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Extraction of phenolic compounds from sulfur-free black liquor thanks to hydrothermal treatment before the production of syngas for biofuels

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Abstract

Nowadays, black liquor, the liquid residue from cooking step in pulp industry is burnt to produce energy for the plant. But as the pulp mills have energy in excess, higher added values applications for black liquor may be looked for. Hydrothermal treatment offers a good opportunity as it is well suited for this kind of wet feedstock. It may be used to depolymerize organic compounds or produce syngas for biofuels applications. The objective of this study is to combine phenols and biofuel production by extracting the small organic molecules formed at moderate temperature prior to complete gasification of black liquor. Hydrothermal experiments from 225 °C to 600 °C have been performed on sulfur-free black liquor in batch reactor. At 280 °C phenol, guaiacol and syringol were found in their highest quantity: 5 % of the initial lignin (which represented 6 wt% of the liquid black liquor) could be converted into these three compounds.

Keywords: sulfur-free black liquor, hydrothermal treatment, lignin, phenol, guaiacol, syringol

1. Introduction

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Lignin gains more and more interest in the field of biomass research [1]. Indeed its aromatic structure, its high functionalization and its natural abundance make it an ideal candidate to produce high added value chemicals as for example bio-sourced phenolic compounds. However, lignin extraction and depolymerization are challenging because of the complexity of its structure and its heterogeneity ([2], [3]).

Nowadays, the most important potential source of industrial lignin is the kraft process which removes lignin from wood chips by an alkaline hydrolysis using NaOH and Na₂S to produce cellulose for paper making. The lignin polyphenolic molecules are then found in the black liquor, the liquid residue of the cooking step. The black liquor also contains carboxylic acids molecules (under carboxylate anion form) resulting from the degradation of part of the hemicelluloses as well as inorganic molecules from the cooking reagents. Black liquor is then burnt to recover the cooking chemicals and produce energy for the plant. This process, used for many decades, works well and is perfectly optimized. More than 70 million tons of wood lignin is burnt every year worldwide ([1], [4]).

However, to diversify their activity, pulp mills have started to change and transform into complete biorefineries by giving better value to the wood components which include hemicelluloses and lignin ([5], [6]). For example, hemicelluloses can be extracted by adding a hydrolysis step (hot water extraction at 170°C) prior to cooking. In a previous study we demonstrated that this process modification, besides allowing hemicelluloses valorization, facilitated wood delignification and enabled cooking without sulfur chemicals [7]. Consequently, with this modified process a different type of black liquor, sulfur-free and poorer in organic acids, will become available. So, instead of burning it, it is anticipated that other types of valorization for lignin could be more easily found.

The present study is part of the European “Pulp & Fuel” project that gathers 10 academics and industrials partners and aims to convert black liquor into biofuels thanks to supercritical water gasification (SCWG). SCWG is an hydrothermal treatment which produces gas and where water above

critical point (374 °C, 22.1 MPa) acts as reactant (source of hydrogen and free radicals), solvent for organic compounds and catalyst [8]. Moreover, this process is compatible with high-water containing feedstocks like black liquor that can then be used directly avoiding a costly drying step. The alkali salts present in black liquor also act as catalysts for the SCWG and would enhance lignin depolymerization ([9]–[11]).

Several studies have investigated the SCWG of black liquor to produce a gas mixture rich in H₂ ([12]–[19]). Temperature appears to be the main parameter influencing gas yield. Hydrogen production increases with the temperature ([12], [17]). Clogging problem have been reported due to the salt precipitation and char formation ([14], [20]).

Additionally, some researchers have studied the hydrothermal treatment of lignin at lower temperature for the production of phenolic molecules ([21]–[25]). Huet et al. [25] have shown that monomeric compounds like phenol, catechol, guaiacol and syringol can be extracted from hydrothermal treatment of black liquor at 250 °C with a yield of 28 g.kg⁻¹ of dry black liquor. Moreover, they demonstrated the advantage provided by the treatment of a black liquor originating from prehydrolyzed wood and therefore depleted in products resulting from hemicelluloses which usually have the effect of causing recondensation of the phenolic fragments.

Our goal in this project is to study the lignin depolymerization and degradation during SCWG of black liquor coming from a soda cooking of prehydrolyzed hardwood chips. Hydrothermal experiments would be done at different temperatures between 225 to 600 °C. By doing so, optimum conditions to find phenolic compounds of interest (like syringol, guaiacol and phenol) can be identified. In fact, the studied process would consist in recovering these small phenolic molecules during the rise in temperature of the SCWG, at a time to be defined, before they have been transformed, and to continue the treatment until complete gasification. The whole process would then produce both gas (CH₄, H₂, CO₂...) and valuable phenolic monomers (syringol, guaiacol, phenol...).

2. Material and methods

2.1. Material

2.1.1. Chemicals and gas

List of chemicals and gas used for the experiments: Sulfuric acid H_2SO_4 4N (prepared from 95–97% H_2SO_4 ACS reagent, Fluka), sodium hydroxide NaOH (>99 %, Carl Roth), vanillin $\text{C}_8\text{H}_8\text{O}_6$ (99 %, Sigma Aldrich), kit poly(styrene sulfonate) sodium salt (PSS), ethyl acetate $\text{C}_4\text{H}_8\text{O}_2$ (ROTISOLV® ≥ 99.9 %, CPG Ultra Grade, Carl Roth), phenol $\text{C}_6\text{H}_6\text{O}$ (PESTANAL® analytical standard, Sigma Aldrich), guaiacol $\text{C}_7\text{H}_8\text{O}_2$ (Rotichrom®GC, Carl Roth), syringol 2,6-dimethoxyphenol $\text{C}_8\text{H}_{10}\text{O}_3$ (analytical standard, Sigma Adrich), phenol- d_6 $\text{C}_6\text{D}_6\text{O}$ (99 atom% D, Sigma Aldrich), Potassium Bromide KBr (for IR spectroscopy, Carl Roth), helium He for GC-MS analysis (ALFAGAZ™ 2 Helium, He ≥ 99.9999 %, Air Liquide), nitrogen N_2 for batch reactor (technical nitrogen, $\text{N}_2 > 99$ %, Air Products).

2.1.2. Black liquor

The raw material used in this study is sulfur-free black liquor provided by our project partner Fibre Excellence R&D kraft, a wood kraft pulp producer located in Saint-Gaudens (France). To produce this black liquor an industrial mix of hardwood chips composed of beech, poplar, oak and chestnut was used. The first step was hemicellulose hydrolysis (hot water extraction at 170 °C during 1 h with a mass ratio of water/dry wood of 3.9). With the temperature increase, the acetyl groups on hemicelluloses are released as acetic acid and acid hydrolysis occurs. Then a soda cooking (32 % NaOH, 5.1 Liquid/dry-wood mass ratio, 170 °C during 55 min) was applied on these hydrolyzed wood chips and the black liquor was recovered.

The main characteristics of this sulfur-free black liquor are presented in Table 1.

