

# Lignin from bark as a resource for aromatics production by hydrothermal liquefaction

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## Abstract

Biorefineries, which are using mostly unused side streams of other existing processes like bark or lignin, have a huge potential to open new resources, for example, chemicals. But with new resources new challenges will be met along the way. These challenges must be addressed and discussed to build a solid and far-sighted process. This work focuses on the formation of monocyclic compounds like catechol as a valuable product during the hydrothermal liquefaction of beech wood bark as well as Kraft lignin from pine wood like Indulin AT. The focus is to get a better knowledge of the behavior of bark during hydrothermal liquefaction for depolymerization aiming at the production of aromatic building blocks for chemicals. Therefore, the influence, for example, of temperature and reaction time, the chemical reaction pathways, and the therefore necessary analytics need to be understood. Several limitations and challenges of common analytical methods are discussed and compared for bark and Kraft lignin, which is relatively well investigated and can act as a reference material to build a common ground and make it possible to build standards for all bioeconomic processes. Hydrothermal conditions increase the yield and selectivity toward bifunctional molecules like catechol. With rising temperatures and longer retention times, the catechol mass yields get lower. At temperatures above 350°C, nearly no catechol could be found any more. Different types of wood deliver different lignin compositions in terms of the monomeric units. However, it can be observed that different lignins show the same trends in regard to the catechol yield concerning temperatures and reaction time dependence, but overall a different product spectrum.

## KEYWORDS

catechol, challenges, characterization of fragmentation products, hydrothermal liquefaction, lignin, platform chemicals

## 1 | INTRODUCTION

Bark, and more specifically the lignin contained in the bark, could be used as a source for aromatic molecules in the production of platform chemicals. Crude oil would be substituted by using an already aromatic functionalized

molecule. The lignin-rich bark is built and used of plants to be resistant against environmental influences and to contribute to mechanical stability. Lignin constitutes of three different monomer basic units: coniferyl alcohol, sinapyl alcohol, and p-cumaryl alcohol (Bunzel & Ralph,

2006). The amount of each unit depends, for example, on the source of the lignin regarding the plant material used and the separation process applied, by which the lignin was obtained. Softwood (like pine) lignin is mostly composed of coniferyl alcohol, while hardwood (like beech) lignin also contains sinapyl alcohol as building block (Bunzel & Ralph, 2006). Therefore, the lignin structure is highly complex and versatile depending on its origin and isolation method (Bauer, Sorek, Mitchell, Ibáñez, & Wemmer, 2012; Donaldson, 2013). From the variety of types of biomass, that is, lignins, different products and product distributions could be gained after decomposition (Dorrestijn, Kranenburg, Poinsoot, & Mulder, 1999; Faravelli, Frassoldati, Migliavacca, & Ranzi, 2010). This needs to be considered when the depolymerization process is investigated. The challenge of liquefaction of lignin for chemical use is to maintain certain functional groups, such as hydroxyl groups (-OH) or methoxy groups (-OCH<sub>3</sub>) and to improve selectivity toward bifunctional components like catechol, which are particularly interesting for production of polymeric materials. Due to the complexity of lignin molecules also the reaction network during decomposition is complex. So far, only a limited number of key substances and reactions are identified, leaving a number of open questions. Within the lignin molecules, several types of chemical bonds of different reactivity may be split. The reactive aryl ether bonds ( $\beta$ -O-4) and other ether bonds like  $\alpha$ -O-4 bonds are predetermined breaking points (Wang & Rinaldi, 2012). Other bonds, like C-C-type bonds, are much more difficult to cleave and may lead to the formation of oligomers and larger, tar-like structural molecules. In this context, the repolymerization of intermediates needs to be investigated. For the gain of platform chemicals like catechol, the reaction pathway toward this monoaromatic structure needs to be understood.

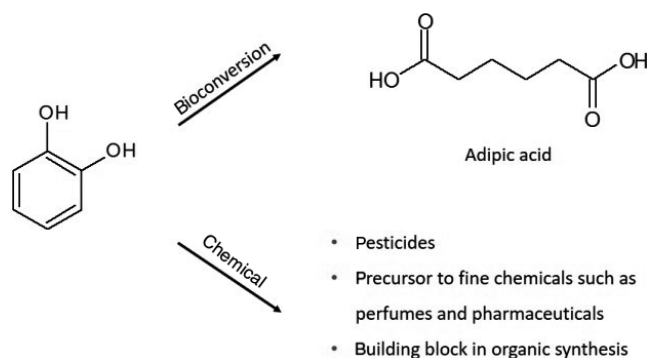
Before lignin is used in a process, it is mostly isolated from the other biomass present. The Kraft process, for example, is the most common process in the pulp and paper industry and the main source for lignin today (Ragnar et al., 2014). In this process, lignin and likewise the bark is usually utilized to produce energy. This makes the Kraft lignin and bark relatively cheap; however, for chemical use of the so-produced lignin its sulfur content can be a problem. In particular, in catalytic processes the sulfur may act as a catalyst poison despite from incriminating the reactor construction materials. Also, the Kraft process is harsh to the lignin structure itself and causes a certain cleavage structure. The organosolv process is more gentle toward the molecule structure, but it is more expensive and not commercially established like the Kraft process (Schulze, Seidel-Morgenstern, Lorenz, Leschinsky, & Unkelbach, 2016;

Unkelbach, Pindel, & Scheweppe, 2009). By using bark, these isolation processes will be omitted, because it gets parted of the trunks directly on-site of the pulp and paper industry. Therefore, this side stream of the pulp and paper industry could be used directly as a concentrated resource.

The three monomeric units of lignin are mainly coupled via ether bonds, biphenylic, or alkyl bridges which have to be split in a depolymerization process. Thermal degradation processes occur via pyrolytic reactions which are mainly radical chain reactions which end up in an enormous number of reaction products. The advantage of solvolytic processes is that especially ether bonds are split very selectively with the help of an alkaline or acid catalyst. Hydrothermal liquefaction (HTL) is a particular case of the solvolysis of lignin and means the reaction with water at near critical conditions (22 MPa, 647 K). At near critical conditions, water is a relatively strong dissociated molecule and a good solvent for organic compounds with a strongly decreasing density. Due to these special properties of water, the hydrothermal lignin depolymerization is more selective than other processes and maintains the functional groups, like hydroxyl (-OH) or methoxy groups (-CH<sub>3</sub>), and improves selectivity toward bifunctional components like catechol. Therefore, it was aimed in this work to keep the already functionalized parts of the lignin molecule via the special properties of water under near and subcritical conditions and to improve the understanding of the underlying reaction pathways, too. An additional focus was set to the characterization and possible use of the oligomers formed during lignin degradation by HTL.

