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Ethanol Organosolv Lignin Depolymerization with Hydrogen over a Pd/C Catalyst

K. Johanna Hakonen,^{*[a]} J. Luis González Escobedo,^[a] Heidi Meriö-Talvio,^[a] Syed F. Hashmi,^[b] Reetta S. Karinen,^[a] and Juha Lehtonen^[c]

[a] K. J. Hakonen, J. L. González Escobedo, H. Meriö-Talvio, Dr. R. S. Karinen

Department of Chemical and Metallurgical Engineering

Aalto University

Kemistintie 1, 02150 Espoo, Finland

E-mail: johanna.hakonen@aalto.fi

[b] S. F. Hashmi

Department of Bioproducts and Biosystems

Aalto University

Vuorimiehentie 1, 02150 Espoo, Finland

[c] Research Prof. J. Lehtonen

Bioenergy & Thermochemical Processes

VTT Technical Research Centre of Finland

Biologinkuja 5, 02150 Espoo, Finland

The effect of a 3% Pd/C catalyst on the depolymerization of the ethanol organosolv lignin (EOL) was studied in ethanol at 300–400 °C and 10–50 bar H₂ pressure. The EOL depolymerized to monoaromatic compounds, oligomers and larger lignin fragments in both catalytic and non-catalytic experiments. In addition, char was formed simultaneously due to repolymerization. The commercial Pd/C catalyst influenced the content of the bio-oil and gas fraction through the secondary reactions of the smaller product molecules. However, the EOL decomposition occurred mainly thermally and possibly autocatalytically due to the inert nature of the catalyst support. The effect of the catalyst on the monoaromatic product distribution was remarkable. With the catalyst, most of the identified products contained a saturated side chain produced by hydrogenation,

whereas without the catalyst, the product distribution was wider, with a large portion of products exhibiting unsaturated and carbonyl side chains. Additionally, the monoaromatic compounds formed in the presence of the catalyst had longer side chains than the components formed in non-catalytic experiments.

Introduction

Lignocellulosic biomass is an abundant and attractive feedstock for the production of biofuels and -chemicals. In future integrated biorefineries, it is economically essential to convert all the main components of lignocellulosic biomass: cellulose, hemicellulose and lignin (15-30% by weight, 40% by energy), to value added products.^[1] Lignin is traditionally burned as a part of black liquor in Kraft pulp mills to provide energy for the pulping process. However, lignin with its unique polyphenolic structure can be regarded as the major aromatic resource of the bio-based economy.^[2] There is a lack of bio-based aromatic fuel components, since most of the currently utilized bio-components are either paraffinic hydrocarbons or alcohols. Especially in jet fuels, aromatic components are required due to their properties e.g. elastomer swelling properties of the fuel. Monoaromatic compounds from lignin have high potential for this purpose. Depending on their boiling point they could be used as gasoline or diesel components, either directly or after typical refinery hydrotreating processing (i.e. as cyclic paraffin). Alternatively, they can be applied as aromatic chemical intermediates for bio-based chemicals and polymers such as phenol-formaldehyde resins. Furthermore, partly degraded oligomeric lignin from the same process has a potential for material applications or it can be further converted to bio-carbon by hydrothermal treatments.

The challenge of the valorization of lignin lies in its structure, which is recalcitrant towards depolymerization and highly prone to repolymerization to more condensed structure with stronger bonds. Lignin is a three-dimensional randomly branched amorphous polymer consisting of three different p-hydroxycinnamyl alcohols (monolignols).^[3] Those are p-coumaryl, coniferyl and sinapyl alcohols, which are linked together by condensed carbon-carbon linkages and ether linkages, of which the β -O-4 linkage (β -aryl ether) is the dominant one.

Separation or pretreatment of lignin is a very essential factor considering the further valorization methods.^[1] The raw material for lignin valorization can either originate from Kraft pulping (e.g. Lignoboost lignin^[4]) or biorefineries based on biomass fractionation and hydrolysis by new technologies (e.g. organosolv lignin). The ethanol organosolv process is one of the strategies currently being studied for the conversion of biomass to biofuels.^[5] In contrast to for example Kraft lignin (up to 10000 g mol⁻¹^[6]), ethanol organosolv lignin (EOL) is sulphur-free low-molecular-weight (e.g. 3300 g mol⁻¹^[6]) product of high purity.

Catalytic technology is considered to be the key-technology for biomass conversion and lignin valorization to monomeric products.^[7] Hydrotreatment or hydrogenolysis appears to be the most promising method to produce phenols from lignin.^[8,9] Compared to pyrolysis, higher lignin conversion and yields of monophenols, and lower char formation are achieved. In solvolysis, lignin is decomposed in a solvent such as tetralin. However, catalytic hydrotreatment in an appropriate solvent and hydrogen pressure gives higher product yields. Various solvents have been studied such as water,^[10] methanol,^[11,12] ethanol,^[10,11,13–16] water-ethanol,^[14,15,17] isopropanol,^[11,18] acetone,^[19] tetralin,^[20,21] hexadecane^[22] and ionic liquids.^[23] Among the studied solvents, ethanol gives the best results.^[11,14] Cheng, Wilks, Yuan, Leitch and Xu^[14] depolymerized alkali lignin in ethanol and water-ethanol, and observed that smaller oily products formed only with pure ethanol. However, there were also more acetone-methanol insoluble large lignin fragments produced with pure ethanol. Kim, Park, Kim and Choi^[11] compared the effects of different alcohols and several carbon supported catalysts in the soda lignin depolymerization. The Pt/C catalyst in ethanol was the best combination producing large amount of bio-oil and the smallest amount of char. Generally, the results were the best with ethanol. Ethanol has also acted as a capping agent by alkylation and as formaldehyde scavenger in solvolysis.^[24] Furthermore, there will be synergy arising from ethanol being produced in biorefineries.

Various catalysts have also been studied in hydrotreatment of lignin, such as bulk nickel in different forms,^[13,23] nickel^[10,11,14,15,18,19,22,25] and noble metals^[10,11,13–15,19] on various supports, as well as different CoMo^[10,13,16] and NiMo^[16,18–21,25] catalysts. In addition, various WP catalysts,^[17] Fe₃O₄-(NiMgAlO)_x and (NiAlO)_x,^[23] and TiN-Ni and TiO₂-Ni^[12] have been tested. Palladium on carbon has been used earlier in the hydrolysis of lignin^[26] and in the solvolysis with formic acid.^[27] In addition, it has been studied in the hydrogenolysis of EOL at low temperatures, 50–200 °C.^[13] In the hydrotreatment study by Kim, Park, Kim and Choi,^[11] Pd/C was also used, but

because different solvents were compared, the product was divided only to acetone-solubles and -insolubles, and gas.

