

# Lignin Depolymerization in the Presence of Base, Hydrogenation Catalysts and Ethanol

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## Supporting information

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## 1. Optimization of reaction conditions

### 1.1. Effect of reaction temperature

The temperature has a distinct impact on lignin depolymerization. Temperatures  $>330^{\circ}\text{C}$  lead to extensive char formation, hence, should be avoided. While performing reaction at temperatures  $<250^{\circ}\text{C}$  does not result in educt depolymerization and precipitation of oligomer products. Thus, a high yield of lignin derived oligomers without formation of char could be granted only in the narrow window of reaction temperatures between  $250\text{-}300^{\circ}\text{C}$ .

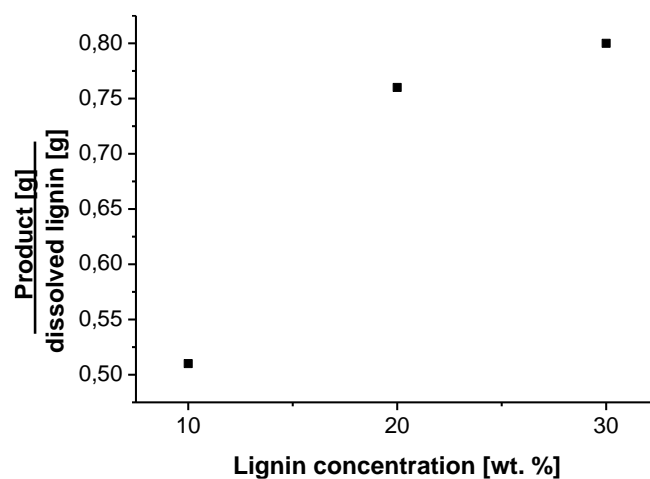
**Table S1.** Effect of temperature on formation lignin oligomers and char.

Entry	Temperature	Yield of retentate, %	Char formation
1	250	-	no
2	300	49	no
3	335	-	extensive

### 1.2. Effect of lignin loading

The influence of the lignin concentration on the yields and characteristics of precipitated oligomers was studied by running reaction with 10, 20 and 30 wt.% of lignin. The concentration of base and catalyst was kept identical for all tests. As it can be seen from Table 5, the yield of product (determined as mass of precipitated lignin oligomers divided by mass of lignin input) increases with increase of lignin concentration from 10 to 20 wt.% (query 1 and 3), however the further increase in lignin concentration to 30 wt.% leads to lower yield (query 3 and 4). It should be noted that maximum solubility of lignin in 80 g of 1M NaOH was determined to be 24.7 g, that means that 5.3 g of lignin remained insoluble at least in the beginning of reaction. Thus, it would be fair to recalculate the product yield taking into consideration the input of soluble lignin. The dependency of product yield from lignin concentration is shown on Figure 6. With an increase of the lignin concentration in the starting mixture the yield of oligomer product increases up to 80 wt.%.

The GPC analysis of obtained oligomers also reveals that products obtained with 20 wt.% lignin loading possess slightly lower molar mass, but higher PDI than the product obtained with 10 wt.% lignin loading. In contrary running reaction with 30 wt.% of lignin results in significant increase of both molar masses (number average and weight average) and PDI. This could result from incomplete solubilization of lignin in reaction media.



**Figure S1.** Effect of lignin concentration on yield of lignin oligomers product normalized by dissolved amount of lignin.

**Table S2.** Characteristics of retentates obtained by lignin depolymerization with lignin concentrations. Lignin depolymerization performed with Kraft lignin (10-30 wt. %) at 300°C for 6 h in the presence of Ru/C catalyst (0.01 wt.%, metal based), ethanol (10 wt.%), 30 bar(120 barg) of H<sub>2</sub> and 0.3-1M NaOH (80 wt.%). DMSO+LiBr was used as an eluent for GPC.