## 1.1 | Possible promising products

As the phenol yield stagnates at a certain value after HTL and cannot be increased, it appears as economically more sustainable to produce different bifunctional compounds in addition to monomeric phenol (Forchheim, Hornung, Kruse, & Sutter, 2014; Jegers & Klein, 1985). Guaiacol is formed as primary product from lignin depolymerization but is an



**FIGURE 1** Possible use of one of the gained products: catechol

intermediate on the way to catechol. Catechol with its two functional groups is an interesting product because it can serve, for example, as a starting material for polymers or for the production of adipic acid (see Figure 1).

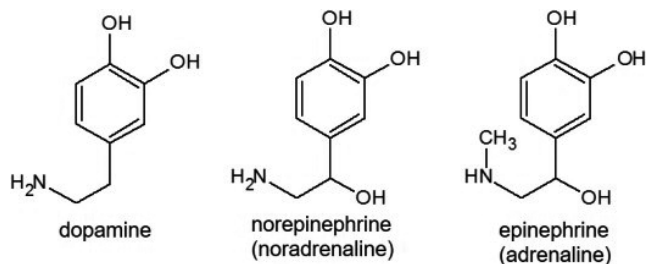
Also, catechol can be used as a precursor for fine chemicals and pharmaceuticals. As an example, it is used to produce neuromodulators for the central nervous system and hormones in the blood circulation; dopamine, norepinephrine, and adrenaline (see Figure 2).

Apart from the mentioned monocyclic products, a lot of oligomers with functional groups are formed which could serve as Bisphenol A substitute, but still a clear characterization of products is missing, just group affiliations are known.

To characterize the reactions pathways of HTL a suitable and reliable analytical set up is required. Analytics is a most challenging part of using biomass as a resource, because of the variable and usually difficult to characterize starting material and a large number of unknown conversion products. Small changes in analytical methods could lead to significantly different results, so it is also important to specify the used methods. These facts make it hard to compare different results. Different challenges met with NMR, GPC, etc. are discussed and compared in this work for bark and Kraft lignin, which is relatively well investigated and can act as a reference material. Different experiments were performed to investigate if the reaction network of Kraft lignin can be transferred to other lignocellulosic biomass sources like bark. Additionally, an oligomer was synthesized and used for HTL (Katahira, Kamitakahara, Takano, & Nakatsubo, 2006) as intermediate between the lignin molecule and the monomeric products. A synthesis of vanillin over  $\beta$ -O-4 bonds was chosen, because  $\beta$ -O-4 is the main common bond in the Kraft lignin.

## 2 | MATERIALS AND METHODS

Beech bark, a residue of the pulping industry provided by Sappi company (Stockstadt, Germany), was used in this study. To compare the gained results and to understand the reactions of lignin, Indulin AT as Kraft lignin was used as a reference. The biomass source of Indulin AT is pine wood which was purchased by WestRock industries



**FIGURE 2** High value products, synthesized via catechol as a precursor

(Atlanta, USA). Potassium hydroxide was used as a homogenous catalyst in HTL. Lignin, respectively bark, and the potassium hydroxide solution are placed in a stainless steel (1.4571) microreactor (10–25 ml, max. 500°C, max. 280 bar) and sealed. The oven used for the heating is a modified GC oven with a heating rate of 40 K/min. After reaction, the autoclaves were immersed in cold water to cool down and to stop the reaction. Samples of each product phase (solid, liquid, and gas) were taken and analyzed by the methods described in the following.

### 2.1 | Analysis via gas chromatography

Gas chromatography (GC) was mainly used for analyzing the monomeric components in the liquid product mixture. The gaseous samples are analyzed by an Agilent 7890 B GC system with an FID and TCD. For the quantitative analysis of the liquid products, a Hewlett Packard 5890-II GC system with a Hewlett Packard 5890 autosampler equipped with an FID-detector was used. An HPChem laboratory data system is used. As column, a nonpolar 30 m Restek Rtx-1 MS crossbond dimethylpolysiloxane column was used with a nominal diameter of 250  $\mu$ m and a nominal film thickness of 25  $\mu$ m. The FID has a temperature of 310°C, with a hydrogen flow of 41 ml/min and an air flow of 450 ml/min. The constant makeup gas flow (nitrogen) is 5 ml/min. The GC front inlet has an initial temperature of 275°C and a carrier gas pressure of 2.4 bar. Fifteen different monomeric aromatic compounds (cyclopentanone, furfural, 2-methylcyclopentanone, cyclohexanone, cyclohexanol, 5-hydroxymethylfurfural, phenol, o-cresol, guaiacol, p-cresol, 4-ethylphenol, syringol, vanillin, 4-ethylcatechol, and catechol) could be quantified by calibration. As water, which is detrimental for the used GC column, is the solvent in the HTL, the samples cannot be measured directly, and a sample preparation method was applied (Forchheim, 2013).

### 2.2 | Analysis via gel permeation chromatography

Gel permeation chromatography (GPC) or size exclusion chromatography (SEC) separates the component mixture based on the size of its components or more precisely on their hydrodynamic volume. It is a separation technique solely based on the diffusion velocity of the molecules through the separation column. There are no interactions (neither physical nor chemical) with the solid phase like in other chromatographic techniques. Larger molecules cannot enter the pores of the solid phase and hence pass the column fast. Small molecules, however, can diffuse in the pores and have a longer way through the column and get eluted later as the bigger molecules. To ensure that there is practically no interaction with the stationary phase for

nonpolar molecules, a nonpolar solid phase is needed, and the other way around. For molecules, which have polar and nonpolar groups, it is complicated to find a suitable solid phase, but it is possible to use mixed columns, which contain polar and nonpolar solid phases (Gey, 2008). Important is also the fact that the hydrodynamic volume of a molecule changes with the solvent (Gey, 2008). The product samples and the synthesized oligomer were tested in dedicated measurements with the company Malvern.