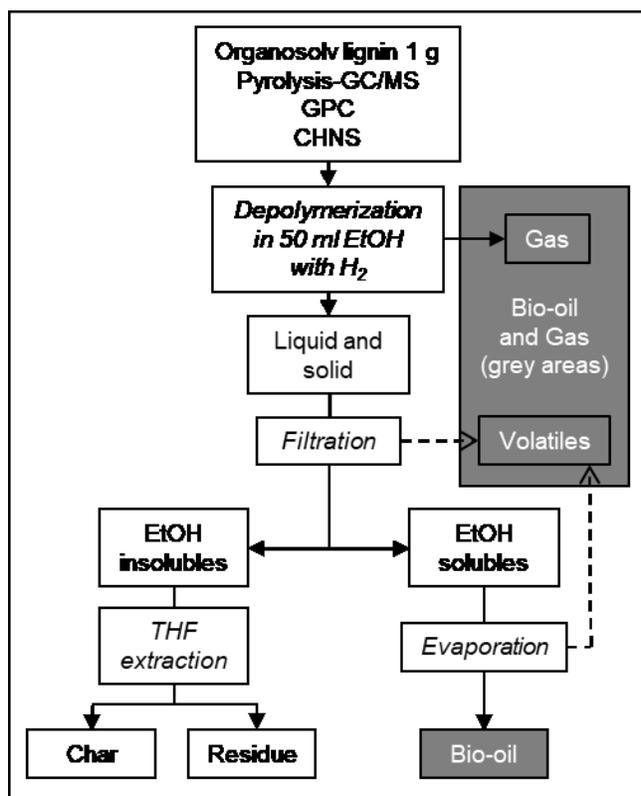
In our recent study^[28] on the non-catalytic hydrothermolysis with the EOL, we concluded that further research with catalysts and co-solvents, for example alcohols, is needed. Thus, in this work, the aim is to produce monoaromatic compounds from EOL by the catalytic hydrotreatment with a high selectivity. The effect of a commercial 3 wt-% Pd/C catalyst on the EOL depolymerization was studied in the presence of hydrogen in ethanol, and it was compared to the non-catalyzed reactions at the same conditions. Furthermore, the product was divided to fractions with two solvents, ethanol and tetrahydrofuran (THF), in order to more thoroughly study the product. The solvent and the product treatment procedure affect the content of the product fractions, and the abundance of those in the literature poses a challenge in the comparison of the results of different research groups. Thus, attention was paid to the fractionation solvent selection so that the yields of the fractions are comparable with the analysis results. In addition, the product fractions were compared to the corresponding extracted EOL fractions, because all the small bio-oil fragments in the product mixture are not produced in the reaction, but also lignin itself contains those.

Results and Discussion

Product Fractions

The feedstock EOL and the product were treated and separated into various fractions according to Scheme 1 which is explained in detail in the Experimental section. The main fractions were the “bio-oil and gas” fraction (with the highest average aromatic ring number of three), the ethanol insoluble but THF soluble “residue” (larger lignin fragments with the highest average aromatic ring number of 16), and the ethanol and THF insoluble “char”. Solubility to ethanol was naturally one dividing factor because ethanol was used as a solvent. In addition, the ethanol insoluble fraction was further divided to get more detailed information on the larger lignin fragments. THF was selected for the purpose because it was the gel permeation chromatograph (GPC) eluent, and thus the residue yields were comparable to the molecular weight results.

The bio-oil and gas fraction contained the most desired components. Part of the bio-oil evaporated during the sample filtration and evaporation at room temperature. This fraction is called the “volatile compounds” containing monoaromatic compounds and linkage fragments such as water and small organic compounds. It may also contain products of linkage fragments and ethanol such as diethoxymethane formed by ethanol and formaldehyde.^[24] The brown viscous bio-oil consisted of the non-volatile monoaromatic compounds and heavier bio-oil i.e. lignin oligomers and larger lignin fragments.



Scheme 1. Procedure for product treatment and analysis. Dashed arrows are showing the volatile compounds evaporated in the vacuum filtration and the solvent evaporation. Grey boxes represent the bio-oil and gas fraction.

EOL Characterization

The product distribution from the pyrolysis-GC analysis of the raw material EOL is shown in Figure 1. Syringaldehyde gave the biggest peak and the next biggest were for 4-methylsyringol and *trans*-propenylsyringol. According to the analysis, the studied feedstock EOL consists of 67% syringyl units, 32% guaiacyl units and 1% *p*-hydroxyphenyl units. This is consistent with the literature for the hardwood lignin.^[1] In addition, the EOL contains 0.32 wt% hexose and 1.90 wt% pentose carbohydrates^[29], which makes the autocatalytic hydrolysis of the EOL possible due to the acetic acid release from hemicellulose.^[30] Elemental analysis gave the following composition: 61.1% carbon, 31.8% oxygen, 6.3% hydrogen, 0.3% nitrogen and 0.4% sulphur.

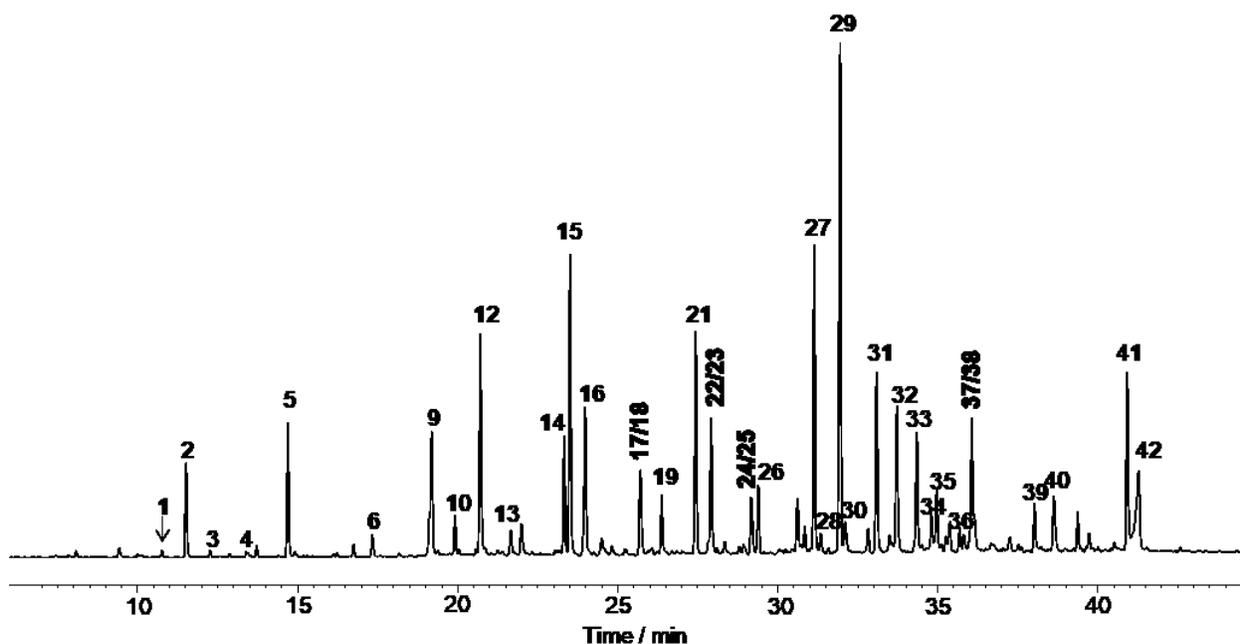


Figure 1. Product distribution of the EOL by Pyrolysis-GC/MS. Peak identities: 1 Phenol; 2 Guaiacol; 3 2-Methylphenol; 4 4-Methylphenol; 5 4-Methylguaiacol; 6 4-Ethylguaiacol; 7 Methylbenzaldehyde; 8 4-Vinylphenol; 9 4-Vinylguaiacol; 10 Eugenol; 11 Catechol; 12 Syringol; 13 *cis*-Isoeugenol; 14 *trans*-Isoeugenol; 15 4-Methylsyringol; 16 Vanillin; 17 4-Ethylsyringol; 18 Homovanillin; 19 Acetoguaiacone; 20 Hydroxybenzaldehyde; 21 4-Vinylsyringol; 22 Guaiacylacetone; 23 4-Allylsyringol; 24 4-(oxy-allyl)guaiacol; 25 4-(1-Hydroxyprop-2-enyl)guaiacol; 26 *cis*-Propenylsyringol; 27 *trans*-Propenylsyringol; 28 Dihydroconiferyl alcohol;

29 Syringaldehyde; **30** cis-Coniferyl alcohol; **31** Homosyringaldehyde; **32** Acetosyringone; **33** trans-Coniferyl alcohol; **34** Syringylacetone; **35** Coniferaldehyde; **36** Propiosyringol; **37** 4-(oxyallyl)syringol; **38** 4-(1-Hydroxy-prop-2-enyl)syringol; **39** Dihydrosinapyl alcohol; **40** cis-Sinapyl alcohol **41** trans-Sinapyl alcohol; **42** Sinapaldehyde.

