Aromatic Monomer Production from Lignin Depolymerization Predicted from Bond Cleavage Data for Lignin Model Compounds

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Lignin depolymerization to form useful aromatic compounds has attracted considerable research attention. Depolymerization of lignin, a complex three-dimensional polymer consisting of aromatic monomers, requires cleavage of C-O-C ether bonds and C-C bonds between the monomers. Previously, we reported the bond cleavage characteristics of several lignin model compounds during treatment with supported metal catalysts in supercritical water in the absence of hydrogen gas. Here, we used our model compound data to predict the yields of aromatic monomers from treatment of lignin (derived from hardwood and softwood biomass) with supported metal catalysts (Pd/C, Rh/C, Pt/C, and Ru/C) in supercritical water. The calculated yields decreased in the order Pd/C > Rh/C > Pt/C > Ru/C, and the calculated yields from hardwood biomass were higher than those from softwood biomass. We also compared the calculated yields with the experimental yields for depolymerization of organosolv-lignin powder. The experimental yields decreased in the same order as the predicted yields but were lower than the predicted yields, possibly because repolymerization during decomposition of the lignin model compounds may have been much less than during lignin decomposition.

Keywords
Lignin depolymerization, Aromatic monomer, Supercritical water, Supported metal catalyst

1. Introduction

Conversion of lignocellulosic biomass to fuels and feedstock chemicals has attracted considerable research attention because of the renewability of lignocellulose1)4). Lignocellulosic biomass consists mainly of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose, which are polymers of sugars, can be readily converted into fuels and feedstock chemicals5)7). However, lignin is a complex three-dimensional polymer consisting of aromatic monomers connected by various types of linkages, so conversion into valuable products is generally difficult, although recent reports have suggested conversion of lignin into useful aromatic products8)12). Lignin depolymerization into aromatic chemicals is important to achieve carbon-efficient use of lignocellulosic biomass.

We previously investigated the conversion of lignin into gaseous products using charcoal-supported palladium, platinum, rhodium, and ruthenium catalysts (Pd/C, Pt/C, Rh/C, and Ru/C) in supercritical water at 673 K13)16). We found that lignin gasification proceeds in two steps: uncatalyzed hydrolysis of lignin to form alkylphenols and formaldehyde in supercritical water, followed by gasification of the alkylphenols and formaldehyde over the supported metal catalysts. In the absence of a catalyst, the alkylphenols and formaldehyde repolymerize to form char. When Ru/C is the catalyst, the lignin monomers are completely converted to gaseous products such as methane, carbon dioxide, and hydrogen. In contrast, Pt/C, Rh/C, and Pd/C show low activity for lignin gasification, but their use suppresses repolymerization resulting in the formation of aromatic products. We also studied the bond cleavage reactions of lignin model compounds over supported metal catalysts in supercritical water17)18); specifically, we determined the yields of aromatic monomers from cleavage reactions of 2-phenethyl phenyl ether, benzyl phenyl ether, biphenyl, diphenyl ether, and bibenzyl, which served as models for lignin compounds with β-O-4, α-O-4, 5-5, 4-O-5, and β-1 linkages, respectively.

In this study, we used our previously reported data on the bond cleavage reactions of lignin model compounds,
along with published data regarding the percentages of various linkage types in lignin derived from softwood and hardwood biomass, to predict the yields of aromatic monomers from lignin by supported metal catalysts in supercritical water. We then compared the predicted yields with the experimental yields determined by depolymerization of a commercial organosolv-lignin powder.

2. Experimental

Pd/C, Pt/C, Rh/C, and Ru/C (5 wt% metal loading) were purchased from Wako Pure Chemical Industries, Ltd. 2-Phenethyl phenyl ether (Wako Pure Chemical Industries, Ltd.), benzyl phenyl ether (Sigma-Aldrich), biphenyl (Wako Pure Chemical Industries, Ltd.), diphenyl ether (Wako Pure Chemical Industries, Ltd.), and bibenzyl (Tokyo Chemical Industry Co., Ltd.) were used as obtained from the suppliers. Lignin (organosolv-lignin powder) was purchased from Aldrich and used as supplied.

Lignin or model compounds were treated with supercritical water in a batch reactor (316 stainless steel tube, volume 6.0 cm³) as described previously. Briefly, lignin or a model compound (0.10 g), catalyst (0.15 g), and water (3.0 g) were loaded into the reactor, which was purged with argon gas to remove air and then submerged in a molten-salt bath (KNO₃-NaNO₃) at 673 K. At this temperature and a water density of 0.5 g cm⁻³, the partial pressure of water was 37.1 MPa in the supercritical phase. After 1 h at 673 K, the reactor was quickly cooled by immersion in a water bath.