Table 1: Characteristics of sulfur-free black liquor used in the study

Black liquor main characteristics		
pH		13.6
Density		1.11
dry matter content (%)		19.4
ash content at 800 °C ¹ (% of dry black liquor)		41
	Na	203,000
	Ca	1,620
ash main element content (mg/kg)	K	1,240
method: ICP/AES NF EN ISO 16967	Si	324
	Mg	116
	Al	97
lignin content ² (% of dry black liquor)		31

¹ 105 °C-oven dried black liquor was introduced in a muffle furnace at 800 °C for 5 hours and the ashes was weighed

²lignin was recovered by centrifugation and freeze drying after acidification of black liquor at pH 3 with H₂SO₄

2.2. Hydrothermal treatment

Hydrothermal treatments were performed in two stirred batch reactors: a 0.6 L stainless steel (type 316) reactor sealed with a screwed jaw from Parr Instruments for temperature below 280°C and a 0.5 L stainless steel (type 1.4980) reactor sealed with dowels and nuts from TOP Industrie for temperature above 280°C. For each experiment, depending of the temperature, between 60 mL and 300 mL of black liquor is introduced in the reactor and N₂ is added to create an inert atmosphere and reach an initial pressure of about 10 bar relative. Then the reactor is heated by a heating collar (of 1.1 kW for Parr reactor and 4 kW for the TOP reactor) at the desired temperature (225, 250, 280, 300, 350, 400, 500 or 600 °C). The heating time depends on the targeted temperature (from 30 minutes to more than 2 hours). Once at temperature the

time is hold for 30 minutes before cooling down with an air coil around the reactor (time of cooling between 30 min and 1h30). During the reaction, the temperature is monitored by a thermocouple (type K) in an immersion sleeve inside the reactor and a relative pressure sensor associated with a pressure gauge indicates the pressure. Data of both sensors (temperature and pressure) are automatically recorded during the experiment in a computerized file.

When the temperature is below 30 °C, the gas analysis is performed. The reactor is opened to collect the liquid and solid phases which are separated by Buchner filtration. The solid is washed with deionized water before analysis. The mass of each phase was determined and the mass yield can be calculated by:

$$\text{liquid phase yield (\%)} = \frac{\text{mass of liquid phase recovered}}{\text{mass of black liquor introduced}} \times 100$$

$$\text{solid phase yield (\%)} = \frac{\text{mass of dry solid phase recovered}}{\text{mass of black liquor introduced}} \times 100$$

$$\text{gas phase yield (\%)} = \frac{n_{\text{gas}} \times \sum_{i=1}^x (M_{\text{gas } i} \times P_{\text{gas } i})}{\text{mass of black liquor introduced}} \times 100$$

where n_{gas} is the number of moles of gas produced during reaction, x the number of gases detected, $M_{\text{gas } i}$ the molar mass of the gas i , $P_{\text{gas } i}$ the molar percentage of the gas i in the total of the gas detected by micro-GC.

2.3. Samples preparation

2.3.1. Lignin extraction

Lignin or high molar mass fractions were extracted from black liquor and liquid phase after hydrothermal treatment. 20 g of sample under stirring was gradually acidified to pH 3 using H_2SO_4 4N. A centrifugation step for 30 minutes at 3076 g in a Sigma 3-16P centrifuge made it possible to recover the precipitated lignin. The lignin was then washed three times with deionized water previously acidified to pH 2 with H_2SO_4 4N and centrifuged after each

washing for 30 minutes at 3076 *g* in a Sigma 3-16P centrifuge. Finally, the washed lignin was freeze dried in a SP VirTis BenchTOP Pro freeze dryer.

2.3.2. Liquid/Liquid extraction

In order to recover the small phenolic compounds from the liquid phase after hydrothermal treatment, liquid/liquid extraction with ethyl acetate were performed. Ethyl acetate was added to the sample in a volumetric ratio of 1:1. After stirring, the mixture was centrifuged for 30 minutes at 3076 *g* in a Sigma 3-16P centrifuge to distinctly separate the two phases.

2.4. Analysis

2.4.1. Gas analysis

At the end of the experiment, gases produced were vented from the reactor and analyzed with an on line micro-Gas Chromatography (CP-4900 from Varian). O₂, H₂, CO and CH₄ were analyzed by a molecular sieve column with argon as carrier gas. C₂H₄, C₂H₆, C₂H₂, C₃H₈, C₆H₆, C₇H₈, CO₂ and H₂S were analyzed on a Poraplot-U column with helium as carrier gas. Temperature was 100°C and carrier gas pressure was 150 kPa. The quantity of the gas produced is calculated with the equation of ideal gas law knowing initial and final temperatures and pressures. The volume of the gas was determined by the volume of the reactor minus the volume of the liquid phase (calculated by the mass divided by the density). The volume of the solid was not taken into account. The uncertainty of the quantification is estimated to be ± 20 %.

2.4.2. Size Exclusion Chromatography (SEC)

Molar mass distributions of liquid phases and precipitated lignin were measured by an alkaline aqueous system gel permeation chromatography. 0.5 mL of liquid sample (or 25

mg of lignin) were dissolved in 4.5 mL (or 5 mL for lignin) of ultrapure water previously adjusted at pH 12 with NaOH. After filtration with a 0.45 μm PTFE membrane, the samples were injected. The chromatography device was composed of a pump (SP Thermo Spectra System P1500), an autosampler (SP Thermo Spectra System AS3500), a guardcolumn (TOSOH TSKgel PWH 0006762), three columns in series (TOSOH TSKgel G3000PW 0005762, TSKgel G4000PW 0005763, TSKgel G3000PW 0005762) and a UV-detector (SP Thermo Spectra System UV6000LP) measuring absorbance at 280 nm. Elution was performed with NaOH solution of pH 12 at flow rate of 0.6 mL.min⁻¹ and injection volume of 10 μL . Four polystyrene sulfonate sodium salts of different molar mass (PSS-psskit Mp 891 Da, 2180 Da, 4210 Da, 9740 Da) and vanillin were injected. The elution volumes at the maximum of the pics were recovered and added on the chromatogram of the samples to help analyze the results.

2.4.3. Gas Chromatography – Mass Spectroscopy (GC-MS)

After liquid/liquid extraction, ethyl acetate extracts were analyzed by GC-MS (PerkinElmer GC Clarus 680 and PerkinElmer MS Clarus SQ 8T). Helium is used as carrier gas at a flow rate of 1 mL.min⁻¹. In the GC oven, the capillary column (Elite 1701- 60 m x 0.25 mm inner diameter; 1.0 μm film thickness) is initially held at the temperature of 45 °C for 10 min and the temperature increase by 6 °C min⁻¹ to 230 °C where it is finally held for 9 min. The identification of compounds was done comparing mass spectra with NIST library. For the quantification, standard compounds (phenol, guaiacol and syringol) were injected at different concentrations to create a calibration curve and phenol-d6 was used as internal standard.

2.4.4. Elemental analysis

Elemental analyses were performed in a CHNS analyser Vario ElCube from Elementar. Helium and dioxygen were used as carrier gas and for the combustion. Content of carbon, hydrogen, nitrogen and sulfur were determined on 10 mg of the solid samples after hydrothermal treatment.

2.4.5. FTIR

Lignin and solid samples after hydrothermal treatment were analyzed by Fourier-Transform Infrared spectroscopy (FTIR). KBr pellet were prepared with 2 mg of samples and 178 mg of KBr. Absorbance spectra were recorded on a FT-IR spectrometer (PerkinElmer Spectrum 65) between 400 and 4000 cm^{-1} , with a resolution of 4 cm^{-1} and 16 scans and analyzed using Spectrum software from PerkinElmer.

3. Results and discussion

3.1. Hydrothermal experiments

Hydrothermal experiments have been performed in batch reactor at different temperatures between 225 °C and 600 °C and for each experiment three phases have been recovered: a solid phase, a liquid phase and a gas phase. Figure 1 represents the mass balance of the hydrothermal experiments. At high temperature, closure of mass balance is more difficult because of the smaller quantity of black liquor introduced but at least 95 % of the initial mass is recovered. For each trial, liquid phase remains the most important recovered phase by weight. With the increase of temperature, the quantity of solid produced increased until 500 °C. A temperature of at least 400 °C must be reached to obtain gas in a significant amount and then the increase of temperature increased the quantity of gas produced. These results are consistent with the study of Gökkaya et al. [26] on supercritical water gasification of phenol which produced a gas quantity nearly zero at 400 °C and which increased afterwards significantly with the temperature rise.

