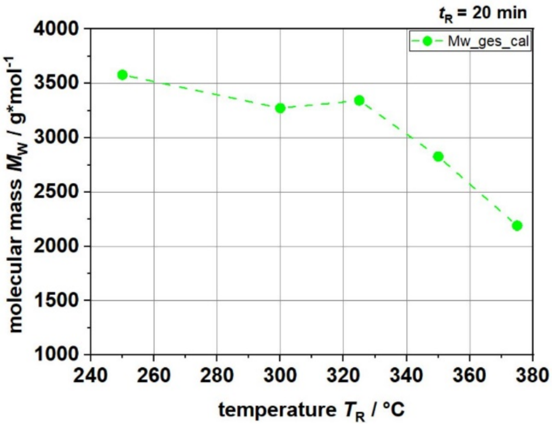

Figure 12: GPC analysis: molecular mass M_W over reaction temperature $T_R = 250 - 375$ °C; $\mathrm{t}_R = 20$ min

In the change of molecular weight over the holding time t_R (see **Figure 13**) the same features are visible. At first, the molecular weight remains relatively stable at about 3200 g/mol, but then decreases just as rapidly at t_R = 20 min. Interestingly, there is a rebound at a longer holding time t_R = 30 min, possibly due to repolymerization effects. However, in general for the GPC analysis, the absolute values of the molecular weight are not very meaningful, because the above-mentioned nature of the lignin (polar/non-polar) is not optimal for the column. Since columns are usually designed for either polar or non-polar substances, it is always possible that interactions between column and sample will occur with lignin. Since we are primarily interested in the relative course, we are nevertheless satisfied with the results.

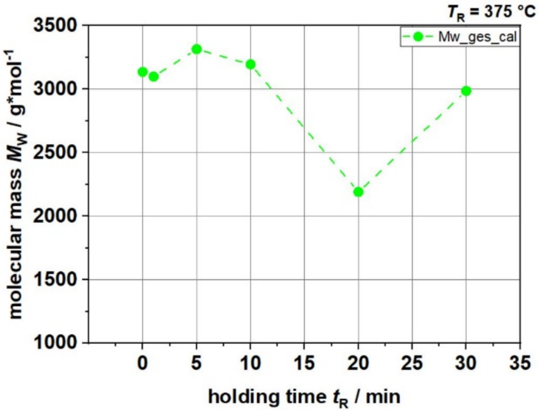

Figure 13: GPC analysis: molecular mass M_W over reaction temperature $t_R = 0 - 30$ min; $\mathrm{T}_R = 375$ °C

4 CONCLUSION

We were able to show with our test series that the direct liquefaction of black liquor works. This is demonstrated by results such as the carbon balance and the aromatic monomers typical for HTL of lignin in the product phase. However, we also saw clear potential for improvement. This is especially true for the organic carbon yield. At the reaction temperatures around T_R = 375 °C and a reactions time of t_R = 20 min, only little organic product phase is obtained. Although a doubling is possible by shortening reaction times t_R, almost half of the carbon still ends up in the solid. One reason mentioned is our batch reaction concept. It is possible that significantly better yields can be achieved at higher temperatures in the continuous phase, since better mixing is possible there. For this purpose, the results of the batch experiments from this study must be compared with continuous experiments of the project partners in subsequent work. Catechol and its derivates are the monomer products as the yields show. Syringol and its derivates are the main intermediates. Phenol is found only in slight amounts. From the data obtained, it was possible to develop a simple reaction pathway describing the depolymerization of lignin. Based on this and the results, the first steps are taken to develop a reaction kinetic model for the depolymerization of lignin in presence of the cooking chemicals from pulping. It is important for this that the analysis of the oligomers is further developed. Using SEC, we were able to show qualitatively the relative progression of molecular weight with increasing reaction temperature T_R and longer reaction time t_R. An additional NMR analysis may be recommended here to evaluate the oligomers based on the functional groups. Finally, it can be concluded that direct HTL of black liquor is a good way to avoid processes such as extracting and re-dissolving the lignin. However, more research needs to be done in some areas to achieve the best possible results.

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