Entry	Base	Lignin content	M <sub>n</sub> , g mol <sup>-1</sup>	M <sub>w</sub> , g mol <sup>-1</sup>	PDI	O/C	Yield of retentate, %
1	1.0 M NaOH	10 wt.%	527	1170	2.2	0.17	59
3	1.0 M NaOH	20 wt.%	493	1160	2.4	0.12	76
4	1.0 M NaOH	30 wt.%	640	1570	2.5	-	66

## 2. Recovery of product and mass balance

The total yield NaOH fraction was determined as the weight of collected NaOH solution divided by the total weight of the starting mixture (100 g). For all performed experiments the yield of NaOH fraction was in the range of 80-90%. The deviation from expected 90-95% wt% are explained by losses of liquid fraction during vacuum filtration, minor leaks during depolymerization process, depressurization as well as some of the liquid was condensed in the upper part of the autoclave and therefore could not be fully removed. From the NaOH liquid phase only monoaromatics could be recovered by means of neutralization of NaOH solution to pH=2 followed by extraction with CHCl<sub>3</sub> and further analyzed by GC-MS. The absolute amount of monoaromatics recovered was small, compared to the main product and never above 2% in yield. The NaOH fraction as obtained was also analyzed by GPC analysis (using NaOH as an eluent) regarding the determination of the molecular weight of lignin derivatives present in this fraction (Fig.2 in manuscript). In order to recover the lignin soluble products, present in NaOH, the solution was acidified to pH=2 and subjected to further filtration. In the case of acidification case less than 500 mg of product could be obtained that in comparison with the starting lignin loading of 10 g is negligible in amount (accounts to a value of 5% from starting share of lignin). After filtration the black color of the filtrate phase suggested that acidification did not result in complete recovery of all the remaining products from solution. The recovered solid black fractions were characterized by elemental analysis and GPC using NaOH as an eluent and the results show that the recovered product fractions are indeed identical to the retentate product based on the O/C ratio. Therefore, we conclude, some part of the products that are oxygen enriched remain dissolved in the liquid fraction even at pH=2.

Based on these observations, it can be concluded that during the depolymerization process resulting in the formation of the quinone methide intermediate, also defunctionalisation seems to play a major role. This defunctionalisation is documented by the changes in the O/C ratio of the retentate product and the starting lignin. Therefore, it can be expected that non-aromatic carbon of the starting material in resinol, cumaran and other linkages like the  $\beta$ -O-4 moieties is lost. These defunctionalisation processes are difficult to follow, as the whole reaction is conducted in basic medium, radical processes driving the defunctionalisation of the aromatic backbone and resulting gaseous products of the linkage moieties are predicted to degrade to carbon dioxide that will be absorbed in the basic solution. Building a full carbon balance is therefore a tedious exercise. The analysis of the respective yields was therefore limited to the products that we can quantify unambiguously, and the proposed mechanism was only discussed from our point of view that can be argued on the basis of the evidence created.