In the extraction at room temperature, 98 wt% of the feedstock EOL was soluble in THF. According to the GPC results shown in Table 1, the number average molecular weight M_n and the weight average molecular weight M_w of the THF soluble feedstock EOL were 726 and 1799 g mol⁻¹, respectively. The feedstock EOL was also divided at room temperature first with ethanol and then the remaining solids with THF to similar fractions as the product according to Scheme 1: the EOL bio-oil, the EOL residue and the EOL char, in order to perceive the effect of the reaction on the yields of the fractions (Table 2). The yield of the ethanol soluble EOL bio-oil fraction was 61 wt% and the M_n and M_w of the fraction were 578 and 932 g mol⁻¹, respectively. The yield of the ethanol insoluble but THF soluble EOL residue fraction was 37 wt%, and the M_n and M_w were 1225 and 3005 g mol⁻¹, respectively.

Table 1. Average molecular weights of the ethanol solubles, the bio-oil and the residue fraction with and without the catalyst in different conditions.

Catalyst	T [°C]	p [bar]	M_n EtOH solubles [g mol ⁻¹]	M_w EtOH solubles [g mol ⁻¹]	M_n bio-oil [g mol ⁻¹]	M_w bio-oil [g mol ⁻¹]	M_n residue [g mol ⁻¹]	M_w residue [g mol ⁻¹]
EtOH/ THF extraction of the EOL ^[a]	rt	-	578	932	-	-	1225	3005
-	300	10	308	491	370	630	816	2221
Pd/C	300	10	323	532	366	622	933	2745
-	300	50	373	625	401	732	1188	3275
Pd/C	300	50	371	599	380	602	1073	3252

-	400	50	292	392	347	574	333	531
Pd/C	400	50	280	353	283	346	245	358

[a] For the whole THF soluble part of the feed EOL (98 wt%): $M_n=726 \text{ g mol}^{-1}$, $M_w=1799 \text{ g mol}^{-1}$.

Table 2. Experimental conditions and product yields.

Catalyst	T [°C]	p [bar]	p_{hot} [bar]	Heating time [min]	Bio- oil and gas yield [wt%]	Bio- oil yield [wt%]	Monoaromatic compound yield [wt%]	Residue yield [wt%]	Char yield [wt%]
EtOH/THF extraction of the EOL	rt	-	-	-	-	61	-	37	2
-	300	10	125	32	70	53	8	11	19
Pd/C	300	10	118	32	73	45	12	5	22
-	300	50	185	28	80	69	6	3	17
Pd/C	300	50	175	30	81	66	12	3	16
-	400	50	298	49	88	56	13	1	11
Pd/C	400	50	298	47	89	49	13	1	10

Hydrotreatment Experiments

Comparison of the EOL and the Product Fractions

In the experiments with hydrogen (Table 2) the EOL was depolymerized at 300 and 400 °C, and various smaller compounds were formed both with the Pd/C catalyst and without any added catalysts. However, some char was also formed and thus repolymerisation took place too. Compared to the room temperature extraction of the EOL, the fraction of residue decreased from

37 to 1–11 wt% (Figure 2) in all the experiments. The average molecular weights of it decreased, except the M_w of the residue at 300 °C and 50 bar, which increased a little as seen in Table 1. This indicates that the EOL was effectively depolymerized in the reaction conditions. The fraction of char increased from 2 to 10–22 wt% compared to the EOL (Figure 2), indicating repolymerization of reactive intermediates especially at the lower reaction temperature. Altogether, the total yield of ethanol insolubles (residue + char) decreased from 39 to 11–30 wt% indicating a favorable change in terms of depolymerization.

Thus, the yield of the bio-oil and gas fraction was 70–89 wt% i.e. clearly higher than the EOL bio-oil amount, 61 wt%, in the EOL extraction (Figure 3). In addition, the average molecular weights ($M_n=280\text{--}373\text{ g mol}^{-1}$, $M_w=353\text{--}625\text{ g mol}^{-1}$) of the product bio-oil were clearly smaller than the ones of the EOL bio-oil fraction (Table 1), indicating the success of the desired depolymerization reaction. This is observed also in Figure 4 where the molecular weight distributions of the fractions of feedstock lignin and reaction product (catalyst, 300 °C and 50 bar) are presented. It can be clearly seen that the bio-oil fraction contains smaller compounds (monoaromatic compounds and dimers) after the catalytic experiment due to the depolymerization. In all the experiments, the yield of bio-oil was less than the yield of the whole bio-oil and gas fraction and hence gaseous/volatile compounds were formed.

Thus, it can be concluded that lignin depolymerized significantly in both catalytic and non-catalytic experiments. This was observed as increased yields of the bio-oil and gas fraction and lower average molecular weights of the bio-oil fraction. On the other hand, some char was formed simultaneously due to repolymerization.

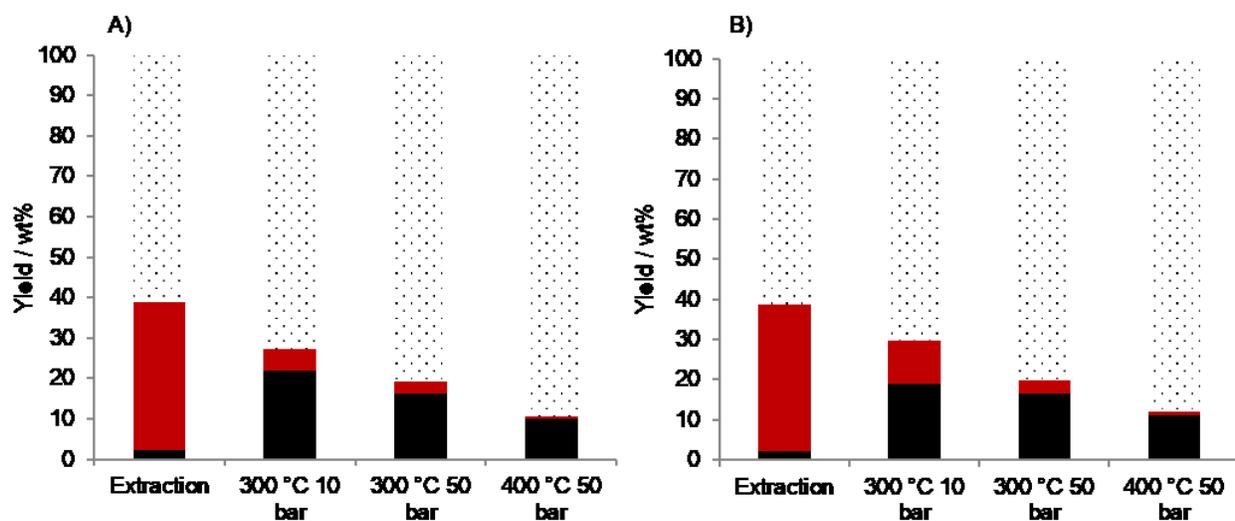


Figure 2. Yields for the main fractions: the bio-oil and gas fraction (dotted), residue (red) and char (black) A) with and B) without the catalyst at different conditions.

