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SELECTIVE DEPOLYMERIZATION OF LIGNIN: ASSESSMENT OF YIELDS OF MONOMERIC PRODUCTS

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A method is developed to assess the limits of selective depolymerization, that is, splitting of aryl ether bonds to yield monomeric aromatic products, of native and technical lignins. The method and respective formula is based on measuring the difference between a sum of aryl ether bonds (α -O-4 and β -O-4) and sum of 5-5 and 4-O-5 bonds. The values calculated based on the proposed formula are correlated with published experimental data on catalytic degradation of lignin. In all cases, wood species and experimental conditions notwithstanding, the yields of monomeric aromatic products are found to be close to theoretically calculated for both softwood (23%) and hardwood (51%). Notice that in the actual experiments the yield in hardwood is twice as much as in softwood. In technical lignins (kraft, organosolv) the yields of monomeric products are lowered due to splitting of α -O-4 and β -O-4 bonds during pulping. The developed method is helpful in evaluation of technologies aiming to bring value-added products from lignin through selective degradation.

KEYWORDS. Lignin, valorization, maximum degree of selective destruction, monomeric products of destruction, wood

INTRODUCTION

Chemical transformation of lignin into value-added products is considered as a priority direction in developing cost-efficient biorefinery.^[1–5] Selective cleavage of alkylaryl ether interunit bonds, mostly of the β -O-4 type, yielding monomeric aromatic products is considered as one of the most promising avenues in this development. To assess available technologies, it could be useful to have a straightforward quantitative method to compare efficiency of lignin depolymerization methods. In case of a partially degradable polymer such as lignin it could be based on the maximum theoretically possible degree of cleavage of alkylaryl ether bonds in the sample considered.

Currently, the following equation is used for rough assessment of the maximum (theoretical) yield of monomeric products in reactions leading to selective degradation of lignin:^[1]

$$Y = \frac{(n-2)P^2}{n} \cdot 100,$$

where Y represents the sum of individual yields of monoaromatics, n is the number of monomers occurring in the polymer chain, and P corresponds to the fraction of cleavable/targeted bonds (e.g., for lignin, β -O-4 linkages).

In our opinion, this equation was derived based on two insufficiently proven assumptions. First, lignin is considered to be a linear polymer. While some literature data suggest a linear structure of low molecular mass fractions

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in separated lignin samples,^[6-10] common is understanding of the structure of lignin as a three-dimensional branched polymer.

Second, the equation does not reflect the known fact of phenylpropane units (PPU) in lignin being bound by essentially two types of bonds: ether (α -O-4 and β -O-4) and carbon-carbon. Therefore, splitting even all interunit alkylaryl ether bonds would not bring about lignin depolymerization into monomeric products.

In this study, we develop an alternative approach to evaluation of the relative efficiency of different methods of lignin depolymerization. It is based on determination of the maximum degree of selective splitting of α -O-4 and β -O-4 bonds available for a selected sample.

RESULTS AND DISCUSSION

Major types of inter-PPU bonds in lignin, as they are currently understood, are presented in Figure 1. Notice that β -aryl ether (1), biphenyl (4) and diaryl ether (5) structures contain only one bond type (etheric or carbon-carbon), while phenylcoumarane (2), resinol (3), dibenzodioxocin (6), and spirodienone (7) contain both bond types. Thus, the majority of PPU units in lignin are bound by two bonds, one stable, and one easily splittable under the typical conditions of lignin depolymerization. Obviously, in the process of selective degradation, splitting of α -O-4 and β -O-4 bonds would not lead to complete depolymerization of lignin. On the other hand, a minor fraction of PPU that are bound