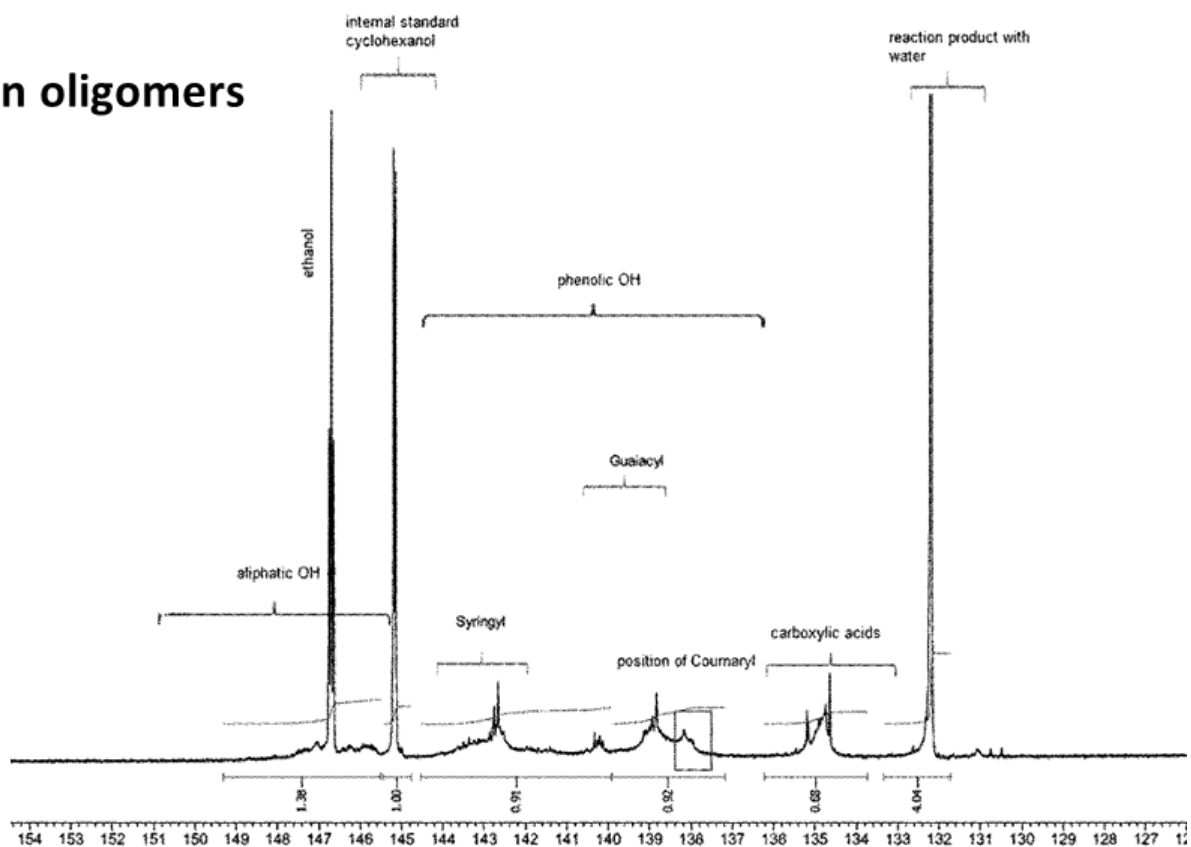
## 3. <sup>31</sup>P NMR data

<sup>31</sup>P NMR was performed from 15 mg sample (lignin or lignin oligomer) were treated w/ 50  $\mu$ i 2-Chlor-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan in 400 ml Pyridine and CDCl<sub>3</sub> (1,6:1 v/v). Additionally, cyclohexanol as internal standard and Cr(III)-Acetylacetonat (as relaxation agent) were added in 150 ml Pyridine/CDCl<sub>3</sub>. The sample was analyzed as "quantitative <sup>31</sup>P-NMR". The <sup>31</sup>P-NMR signals were attributed according to literature. [1] The sample shows signals for aliphatic-OH, phenolic-OH and carboxylic acids. Syringyl. And Guaiacyl-rings can be distinguished. The total amount of aliphatic, phenolic and carboxylic OH were determined. Table S3 shows the differences in the signals between lignin starting material and lignin oligomer (Figure S2).