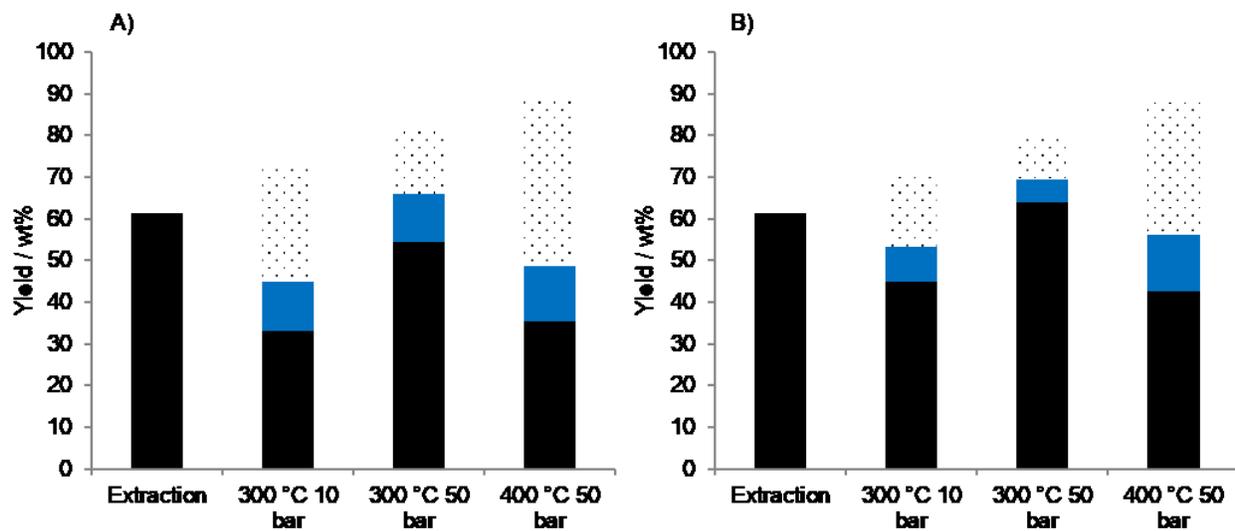


Figure 3. Yields for the bio-oil and gas fraction: gaseous/volatile compounds (dotted), monoaromatic compounds (blue) and heavier bio-oil (black) A) with and B) without the catalyst at different conditions.

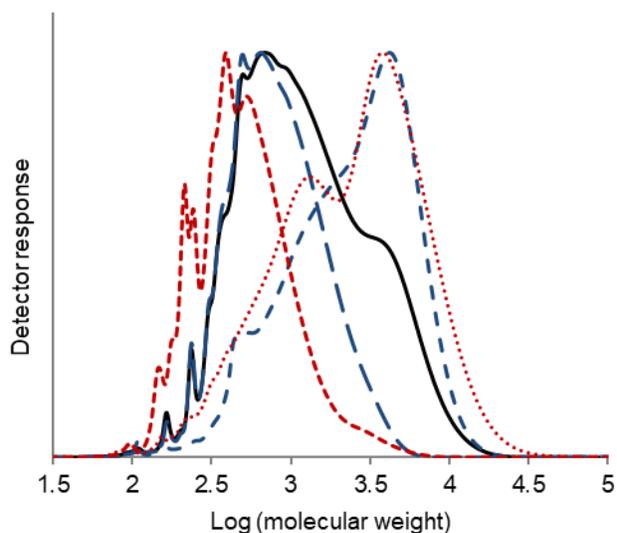


Figure 4. Molecular weight distributions of lignin and derivatives. From feed EOL, THF-soluble part (black solid). From ethanol extraction, the EOL bio-oil fraction (blue long dashed) and the EOL residue fraction (blue dashed). From the product of a representative catalyzed experiment at 300 °C and 50 bar (60 min), bio-oil (red short dashed) and residue (red dotted).

Comparison to the EOL Hydrothermolysis

The hydrothermolysis of this EOL^[28] was performed in water in the absence of a catalyst in our previous study. The water-insoluble solid reactor residue was divided to the char and the residual lignin (RL) with NaOH, so those fractions are not directly comparable to our ethanol-insoluble char and residue separated with THF. In addition, the bio-oil in water fraction was extracted with ethyl acetate, leading to the bio-oil and the water-soluble product fractions. Thus, the difference between the hydrothermolysis and the reaction in our study is not possible to be distinguished from the effect of the separation of the fractions.

The bio-oil yield, 15 wt%, in the EOL thermolysis^[28] at 310 °C is remarkably lower than the yield, 53 wt%, without the catalyst at 300 °C and 10 bar in this study (Figure 3). Even the combined yield of the bio-oil and the water-soluble compounds, 37 wt%, was lower than the yield of the bio-oil here. However, this can be explained by the larger EOL fragments which are less soluble to water than to ethanol and hence remain in the solid residue. This is supported by the average molecular weights M_n and M_w of the bio-oil in the thermolysis, 258 and 256 g mol⁻¹, respectively, which are

lower than the ones in this study, 308 and 491 g mol⁻¹ (Table 1), respectively. In addition, the yield of the thermolysis RL, 43 wt%, was considerably larger than the yield of the residue, 11 wt% (Figure 2), in this study. This can be explained by the EOL being less soluble to water compared to ethanol but also NaOH dissolving the solids probably more efficiently than THF, leading to higher amount of RL than THF separation. This can be seen from the yield of the char divided by NaOH, 12 wt%, which is less than the yield of the char divided by THF, 19 wt% (Figure 2), in this research.

However, there was a remarkable difference between the yields of the gaseous/volatile compounds, which were 8 wt% in the EOL hydrothermolysis^[28] and 17 wt% (Figure 3) in this study. The monoaromatic compound distribution was also affected to a great extent. In the hydrothermolysis, syringol and 3-methoxycatechol were clearly the most abundant monoaromatic products, and the next ones were guaiacol and 4-methylsyringol. Here the most abundant monoaromatic compounds were 4-methylsyringol, syringol, syringaldehyde and 4-propylsyringol, as can be seen in Figure 5. The product distribution was more even than in the hydrothermolysis, and the yield of the monoaromatics with a longer side chain was relatively larger. The total yield was not calculated for the monoaromatic products in the hydrothermolysis, but the yield of the 8 quantified compounds was 7 wt%. According to the chromatograms in that study, only a small portion was missing from that amount. In this study, the same 8 compounds gave the yield of 3 wt% and the total yield was 8 wt%. The monoaromatic products were quantified in different ways, and the yield estimation in this research is discussed later. It can be concluded, nonetheless, that the different conditions between the studies did not affect the total yield of the monoaromatic products significantly.