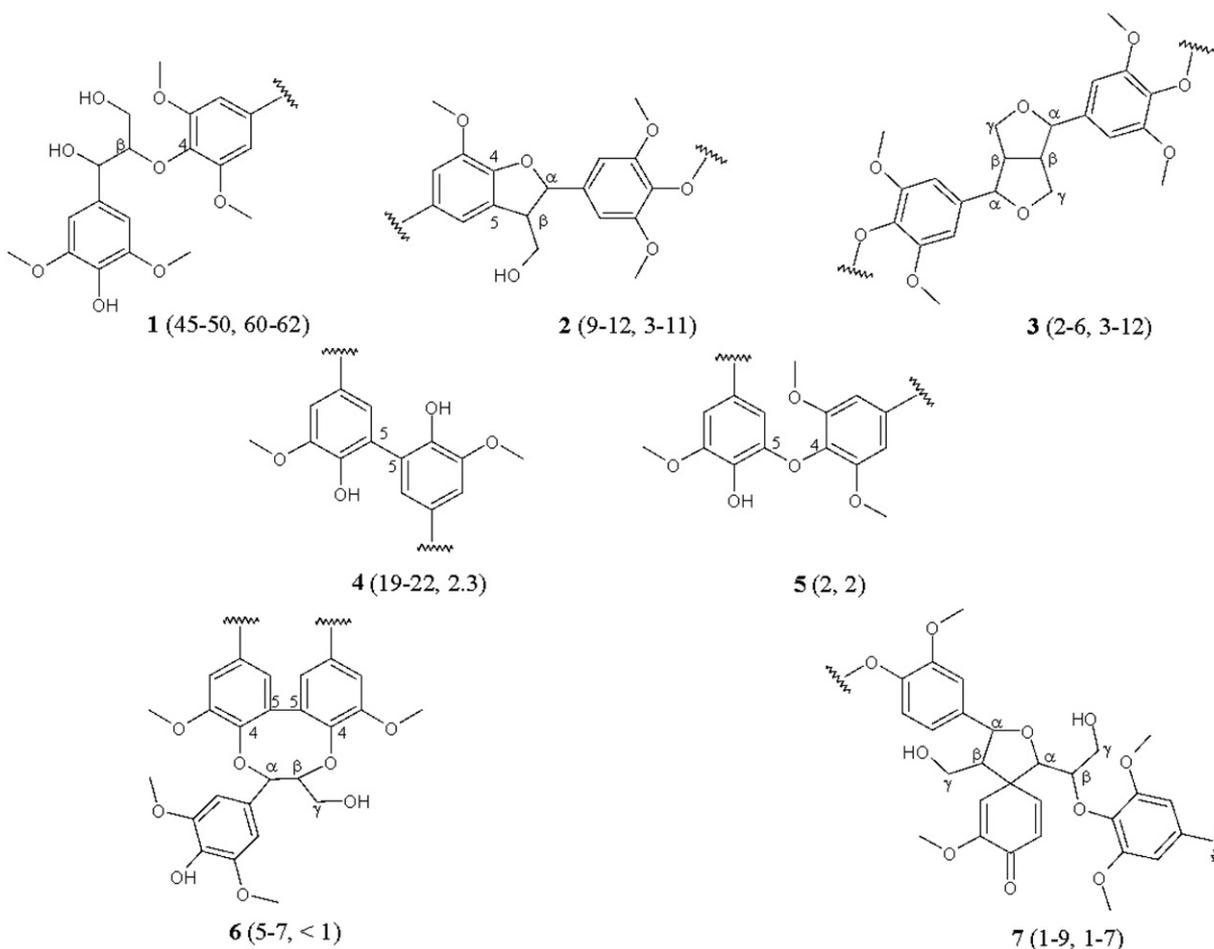


FIGURE 1. Types of inter-unit bonds in lignin [1] (for 4, see [12, 13]). The content of respective bonds is given in parentheses as n/100 PPU (softwood, hardwood).

TABLE 1. Yields of monomeric products of selective degradation of lignin.

