# Lignin Depolymerization over Ni/C Catalyst in Methanol, a Continuation: Effect of Substrate and Catalyst Loading

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# Lignin Depolymerization over Ni/C Catalyst in Methanol, a Continuation: Effect of Substrate and Catalyst Loading

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**Abstract:** Conversion of lignin to fuels and chemicals is a significant challenge given the intrinsic heterogeneity of lignin. Towards development of selective processes for lignin depolymerization, herein we further expand on a catalytic system, Ni/C in methanol, for the conversion of wood lignin into methoxypropylphenols (Song *et al., Energy Environ. Sci*. **2013**, *6*, 994–1007). We find that the product spectrum and yield vary significantly across catalyst loading and biomass type and origin. Poplar and eucalyptus result in lower monomer yields than those found for birch. These results suggest that catalytic systems for selective lignin depolymerization must carefully consider the nature of the substrate to achieve high yields of individual, upgradeable products.

Lignin, accounting for 15-30% by weight of dry biomass, is formed from three phenylpropanoid monomers that are linked together during biosynthesis by a variety of C-O and C-C bonds. Given its intrinsic heterogeneity as a polymer in lignocellulosic biomass, most depolymerization processes including thermal, catalytic, and biological, yield a heterogeneous mixture of oxygenated aromatics, making lignin conversion to fuels and chemicals a significant challenge in modern lignocellulosic biorefineries.[1-2] Currently, most production facilities for cellulosic ethanol utilize only the carbohydrate components of biomass,[3-4] and lignin is isolated as a lignin-enriched “cake.” Given a general lack of catalysts that can selectively cleave C-O and C-C bonds in polymeric lignin to produce a manageable product slate at high yields, biorefinery lignin is typically burned to produce electricity.[1] Moreover, the development of processes to effectively convert a large mixture of oxygenated aromatics into a single product is still a nascent endeavor, warranting the development of selective depolymerization catalysts to produce high yields of a manageably narrow product slate that can be upgraded to fuels and chemicals.[5]

Conversion of wood lignin with Raney Ni, Pd/C, Rh/C, Rh/$Al_2O_3$ and Ru/$Al_2O_3$ catalysts are some of the first examples of reduced metal catalytic depolymerization of lignin via hydrogenolysis.[6-8] Using spruce wood, studies with Rh/C catalyst achieved maximum 34% conversion of total available lignin and yielded six different phenolic products. The Raney nickel catalyzed reaction enabled only 16% conversion of total available lignin in 1:1 dioxane/water (v/v) at 195 ºC, 34 bar $H_2$, and 5 h reaction time.[6] Catalytic depolymerization of lignin has also been extensively studied over the past several decades,[9-12] but with limited success in terms of yields and selectivity of the phenolic products. For example, Pd/C and HZSM-5 is capable of cleaving C-O bonds in monomeric and dimeric phenol substrates to give mixtures of cyclohexane products.[11a] Base hydrolysis of lignin results in phenolic products that repolymerize to refractory material that is very difficult to upgrade leaving poor yields of isolable monomeric or oligomeric phenols. Lercher and coworkers have shown that capping/protection of monomeric groups with borate groups improves the yields of phenolic products.[11b,c] Rinaldi and Wang have recently reported on transfer hydrogenation using isopropanol over a raney nickel and an acidic β-zeolite for lignin model substrates and organosolv lignin, in which demethoxylation and dihydroxylation of phenol intermediates were noted.[12]

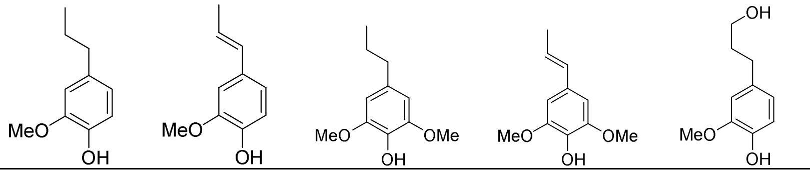
More recently, Song *et al*. reported a process for depolymerization of Soxhlet extracted birch sawdust with a number of catalysts without a direct need for externally added $H_2$.[13] Among several reactions, the authors reported that a Ni/C catalyst achieved the best results, enabling 54% lignin derived products from intact birch sawdust in methanol at 200 ºC and at 2 bar inert atmosphere. As discussed by the authors, this reaction likely formed hydrogen *in situ* from methanol. The major products reported were 2-methoxy-4-propylphenol (dihydroeugenol, DHE) and 2,6-dimethoxy-4-propyl-phenol (DMPP) with selectivity of 22 and 67%, respectively (Figure 1). These promising results prompted us to further examine and expand the activity of the Ni/C catalyst for the conversion of birch and other biomass substrates, namely, poplar and eucalyptus wood.