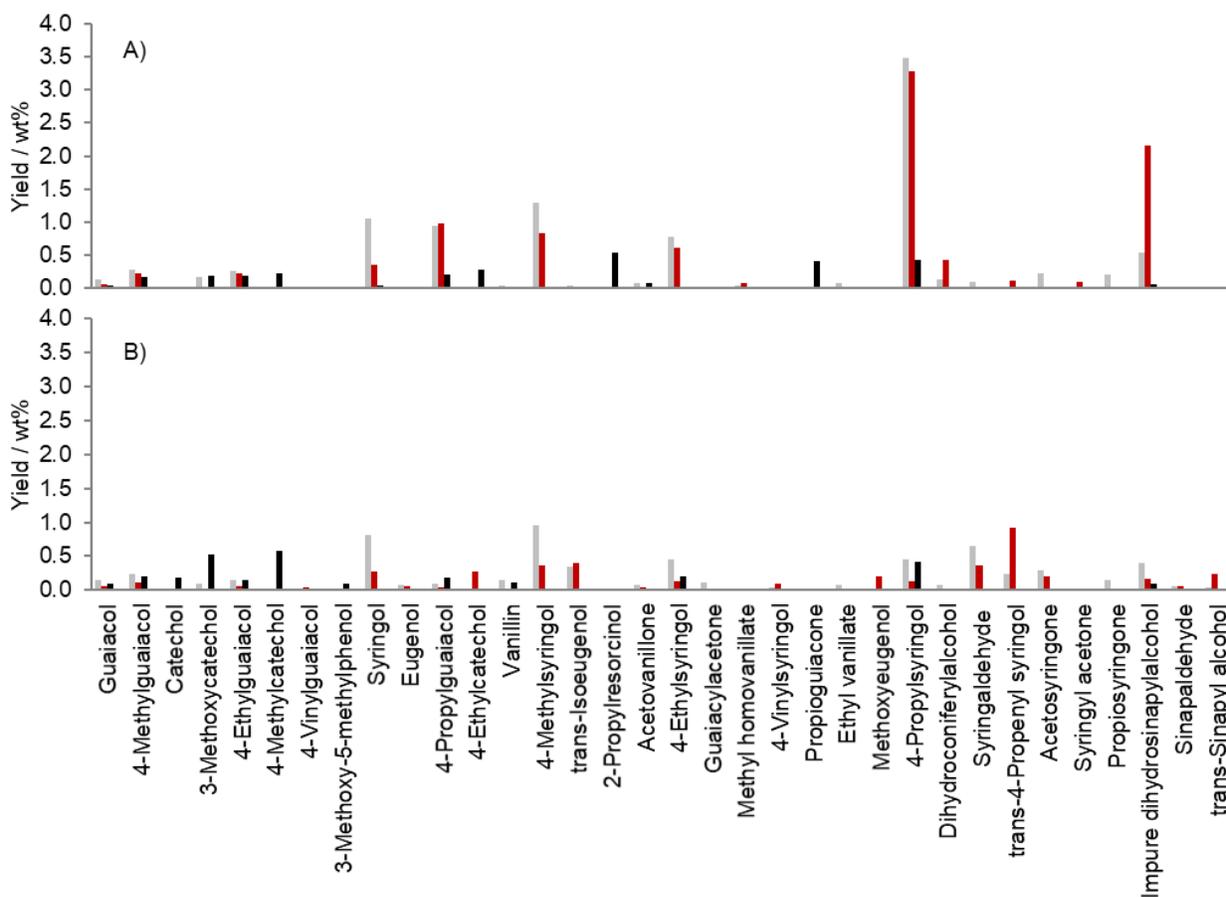


Figure 5. Monoaromatic product yields A) with and B) without the catalyst at different conditions: 300 °C and 10 bar (grey), 300 °C and 50 bar (red), and 400 °C and 50 bar (black).

Effect of the Catalyst

The Pd/C catalyst affected clearly (Figure 3) the composition of the bio-oil and gas fraction through the secondary reactions of the smaller product molecules, which accessed easily the catalyst surface. The catalyst had a remarkable effect on the monoaromatic product distribution, as will be explained later. In addition, with the catalyst there were less non-volatile bio-oil and more gaseous/volatile compounds formed than without the catalyst. The increasing amount of gaseous/volatile compounds with the catalyst is consistent with the literature.^[11,31] The comparison

of the bio-oil yields to the results in the literature is more difficult due to the different fractionation methods and lignins. It has been observed^[10,11] that the yield of the bio-oil increases with the catalyst. However, in the case of the Pd/C catalyst,^[11] the bio-oil was separated with acetone instead of ethanol, and soda lignin was used. In the hydrotreatment of the organosolv lignin with the noble metals, nickel and cobalt on the acidic supports at 260 °C and 20 bar,^[10] the bio-oil was separated similarly with ethanol as in our study. The yield of the bio-oil increased from 63 wt% without the catalyst to 65-84 wt% with the catalyst. The probable explanation is the acidity of the support enhancing the depolymerization of the lignin.

The presence of the catalyst had only a small effect on the main fraction yields as can be seen in Figure 2. Kim, Park, Kim and Choi^[11] observed clearly less char at 350 °C and 30 bar with the Pd/C catalyst than without it, but the char was separated with acetone instead of THF. In addition, the yield with the catalyst, ca. 5 wt%, was less than our lowest yield, 10 wt% at 400 °C and 50 bar, but it was much higher, ca. 35 wt%, than our highest yield without the catalyst, 19 wt% at 300 °C and 10 bar. The average molecular weights of the bio-oil and the residue in our study were also on a similar level with and without the catalyst (Table 2). The M_w of the residue at 300 °C and 10 bar was clearly lower without the catalyst than with the catalyst. This is explained by a big peak of smaller compounds, which remained in the residue sample in the non-catalytic experiment. Thus, it seems that with this catalyst, lignin decomposes mainly thermally, and possibly autocatalytically by acid hydrolysis, because carbon is not an acidic cracking support.

Effect of the Conditions on the Main Fractions

In contrast to the effect of the catalyst, conditions affected significantly the distribution of main fractions, as can be seen in Figure 2. The effects of the pressure and the temperature were the same with and without the catalyst. When the hydrogen cold pressure in the reactor was increased from 10 to 50 bar at 300 °C, the yields of char and residue decreased and the yield of the bio-oil and gas fraction increased in both catalytic and non-catalytic experiment. The average molecular weights of the residue increased with the pressure (Table 1), and the M_w for the product was even higher than for the feed lignin. Thus, there was less residue but the fragments were larger.

It has been observed that the gas phase being nitrogen or hydrogen has only an insignificant effect on the thermolysis of kraft lignin at 345 °C.^[32] Thus, hydrogen requires a catalyst in order to be

reactive. The effect of the pressure increase on the product distribution also without the catalyst can be explained with the supercritical conditions. At higher pressure, more hydrogen is dissolved in the liquid phase, and also more small products remain in the liquid phase. As a result, the reaction mixture is more diluted and repolymerization is slowed down. On the other hand, when more hydrogen is present at higher pressure, the catalyst is able to promote the capping of the reactive product fragments by hydrogenation and thus stabilizing the reaction mixture. However, the dilution might be a remarkable factor in both cases, because the access of the larger lignin product fragments to the catalyst active sites is more hindered.

Increasing the temperature had a similar effect on the product distribution as increasing the pressure. Even less char and residue and even more bio-oil and gas was formed (Figure 2), because depolymerization becomes faster as a function of temperature. Actually, the residue was almost disappeared at 400 °C. In addition, the average molecular weights of the residue decreased with the temperature. At 400 °C, the M_n of the residue was even smaller than the M_n of the bio-oil, which can be explained by the very small yield of the residue and some monoaromatic compounds remaining in the residue sample.

Effect of the Catalyst and the Conditions on the Bio-oil and Gas Fraction

Effect of the Catalyst and the Conditions on the Monoaromatic Compound Distribution

To evaluate the composition of the bio-oil and gas fraction in more detail, the monoaromatic distribution is discussed first. With the catalyst the estimated yield of the monoaromatic compounds is almost the same, 12–13 wt%, in all studied conditions as presented in Figure 3. Without the catalyst, the yield is between 6–13 wt%, with the biggest yield obtained in the most severe conditions. It has been observed earlier^[11] that several carbon supported catalysts enhanced little the yield of monoaromatic compounds, which is also seen here.

However, the monoaromatic yields do not contain all the monoaromatic products because some of those are evaporated and escaped during the sample preparation. This was observed with the GPC and GC/MS analyses when comparing the results for the filtrated and evaporated products. In addition, these yields are estimations because the response factor of one was used for all the compounds since response factors are not available for all the product molecules. This leads to too

low amounts for the smallest monoaromatic compounds. Actually, the response factors vary a lot from each other depending on e.g. functionality and boiling point. For example, the response factor of 1.6 was determined for guaiacol and 0.9 for 4-propylguaiacol. Thus, the product distribution affects the estimation: the more there are smaller monoaromatic compounds the smaller the estimated amount is compared to the real amount. Hence, based on the analyzed composition of the products of each experiment, it can be approximated that the real amount at 300 °C and 10 bar was more than the estimated 8 wt% without the catalyst and about the estimated 12 wt% with the catalyst. At 300 °C and 50 bar it was less than the estimated values, 6 wt% without the catalyst and 12 wt% with the catalyst, whereas at 400 °C and 50 bar it was larger than the estimated 13 wt% in both cases. In addition, it is possible that all of the high boiling products do not go through the GC/MS although even *trans*-sinapyl alcohol with a boiling point of 382 °C was observed.