No.	Wood sample	Process	Yields of monomeric products of lignin degradation, mass % to lignin	References
Softwood				
1	Spruce (<i>Picea glauca</i> Moench (Voss))	Dioxane/water (1:1) Pd/C, 468 K, 5 h, 3.4 MPa H ₂	24	[17]
2	Spruce (<i>Picea excelsa</i>)	Benzene, Co ₂ (CO) ₈ , 443 K, 24 h, 10 MPa H ₂ /CO (1:1)	24.5	[18]
3	Pine (<i>Pinus sylvestris</i>)	EtOH/H ₂ O, Pd/C (5 mol%), 195 °C, 1 h	23	[19]
4	Pine (<i>Pinus radiata</i>)	Dioxane/water (1:1) Pd/C, 468 K, 24 h, 3.45 MPa H ₂	21	[20]
5	Pine*	Methanol, Pd/C, ZnCl ₂ , 498 K, 12 h, 3.4 MPa H ₂	19	[21]
6	Pine*	Water, H ₃ PO ₄ , LiTaMoO ₆ , Ru/C, 503 K, 24 h, 6 MPa H ₂	21.2	[22]
Hardwood				
7	Birch (<i>Betula pendula</i>)	EtOH/H ₂ O, Pd/C (5 mol %), 195 °C, 1 h	49	[19]
8	Birch (<i>Betula pendula</i>)	Methanol, Ru/C, 523 K, 3 h, 1 MPa H ₂	47.2	[23]
9	Birch (<i>Betula platyphylla</i> Suk)	Dioxane/water, H ₃ PO ₄ , Pt/C, 473 K, 4 h, 4 MPa H ₂	46.4	[24]
10	Birch*	Methanol, Pd/C, ZnCl ₂ , 498 K, 12 h, 3.4 MPa H ₂	55	[21]
11	Birch*	Water, Ni-W ₂ C/AC, 508 K, 4 h, 6 MPa H ₂	46.5	[25]
12	Birch*	Methanol, Ni/C, 473 K, 6 h, argon	54	[26]

*Species not fully identified.

by alkyl aryl ether bonds only, could easily split as monomers; likely, such PPU are located on periphery of the macromolecule.

The content of this PPU fraction (monomer yield) can be estimated based on the difference between the contents of (a) alkylaryl ether bonds and (b) stable bonds in a sample. It is known that splitting of 1% of inter-PPU bonds results in dissolution of 1% lignin.^[11]

In Bjorkman spruce lignin (*Picea abies*), the summary bonds/PPU ratios are: (α -O-4 + β -O-4) = 61/100 PPU, and (5-5 + 4-O-5) = 38/100 PPU, the latter characterizing a degree of condensation.^[14] The difference is 23/100 PPU (23% based on the total bonds that is 99/100 PPU). Otherwise, Bjorkman

spruce lignin contains 23% inter-PPU alkylaryl ether bonds splitting of which would yield 23% monomeric depolymerization products. In native wood lignin of softwood (spruce, pine), the total content of alkylaryl ether bonds is 79/100 PPU.^[15] If we assume the same degree of condensation in native lignin as in Bjorkman lignin (38/100 PPU), the expected yield of monomers would be the same 23% based on lignin in wood.

In Bjorkman eucalyptus lignin (*E. grandis*), the summary bonds/PPU ratios are: (α -O-4 + β -O-4) = 64/100 PPU, and (5-5 + 4-O-5) = 21/100 PPU, the latter characterizing a degree of condensation.^[16] The difference is 43/100 PPU (51% based on the total bonds

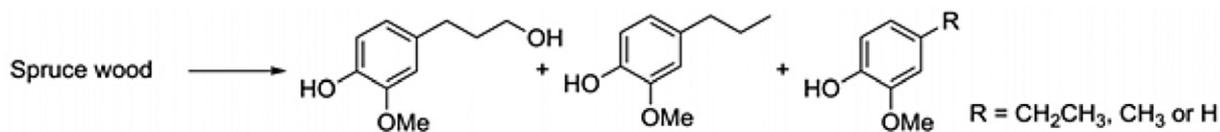


FIGURE 2. Products of hydrogenolysis of spruce wood (dioxane/water 1:1, H₂ at 3.4 MPa, 468 K, 5 h).^[2]

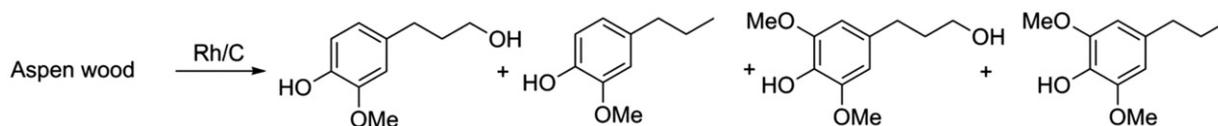


FIGURE 3. Products of hydrogenolysis of aspen wood (dioxane/water 1:1, H₂ at 3.4 MPa, 468 K, 5 h).^[2]

that is 85/100 PPE). Based on these estimate, the projected yield of monomeric products of selective degradation of lignin in hardwood is more than twice as much as in softwood.

Independent verification of the proposed estimate is based on their comparison to actual data on selective lignin degradation (Table 1).