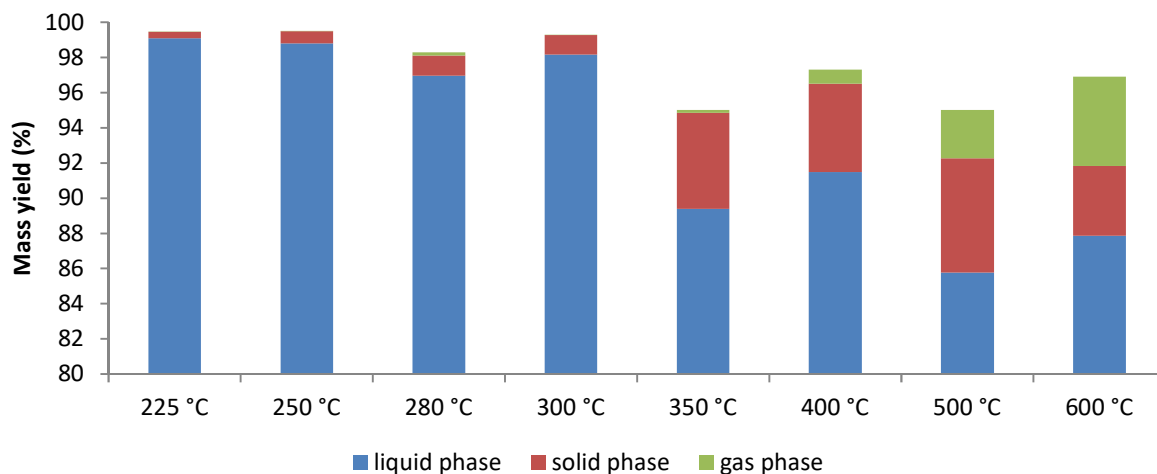


Figure 1: Mass yield of hydrothermal experiments at different temperatures

3.2. Gas phase

Concerning the gas composition, the main gas produced in our experiments were CH₄, H₂, CO₂ and C₂H₆. Figure 2 shows the quantity of gas produced for hydrothermal treatments at 400 °C, 500 °C and 600°C. Except for H₂ between 500 °C and 600°C, their quantity increased with the temperature. At 600 °C their molar proportions were 46 %, 25 %, 19 % and 9 % respectively for CH₄, H₂, CO₂ and C₂H₆. Other gases were present in the gas phase in much smaller quantity. Among them, toluene, benzene, propane and ethylene. CO was not found because of the water-gas shift reaction converting CO into CO₂ (CO + H₂O → CO₂ + H₂). This latter reaction is catalyzed by alkali salts which are present in high quantity in black liquor ([15], [24]). The CO₂ production is underestimated as part of the CO₂ will dissolve in water especially in alkaline media. The carbonic acid formed by this dissolution will gradually consume alkalinity and decrease the pH. Indeed, the pH of the liquid phase is changing depending on temperature: it stays at a value of about 13 up to 350 °C. Then, it gradually decreases to around 10 at 600°C. This pH drop would be essentially linked to an increase of CO₂ dissolved in the liquid phase.

In the Pulp & Fuel process, the H₂ from SCWG will be used to adjust CO/H₂ ratio of the syngas coming from bark gasification so that it is suitable for the Fischer-Tropsch process [27]. The production of H₂ should increase at higher temperatures than 600 °C ([18], [28], [29]). These temperatures cannot be

reached in our batch equipment but will be tested in a new reactor (continuous) that we will receive soon. The co-produced CH₄ may be valorized as energy for the mill.

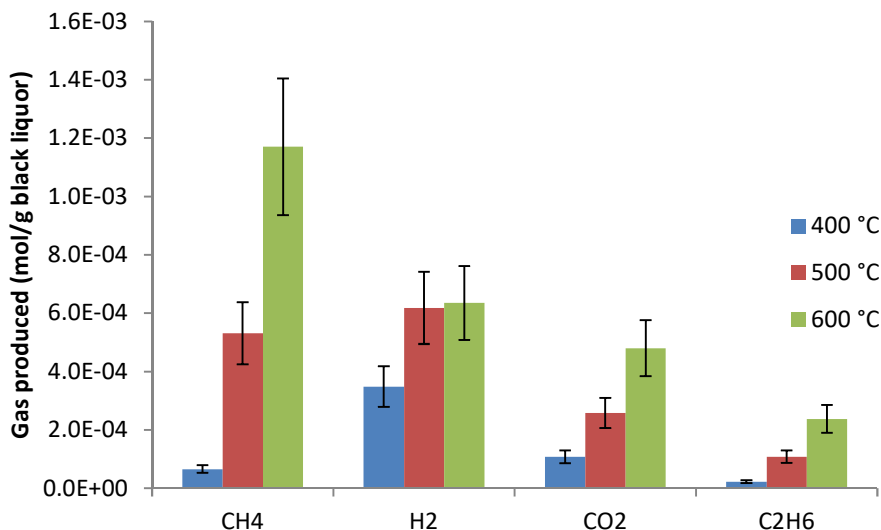


Figure 2: Main gas products in mol per g of raw black liquor

3.3. Liquid phase

The goal of this study is to look for interesting phenolic compounds coming from lignin depolymerization during hydrothermal treatment of the black liquor. These molecules of interest are found in the liquid phase at the end of the experiment. First of all, the whole liquid phase was analyzed by SEC, and then the small phenolic compounds were extracted to be identified and quantified. Finally, the high molar mass fraction were precipitated and characterized.

Figure 3 show the Size Exclusion Chromatography analysis on black liquor and liquid phases recovered after hydrothermal treatments at different temperatures. Compared to the initial black liquor, the liquid phase after 225 °C experiment is already significantly depolymerized: the highest molar mass have disappeared and the molar mass at the peak shifted from 2180 Da to 891 Da. Then, by increasing the temperature of the hydrothermal treatment further the high molar mass peak regularly decreases in intensity but stays around 890 Da. From 350°C and above, the signal is too low to be properly observed in this analysis. This decrease in intensity would reflect a change in the chemical structure of the

components (which would absorb less in UV at 280 nm). This will be confirmed below by FTIR spectroscopy of recovered lignin.

The black liquor curve exhibits a second peak after 25 mL which can be attributed to small oligomers of lignin with a degree of polymerization of 2 to 3. These small compounds are significantly degraded by the hydrothermal treatment from the lowest temperatures studied.

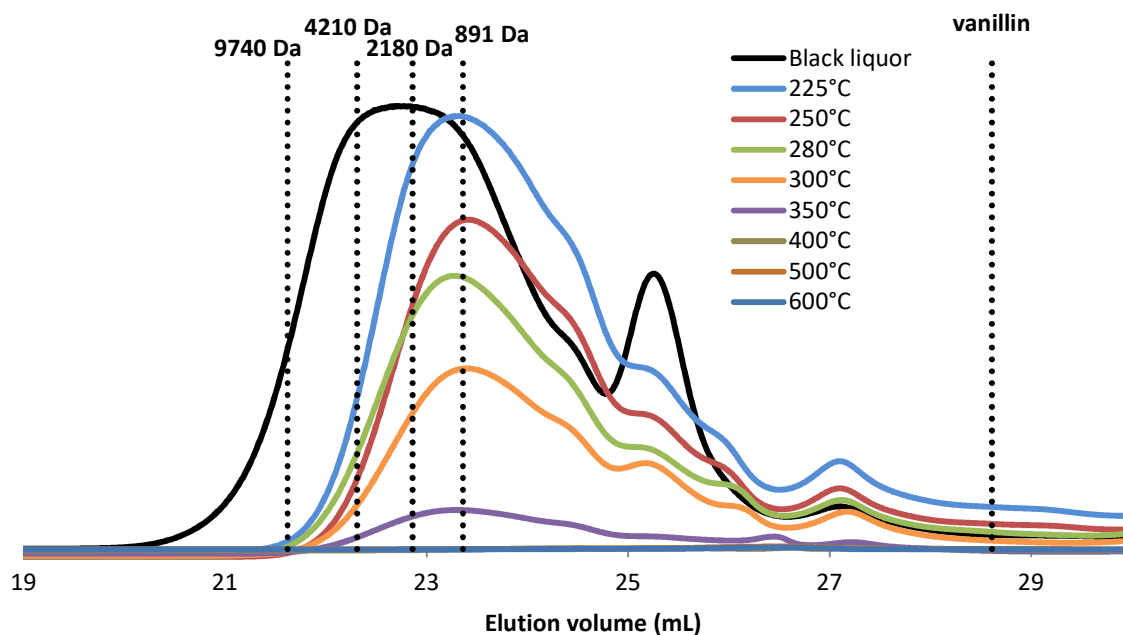


Figure 3: SEC analysis of black liquor and liquid phases after hydrothermal treatments at different temperatures