However, the monoaromatic compound distributions are presented and discussed here because there were clear differences with and without the catalyst. With the catalyst, the identified products (Table 3) were mainly compounds with a saturated side chain produced by hydrogenation (Figure 6). Without the catalyst, only thermal cracking, or free radical reactions, took place, and there was wider product distribution with large portions of products with unsaturated and carbonyl side chain at 300 °C. At 400 °C much wider distribution of different compounds was formed compared to 300 °C with and without the catalyst. The fraction of identified products was only 20–21%, compared to 74–81% at 300 °C. A large portion of the identified products at 400 °C were various dihydroxybenzenes formed by demethylation. A large number of unidentified compounds were also clearly dihydroxybenzenes according to the mass-to-charge ratios but those were not identified with certainty. Differences in the monoaromatic composition can be also seen in the molecular weight distribution curves (Figures 7 and 8). The lower molecular weights are emphasized more in the absence of the catalyst at 300 °C as shown in Figure 8. However, quantitative analysis by GPC is not possible because the amount and the quality of the chromophores in the compounds affect the detector response.

Table 3. List of identified monoaromatic products.

Entry	Compound	IUPAC Name	Retention time [min]

1	Guaiacol	2-Methoxyphenol	12.6
2	4-Methylguaiacol	2-Methoxy-4-methylphenol	15.7
3	Catechol	Benzene-1,2-diol	15.8
4	3-Methoxycatechol	3-Methoxybenzene-1,2-diol	17.6
5	4-Ethylguaiacol	4-Ethyl-2-methoxyphenol	18.0
6	4-Methylcatechol	4-Methylbenzene-1,2-diol	18.3
7	4-Vinylguaiacol	4-Ethenyl-2-methoxyphenol	19.0
8	3-Methoxy-5-methylphenol	3-Methoxy-5-methylphenol	19.2
9	Syringol	1,3-Dimethoxy-2-hydroxybenzene	19.9
10	Eugenol	4-Allyl-2-methoxyphenol	20.2
11	4-Propylguaiacol	2-Methoxy-4-propylphenol	20.3
12	4-Ethylcatechol	4-Ethylbenzene-1,2-diol	20.7
13	Vanillin	4-Hydroxy-3-methoxybenzaldehyde	21.2
14	4-Methylsyringol	2,6-Dimethoxy-4-methylphenol	22.4
15	trans-Isoeugenol	2-Methoxy-4-[(1E)-1-propen-1-yl]phenol	22.5
16	2-Propylresorcinol	2-Propyl-1,3-benzenediol	23.0
17	Acetovanillone	1-(4-Hydroxy-3-methoxyphenyl)ethanone	23.3
18	4-Ethylsyringol	4-Ethyl-2,6-dimethoxyphenol	24.3
19	Guaiacylacetone	1-(4-Hydroxy-3-methoxyphenyl)propan-2-one	24.4
20	Methyl homovanillate	Methyl 2-(4-hydroxy-3-methoxyphenyl)acetate	24.9
21	4-Vinylsyringol	2,6-Dimethoxy-4-vinylphenol	25.3
22	Propioguiacone	1-(4-Hydroxy-3-methoxyphenyl)propan-1-one	25.7
23	Ethyl vanillate	Ethyl-4-hydroxy-3-methoxybenzoate	25.8

24	Methoxyeugenol	2,6-Dimethoxy-4-prop-2-enylphenol	26.2
25	4-Propylsyringol	2,6-Dimethoxy-4-propylphenol	26.3
26	Dihydroconiferyl alcohol	4-(3-Hydroxypropyl)-2-methoxyphenol	27.3
27	Syringaldehyde	4-Hydroxy-3,5-dimethoxybenzaldehyde	27.4
28	trans-4-Propenyl syringol	2,6-Dimethoxy-4-[(E)-prop-1-enyl]phenol	28.3
29	Acetosyringone	4'-Hydroxy-3',5'-dimethoxyacetophenone	29.1
30	Syringyl acetone	1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-2-one	29.8
31	Propiosyringone	1-(4-Hydroxy-3,5-dimethoxyphenyl)propan-1-one	30.9
32	Dihydrosinapyl alcohol with an impurity (M=240 g/mol)	4-(3-hydroxypropyl)-2,6-dimethoxyphenol	32.2
33	cis-Sinapyl alcohol	4-[(Z)-3-Hydroxyprop-1-enyl]-2,6-dimethoxyphenol	32.8
34	Sinapaldehyde	3-(4-Hydroxy-3,5-dimethoxyphenyl)prop-2-enal	34.1
35	trans-Sinapyl alcohol	4-[(E)-3-Hydroxyprop-1-enyl]-2,6-dimethoxyphenol	34.3

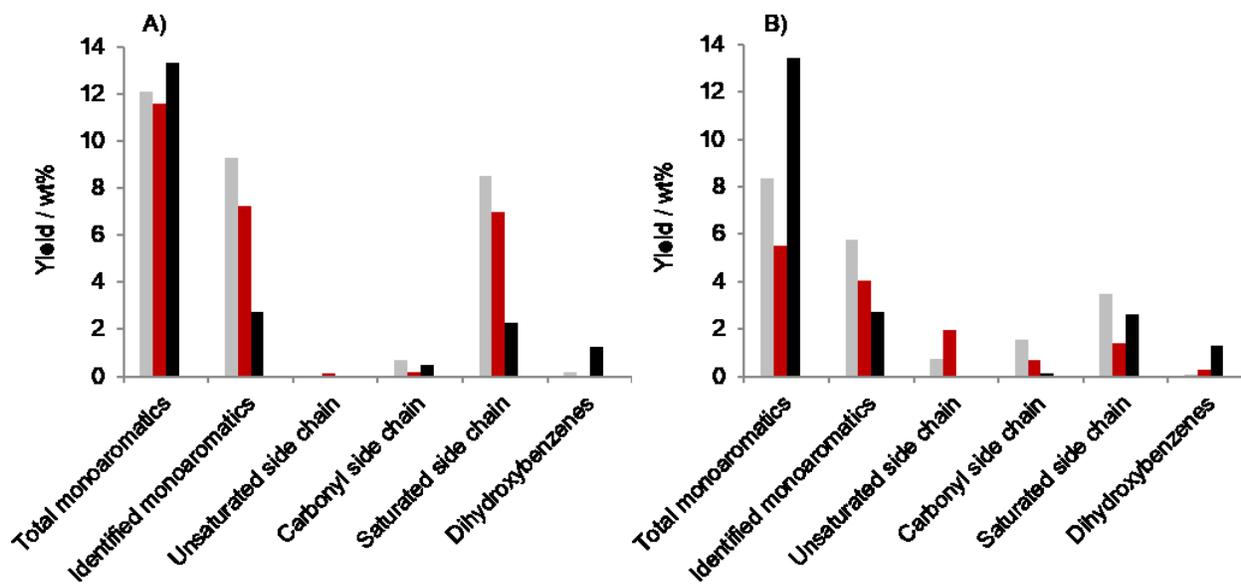


Figure 6. Yields of various types of monoaromatic products A) with and B) without the catalyst at different conditions (300 °C and 10 bar: grey; 300 °C and 50 bar: red; 400 °C and 50 bar: black).