The data presented in Table 1 show the yields of monomeric products to be close to the theoretical maximum in both softwood (23%) and hardwood (51%), the exact species and experimental conditions notwithstanding. Thus, the experimental data support the proposed method of evaluation of theoretical maximum of lignin depolymerization. Typical products of selective degradation of softwood and hardwood lignins are presented in Figures 2 and 3.

The data described are obtained on native lignin in wood. Under the harsh conditions of alkaline pulping, the bulk of α -O-4 and β -O-4 bond in lignin is splitted. For example, only 23/100 PPE of such bonds remains in kraft spruce lignin.^[15] Then, it is not surprising that catalytic hydrogenolysis (Ru/C) of kraft lignin in methanol yields less than 4% monomeric products.^[1, 27] Selective degradation of birch organosolv lignin yields 14% monomers.^[2, 26]

For comparison, when a synthetic β -O-4 polymer ($M_n = 2693$, $M_w = 6007$) underwent reductive depolymerization (EtOAc/H₂O, 5 mol % Pd/C, 10 mol % NaBH₄, 80 °C, 1 h) the monomeric product formed with 99% yield.^[28] Under similar conditions, spruce

wood (i.e., native lignin) yielded only 23% monomeric products.^[19]

Based on the presented data, we suggest the following formula for the assessment of the maximum degree of selective degradation of lignin:

$$Y = \frac{A-C}{A+C} \cdot 100,$$

where Y is a summary yield of monomeric aromatic products (%), A is a sum of α -O-4 and β -O-4 ($n/100$ PPU), and C is a sum of 5-5 and 4-O-5 bonds ($n/100$ PPU).

More detailed description and proofs of correctness of the equation are provided in Supporting information.

CONCLUSION

The developed method could be helpful in assessing methods of producing value-added products from lignin. Nowadays, prospective technologies provide yields of monomeric lignin degradation products from wood that are close to theoretically possible in both softwood (23%) and hardwood (51%), (cf. to data in Table 1). However, comparative economic validation is often difficult being dependent on further processing of residual wood containing carbohydrates and lignin. Some of proposed methods utilize complicated and expensive catalytic processes where regeneration becomes a special issue. Also, high temperatures and hydrogen pressure require expensive equipment. In case of technical lignins, the yields of monomeric

products are low. Even in case of untreated wood, as it is demonstrated in this study, lignin depolymerization is decisively incomplete and limits to the improvement do exist. Therefore, in our opinion, selective lignin degradation could be considered only as one of several, and not necessarily major avenue of lignin utilization; more methods allowing transformation of most of wood lignin into value-added products should be developed.

SUPPORTING INFORMATION

Example of calculations 1 (Bjorkman spruce lignin)

The sum of bonds α -O-4 and β -O-4 = 61/100 PPU

The sum of bonds 5-5 and 4-O-5 = 38/100 PPU

Difference: 61 – 38 = 23/100 PPU

If to consider from the sum of these bonds:

$$\frac{23}{63 + 38} = \frac{23}{99} \cdot 100 = 23.2 \sim 23\%$$

Otherwise, Bjorkman spruce lignin contains 23% bonds, splitting of which would yield 23% monomeric depolymerization products.

In **native wood lignin** of softwood (spruce, pine), the total content of alkylaryl ether bonds is 79/100 PPU. If we assume the same degree of condensation in native lignin as in Bjorkman lignin (38/100 PPU), the sum of bonds 5-5 and 4-O-5:

$$\frac{79 \cdot 38}{61} = 49.2 \sim 49/100 \text{ PPU}$$

Difference between two types of bonds: 79 – 49 = 30/100 PPU

If to consider from the sum of these bonds:

$$\frac{30}{79 + 49} = \frac{30}{128} \cdot 100 = 23.4 \sim 23\%$$

Example of calculations 2 (Bjorkman eucalyptus lignin)

The sum of bonds α -O-4 and β -O-4 = 64/100 PPU

The sum of bonds 5-5 and 4-O-5 = 21/100 PPU

Difference: 64 – 21 = 43/100 PPU

If to consider from the sum of these bonds:

$$\frac{43}{64 + 21} = \frac{43}{85} \cdot 100 = 50.6 \sim 51\%$$

Otherwise, Bjorkman eucalyptus lignin contains 51% bonds, splitting of which would yield 51% monomeric depolymerization products.

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