THE CATALYTIC EFFECT OF CARBON-SUPPORTED RUTHENIUM ON THE DEPOLYMERIZATION OF HYDROLYTIC LIGNIN

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Introduction

Biomass consists of an assortment of recalcitrant polymers such as cellulose and lignin. Prior to use in gasification streams, these polymers are subjected to degradation/depolymerization reactions for the purpose of liberating smaller, more volatile and reactive species.

It is well known that carbohydrates can be depolymerized in an acid hydrolysis reaction with the depolymerization effectively catalyzed using a carbon-supported ruthenium catalyst (1-5). Under relatively mild conditions, carbon-supported ruthenium can also effectively catalyze the hydrogenation of highly hindered aromatic rings, such as those found in rosin (6, 7). More recently, alumina-supported ruthenium and other forms of ruthenium have been studied as hydrodesulfurization and coal liquefaction catalysts (8-11).

While it is known that ruthenium can catalyze carbohydrate depolymerization, less is understood when reacting whole biomass, as hydrolytic lignin remains and must be separated from the catalyst. Base hydrolysis at 280-320°C has been used to solubilize and react the hydrolytic lignin to phenolic compounds (2, 12). However, little is known about the effect of the ruthenium on the hydrolytic lignin under the base hydrolysis reaction conditions. In this study, the catalytic effect of ruthenium on the degradation of lignin polymers has been explored.

Experimental

Commercially available hydrolytic lignin was obtained from Aldrich Chemical Co. and used as the starting material. Reagent grade sodium hydroxide and concentrated hydrochloric acid were also obtained from Aldrich. The ruthenium catalyst (5% ruthenium loaded on a carbon support) was obtained from Aldrich.

Reactions were performed with and without ruthenium catalyst. For the latter, the catalyst loading was a 1% metal loading. Tubing reactors (~25 mL) were loaded with 1.5 g of hydrolytic lignin and 10 mL of 10% aqueous sodium hydroxide. The reactors were initially purged with nitrogen to remove air and charged to 4.5 MPa with hydrogen gas. An ebulating sand bath was utilized to obtain temperatures of 280, 300 and 320°C in three experiments, each of which had a residence time of 1 hour.

The reacted materials were processed according to the flow chart shown in Figure 1. Solid and liquid products were separated by filtration. The liquid material was then acidified to a pH of approximately 2.0 and separated into acid-soluble and acid-insoluble fractions. Acid-soluble compounds were then extracted with diethyl ether, which was then evaporated to determine yield. Not all acid soluble compounds were soluble in diethyl ether. The yield of residual acid-solubles and gases were determined by difference.

The ether soluble fraction was analyzed by gas chromatography-mass spectrometry (GC-MS) using a Shimadzu QP-5000 mass spectrometer. The acid-soluble fraction was analyzed using a Chemagnetics M100S solid-state nuclear magnetic resonance (NMR) spectrometer operating at a field strength of 2.4 T and utilizing a spinning speed of 3.5 kHz. The technique of cross polarization with magic angle spinning was employed.

To simplify the discussion, the ether-soluble fraction will be referred to as LMW (low molecular weight), the acid-insoluble as HMW (high molecular weight), and the residual soluble material following extraction with diethyl ether as AS-LMW (acid-soluble-low molecular weight) materials.

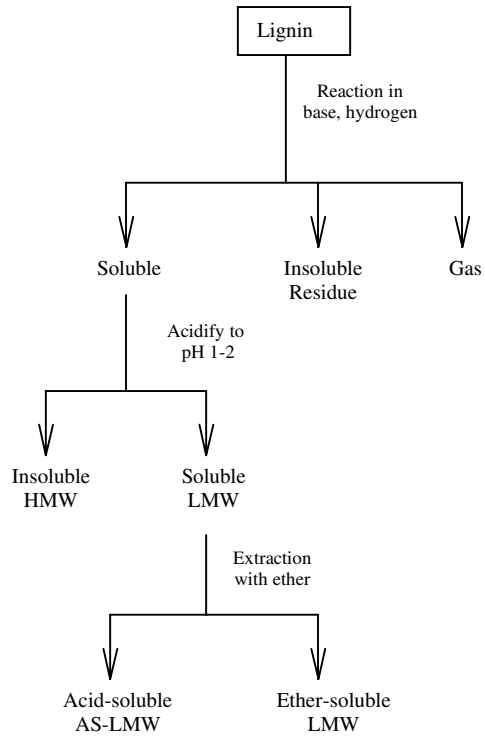

Figure 1: Schematic of procedure to separate products.