3.3.1. Small phenolic compounds analysis

The goal of this study was to find the best temperature of the hydrothermal treatment to recover the highest quantity of interesting phenolic compounds. For each hydrothermal experiment the small phenolic compounds were extracted from liquid phase by ethyl acetate. These ethyl acetate extracts were analyzed by gas chromatography coupled with mass spectrometry (GC-MS). As shown as example in Figure 4, many different aromatic compounds have been identified in the samples depending of the temperature of the hydrothermal treatment. At 280 °C, most of the compounds are methoxylated

phenol while at 500 °C the latter have disappeared in favor to alkyl phenol. Kang et al. ([23], [24]) have observed the same trend during hydrothermal treatment of lignin which may be explained by demethoxylation reactions that are favored at higher temperature, followed by radical coupling with alkyl groups.

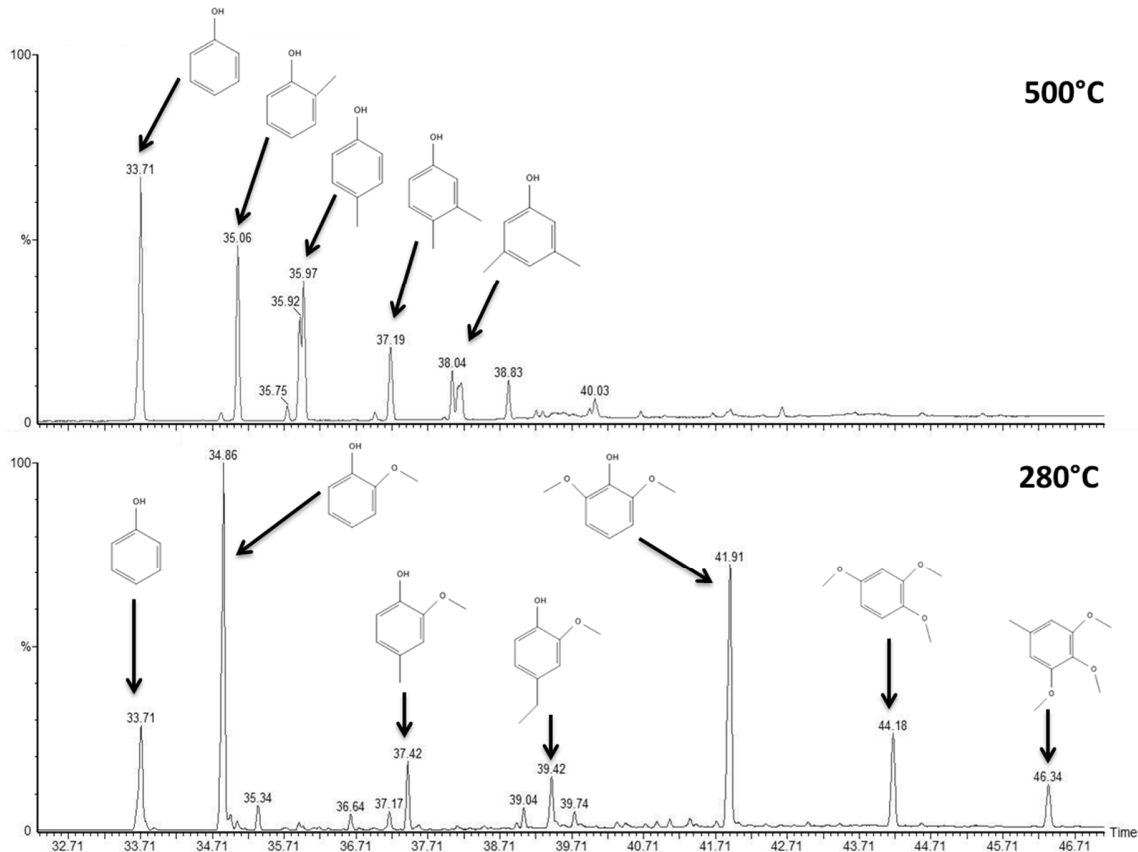


Figure 4: Example of GC-MS chromatogram of ethyl acetate extracts after hydrothermal treatment of black liquor at 280 °C and 500 °C

Three of the most abundant compounds (phenol, guaiacol and syringol) have been targeted and quantified thanks to calibration with model compounds: Figure 5 gives their concentration in all the samples.

The three molecules (coming from syringyl, guaiacyl and hydroxyl-unit of hardwood lignin) were already present in small quantity in black liquor but the depolymerization induced by the hydrothermal treatment increased their quantity. At low temperatures (up to 250°C), syringol was found in the highest quantity and as the temperature increased guaiacol became progressively dominant and finally at 350°C and above, only phenol was present. Several explanations can be suggested: The most methoxylated units may be the most easily extracted from lignin since they are supposed to carry less interunit C-C linkages ; also, demethoxylation reactions would occur more and more as the temperature increases [24] to eventually lead to phenol, which is rather stable at the investigated temperatures ([30], [31]).

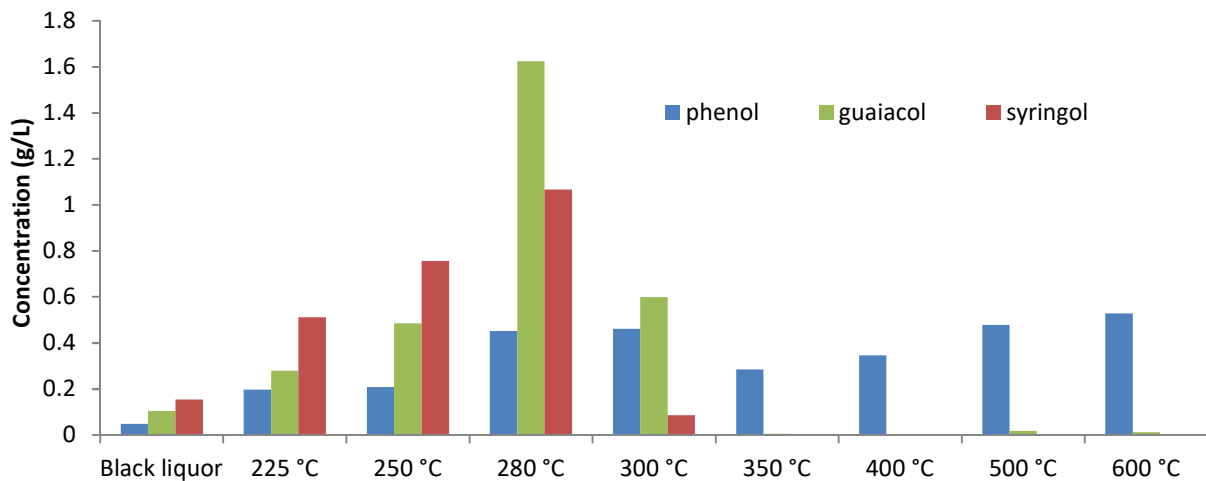


Figure 5: Concentration of phenol, guaiacol and syringol in liquid phase

Regarding these results, a treatment at 280 °C appears to lead to the highest quantity of small phenolic molecules: 3.15 g of phenol, guaiacol and syringol was extracted from one liter of liquid phase. So, calculation gives 5 % of the initial lignin which was converted into these small phenolic compounds.

