

Partial Depolymerization of Lignin Using Hydrogenolysis over Raney Nickel

Daniel Leong¹, Junna Xin², Jinwen Zhang²

1. Olin College of Engineering, 2. Washington State University

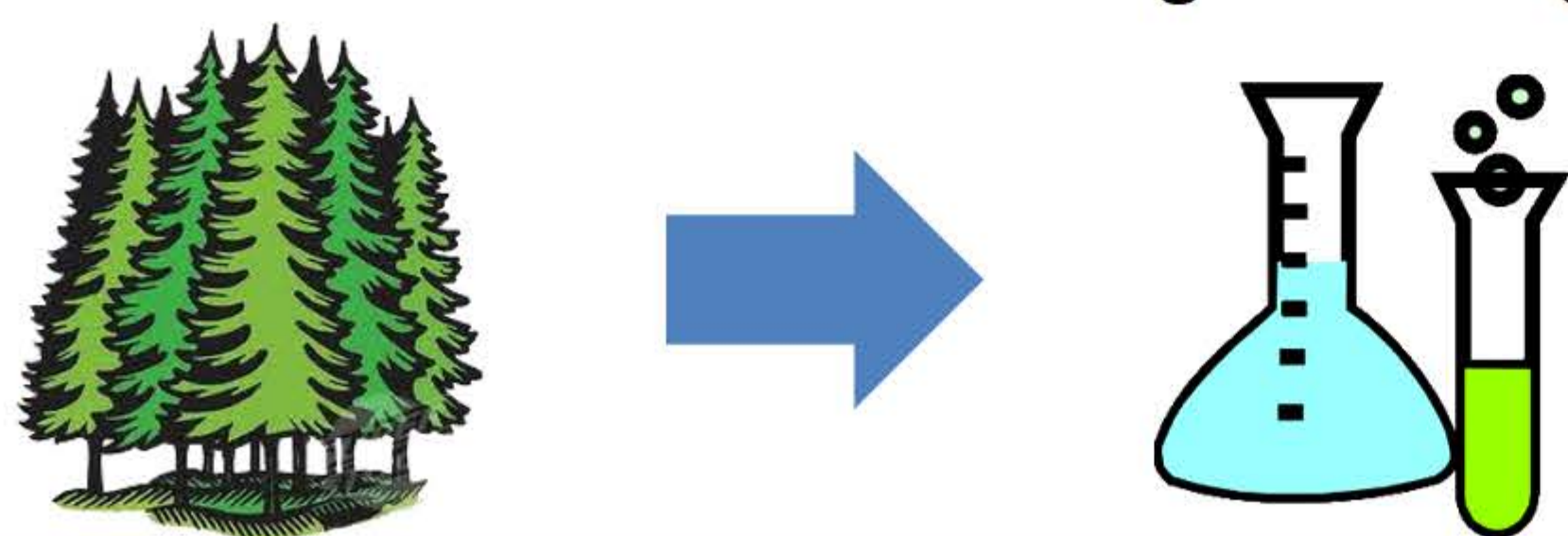
NARA Program, Composite Materials and Engineering Center, Washington State University



Olin College

1. Introduction

For many years, scientists have been searching for a novel way to create engineering polymers from renewable resources. Lignin, a highly branched amorphous polymer, could be the most promising substance for realizing this goal. Its molecular structure suggests that it could be a valuable source of chemicals. To exploit the wide application of lignin in polymer materials, in this study mild hydrogenolysis over Raney Ni catalyst was successfully performed to convert lignin to polymer units with low molecular weight and high hydroxyl value.