Results and Discussion

Non-catalytic Reactions. Table 1 shows the conversions and yields of HMW, LMW and AS-LMW/gas fractions for 280, 300 and 320°C reaction conditions. In each case, conversion to either LMW, HMW, or AS-LMW/gas was nearly complete. Shown in Figure 2 are the GC-MS chromatograms for the LMW fraction and in Figure 4 are solid-state ^{13}C-NMR spectra for the HMW fraction. Relative yields, which are listed in Table 1, indicate that as the reaction severity increases, the yield of HMW product and LMW product decreases, while the AS-LMW/gas yield increases, particularly at 320°C.

Table 1. Conversion and Yield Data for Reaction of Hydrolytic Lignin With and Without Ruthenium Catalyst

Reaction Temp (°C)[a]	Catalyst	Conversion (wt %)	Yield HMW (wt %)	Yield LMW (wt %)	Yield AS-LMW /Gas (wt%)[b]
280	none	99.7	52.0	22.1	25.6
300	none	98.1	38.2	14.6	45.3
320	none	98.6	24.0	8.1	66.5
280	Ru	97.6	22.6	27.5	47.5
300	Ru	90.4	23.6	23.7	43.1
320	Ru	93.5	21.2	16.9	55.4

a All reactions were run for 1 hour, under 4.5 MPa of hydrogen.
b Yield determined by difference.

GC-MS analyses of the LMW fraction (Figure 2) show a product distribution of primarily phenols and catechols, which are compounds typical of lignin degradation reactions. At 280°C, guaiacol is a major product, as well as other methoxyl-substituted aromatic compounds. As the reaction temperature increases, the abundance of methoxyl-substituted aromatics dramatically decreases, with 2,6-di-tert-butyl-p-cresol surviving the more degradative conditions.

Based on the solid-state NMR data (Figure 4), the HMW fraction was found to undergo reactions consistent with those previously reported in lignin maturation investigations (13-19). The primary reaction results in the loss of methoxyl (Figure 4: 74 ppm) and catechol (Figure 4: 148 ppm) functionality with some preservation of phenol-like moieties (Figure 4: 154 ppm).

Catalytic Reactions. When reactions were carried out in the presence of ruthenium catalyst, the conversion was slightly lower than for the corresponding reactions without ruthenium. At all three reaction temperatures, yield of HMW does not change significantly, while the LMW decreases with increasing reaction temperature. However, the depolymerization of the starting material appears to be suppressed under the catalytic reaction conditions at the higher reaction temperature.

GC-MS analyses of the LMW fraction (Figure 3) show the fraction is composed primarily of phenols and catechols, similar to non-catalytic reaction conditions. At 280°C, guaiacol is a major product, as well as other methoxyl-substituted aromatic compounds. As the reaction temperature increases, the methoxyl-substituted aromatics dramatically decrease, with 2,6-di-tert-butyl-p-cresol surviving the more degradative conditions.

The HMW fraction yield did not change as significantly with temperature. The most notable effect on functional group distributions was the loss of the methoxyl (Figure 5: 74 ppm) moieties, while there was some preservation of catechol (Figure 5: 148 ppm) and phenol (Figure 5: 154 ppm) groups within the structure.

Comparison of Non-catalytic and Catalytic Reactions. At 280°C, the extent of depolymerization appears greater for the catalytic reactions. The AS-LMW/gas yield is higher for the catalyzed reaction, and NMR of the HMW fraction shows a greater loss of oxygen functionality when catalyst is in the reaction. The GC-MS data for the LMW also shows fewer oxygen substituted compounds compared to the non-catalytic reaction, another indication of an increased rate of reaction.

However, at 300 and 320 °C, the ruthenium appears to suppress the depolymerization of the hydrolytic lignin compared to the non-catalyzed reactions. The AS-LWM/gas yield is lower for the catalytic reactions. Results of NMR analyses suggest that for the non-catalyzed reactions, the HMW fraction loses more oxygen functionality, particularly as phenols and catechols while the aromaticity increases, compared to the catalytic reactions. The GC-MS data obtained for the LMW fractions indicates a lower percentage of oxygenated compounds, with relatively more substituted aromatics, than in the catalytic reactions.

So what is the role of the ruthenium under these reaction conditions? Ruthenium is a known hydrogenation catalyst, particularly selective for hydrogenating carbonyl functional groups and hindered aromatics (1, 6, 7). However, the hydrogenation activity is highest at 25-200°C. At temperatures of 200-300°C, it has been reported that dehydrogenation activity of aromatics is more dominant (20-21). The reaction system we are investigating is slightly different in that it is a base hydrolysis as well as a hydrogenation reaction.

As observed in the non-catalytic reaction, it is thought that the base participates in breaking the β-O-4 bonds. As radicals are generated through the reaction of the hydrolytic lignin, at 280°C, the ruthenium may be catalyzing the capping of methoxyl radicals with hydrogen and keeping the radicals from re-reacting with the HMW structure. At higher temperatures, the ruthenium appears to promote hydrogenation of the oxygen radicals on the aromatic structures and preserve the phenols and catechols in the HMW structure. It may also function to hydrogenate the carbonyl groups on the generated monomers.