### 2.3 | Analysis via nuclear magnetic resonance spectrometry

NMR measurements were performed with starting material as well as the solid and liquid products in a Bruker Avance 250 MHz instrument. The lignin structures were investigated by two-dimensional (2D) NMR measurements. To get information about the lignin structure and the influence of the applied isolation processes, heteronuclear single quantum coherence (HSQC) measurements (according to Bunzel & Ralph, 2006; Mansfield, Kim, Lu, & Ralph, 2012) were performed for the lignins used. In contrast to 1D-NMR measurements, couplings between individual nuclei become visible in 2D-NMR experiments. Indirect couplings are present via bonds as well as directly across the space. Thus, information about the spatial structure of the molecules under consideration of the different biomass sources and isolation methods can be obtained. Product analysis by NMR was carried out with different solvents.

## 3 | RESULTS AND DISCUSSION

As mentioned earlier, analytics is crucial for the understanding and further elucidation of reactions networks. The monomers obtained from HTL of all lignin-based biomass are similar in their structure consisting of an aromatic ring with different side groups and chains. The resulting superposition of signals is in general for several analytical methods one main reason why analysis of lignin-derived components in the liquid phase is complex, hampering quantification of substances, and interpretation of the data. In the following, challenges met within this work are described and discussed. Lessons learned are derived improving the understanding of lignin and HTL of lignin.

### 3.1 | Gas chromatography

Even with GC, it is hard to analyze the individual products, because of their complex variety and similarity of products formed in terms of molecular weight and functionality. There is no database for lignin degradation products available, so a calibration of more than 10 products is already work-intensive. Also, the amounts of the single products

vary significantly with the different reaction parameters. Consequently, quantification of components in the right range of the calibration requires many measurements in different dilutions.

There are always numerous peaks which cannot be separated properly or identified (Figure 3). The signal-to-noise ratio can also be a problem in GC measurements. Meanwhile, 15 different monomers can be quantified in our laboratory. This allows for analysis of the main monomeric compounds from HTL and improved the understanding of the reaction networks by using different biomass feedstocks like bark. GC is also the most common method for monomeric phenolics gained out of lignin, and it is a reliable method because several measurements done via HPLC or GC-MS confirm the gained results.

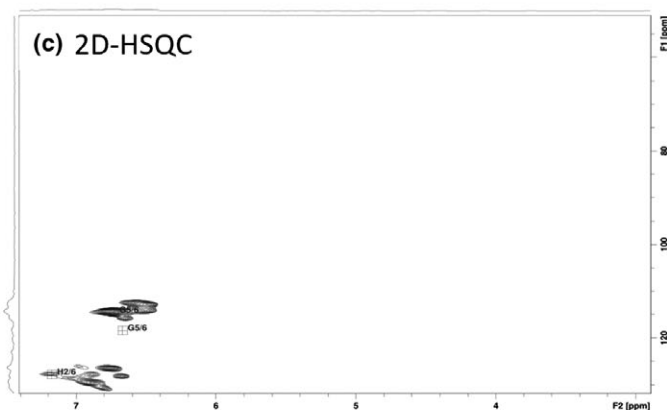
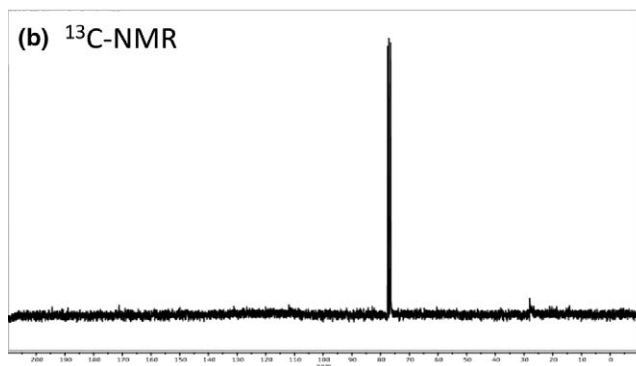
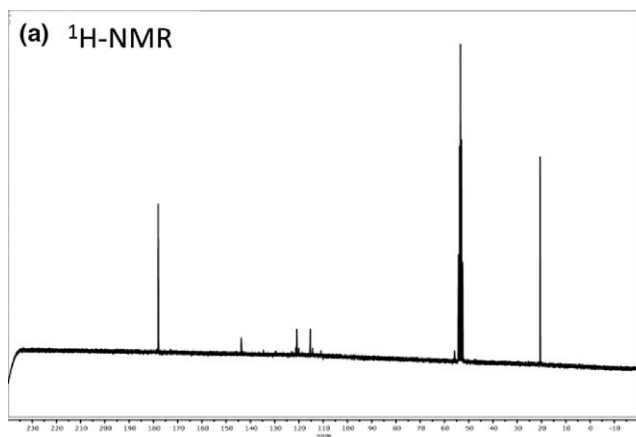
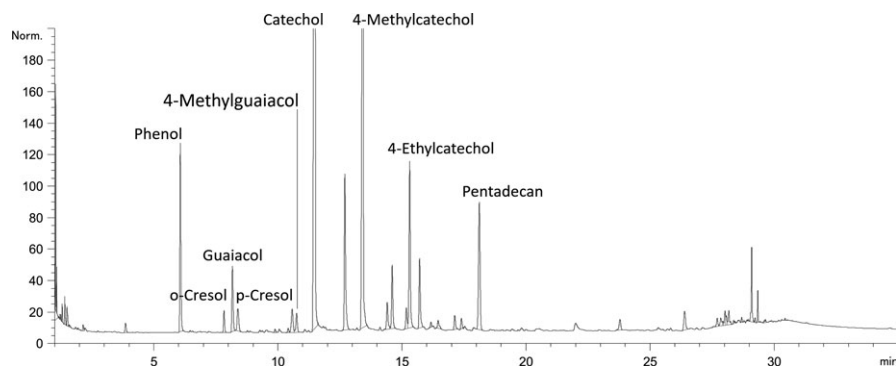
### 3.2 | Analysis via NMR

Also, by NMR measurements it is not easy to obtain a clear spectrum, which makes the structure analysis highly complicated. There is also a superposition of signals, due to the broad product spectra. Furthermore, different problems occurred with different solvents and measuring techniques. Figure 4 shows three different examples of NMR measurements.