Ni/C catalyst, containing 11 wt% Ni, was prepared by incipient wetness impregnation method by following the procedure of Song et al.[13] and characterized by FE-SEM, HRTEM, grazing incidence X-ray diffraction (GIXD) and BET surface area analyzer. HRTEM image (Figure S1A) shows spherical nanoparticles of dimensions approximately 4-8 nm are uniformly distributed. FE-SEM image (Figure S1B) reveals that the spherical nanoparticles are aggregated to form big particles in some parts of the sample. Wide angle GIXD pattern (Figure S1C) suggests that the material is amorphous with two broad peaks center around $2\theta = 44.2$ and $51.9^o$, which matches with peaks of standard JCPDS (JCPDS # 4-850) data of Ni metal. Three sharp peaks at $2\theta = 21$, 22 and 29° are likely contributed by the carbon support as these peaks match with those observed in the GIXD profile of the support. $N_2$ adsorption-desorption study at 77 K shows BET surface area of the catalyst is 893 $m^2$ $g^{-1}$.

Under identical reaction conditions (200 °C, 6 h, 5 wt% Ni/C, and stirring speed of 500 rpm under 2 bar $N_2$) to those used by Song et al.,[13] we carried out several experiments for the conversion of dried, knife milled and Soxhlet extracted birch wood. These results, summarized in Table 1, showed the yield of 20% lignin derived products based on available lignin in birch. The observed yield is ca. 30% lower than the reported yield by Song et al. We also found the propenyl derivatives isoeugenol (i-EuOH) and methoxyisoeugenol (Mi-EuOH) (Figure S2) are the primary products with their respective yields of 8 and 12 % (Entry 1, Table 1), respectively. i-EuOH and Mi-EuOH are also detected as the major products from poplar and eucalyptus wood with total yields of the lignin derived products as 6 and 16%, respectively (Table 1 and Figures S3-S4). Birch wood appeared to be a better feedstock, enabling higher lignin derived products. While the exact reason for the superior activity of birch wood is not known, lower complexity of xylan-enriched hemicellulose, differences in lignin-carbohydrate complex linkages, and higher uniformity of lignin in birch could be among the possible reasons for its higher activity.[14]

When the above reactions were repeated with 10 wt% Ni/C, the yields and products distribution changed significantly (Table 1 and Figures S5-S7). Complete hydrogenation of i-EuOH and Mi-EuOH led to the formation of DHE (10%) and DMPP (18%) as major products from birch wood with a small amount of the corresponding propenyl derivatives (Entry 4 in Table 1 and Figure S4). Total yields of the lignin-derived products also improved to 32% based on lignin content. The reaction profile (Figure 1) for birch wood depolymerization with 10 wt% Ni/C showed that the initial product solutions predominantly contained i-EuOH and Mi-EuOH, which were further hydrogenated to DHE and DMPP, respectively, as the reaction progressed. Interestingly, after 6 h reaction time with 10 wt% catalyst on birch, the total pressure inside the reactor after cooling down the reactor to ambient temperature was significantly higher (9.4 bar) than the initial pressure (2 bar). In the case of birch wood conversion with 5 wt% Ni/C, pressure buildup inside the reactor was considerably lower (3.5 bar). The reason for high pressure buildup in the presence of 10 wt% Ni/C loading could be due to the formation of more $H_2$ from the methanol solvent during the reaction. Poplar and eucalyptus wood also yielded higher lignin-derived products (26 and 28% respectively) in the presence of 10 wt% Ni/C. However, i-EuOH and Mi-EuOH were formed as the primary products from poplar, possibly due to the presence of less produced $H_2$ as evidenced from lower final pressure (5.5 bar) inside the reactor (Entry 5, Table 1). A comparison of the results with different biomass substrates and catalyst loading is shown in Figure 2.