Gaseous products were collected using a glass syringe and analyzed by gas chromatography (GC-8A, Shimadzu Corp.) equipped with a thermal conductivity detector and a ShinCarbon ST column. The reactor contents were recovered by rinsing the reactor with tetrahydrofuran and filtering the rinse liquid to remove any solids (supported metal catalysts). The products dissolved in the filtrate were quantitatively analyzed using a gas chromatograph (Agilent Technologies Japan Ltd., HP-6890) equipped with a flame ionization detector and a DB-WAX capillary column. The yield of each product was calculated by the following equation: C% = (moles of carbon in product)/(moles of carbon in reactant) × 100. The amount of solid product was estimated by subtracting the weight of the catalyst loaded in the reactor from the weight of the tetrahydrofuran-insoluble solid fraction.

3. Results and Discussion

3.1. Bond Cleavage Reactions of Lignin Model Compounds

As mentioned above, we previously reported data on the bond cleavage reactions of lignin model compounds catalyzed by Pd/C, Pt/C, Rh/C, and Ru/C in supercritical water. The metal dispersions of Pd/C, Pt/C, Rh/C and Ru/C were 11, 21, 19, and 43 %, respectively, as determined by adsorbed hydrogen at 313 K in a volumetric unit (Quantachrome, Autosorb-1). We used 2-phenethyl phenyl ether, benzyl phenyl ether, biphenyl, diphenyl ether, and bibenzyl as the models for lignin compounds with β-O-4, α-O-4, 5-5, 4-O-5, and β-1 linkages, respectively. Table 1 shows the percentages of monomeric and dimeric aromatic compounds produced by treatment of lignin model compounds with supercritical water for 1 h at 673 K and a water density of 0.5 g cm⁻³ in the presence or absence of a catalyst.

| Model compound               | Catalysts          |
|------------------------------|--------------------|
|                              | Pd/C       | Pt/C       | Rh/C       | Ru/C       | None     |
| 2-Phenethyl phenyl ether     | 79.6       | 63.2       | 61.3       | 10.2       | 64.1     |
|                              | (0.0)      | (0.0)      | (0.2)      | (1.3)      | (0.9)    |
| Benzyl phenyl ether          | 62.2       | 44.0       | 41.9       | 5.0        | 65.1     |
|                              | (0.0)      | (0.1)      | (0.0)      | (0.0)      | (0.0)    |
| Biphenyl                     | 4.4        | 1.2        | 3.1        | 4.4        | 0.4      |
|                              | (90.4)     | (60.7)     | (30.3)     | (4.4)      | (89.6)   |
| Diphenyl ether               | 30.4       | 37.2       | 54.9       | 7.4        | 4.8      |
|                              | (59.7)     | (34.3)     | (1.3)      | (0.2)      | (97.1)   |
| Bibenzyl                     | 9.1        | 8.2        | 39.9       | 11.6       | 3.1      |
|                              | (69.3)     | (61.9)     | (30.3)     | (4.4)      | (89.6)   |
of both monomeric and dimeric aromatic compounds were low because this catalyst shows activity for gasification of aromatic compounds under these reaction conditions. Gas yield decreased in the order Ru/C > Rh/C > Pt/C > Pd/C. No solid products were observed from all lignin model compounds. The Pd/C-, Pt/C-, and Rh/C-catalyzed reactions of lignin model compounds cross-linked by C-O-C ether bonds afforded mainly monomeric aromatic compounds. In contrast, lignin model compounds cross-linked by C-C bonds were difficult to convert to monomeric aromatic compounds.