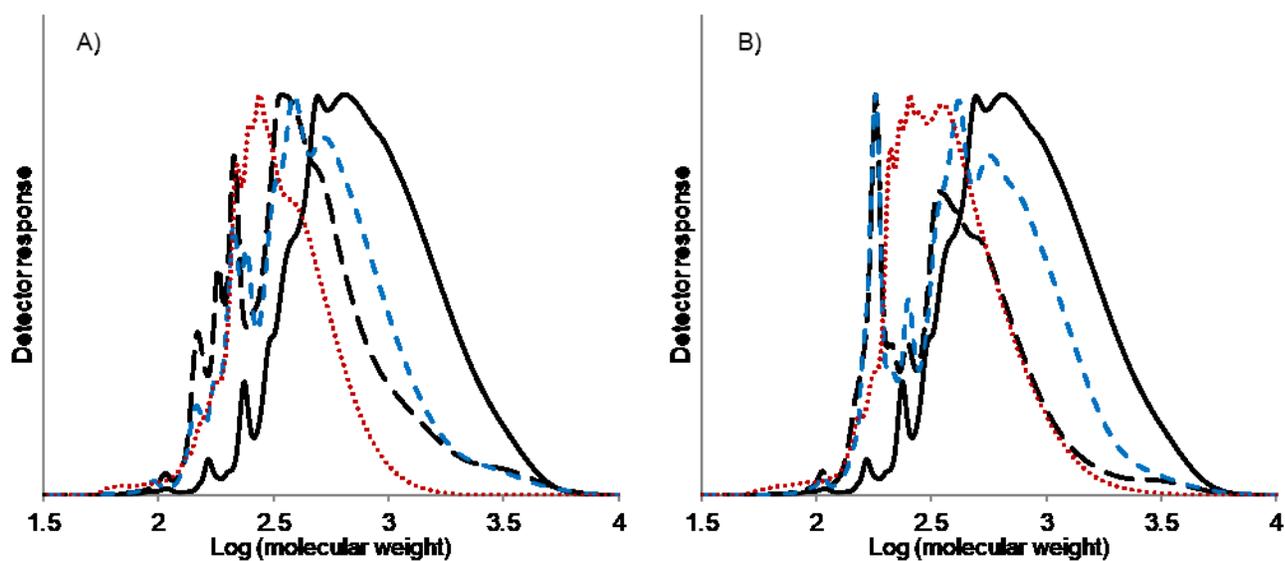


Figure 7. Molecular weight distributions of the ethanol solubles A) with and B) without the catalyst at different conditions (300 °C and 10 bar: black long dashed; 300 °C and 50 bar: blue dashed; 400 °C and 50 bar: red dotted) compared to the feed EOL bio-oil (black solid).

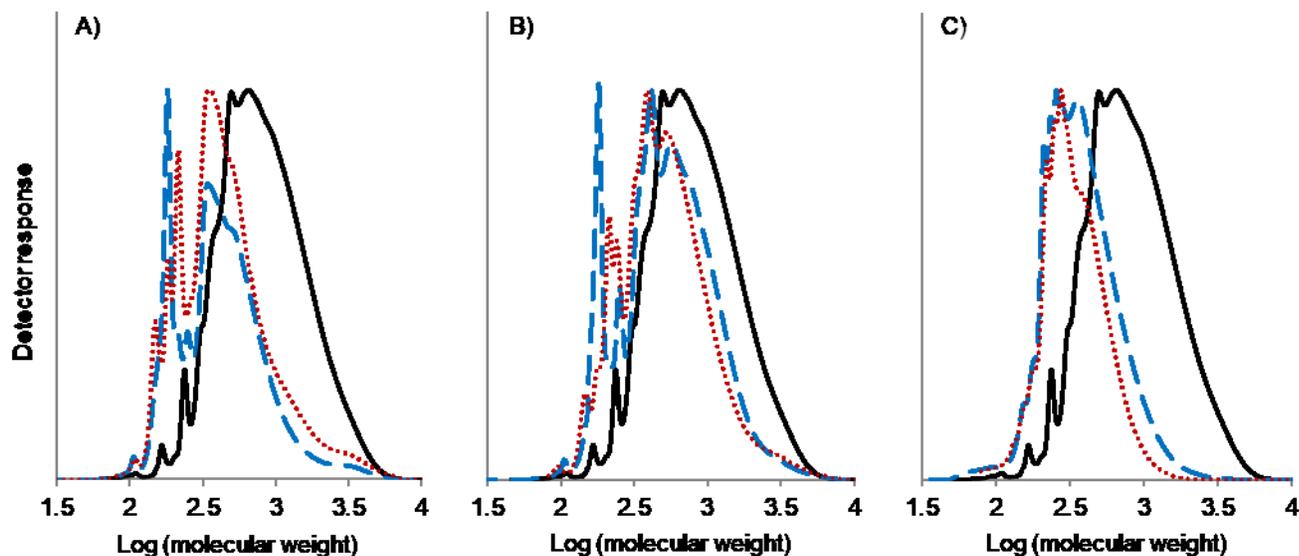


Figure 8. Molecular weight distributions of the ethanol solubles with (red dotted) and without (blue dashed) the catalyst at different conditions compared to the feed EOL bio-oil (black solid). A) 300 °C and 10 bar, B) 300 °C and 50 bar, and C) 400 °C and 50 bar.

Furthermore, the portion of the longer side chain products was larger with the catalyst in all the conditions as can be seen in Figure 5, because hydrogenation prevents further decomposition of the side chain. According to literature^[33] vinyl and allyl substituents are converted to ethyl and propyl groups in solvolysis with tetralin as a hydrogen donor. Kim, Park, Kim and Choi^[11] observed also that the catalysts enhanced the production of alkyl guaiacols and syringols at 350 °C and 30 bar hydrogen in methanol, ethanol and 2-propanol. In our study, there were much more 4-propylsyringol and 4-propylguaiacol formed with the catalyst at 300 °C and 10 bar, whereas the major products without the catalyst were syringol, 4-methylsyringol and syringaldehyde. The monoaromatic product distribution with the catalyst was similar to the one observed by Patil, Armbruster, Richter and Martin.^[10] They studied the 5% Ru/ γ -Al₂O₃ at 260 °C and 20 bar hydrogen, and 4-propylsyringol was clearly the biggest product. 4-Propylsyringol and dihydrosinapyl alcohol were the major product with the catalyst at 300 °C and 50 bar in our research. In these conditions there was a significant portion of unsaturated products (45%) without the catalyst, trans-4-propenylsyringol being the major product. Thus, at higher pressure the side chains of the products were even longer. Again, the presence of the catalyst promotes the capping

of the products, which is enhanced at higher pressure due to the higher amount of hydrogen. Without the catalyst, the higher hydrogen pressure leads to dilution of the reaction mixture and reduces the occurrence of free radical reactions. At 400 °C the dihydroxybenzenes had longer side chains with the catalyst, too, major products being 2-propylresorcinol and 2-ethylcatechol, compared to the products without the catalyst, major ones being 3-methoxycatechol and 4-methylcatechol. This affects the estimated amounts via different response factors and volatilities and might explain the result that there are less monoaromatics formed without the catalyst than with the catalyst at 300 °C.

Effect of the Conditions on the Bio-oil and the Gaseous/volatile Compounds

The effect of the reaction conditions were the same with and without the catalyst in the case of the bio-oil and the gaseous/volatile compounds (Figure 3), too. The yield of the bio-oil increased and thus the yield of gaseous/volatile compounds decreased with the pressure at 300 °C with and without the catalyst. This is consistent with the monoaromatic product distribution: the side chain length was longer at 50 bar and thus the ethanol soluble products were less volatile. The average molecular weights of the bio-oil also increased with the pressure as can be seen in Table 1. Compared to the EOL bio-oil fraction of the room temperature extraction, the fraction of the bio-oil decreased from 61 to 45–53 wt% at 10 bar and increased to 66–69 wt% at 50 bar due to the different volatility of the product bio-oil.