While ruthenium catalyst might suppress the complete gasification of the hydrolytic lignin, it does appear to selectively hydrogenate and retain some oxygen in the solid carbonaceous material. The possible result would be less oxygen in the gas products and less CO/CO_2 generation. Rather than focusing on the complete depolymerization of lignin, the goal could be to focus on finding value-added applications for the products in order to improve the economics for the entire process.

Conclusions

Results indicate that the overall lignin conversion is reduced slightly with increasing temperature compared to non-catalytic reactions. Acid-insoluble compounds retain oxygen functionality, as determined by solid state ^{13}C NMR, when compared to their non-catalytic counterparts. For all reactions, the NMR data showed the oxygen is lost as ether, phenol, and catechol moieties. However, in the non-catalytic reactions, the rate of loss of these moieties and the increase is aromaticity is greater than in the catalytic reactions. If the ruthenium does act to suppress the depolymerization of hydrolytic lignin at higher temperatures, it may selectively suppress loss of oxygen and therefore produce less CO/CO_2. In that case, making value added materials from the remaining material could increase the viability of the entire process. Future work will include using an inert gas, such as N_2 in the reaction, determining the gas composition and yield with and without hydrogen, and searching for uses of the remaining solid.

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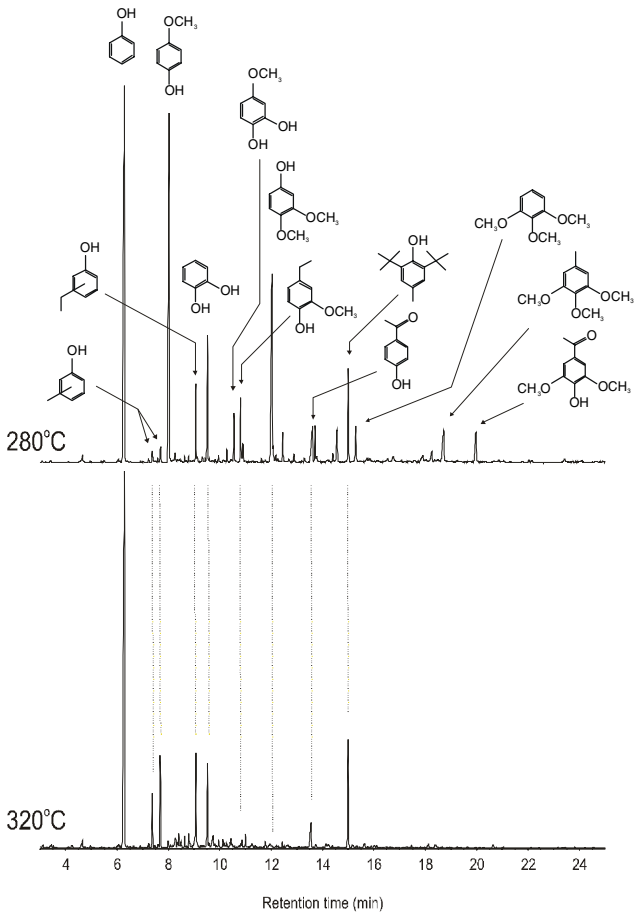

Figure 2: GC-MS spectra of LMW for non-catalytic reactions at 280 and 320°C.

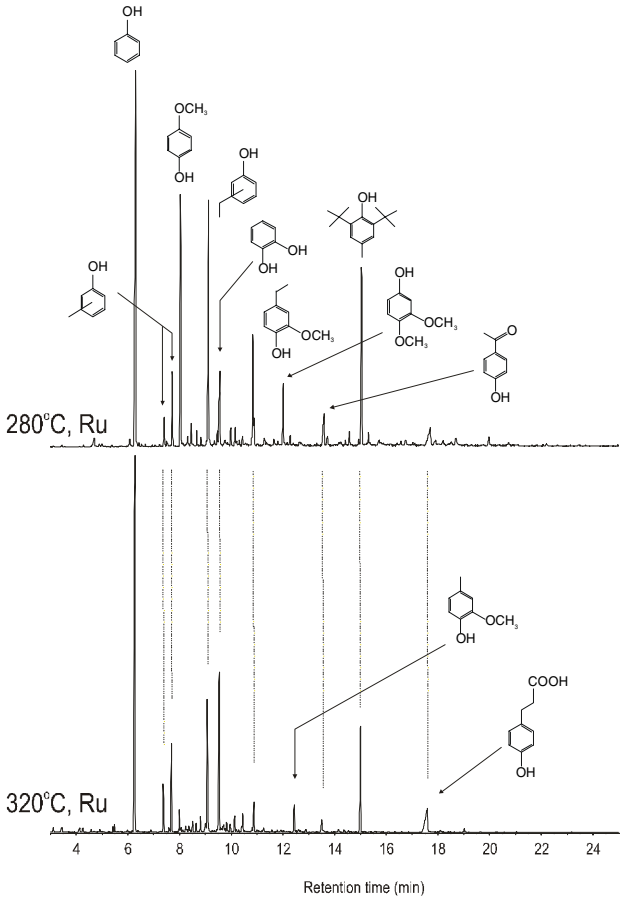

Figure 3: GC-MS spectra of LMW for catalytic reactions at 280 and 320°C.