Figure 4a shows a  $^1\text{H}$ -NMR spectrum of an HTL product mixture in deuterated methanol with a superposition of different signals. Figure 4b shows the corresponding  $^{13}\text{C}$ -NMR. The low noise-to-signal ratio makes it impossible to analyze a single signal. 2D-HSQC spectra can help to identify the molecular structure depending in terms of aromatic or aliphatic bond atoms. For instance, for an aromatic ring signal for the  $\text{C}_2$ ,  $\text{C}_5$ , and  $\text{C}_6$  atoms should appear in the lower field (low left corner) of the spectra, while their bond types appear in the high field (upper right corner). Figure 4c shows the 2D-HSQC spectra of a product mixture; it shows signals in the aromatic area but not in the aliphatic area. But there are just signals of the  $\text{C}_5$  and  $\text{C}_6$  ring atoms, the signal for the  $\text{C}_2$ -atom is missing. This usually indicates ring cleavage, but the lack of a shift to signals in the aliphatic area is contradictory to this assumption. Also, signals expected for existing bonds are missing. This phenomenon appeared in several measurements and could not be explained until now. These examples show how difficult it is to gain clear information out of product spectra from NMR measurements.

Fractionation of the liquid product could be a next logical step to get better results. But separation of the whole product mixture cannot simply be performed by distillation or solvent extraction. Usually products with similar properties are recovered by one or the other method, which still leads to superposition of the signals in NMR or chromatography analysis.

**FIGURE 3** GC chromatogram of a liquid phase product mixture sample, the labeled components are quantified compounds

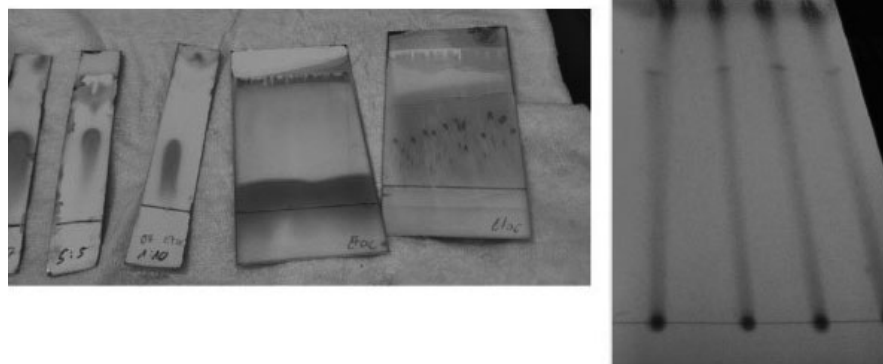


**FIGURE 4** NMR signal of liquefaction product mixtures obtained by different methods and solvents. (a)  $^1\text{H}$ -NMR of a product mixture in deuterated methanol. (b) corresponding  $^{13}\text{C}$  NMR to a). (c) 2D-NMR spectrum

Also, by thin layer chromatography, separation of the single compounds is not satisfactorily achievable for the same reason. Different solvents and mixing ratios were used, but still then complete separation was not possible (see Figure 5). Instead of the expected dots of individual components on the thin layer chromatography plate, just lines become visible indicating that the separation is not completed. Because of the complexity of the fractionation of the products, fractionated lignins as a starting material could also lead to a more defined product mixture and help with the separation and the analytical methods (Rohde et al., 2018).

### 3.3 | Analysis via size exclusion chromatography

The biggest challenge in the analysis of lignin-derived compounds is the analysis of oligomers. SEC seems to be the method of choice, but the lignin structure has both non-polar and polar regions, which makes it very complicated to apply a suitable SEC method. By this method, the product mixture is separated based on the size of its components or more precisely on their hydrodynamic volume. There are no interactions (neither physical nor chemical) with the solid phase like in other chromatographic



**FIGURE 5** Thin layer chromatogram plates with different solvents, mixtures, and ratios of the liquefaction product mixtures

techniques. Larger molecules cannot enter the pores of the solid phase and hence pass the column fast. Small molecules, however, can diffuse in the pores and have a longer way through the column and get eluted later as the bigger molecules. To ensure that there is practically no interaction with the stationary phase for nonpolar molecules, a nonpolar solid phase is needed, and the other way around. For molecules, which have polar and nonpolar groups, it is complicated to find a suitable solid phase, but it is possible to use mixed columns, which contain polar and nonpolar solid phases (Gey, 2008). Important is also the fact that the hydrodynamic volume of a molecule changes with the solvent (Gey, 2008; see Figure 6).

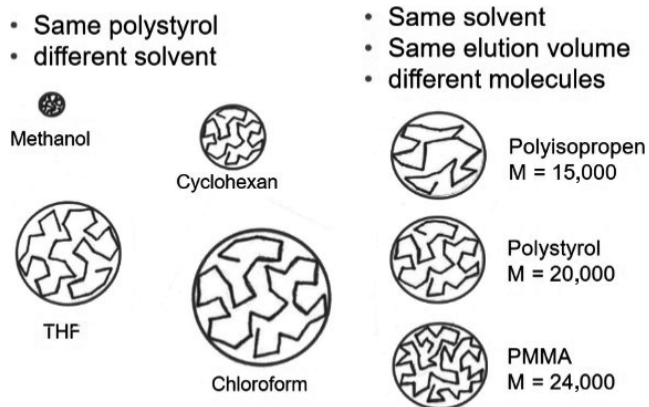
To get an intermediate between the lignin molecule and the monomeric products, an oligomer molecule (Figure 7) was synthesized and also investigated (Katahira et al., 2006).