The extraction and valorization of these phenolic compounds might be of great interest for pulp mills as the demand for biobased compounds increases and the phenol market is expected to grow in the coming years ([2], [32]).

The phenolic extract contains several compounds that could be valorized directly as a mixture by substituting petroleum-based phenol for the production of green phenol-formaldehyde resins ([24],

[33]). However, the purification and isolation of some specific compounds may be a good opportunity to target higher added value applications. Indeed, these phenolics have particular properties like antioxidant, antiseptic, anti-diarrhea and germicidal activity which can be used for the synthesis of specialty polymers, pharmaceutical products, adhesives, food additives etc. ([24], [34], [35]). For example, guaiacol can be used as smoky odor in synthetic flavors and fragrances; syringol can be used in pharmaceutical (platelet aggregation, anti-dermatophyte activity); 4-ethylguaiacol can be used in ice cream, gelatins or puddings ([35]–[38]).

3.3.2. Higher molar mass fraction

As observed before, the depolymerization already occurs significantly at 225 °C. In order to investigate the structural modification of lignin, the high molar mass fraction of the liquid phases from hydrothermal treatments between 225 °C and 300 °C were isolated by the same precipitation method used to extract lignin from black liquor. This temperature zone has been studied because as seen in the previous part, it is in this range that the small phenolic molecules should be extracted in the framework of this project. The presence of potentially valuable oligomers could be interesting information as well.

Table 2 gives the weight percentage of the precipitate called here “lignin”. The quantity of high molar mass fraction that could be extracted by acid precipitation decreased with the increased intensity of the treatment. These results are consistent with the reduction of UV absorbance observed in the SEC of the whole liquid phase (Figure 3) and follow the degradation of the lignin.

Table 2: Content of “lignin” in the wet liquid phases (in weight)

	Black Liquor	225 °C	250 °C	280 °C	300 °C
Lignin content (% of liquid phase in weight)	6.0	5.4	5.1	4.9	4.2

The molar mass distribution of the precipitated lignin was also analyzed by SEC (Figure 6). Compared to Figure 3 the molar mass distribution of lignin samples in Figure 6 is narrower but the main peaks are still

centered on the same molar mass. All the small molar mass compounds are reduced in quantity because part of them did not precipitate under acidification.

In Figure 6, compared to the lignin extracted from the initial black liquor, the lignin precipitated from the liquid phase at 225 °C experiment is already significantly depolymerized. With the increase of the temperature of the hydrothermal treatment (from 225°C to 300°C), the molar mass of the lignin precipitate decreased a little further to an average polymerization degree of about 4 (800 - 900 Da). Zhou [39] and Wahyudiono et al. [21] have observed similar trend during the hydrothermal treatment of isolated alkaline lignin. Lignin depolymerization occurs during hydrothermal treatment by hydrolysis of ether bonds like β -O-4 linkages and cleavage of aliphatic C-C bonds ([21], [24], [39], [40]). These results are also consistent with the presence of small phenolic compounds in the liquid phases as detailed in the previous part.

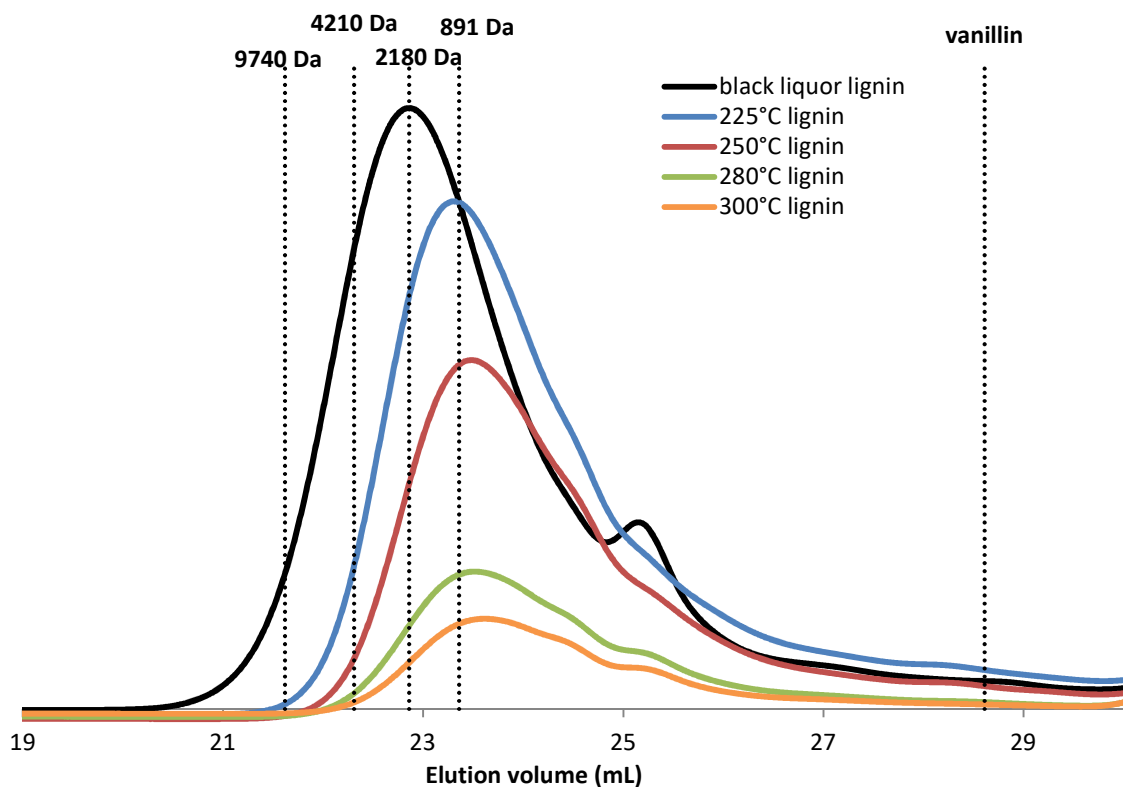


Figure 6: SEC analysis on lignin extracted from black liquor and liquid phases after hydrothermal treatment

At the same time when the temperature increased, the intensity of the global signal was reduced. As the SEC is equipped with a UV detector, the lower absorbance would indicate that the phenolic character of the precipitate is progressively lost.

FTIR spectra of the lignin samples recovered from the liquid phase are presented in Figure 7. The intensity of absorption band between 3100 and 3600 cm^{-1} ascribed to hydroxyl group decreased with the rise of reaction temperature. Likewise the absorption bands between 1400 and 1600 cm^{-1} ascribed to carbons of aromatic skeleton tended to decrease with the increase in temperature. The absorption band at 1463 cm^{-1} assigned to lignin OCH_3 groups also progressively decreased in intensity with the hydrothermal treatment. The same observation could be done for the absorption bands at 1329, 1271, 1150, 1030 cm^{-1} related to vibrations of C-C, C-O and C-H of syringyl and guaiacyl unit.

Thereby, with the increase of the temperature, lignin is not only more depolymerized by ether and aliphatic C-C bonds cleavage, but it is also more intensely degraded leading to more structure and functional groups changes. Demethoxylation, dealkylation, alkylation and condensation reactions occurred in a greater extent [24]. Demethoxylation reactions are in line with the observations on FTIR spectra about the reduced intensity of adsorption band assigned to syringyl and guaiacyl units.