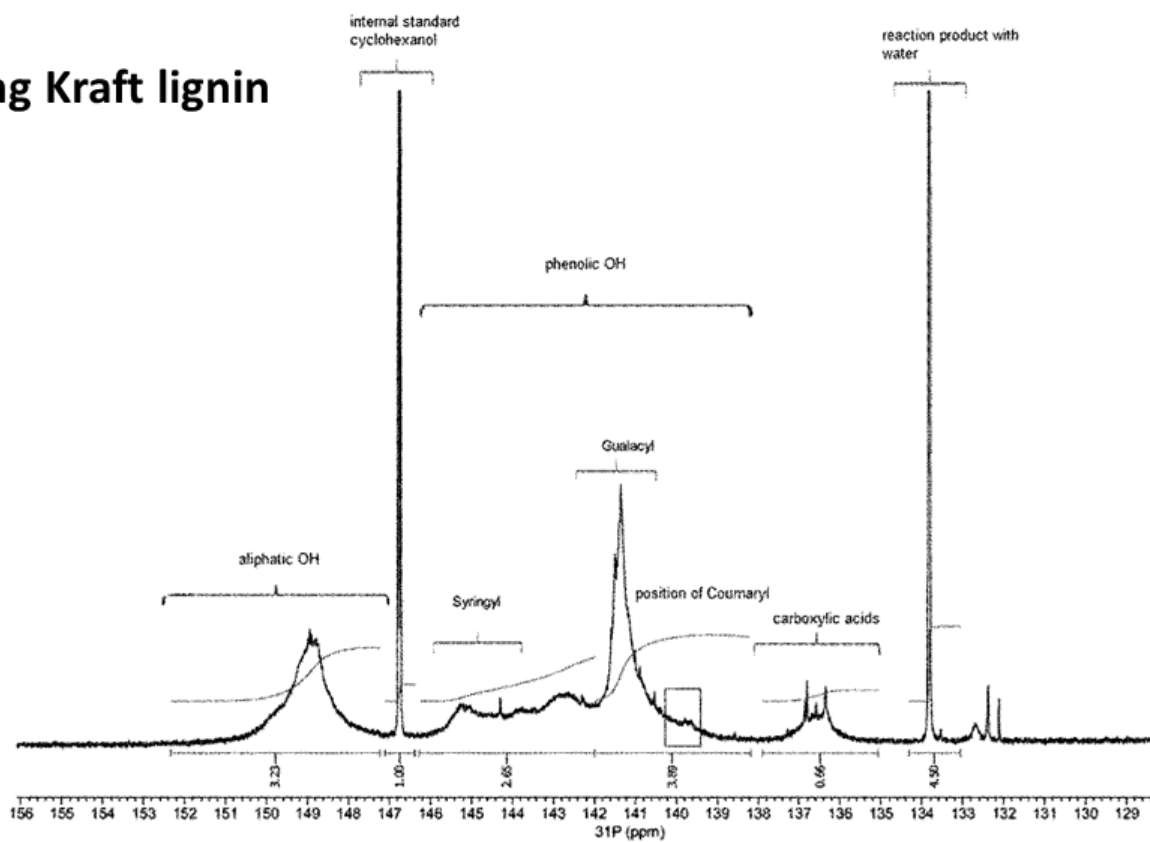
**Table S3.** Distribution of aromatic and aliphatic OH in the starting Kraft lignin and lignin oligomers obtained under standard conditions: Kraft lignin (10 wt. %) at 300°C for 6 h in the presence of Ru/C catalyst (0.01 wt.%, metal based), ethanol (10 wt.%), 30 bar(120 barg) of H<sub>2</sub> and 1M NaOH (80 wt.%).

Compound	Sample amount [mg]	Aliphatic OH, mmol/g	Syringyl and phenolic OH, mmol/g	Guaiacyl OH, mmol/g	Carboxylic OH, mmol/g	Total phenolic OH, mmol/g	Total OH, mmol/g
Lignin oligomer	14.16	0.93	0.61	0.62	0.46	1.23	2.62
Lignin	15.03	1.54	1.26	1.86	0.32	3.12	4.98

## Lignin oligomers



## Starting Kraft lignin



**Figure S2** <sup>31</sup>P NMR spectrum of Lignin oligomers and starting Kraft lignin

**References:**

1. Granata, A.; Argyropoulos, D.S. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a Reagent for the Accurate Determination of the Uncondensed and Condensed Phenolic Moieties in Lignins J. *Agric. Food Chem.* **1995**, *43*, 1538-1544.