The measurements were performed by Malvern Instruments to find a suitable method. The analysis of the synthesized oligomers as well as of the liquid reaction products obtained from HTL (at 300°C & 30 and 60 min, and 400°C & 30 min) shows promising results. The

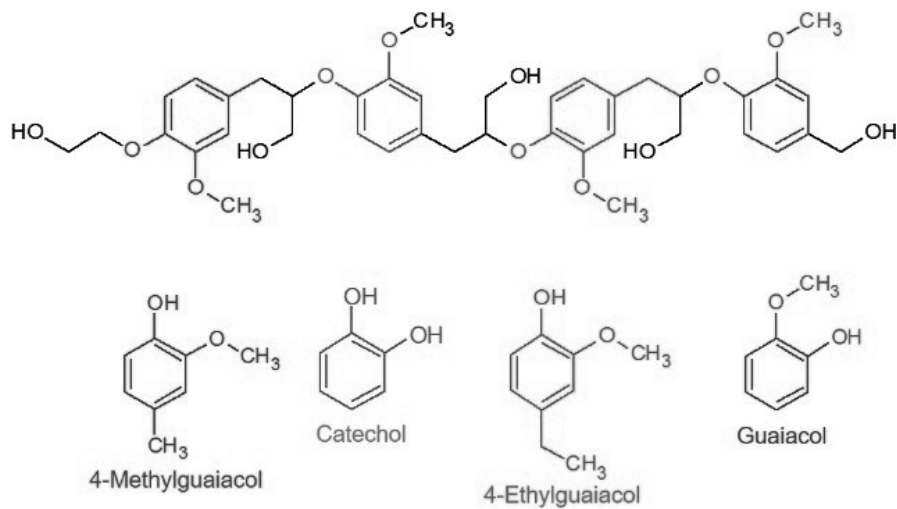
samples were measured in dimethyl sulfoxide (DMSO) as a solvent with a mixed column (polar and nonpolar solid phase) and calibrated against pullulan (water-soluble polysaccharide consisting of maltotriose units). The mixed column shall help with the polar and nonpolar regions of the oligomers.

Figure 8 shows an SEC chromatogram where the retention volume, respectively, time is plotted on the x-axis. The larger molecules leave the column first, while smaller ones are retained in the pores of the solid phase. The peak area can be integrated and is equivalent to the amount of the analyzed molecule. Wide peaks represent several molecules of comparable size, where a proper separation was not possible. With a longer reaction time at 300°C, the valley between the two main peaks (~11 ml retention volume) gets lower. This means, that the molecule variety gets higher and the separation of them even worse. But the separation of the molecules in this size region is not completed. This is another problem of the SEC with lignin-based samples: The range of molecule sizes is too large, which makes it complicated to cover it all. With 400°C and 30 min reaction time, the chromatogram shows a shift to the right side, which means that the molecules become smaller than those obtained at 300°C. The synthesized lignin oligomer delivers the clearest chromatogram (Figure 9).

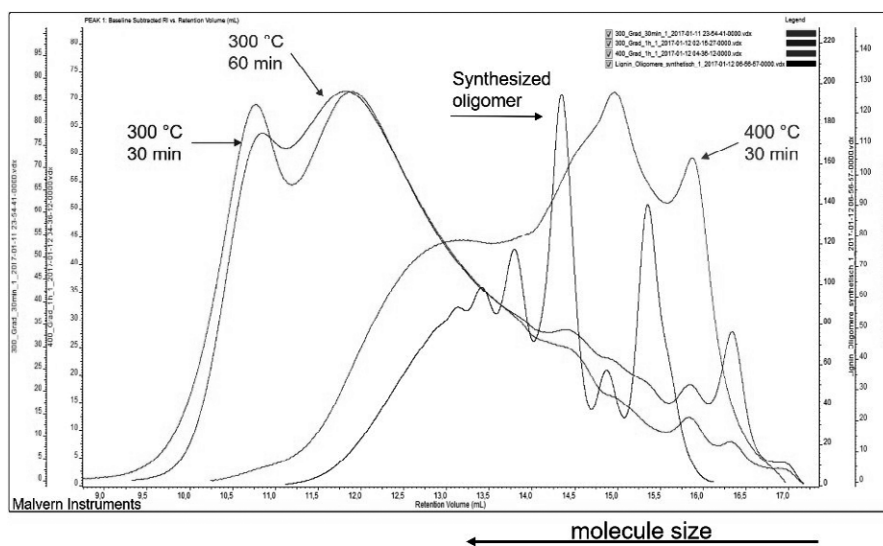
Standards for the calibration of SEC hardly are commercially available (Artemyeva, Diprospero, Smoliakova, Kozliak, & Kubátová, 2015; Artemyeva, Kozliak, & Kubátová, 2015; Diprospero, Artemyeva, Kubátová, & Smoliakova, 2015). Often polystyrene is used as standard, but it is a nonpolar hydrocarbon chain unlike to the lignin-derived molecules. With the synthesized oligomer, the calibration could be extended. Figure 9 shows the chromatogram of the synthesized oligomer along with the calibration curve. Chain lengths of four (15.5 ml retention time) and up to eight monomeric units (13.3 ml retention time) can be observed. These results were included in the calibration. The expected shift of molecular weight applying higher temperatures and longer reaction times to



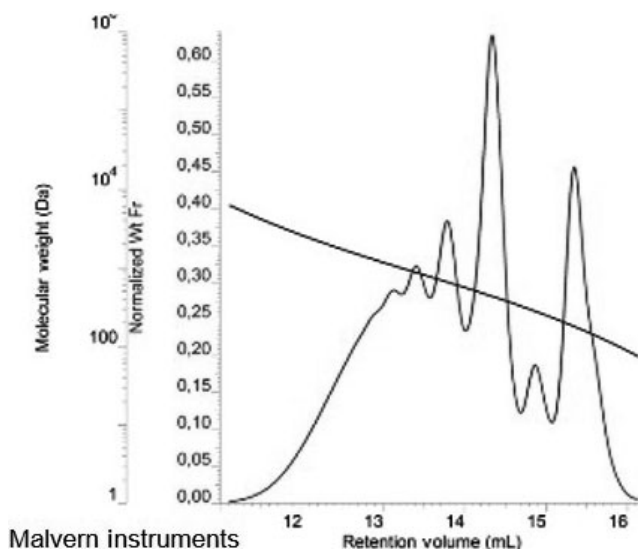
**FIGURE 6** Schematic of hydrostatic volumes of the same molecule in different solvents and different molecules in the same solvent (only pps-polymer; pss-polymer, 2016)



**FIGURE 7** One possible lignin oligomer molecule, synthesized according to Rui et al. and some of the formed HTL products (Katahira et al., 2006)



**FIGURE 8** SEC chromatogram of HTL products (at 300 °C and 30 min, 300 °C and 60 min, 400 °C and 30 min) and of the synthesized oligomer as received by Malvern Instruments (2017)



**FIGURE 9** SEC chromatogram of the synthesized oligomer with calibration (conducted by Malvern Instruments, 2017)

smaller molecules could be observed and valued via this new GPC method (see Figure 8). This method shows benefits to the analysis of HTL products because now additional reaction steps can be suggested and included in the reaction network. However, further evaluation of the method is needed besides the fact, that the method requires high practical efforts. Also, possible side chains of real samples cannot be simply measured via the integration of the plain chain of monomeric units and need further investigation. This extended method does not only allow for a more proper analysis of oligomers thus improving the understanding of HTL reaction networks, but also is the basis to develop potential separation process to obtain oligomers as products in addition to the monomeric substances.