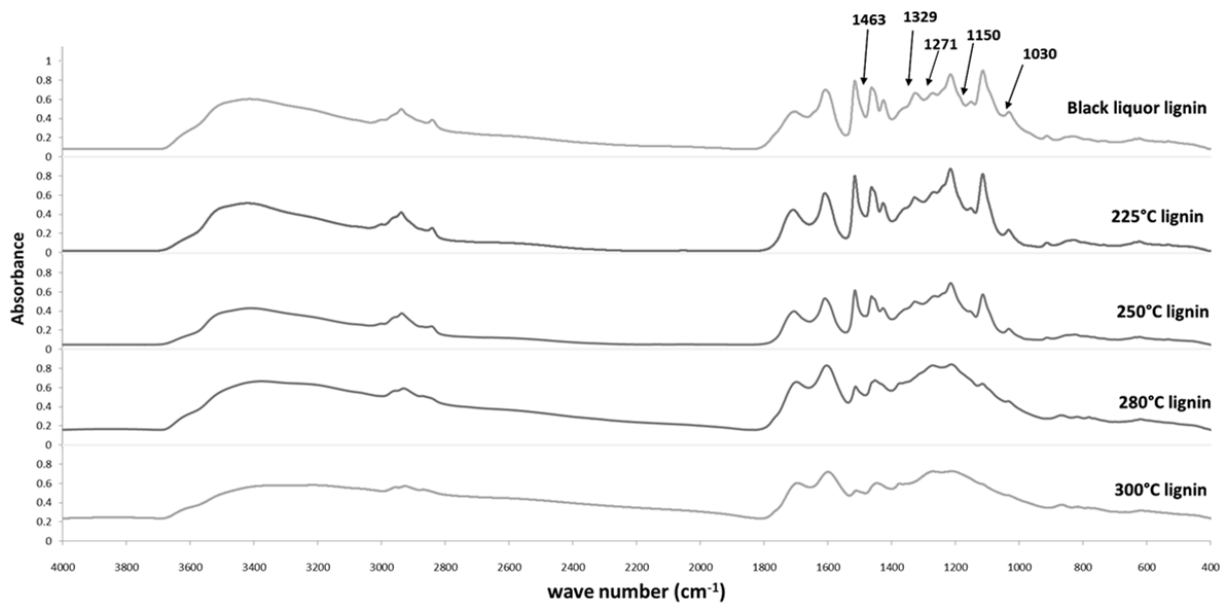


Figure 7: FTIR analysis of the precipitate recovered from black liquor and liquid phases after hydrothermal treatment

So, with the increase of temperature, lignin structure was progressively degraded and lost its polyphenolic character.

3.4. Solid phase

To fully apply the concept of biorefinery, all the side products of the process should be valorized to optimize the use of natural resources. Regarding solid from hydrothermal experiment, some authors have proposed application as active carbon for gas storage or heavy metal adsorption ([41]–[43]). With this in mind, the solid phases produced in this study have been characterized.

Solid phases recovered at the end of hydrothermal treatments were analyzed after thorough washing with deionized water. No sample could be recovered in sufficient quantity below 300 °C.

Table 3 shows the result of elemental analysis of the solid produced in comparison with the dried black liquor.

Table 3: Elemental analysis of dried black liquor (BL) and solid phase after hydrothermal treatments at different temperatures

- "others" (calculated by difference) include oxygen atom and Na, K, Ca, Al, Mg etc. in inorganics.

	Dried BL	300 °C	350 °C	400 °C	500 °C	600 °C
C (%)	25.9	70.5	76.8	84.2	87.7	91.6
H (%)	5.3	5.2	5.4	5.2	5.1	2.6
N (%)	0.1	0.4	0.3	0.3	0.3	0.3
S (%)	0.2	0.1	0.1	0.1	0.2	0.1
Others (%)	68.6	23.8	17.4	10.2	6.7	5.3
H/C (mol/mol)	2.5	0.9	0.8	0.7	0.7	0.3

There is a significant difference between the elemental composition of dried black liquor and the solid after a hydrothermal treatment already at 300 °C. This is essentially due to the high quantity of inorganics present in dried black liquor which stay in the liquid phase after the hydrothermal experiment as the reactor is cooled down to the room temperature before opening.

The results in Table 3 shows an increase in carbon content in the solid with the increase of the temperature of the treatment. This can be explained by the removal of oxygen atom (elimination of OCH₃ on aromatic structures and OH on lignin side chains) as shown by the decrease of the "others" category. The hydrogen content and the H/C ratio slowly decreased with the temperature up to 600 °C where an important drop was observed. As suggested by Hu et al. [44], the increase of the temperature induces the elimination of functional groups and then carbonization in the solid residues.

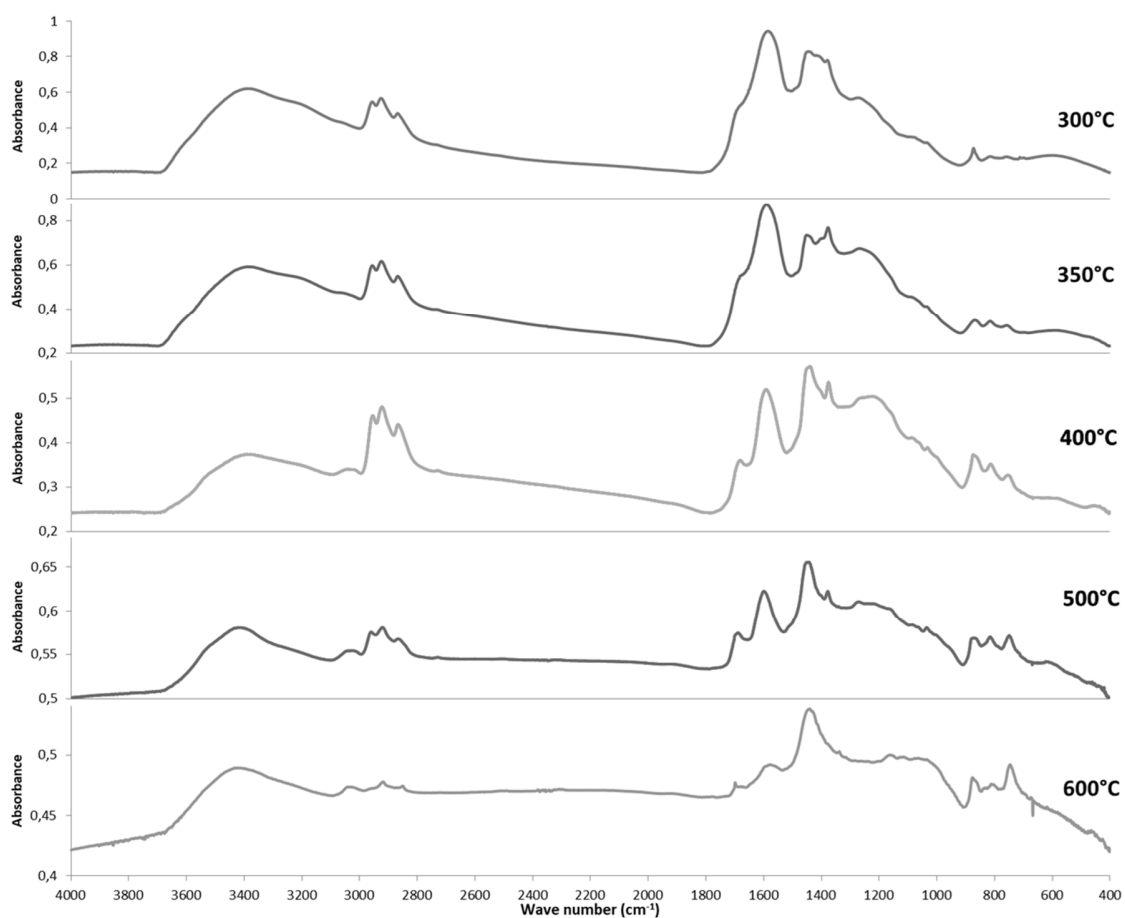


Figure 8: FTIR analysis of solid phases after hydrothermal treatment

The FTIR analyses of solid phases (Figure 8) highlight the decrease of OH groups (band between 3100 and 3600 cm^{-1}) with the increase in temperature.