**Table 1**. Depolymerization results of birch, poplar and eucalyptus wood with 5 and 10 wt% Ni/C catalyst in methanol.



| Entry | Substrate, Ni/C catalyst loading | DHE[a] | i-EuOH[a] | DMPP[a] | Mi-EuOH[a] | DHE-OH[a,b] | Total % yield[c] | Final pressure (bar)[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | Birch, 5 wt% | - | 8 | - | 12 | - | 20 | 3.5 |
| 2 | Poplar, 5 wt% | - | 2 | - | 2 | 2 | 6 | 2.4 |
| 3 | Eucalyptus, 5 wt% | - | 6 | - | 8 | 2 | 16 | 3.6 |
| 4 | Birch, 10 wt% | 10 | 1 | 18 | 3 | - | 32 | 9.4 |
| 5 | Poplar, 10 wt% | 1 | 8 | 2 | 15 | - | 26 | 5.5 |
| 6 | Eucalyptus, 10 wt% | 6 | 3 | 8 | 11 | - | 28 | 8.5 |

Reaction conditions: wood biomass = 1.0 g, catalyst = 0.05 g (5 wt%) or 0.1 g (10 wt%), T = 200 ºC, 2 bar $N_2$ and 6 h reaction time. [a] yields (%) are calculated from the theoretical lignin content in wood and the mass of the products quantified by GC-FID (Supporting Information). Lignin analysis data of birch, eucalyptus and poplar are shown in Table S1. [b]DHE-OH = 4-(3-hydroxypropyl)-2-methoxyphenol. [c]Total yields (%) represent the sum of all lignin derived products. [d]Pressure inside the reactor after cooling down the reactor to ambient temperature after 6 h reaction time.

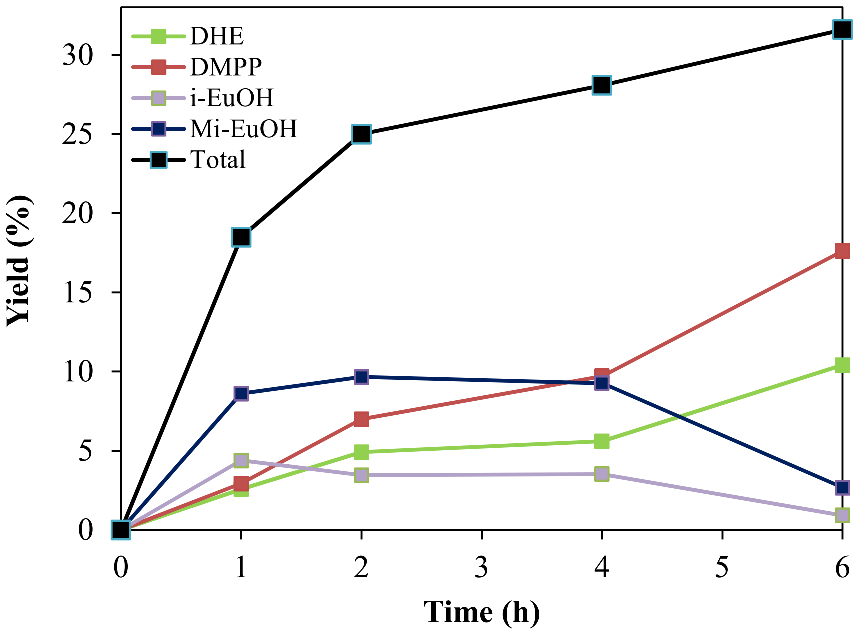


**Figure 1.** The reaction profile for the production of lignin monomers from birch wood. Reaction conditions: birth wood = 1.0 g, Ni/C = 0.10 g (10 wt%), T = 200 ºC, $N_2$ = 2 bar.