Recent studies like the work of Sheng et al. (2017) apply a procedure which is using negative ion-mode electrospray ionization (ESI) with NaOH as a dopant and collision-activated dissociation (CAD) fragmentation pattern. With this, they could provide new information about

synthesized oligomer model compounds from coniferyl alcohol with  $\beta$ -O-4 and/or 5-5 bonds, which could help to analyze and better interpret real biomass samples. Also, in this case several aspects must be still understood and considered. As an example, the synthesized oligomers always have a coniferyl alcohol end group; this could influence the fragmentation patterns of the deprotonated molecules (Sheng et al., 2017). However, this method shows potential for analysis of oligomers, but it is also highly complex and expensive. Several main requirements must be fulfilled (e.g., no fragmentations, only ions containing an entire intact molecule; Sheng et al., 2017) to get clear results. In addition, only straight chains were investigated, side chains could complicate the interpretation of the results.

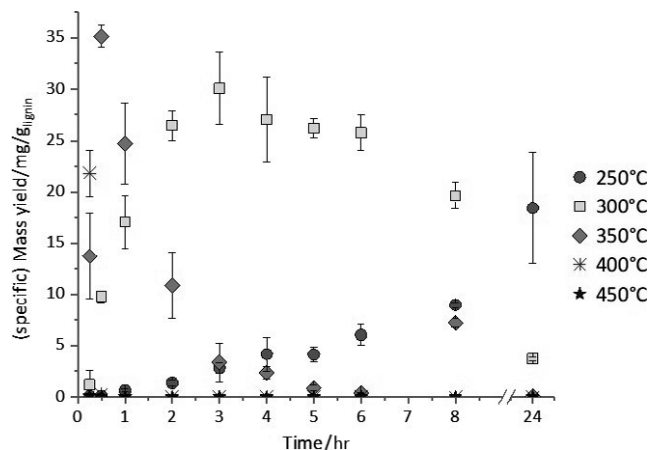
In (Liu, Li, Liu, & Shen, 2017), new advantages of GC-MS and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements are presented. The authors investigated the degradation of lignin to aromatic compounds in isopropanol under mild, microwave-assisted heating and could show the different ranges of the oligomeric and monomeric product spectra of the lignin degradation. Exact molecular masses can hardly be identified this way, even if more information of the molecular structure is available.

Other studies like (McClelland et al., 2017) combining NMR, Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR), and SEC analyses delivered also new information of lignin degradation pathways via oligomeric compounds. The SEC method was performed with THF as mobile phase and calibration with polystyrene, so solubility and calibration issues must be considered. Via FT-ICR number average molecular weight and element ratios could be obtained. But these results are not sufficient to derive a clear structure of the oligomers. NMR measurements should help to gain more information of the molecule structure; however, because of superposition of signals only ranges can be identified for certain functional groups. So, an idea of the starting structures is possible, but further understanding is still necessary.

Recent advantages of new and extended analysis methods and their combination improved the understanding of the degradation process of lignin and the intermediate oligomeric structures. But the interpretation of the measured results and the measurement itself is still difficult, highly complex, and also expensive. In addition, more standard measurements should be developed for a better comparability between different works.

### 3.4 | Different lignin sources as starting materials

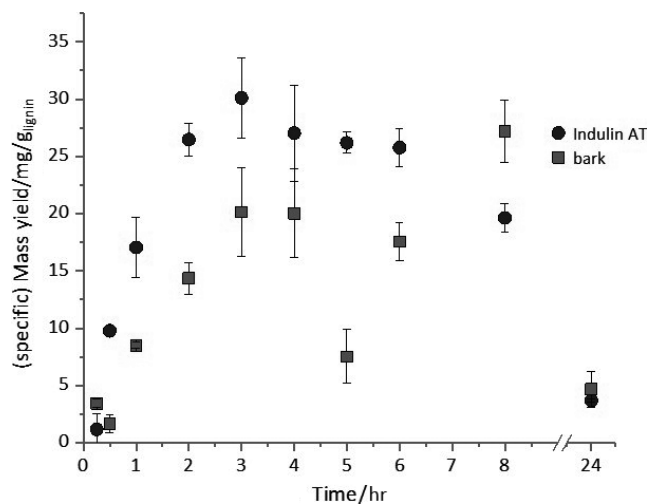
With higher reaction temperatures, longer reaction times, and a higher concentration of the homogenous catalyst KOH, the rate of gas formation and further reactions of the



**FIGURE 10** Mass yield of the catechol obtained by HTL in mg per g lignin from beech bark over the different reaction times (0.25–24 hr) and temperatures (250–450°C) and 1 wt.% KOH

**TABLE 1** Different products of the HTL; Mass yields of syringol and guaiacol obtained at 300°C, 120 min and 1 wt.% KOH solution

300°C, 120 min	Indulin AT	Bark
Syringol mg/g <sub>lignin</sub>	0.03	3.27
Guaiacol mg/g <sub>lignin</sub>	11.2	5.80