The three absorption bands below 3000 cm^{-1} assigned to stretching vibrations of aliphatic C-H decreased only above 400°C and have almost disappeared at 600 °C. It is consistent with the elemental analysis where a drop of H/C ratio from 0.7 to 0.3 was observed between 500 °C and 600 °C. Kruse et al. [45] by treating wood hydrochar between 490 °C and 700 °C also observed a decrease of bands characteristic for alkyl-chain and alcohols.

The absorption band between 1400 cm^{-1} and 1600 cm^{-1} ascribed to carbons of aromatic skeleton were present in all the spectra even if their intensity tended to decrease with increasing temperature.

From 400 °C, an absorption band just above 3000 cm⁻¹ can be distinguished; it is ascribed to C-H aromatic stretching vibrations. Moreover, the presence of the absorption band between 700 cm⁻¹ and 900 cm⁻¹, related to C-H out of plan deformation in mono, di or tri-substituted benzene ring confirms that the solid structure is highly aromatic and condensed. This conclusion is in line with the high carbon content observed in elemental analysis and the low H/C ratio.

4. Conclusion

The objective of this study was to find the optimal temperature to recover monomeric phenolic compounds during the hydrothermal gasification process applied on black liquor. Hydrothermal batch experiments from 225 °C to 600 °C have been performed on black liquor coming from soda cooking of autohydrolyzed hardwood chips. It was shown that lignin depolymerization has already occurred at 225 °C. The molecular weight of lignin continued to decrease with increasing temperature. However it is at 280 °C that the quantity of phenolic monomers (phenol, syringol and guaiacol) was the most important. These three compounds represented 5 % of the initial lignin present in the black liquor (by weight). This work makes it possible to envisage a complete process producing both syngas and phenolic monomers of interest in which the latter are extracted at around 280 °C well below the start of gas formation (400 °C).

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References

- [1] D. S. Bajwa, G. Pourhashem, A. H. Ullah, and S. G. Bajwa, "A concise review of current lignin production, applications, products and their environmental impact," *Ind. Crops Prod.*, vol. 139, p. 111526, Nov. 2019, doi: 10.1016/j.indcrop.2019.111526.
- [2] H. Wang, Y. Pu, A. Ragauskas, and B. Yang, "From lignin to valuable products—strategies, challenges, and prospects," *Bioresour. Technol.*, vol. 271, pp. 449–461, Jan. 2019, doi: 10.1016/j.biortech.2018.09.072.
- [3] P. Azadi, O. R. Inderwildi, R. Farnood, and D. A. King, "Liquid fuels, hydrogen and chemicals from lignin: A critical review," *Renew. Sustain. Energy Rev.*, vol. 21, pp. 506–523, May 2013, doi: 10.1016/j.rser.2012.12.022.
- [4] H. Luo and M. Abu-Omar, "Chemicals From Lignin," in *Reference Module in Earth Systems and Environmental Sciences*, 2017. doi: 10.1016/B978-0-12-409548-9.10235-0.
- [5] C. Chirat, D. Lachenal, and A. Dufresne, "Biorefinery in a kraft pulp mill: from bioethanol to cellulose nanocrystals," *Cellul. Chem. Technol.*, vol. 44, no. 1–3, pp. 59–64, 2010.
- [6] M. Moshkelani, M. Marinova, M. Perrier, and J. Paris, "The forest biorefinery and its implementation in the pulp and paper industry: Energy overview," *Appl. Therm. Eng.*, vol. 50, no. 2, pp. 1427–1436, Feb. 2013, doi: 10.1016/j.applthermaleng.2011.12.038.
- [7] H. Curmi, C. Chirat, M.-C. B. Salon, and D. Lachenal, "Effect of autohydrolysis on alkaline delignification of mixed hardwood chips and on lignin structure," *Holzforschung*, vol. 72, no. 8, pp. 631–636, Jul. 2018, doi: 10.1515/hf-2017-0196.
- [8] Y. Hu, M. Gong, X. Xing, H. Wang, Y. Zeng, and C. C. Xu, "Supercritical water gasification of biomass model compounds: A review," *Renew. Sustain. Energy Rev.*, vol. 118, p. 109529, Feb. 2020, doi: 10.1016/j.rser.2019.109529.
- [9] E. Pérez and C. O. Tuck, "Quantitative analysis of products from lignin depolymerisation in high-temperature water," *Eur. Polym. J.*, vol. 99, pp. 38–48, Feb. 2018, doi: 10.1016/j.eurpolymj.2017.11.053.
- [10] N. Abad-Fernández, E. Pérez, and M. José Cocero, "Aromatics from lignin through ultrafast reactions in water," *Green Chem.*, vol. 21, no. 6, pp. 1351–1360, 2019, doi: 10.1039/C8GC03989E.
- [11] Y. Hawangchu, D. Atong, and V. Sricharoenchaikul, "The effect of alkali on the product distribution from black liquor conversion under supercritical water," *Environ. Technol.*, vol. 38, no. 13–14, pp. 1742–1750, Jul. 2017, doi: 10.1080/09593330.2017.1323954.
- [12] M. Huet, A. Roubaud, and D. Lachenal, "Conversion of sulfur-free black liquor into fuel gas by supercritical water gasification," *Holzforschung*, vol. 69, no. 6, pp. 751–760, Aug. 2015, doi: 10.1515/hf-2014-0254.
- [13] O. N. Fedyaeva, A. A. Vostrikov, A. V. Shishkin, and D. Yu. Dubov, "Conjugated processes of black liquor mineral and organic components conversion in supercritical water," *J. Supercrit. Fluids*, vol. 143, pp. 191–197, Jan. 2019, doi: 10.1016/j.supflu.2018.08.015.
- [14] E. Purkarová, K. Ciahotný, M. Šváb, S. Skoblia, and Z. Beňo, "Supercritical water gasification of wastes from the paper industry," *J. Supercrit. Fluids*, vol. 135, pp. 130–136, May 2018, doi: 10.1016/j.supflu.2018.01.015.
- [15] J. Lappalainen *et al.*, "Sub- and Supercritical Water Liquefaction of Kraft Lignin and Black Liquor Derived Lignin," *Energies*, vol. 13, no. 13, Art. no. 13, Jan. 2020, doi: 10.3390/en13133309.
- [16] B. H. Y. Ong, T. G. Walmsley, M. J. Atkins, and M. R. W. Walmsley, "Hydrothermal liquefaction of Radiata Pine with Kraft black liquor for integrated biofuel production," *J. Clean. Prod.*, vol. 199, pp. 737–750, Oct. 2018, doi: 10.1016/j.jclepro.2018.07.218.