In summary, Song et al. has recently reported on the exciting use of Ni/C as an effective catalyst for one-pot conversion of treated birch sawdust in methanol, enabling 54% wood lignin conversion with a total of 89% selectivity for DHE and DMPP. We have investigated and expanded the application of this system to poplar and eucalyptus wood by adopting the reported reaction conditions. Our results show that the propenyl analogs of DHE and DMPP, i-EuOH and Mi-EuOH, are the main products from all wood substrates using 5 wt% Ni/C, and that total yields range from < 10% to > 30% depending on the biomass substrate. Furthermore, in the presence of higher Ni/C (10 wt%), DHE and DMPP become the major products from birch wood, which is presumably due to the presence of more $H_2$ produced from methanol reforming over Ni/C as noted by Song et al.[13] While the exact reason for discrepancies between our results and those reported by Song et al. is difficult to speculate, biomass composition is known to vary across regions and growing seasons.[15] Perhaps, natural chemical variation between birch from coastal China and birch from inland United States may have contributed to the observed differences.

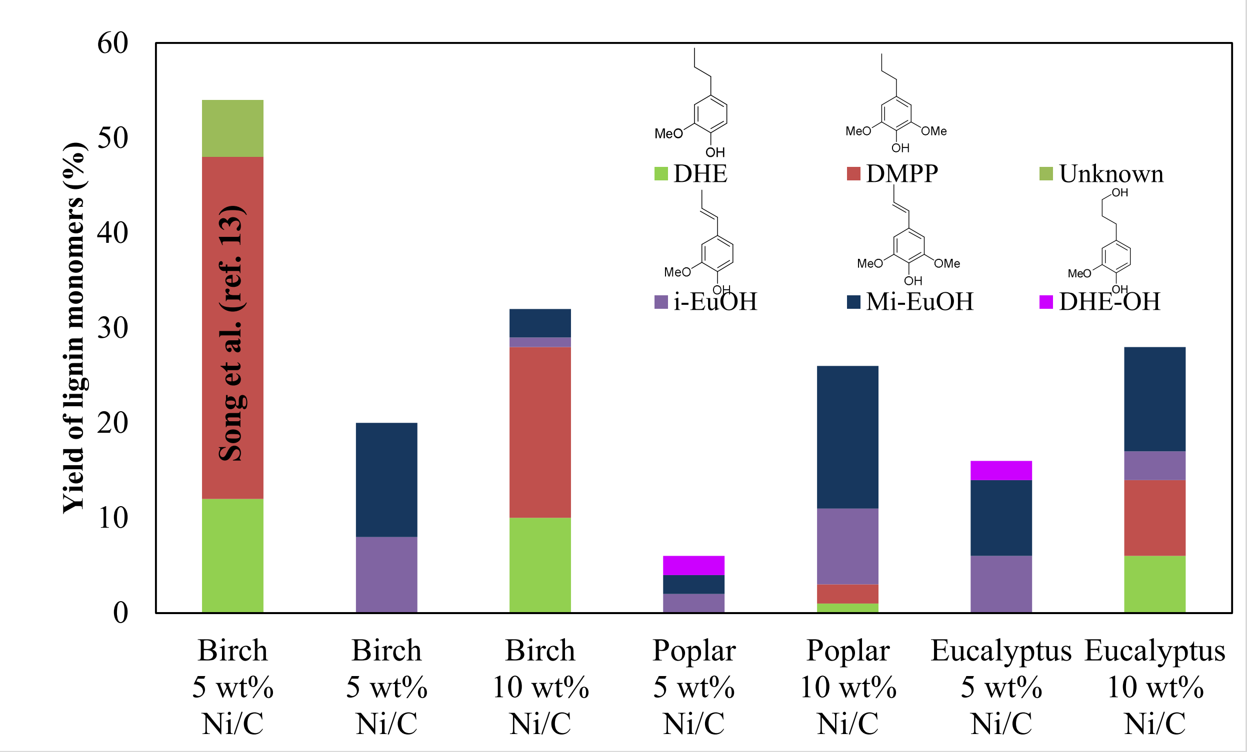


**Figure 2**. A comparison of lignin depolymerization using various biomass substrates and catalyst loading.

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