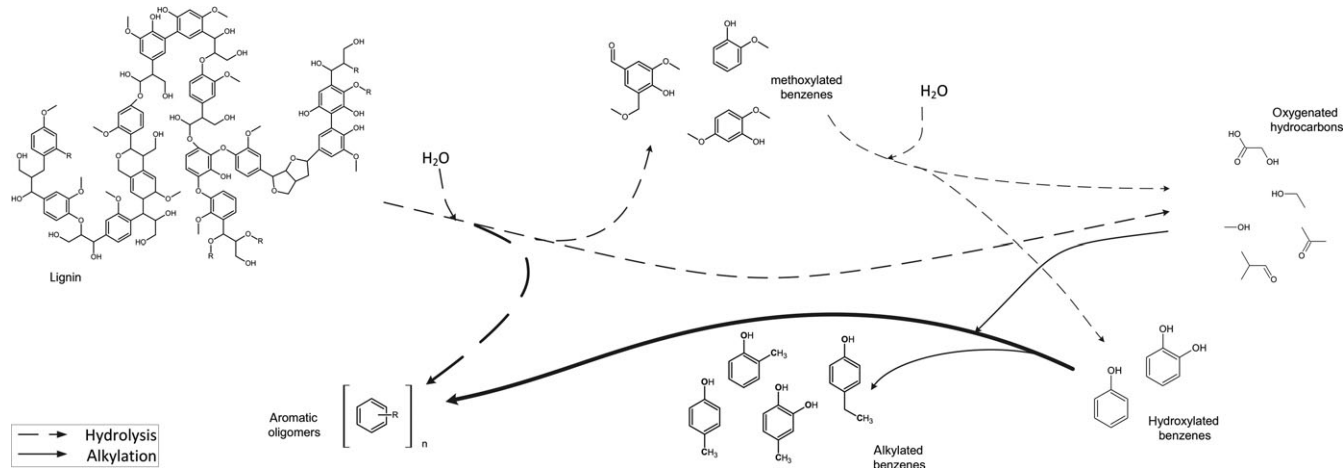


**FIGURE 11** Mass yield of the obtained catechol in mg per g used lignin by HTL at the different reaction times (0.25–24 hr), 300°C and a KOH concentration of 1 wt.% of four different lignin sources (Indulin AT [circle], beech bark [square])

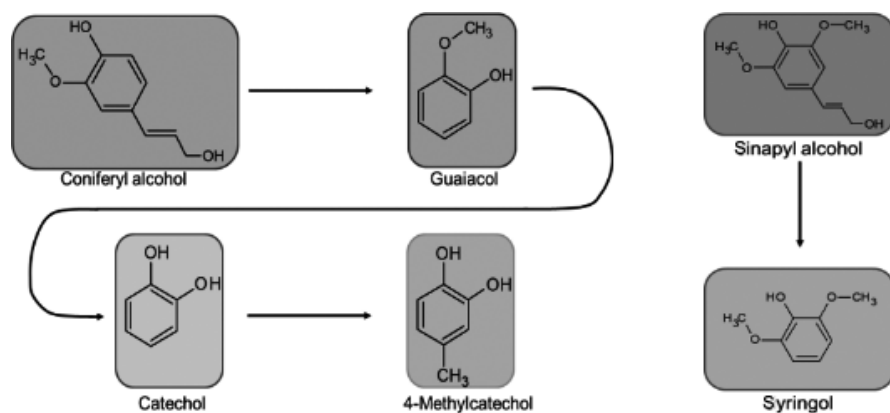
lignin molecule fragments toward smaller molecules is getting higher. Figure 10 shows the mass yields of the catechol obtained by HTL from beech bark at the different reaction times and temperatures with 1 wt.% KOH.

With higher temperatures and longer retention times, the catechol mass yields get lower. At temperatures above 350°C practically no catechol could be found anymore. At some temperatures and reaction times, out-of-trend results

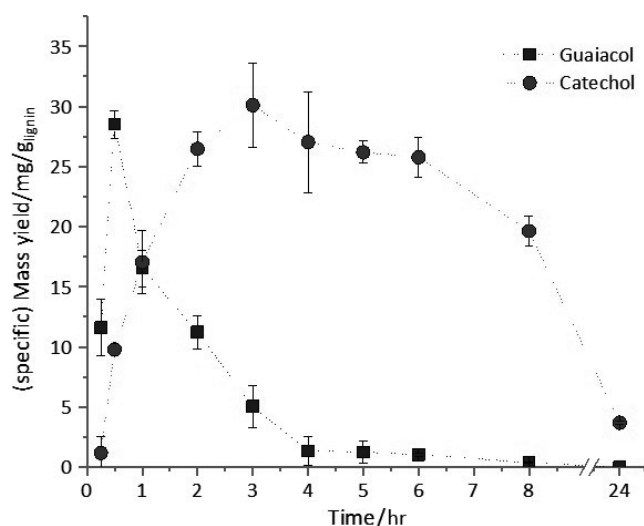




**FIGURE 12** Reaction pathways of lignin toward liquid and solid products (Barbier et al., 2012; Kang et al., 2013)



**FIGURE 13** Product examples from coniferyl alcohol and sinapyl alcohol

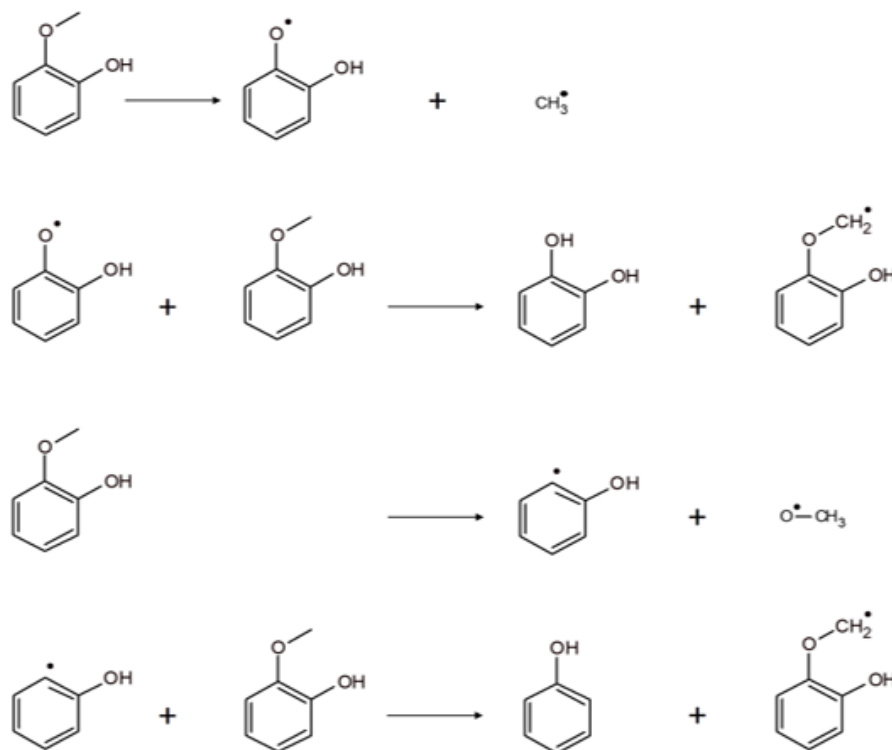


**FIGURE 14** Mass yield of the obtained guaiacol (square) and catechol (circle) in mg per g lignin at different reaction times (0.25–24 hr) at 300°C and a KOH concentration of 1 wt.%