3.2. Prediction of Aromatic Products of Lignin Depolymerization

The reported percentages of linkage types in lignin obtained from softwood and hardwood biomass are shown in Table 2 (\textsuperscript{18,19}). On the basis of these data and our previous data for bond cleavage reactions of model compounds, we calculated the product distributions for lignin depolymerization as follows. We treated lignin as an infinite straight chain of aromatic monomers a and b cross-linked by bonds A, B, and C, as shown in Fig. 1. Monomer a, for example, can be obtained by cleavage of bonds A and B, whereas the a-b dimer can be obtained by cleavage of bonds A and C and retention of bond B. The yields of products with \(n\) aromatic rings \((Y_n)\) can be calculated by the following equation:

\[
Y_n = \left(\sum A_i c_i\right)^2 \left(\sum A_i r_i\right)^{n-1}
\]  

(1)

where \(i\) designates the type of linkage (\(\beta\)-O-4, \(\alpha\)-O-4, 5-5, 4-O-5, or \(\beta\)-1), \(A_i\) is the probability that linkage \(i\) is present, \(c_i\) is the probability of cleavage of linkage \(i\) to produce aromatic monomers, and \(r_i\) is the probability that linkage \(i\) remains uncleaved. For example, when the Pd/C catalyst is used for the 5-5 bond (biphenyl), \(c_{5-5} = 0.044\) and \(r_{5-5} = 0.904\). We did not carry out bond cleavage reactions of lignin model compounds with \(\beta\)-5 and \(\beta\)-\(\beta\) linkages, which have both C-O-C ether bonds and C-C bonds. For these linkages, we used the probability of bond cleavage and the probability of the lack of bond cleavage for bibenzyl, which has C-C bond cross-links; this choice was based on the fact that in supercritical water at 673 K, C-C bonds are more difficult to cleave than C-O-C ether bonds (as indicated by the data in Table 1). The yields of products with \(n\) aromatic rings calculated by Eq. (1) and the data in Tables 1 and 2 are shown in Fig. 2. For softwood biomass, the aromatic monomer yields were calculated to be 21.5, 13.5, 18.3, and 0.7 % using Pd/C, Pt/C, Rh/C, and Ru/C, respectively, and

| Linkage type | Softwood\textsuperscript{a)} | Softwood\textsuperscript{b)} | Hardwood\textsuperscript{a)} | Hardwood\textsuperscript{b)} |
|--------------|-----------------|-----------------|-----------------|-----------------|
| \(\beta\)-O-4 | 43-50           | 48              | 50-65           | 61              |
| \(\alpha\)-O-4| 6-8             | 7               | 4-8             | 7               |
| \(\beta\)-5  | 9-12            | 11              | 4-6             | 5               |
| 5-5          | 10-25           | 22              | 4-10            | 8               |
| 4-O-5        | 4               | 4               | 6-7             | 7               |
| \(\beta\)-1  | 3-7             | 5               | 5-7             | 6               |
| \(\beta\)-\(\beta\)| 2-4 | 3               | 3-7             | 6               |

\textsuperscript{a)} Values obtained in previous studies\textsuperscript{18,19}.  
\textsuperscript{b)} Values used for the calculation in this manuscript.
13.1 % in the absence of catalyst. The low monomer yield calculated for Ru/C was due to gasification of the aromatic products. For hardwood biomass, the monomer yields were calculated to be 32.4, 20.9, 26.2, and 0.9 % using Pd/C, Pt/C, Rh/C, and Ru/C, respectively, and 19.8 % in the absence of catalyst. The calculated yields for hardwood biomass were higher than those for softwood biomass, owing to the presence of a larger number of β-O-4 bonds in hardwood biomass (Table 1) and to the ease of β-O-4 bond cleavage in supercritical water. The calculated product yields decreased as the number of aromatic rings in the products increased for both types of biomass.

### 3.3. Comparison of Predicted and Experimental Aromatic Monomer Yields from Lignin Depolymerization

Commercial organosolv-lignin powder was depolymerized in supercritical water at 673 K for 1 h with catalysis by Pd/C, Pt/C, Rh/C, and Ru/C and in the absence of a catalyst (Fig. 3). The molecular formula and molecular weight of the organosolv-lignin powder was C42.39H45.46O12.15 and 1000-1500, respectively, as determined by an ultimate CHNS analyzer (Perkin-Elmer, model 2400) and a gel permeation chromatography system (Waters, GPC150Cplus). The origin of the lignin powder was unknown (softwood or hardwood biomass). The yields of obtained aromatic monomers were 10.7, 6.4, 7.8, and 1.8 % using Pd/C, Pt/C, Rh/C, and Ru/C, respectively, and 1.9 % in the absence of a catalyst. That is, the activities of the catalysts decreased in the order Pd/C > Rh/C > Pt/C > Ru/C, which is the same as the order of predicted activities. However, the experimental monomer yields were lower than the predicted yields. Experimental errors of yields for each aromatic monomer and total aromatic monomers were less than 5 %, determined by carrying out the same experiments more than three times to confirm the reproducibility.