When the temperature was increased at 50 bar, the yield of the bio-oil decreased and the yield of the gaseous/volatile compounds increased remarkably, shown in Figure 3, due to the enhanced lignin and product side chain decomposition by demethylation. It can be assumed that more gaseous products are formed at higher temperatures, when more lignin is decomposed.^[34] The average molecular weights of bio-oil were also lower at 400 °C which means that it consisted of smaller lignin fragments.

Conclusions

The hydrotreatment of lignin has great potential in developing the production of biobased aromatic fuels and chemicals. In this study, ethanol organosolv lignin was depolymerized on a 3% Pd/C catalyst at 300–400 °C with 10–50 bar H₂ pressure. Non-catalytic, thermal reaction was studied at the same conditions. In addition, a product treatment and fractionation procedure was developed in order to analyze the product mixture completely.

Monoaromatic compounds were the main target of the depolymerization reaction, and their production was proved in the studied reaction conditions. However, lignin fragment repolymerization took also place and char was formed. The monoaromatic product distribution was affected clearly by hydrogenation reaction which took place in the presence of the Pd/C catalyst. The monoaromatic components formed in the presence of the catalyst had longer side chains than the components formed in the non-catalytic experiments. Higher hydrogen pressure also affected the saturation of the side chain. Increasing the hydrogen pressure further increased the length of the side chains.

However, this catalyst is not optimal in the depolymerization of the lignin, because decomposition occurred mainly thermally and possibly autocatalytically due to the inert support material. Thus, an extensive catalyst screening with acidic cracking supports and process concept development is required to optimize the production of monoaromatic components from lignin.

Supporting Information Summary

Experimental section is available in the Supporting Information.

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Keywords: depolymerization • heterogeneous catalysis • hydrogen • lignin • monoaromatic compounds

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Supporting Information

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Experimental Section

Chemicals and materials

The beech EOL was prepared in an organosolv fractionation process with ethanol/water by Fraunhofer Center for Chemical-Biotechnological Processes.^[1] Characterization of the EOL was also performed and reported by Lê, Zaitseva, Pokki, Ståhl, Alopaeus and Sixta.^[2] 3 wt% Pd/C catalyst from Degussa was ground to the particle size of 0.30–0.42 mm. All chemicals were purchased from commercial suppliers and used without further purification: hydrogen (Aga, 99.999%), nitrogen (Aga, 99.999%), ethanol (Altia, ≥99.5%), tetrahydrofuran (THF) (Merck, Lichrosolv®), pyridine (Merck, ≥99.5%), cumene (Fluka, ≥99.5%), toluene (Analar NORMAPURE®, ≥99.5%), syringol (Aldrich, 99%) and 2,2'-dihydroxybiphenyl (Fluka, >99%). Polystyrene standard with the peak molecular weight of 208 g/mol (PS208) was purchased from American Polymer Standards Corp., PS18000 from Polymer Standard Service – USA Inc., PS474 and PS3470 were purchased from Fluka, and PS1270, PS7000 and PS76600 from Polymer Laboratories.

Catalytic experiments

Experiments were carried out in a 100 ml Parr batch reactor of Hastelloy C (Moline, Illinois, USA) equipped with a spinning catalyst basket stirrer. In the experiments EOL (1 g) was heated to 300 or 400 °C in ethanol (50 ml). Experiments were performed with and without the catalyst (100 mg). Before heating, the reactor was flushed three times with nitrogen to remove the air and then pressure tested. Then the reactor was flushed three times with hydrogen and pressurized to 10 or

50 bar hydrogen. Reaction time was 60 min and stirring speed 1000 rpm. After the reaction, the reactor was cooled down to room temperature in a water bath. Gas was released into ventilation.

Product treatment procedure and fraction definitions

A reaction product treatment procedure as shown in Scheme 1 was developed. After recovering the product mixture, the reactor and the stirrer were washed with known amount of ethanol and the washing solution was combined with the product. The liquid and solid products were separated by vacuum filtration (Whatman glass microfiber filter 1 μm) to ethanol soluble and insoluble fractions. The ethanol insoluble fraction was dried and extracted with THF. The THF insoluble fraction (char) was separated from the soluble fraction (residue) by vacuum filtration. The yield of the residue was calculated by subtracting the yield of the char from the total yield of the THF insoluble fraction. Ethanol soluble compounds were separated from the solvent ethanol by evaporation at room temperature. The remaining brown oil was called the bio-oil consisting of the non-volatile monoaromatic compounds and the heavier bio-oil. The yield of the fraction “bio-oil and gas” was calculated by subtracting the yields of the residue and the char from the amount of the EOL used in the experiment.

All of the ethanol soluble fragments in the product are not produced in the reaction but EOL itself contains ethanol soluble fragments. Thus, to properly compare the EOL and the products, the EOL was also divided to similar fractions as the product: it was extracted at room temperature with ethanol (the EOL bio-oil) and then the remaining solids with THF (the EOL residue and the EOL char). In addition, the EOL was extracted at room temperature with THF. The yields of the fractions were calculated by using the Equation (1).

$$\text{Yield of the fraction} = 100\% \left(\frac{\text{weight of the fraction}}{\text{weight of the lignin}} \right) \quad (1)$$

Analysis methods

Monoaromatic compounds shown in Table 3 were identified with an Agilent 7890A GC/MS 5975C (Santa Clara, California, USA). The column was HP-5 (length 30 m, inner diameter 0.25 mm and film thickness 0.25 μm). Solvent for the evaporated samples was pyridine and the inner

standard cumene. Inlet temperature was 280 °C. Temperature was kept at 40 °C for 1 min, then increased 5 °C min⁻¹ to 300 °C, and kept there for 10 min. Samples were filtrated with a 0.2 µm syringe filter. Standards, the NIST database and literature^[3] were used for the interpretation of the results. The amount of Monoaromatic compounds was estimated from the GC/MS results with the response factor of 1 for all the compounds. All of the compounds were not observed due to the solvent delay.

The molecular weight distributions and the number and weight average molecular weights (M_n , M_w) of the EOL, the ethanol solubles, the bio-oil and the residue were determined by gel permeation chromatography (GPC) with an Agilent 1100 HPLC/VWD (Santa Clara, California, USA). The UV wavelength was 280 nm and the flow rate of the eluent THF 1 ml min⁻¹. The columns were a Phenogel pre-column (length 50 mm, inner diameter 7.8 mm and particle size 5 µm) and two Phenogel size exclusion columns of styrene-divinylbenzene (length 300 mm, inner diameter 7.8 mm and particle size 5 µm) with pore sizes 50 and 1000 Å. Calibration was performed with two standard solutions, the other containing toluene, syringol, 2,2'-dihydroxybiphenyl, PS474, PS3470 and PS76600, and the other toluene, polystyrene dimer PS208, PS1270, PS7000 and PS18200. The standard PS474 was divided by the columns to several oligomer peaks, of which polystyrene trimer PS312, tetramer PS417 and pentamer PS521 were used in the actual calibration. The concentration of the samples was 2 mgml⁻¹ and those were filtrated with a 0.45 µm syringe filter. Acetylation was not performed because the feed EOL solubility to THF was high, 98 wt%. The composition of the lignin was analyzed by a Pt-filament pulse pyrolyzer Pyrola2000 (Pyrol AB, Lund, Sweden) (2 s, 600 °C), which was connected to a Varian 3800/2000 GC/MS instrument (Agilent Technologies, Inc., Santa Clara, California, USA).^[4] The elemental analysis of lignin was performed with a Perkin Elmer 2400 Series II CHNS elemental analyzer (Waltham, MA, USA).

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