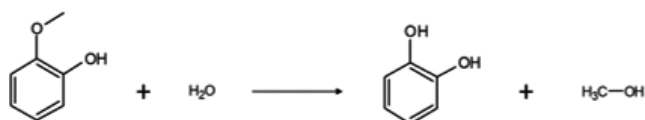
can be seen in all performed experiments, for example, at 300°C and 5 hr reaction time. Formation of intermediate oligomers and their repolymerization can happen at any

time under hydrothermal conditions. So, with longer reaction times newly formed polymeric structures may be cleaved again. Also in between, for example, at 350°C and 1 hr reaction time, these undefined repolymerization reactions show results in unexpended ways. Because of the unsatisfactory oligomeric analytics, these trends cannot be explained properly by now.

As mentioned above the ratio of coniferyl alcohol, sinapyl alcohol, and p-cumaryl alcohol is different for different types of biomass (Bunzel & Ralph, 2006). With the HTL products obtained, it is possible to infer about the monomer units of the used lignin without additional structural analytics. Syringol is a degradation product of sinapyl alcohol and guaiacol that of coniferyl alcohol (Bunzel & Ralph, 2006; Donaldson, 2013; Faravelli et al., 2010; Feng, Cheng, Yuan, Leitch, & Xu, 2013). Table 1 shows the product yield of syringol and guaiacol of the HTL of Indulin AT and bark. The investigated Indulin AT structure contains mostly coniferyl alcohol, then second most p-cumaryl alcohol, while no sinapyl alcohol units could be observed. The used beech bark lignin is built half of sinapyl alcohol and only around 20% of coniferyl alcohol.



**FIGURE 15** Reaction pathways of guaiacol decomposition under hydrothermal conditions in the near critical region with radical formation (Yong & Yukihiro, 2013)



**FIGURE 16** Hydrolysis of guaiacol under hydrothermal conditions in subcritical regions (Yong & Yukihiro, 2013)

Catechol is a consecutive product of guaiacol and experiments with guaiacol as a starting material confirmed the assumption that 4-methylcatechol is a consecutive product of catechol and guaiacol (see next section). It can be observed that different lignins show the same trends in regard to the catechol yield with respect to temperatures and reaction time dependence (see Figure 11).

#### 4 | CLEAVAGE REACTIONS

Lignin liquefaction usually delivers three product phases: gaseous, liquid, and solid, depending on the treatment method (hydrothermal, pyrolysis, acid or base catalyzed, etc.). The gaseous main products of the HTL consist mostly of carbon dioxide and methane. They are formed through direct degradation of the lignin molecule, especially through the split-off of small side groups like methoxy or hydroxy groups. Also, the degradation of intermediates and the split-off of their side chains or functional groups lead to gas formation (Barbier et al., 2012; Kang, Li, Fan, & Chang, 2013; Kruse, Funke, & Titirici, 2013).

The main reactions occurring during HTL are hydrolysis and alkylation reactions by ionic or radical reactions, depending on the conversion temperature (see Figure 12). At high temperatures, increasingly more radicals are formed, which accelerate the cleavage but also the repolymerization reactions. Through hydrolysis in the presence of water, which acts as a solvent and reaction partner in HTL processes, methoxylated benzenes occur as intermediates. Also, via hydrolysis, they further react to the hydroxylated benzenes like catechol. The further cleavage of oligomeric intermediates is stopped through saturation with hydrogen, and this way stable oligomeric aromatics can form directly out of lignin. Hydrolysis reactions furthermore deliver oxygenated hydrocarbons, which are used in alkylation reactions as reactants then (Barbier et al., 2012; Kang et al., 2013).

The reaction pathway from coniferyl alcohol to catechol, for example, proceeds via guaiacol (see Figure 13) and then further to 4-methylcatechol (Jegers & Klein, 1985; Wahyudiono, Sasaki, & Goto, 2008, 2011). This is confirmed by our measurements as shown in Figure 14, where guaiacol shows the typical behavior of intermediate within a consecutive reaction.

Several reaction pathways forming catechol can be described, depending on the reaction conditions. In near critical regions with rising temperature, increasingly radical reactions take place (Figure 15). The reaction rate is increased this way delivering an increasing number of intermediates and products.

Besides this, repolymerization reactions can be promoted by the unstable radicals and numerous reactions

happening simultaneously. In subcritical conditions, ionic reactions occur and guaiacol gets hydrolyzed with water to catechol (Figure 16).

However, this is assumed to be only one of different reaction pathways toward catechol (also described in Wahyudiono et al., 2011); another one might be the direct cleavage out of larger molecules and even out of the lignin by spitting of  $\beta$ -O-4-bonds.

Sinapyl alcohol reacts toward syringol as an intermediate, which can also further react toward catechol but not as easy as guaiacol (compare Figure 12). This explains why the catechol yield is different when the bark is used as a starting material (see Figure 11). Because of this and other degradation products, we can conclude that there is less coniferyl alcohol in the bark but more sinapyl alcohol, so less guaiacol and less catechol are formed during degradation.

This work improved the understanding of lignin itself and its behavior as a feedstock in HTL. Lignin liquefaction via hydrothermal treatment leads to functional molecules, and this process can be transferred to other lignin sources like bark. The oxygen in the functional side groups will not be removed completely; the products are still functionalized and can therefore be considered as platform chemicals for further utilization. This would allow to set up a process concept for a biorefinery, where not only the sugars from cellulose and hemicellulose are used for chemicals production, but also the lignin. Also, the gained results verified common trends in product formation during HTL of different biomasses. By this, a model is being developed to predict the product composition of key compounds for different temperatures and reaction times during HTL for the degradation of coniferyl alcoholic based lignin of different biomass sources toward the main monomeric compounds. Several limitations of common analytical methods occurred and have been discussed in this work. Since no commonly agreed protocols and standards are in place today, further improvements of analytical methods are necessary requiring comparatively high efforts and costs. But even the met challenges in this work led to a better understanding of biomass and to an improvement of analytical standards in this field.

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