Lignin was treated as an infinite chain of aromatic monomers, but the molecular weight of actual organosolv-lignin was 1000-1500, indicating that bonds between the aromatic monomers in the organosolv-lignin had already undergone partial cleavage. In previous studies, we gasified lignin over Pd/C, Pt/C, Rh/C, and Ru/C in supercritical water at 673 K and found that lignin gasification involves two steps: hydrolysis of lignin to form alklyphenols and formaldehyde, and subsequent gasification of the alklyphenols and formaldehyde over the supported metal catalyst. In the absence of a catalyst, the alklyphenols and formaldehyde polymerized to form solid char. The extent of repolymerization during the decomposition of lignin model compounds is likely to be much less than that during the repolymerization of actual lignin because the actual lignin monomers have many functional groups. This may partially explain the difference between the predicted and experimental monomer yields. The predicted monomer yields in the absence of a catalyst were 19.8 % for hardwood biomass and 13.1 % for softwood biomass, but the experimental monomer yield in the absence of a catalyst was only 1.9 %. This result suggests that repolymerization was rapid during lignin decomposition in the absence of a catalyst.

Lignin monomers connected by a β-O-4 linkage contain Cα-OH functional groups; these functional groups are reported to be unstable in high-temperature water during cleavage of β-O-4 bonds, and therefore cleavage of the C-O bond can occur in the presence of a catalyst. Under certain conditions, the Cα-OH group can undergo dehydrogenation to form a carbonyl group, and therefore aromatic products with a carbonyl group can be obtained. Our lignin model compound with β-O-4 linkages was 2-phenethyl phenyl ether, which does not have a Cα-OH functional group. Therefore, accurate prediction of the yields of aromatic monomers will require study of the cleavage reactions of lignin model compounds containing a Cα-OH group.

### 4. Conclusion

Using bond cleavage data obtained from our experiments with lignin model compounds, we predicted the yields of aromatic monomers from the decomposition of lignin, derived from hardwood and softwood biomass, by treatment with supercritical water in the presence of supported metal catalysts. For hardwood biomass, the calculated aromatic monomer yields were 32.4, 20.9, 26.2, and 0.9 % with catalysis by Pd/C, Pt/C, Rh/C, and Ru/C, respectively, and 19.8 % in the absence of a catalyst. The calculated yields reflecting the catalyst activities decreased in the order Pd/C > Rh/C > Pt/C > Ru/C. We also found that the calculated yields from...
hardwood biomass were higher than those from softwood biomass. We compared these predicted yields with the experimental yields from decomposition of organosolv-lignin powder, which were 10.7, 6.4, 7.8, and 1.8 % with catalysis by Pd/C, Pt/C, Rh/C, and Ru/C, respectively and 1.9 % with no catalyst. The experimental yields decreased in the same order as the predicted yields. However, the experimental yields were lower than the predicted yields, possibly due to the difference between the extent of repolymerization for the lignin model compounds and the extent of repolymerization for actual lignin.

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要  旨
リグニンモデル化合物の分解挙動から予想されるリグニン解重合反応による芳香族モノマー製造

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リグニン解重合反応による有用な芳香族化合物製造は、リグニノセルロース系バイオマスの有効利用の観点から注目されてい
る。リグニンは、芳香族化合物モノマーが様々な結合で繋がっ
た複雑な三次元的な高分子である。リグニン解重合には、モノ
マー間に存在するC-Oエーテル結合およびC-C結合を開裂す
る必要がある。我々は、担持金属触媒を用いて超臨界水中にて
リグニンのモデル化合物の結合開裂挙動を報告している。本論
文では、リグニンモデル化合物の結合開裂挙動の結果から、リ
グニンから得られる芳香族モノマー収率を予想した。予想され
るモノマー収率は、Pd/C > Rh/C > Pt/C > Ru/C の順となり、針
葉樹より広葉樹のリグニンからより多くの芳香族モノマーが得
られる。さらに、我々はオルガノソルブリグニンの解重合反応
によるモノマー収率の予測と実験結果を比較した。実験で実際
に得られるモノマー収率は予想結果と同じ担持金属触媒の順とな
る。しかし、実験結果でのモノマー収率は予想されるモノ
マー収率よりも低くなった。これは、モデル化合物の分解反応
中には再重合反応があるよう進行しないのに対して、リグニンの
解重合反応中には再重合反応が進行するためと考えられる。