- [17] C. D. Blasio *et al.*, "A study on supercritical water gasification of black liquor conducted in stainless steel and nickel-chromium-molybdenum reactors," *J. Chem. Technol. Biotechnol.*, vol. 91, no. 10, pp. 2664–2678, 2016, doi: 10.1002/jctb.4871.
- [18] K. Özdenkçi, M. Prestipino, M. Björklund-Sänkiäho, A. Galvagno, and C. De Blasio, "Alternative energy valorization routes of black liquor by stepwise supercritical water gasification: Effect of process parameters on hydrogen yield and energy efficiency," *Renew. Sustain. Energy Rev.*, vol. 134, p. 110146, Dec. 2020, doi: 10.1016/j.rser.2020.110146.
- [19] C. Cao, Y. Xie, L. Mao, W. Wei, J. Shi, and H. Jin, "Hydrogen production from supercritical water gasification of soda black liquor with various metal oxides," *Renew. Energy*, vol. 157, pp. 24–32, Sep. 2020, doi: 10.1016/j.renene.2020.04.143.
- [20] C. De Blasio, S. De Gisi, A. Molino, M. Simonetti, M. Santarelli, and M. Björklund-Sänkiäho, "Concerning operational aspects in supercritical water gasification of kraft black liquor," *Renew. Energy*, vol. 130, pp. 891–901, Jan. 2019, doi: 10.1016/j.renene.2018.07.004.
- [21] Wahyudiono, M. Sasaki, and M. Goto, "Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water," *Chem. Eng. Process. Process Intensif.*, vol. 47, no. 9, pp. 1609–1619, Sep. 2008, doi: 10.1016/j.cep.2007.09.001.
- [22] W. Jiang, G. Lyu, S. Wu, and L. A. Lucia, "Near-critical water hydrothermal transformation of industrial lignins to high value phenolics," *J. Anal. Appl. Pyrolysis*, vol. 120, pp. 297–303, Jul. 2016, doi: 10.1016/j.jaap.2016.05.017.
- [23] S. Kang, X. Li, J. Fan, and J. Chang, "Classified Separation of Lignin Hydrothermal Liquefied Products," *Ind. Eng. Chem. Res.*, vol. 50, no. 19, pp. 11288–11296, Oct. 2011, doi: 10.1021/ie2011356.
- [24] S. Kang, X. Li, J. Fan, and J. Chang, "Hydrothermal conversion of lignin: A review," *Renew. Sustain. Energy Rev.*, vol. 27, pp. 546–558, Nov. 2013, doi: 10.1016/j.rser.2013.07.013.
- [25] M. Huet, A. Roubaud, C. Chirat, and D. Lachenal, "Hydrothermal treatment of black liquor for energy and phenolic platform molecules recovery in a pulp mill," *Biomass Bioenergy*, vol. 89, pp. 105–112, Jun. 2016, doi: 10.1016/j.biombioe.2016.03.023.
- [26] D. Selvi Gökkaya, M. Saglam, M. Yüksel, and L. Ballice, "Supercritical water gasification of phenol as a model for plant biomass," *Int. J. Hydrog. Energy*, vol. 40, no. 34, pp. 11133–11139, Sep. 2015, doi: 10.1016/j.ijhydene.2015.04.078.
- [27] M. Ostadi, E. Rytter, and M. Hillestad, "Boosting carbon efficiency of the biomass to liquid process with hydrogen from power: The effect of H₂/CO ratio to the Fischer-Tropsch reactors on the production and power consumption," *Biomass Bioenergy*, vol. 127, p. 105282, Aug. 2019, doi: 10.1016/j.biombioe.2019.105282.
- [28] S. N. Reddy, S. Nanda, A. K. Dalai, and J. A. Kozinski, "Supercritical water gasification of biomass for hydrogen production," *Int. J. Hydrog. Energy*, vol. 39, no. 13, pp. 6912–6926, Apr. 2014, doi: 10.1016/j.ijhydene.2014.02.125.
- [29] A. Kruse, D. Meier, P. Rimbrecht, and M. Schacht, "Gasification of Pyrocatechol in Supercritical Water in the Presence of Potassium Hydroxide," *Ind. Eng. Chem. Res.*, vol. 39, no. 12, pp. 4842–4848, Dec. 2000, doi: 10.1021/ie0001570.
- [30] A. Kruse, P. Bernolle, N. Dahmen, E. Dinjus, and P. Maniam, "Hydrothermal gasification of biomass: consecutive reactions to long-living intermediates," *Energy Environ. Sci.*, vol. 3, no. 1, pp. 136–143, 2010, doi: 10.1039/B915034J.
- [31] J. Yu *et al.*, "Catalytic gasification of phenol in supercritical water with Ru/graphitized carbon black," *RSC Adv.*, vol. 6, no. 79, pp. 75512–75521, 2016, doi: 10.1039/C6RA15601K.
- [32] M. J. Bidy, C. Scarlata, and C. Kinchin, "Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential," National Renewable Energy Lab. (NREL), Golden, CO (United States), NREL/TP-5100-65509, Mar. 2016. doi: 10.2172/1244312.

- [33] J. Xu, J. Jiang, W. Lv, W. Dai, and Y. Sun, "Rice husk bio-oil upgrading by means of phase separation and the production of esters from the water phase, and novolac resins from the insoluble phase," *Biomass Bioenergy*, vol. 34, no. 7, pp. 1059–1063, Jul. 2010, doi: 10.1016/j.biombioe.2010.01.040.
- [34] C. Amen-Chen, H. Pakdel, and C. Roy, "Separation of phenols from Eucalyptus wood tar," *Biomass Bioenergy*, vol. 13, no. 1–2, pp. 25–37, Jan. 1997, doi: 10.1016/S0961-9534(97)00021-4.
- [35] J. N. Murwanashyaka, H. Pakdel, and C. Roy, "Separation of syringol from birch wood-derived vacuum pyrolysis oil," *Sep. Purif. Technol.*, vol. 24, no. 1, pp. 155–165, Jun. 2001, doi: 10.1016/S1383-5866(00)00225-2.
- [36] H. Fiege *et al.*, "Phenol Derivatives," in *Ullmann's Encyclopedia of Industrial Chemistry*, American Cancer Society, 2000. doi: 10.1002/14356007.a19_313.
- [37] I. F. S. T. and F. Y., "[Anti-dermatophyte activity of phenolic compounds in 'mokusaku-eki'].," *Yakugaku Zasshi*, vol. 118, no. 1, pp. 27–30, Jan. 1998, doi: 10.1248/yakushi1947.118.1_27.
- [38] J. A. Maga and I. Katz, "Simple phenol and phenolic compounds in food flavor," *C R C Crit. Rev. Food Sci. Nutr.*, vol. 10, no. 4, pp. 323–372, Dec. 1978, doi: 10.1080/10408397809527255.
- [39] X.-F. Zhou, "Conversion of kraft lignin under hydrothermal conditions," *Bioresour. Technol.*, vol. 170, pp. 583–586, Oct. 2014, doi: 10.1016/j.biortech.2014.08.076.
- [40] R. Singh *et al.*, "Hydrothermal conversion of lignin to substituted phenols and aromatic ethers," *Bioresour. Technol.*, vol. 165, pp. 319–322, Aug. 2014, doi: 10.1016/j.biortech.2014.02.076.
- [41] E. Pérez, C. O. Tuck, and M. Poliakoff, "Valorisation of lignin by depolymerisation and fractionation using supercritical fluids and conventional solvents," *J. Supercrit. Fluids*, vol. 133, pp. 690–695, Mar. 2018, doi: 10.1016/j.supflu.2017.07.033.
- [42] W. Sangchoom and R. Mokaya, "Valorization of Lignin Waste: Carbons from Hydrothermal Carbonization of Renewable Lignin as Superior Sorbents for CO₂ and Hydrogen Storage," *ACS Sustain. Chem. Eng.*, vol. 3, no. 7, pp. 1658–1667, Jul. 2015, doi: 10.1021/acsuschemeng.5b00351.
- [43] Y. Zhao, Y. Tian, H. Zhou, and Y. Tian, "Hydrothermal conversion of black liquor to phenolics and hydrochar: Characterization, application and comparison with lignin," *Fuel*, vol. 280, p. 118651, Nov. 2020, doi: 10.1016/j.fuel.2020.118651.
- [44] J. Hu, D. Shen, S. Wu, H. Zhang, and R. Xiao, "Effect of temperature on structure evolution in char from hydrothermal degradation of lignin," *J. Anal. Appl. Pyrolysis*, vol. 106, pp. 118–124, Mar. 2014, doi: 10.1016/j.jaap.2014.01.008.
- [45] A. Kruse and T. A. Zevaco, "Properties of Hydrochar as Function of Feedstock, Reaction Conditions and Post-Treatment," *Energies*, vol. 11, no. 3, Art. no. 3, Mar. 2018, doi: 10.3390/en11030674.



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