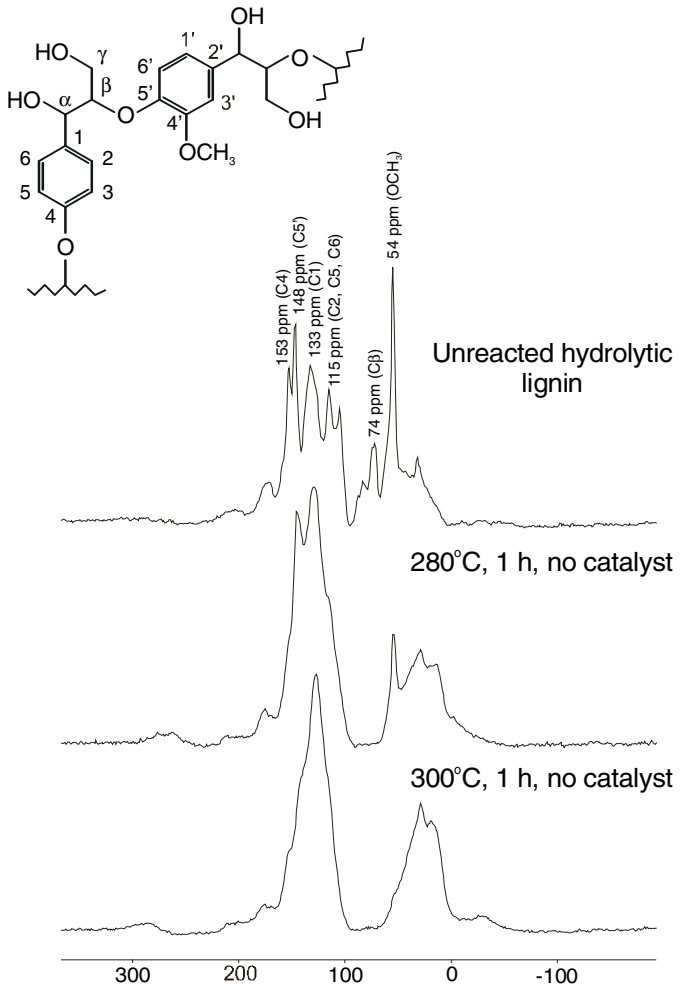

Figure 4: ^{13}C NMR spectra of unreacted lignin and catalytically reacted HMW at 280 and 300°C.

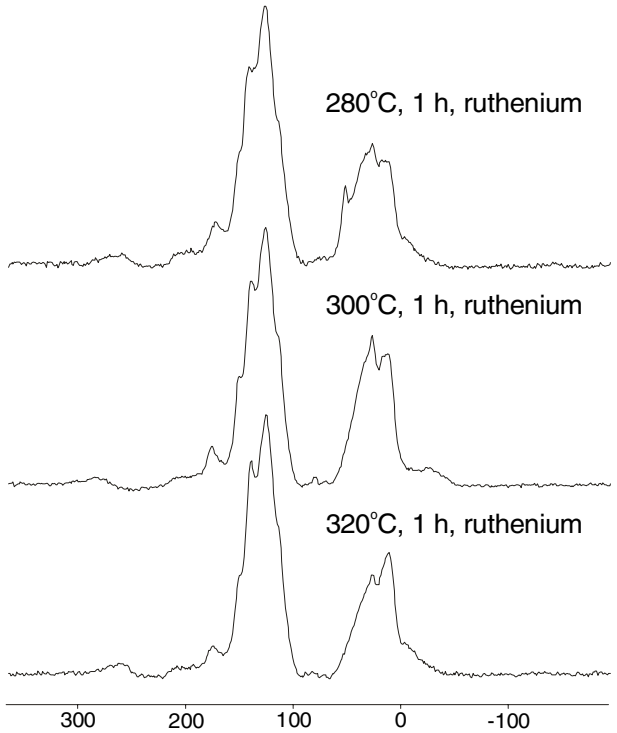

Figure 5: ^{13}C NMR spectra of reacted HMW from catalytic reactions at 280, 300, and 320°C.