2. Procedure

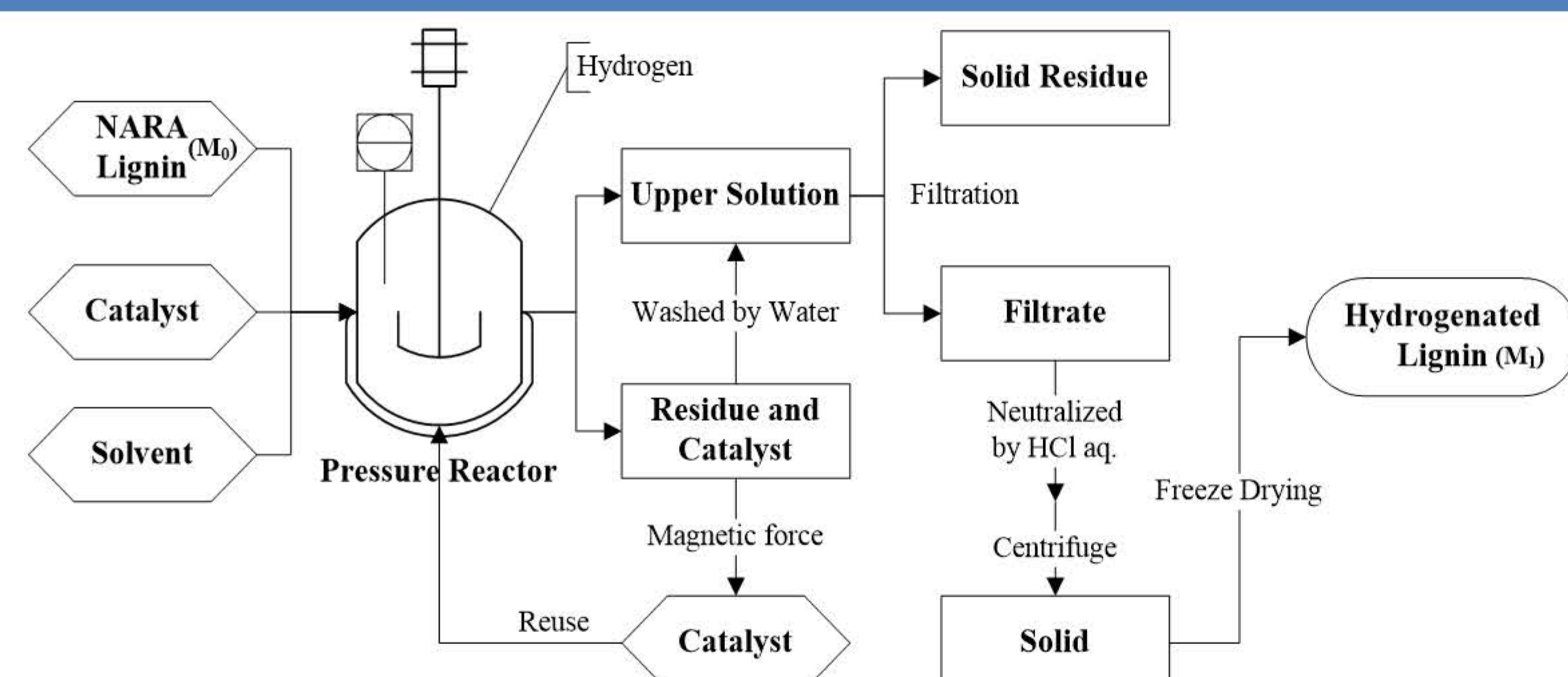


Figure 1: Process diagram for hydrogenolysis reaction

We conducted the following hydrogenolysis reaction for five temperatures between 120 and 200 °C:

1. Pretreat NARA lignin to remove carbohydrates.
2. Charge the pretreated lignin, Raney Ni and 3% NaOH in ethanol/H₂O (v/v, 1/1) to a pressure reactor; Purge the reactor with hydrogen and react for 3.5 h (Figure 2).
3. Remove the catalyst using a magnet and filtrate.
4. Neutralize the filtrate with hydrochloric acid (Figure 3).
5. Collect the product by centrifuge.
6. After removing liquid, place remaining solid residue in freeze dryer (Figure 4). The yield was obtained by M_1/M_0 .



Figure 2: Reactor and temperature controller.



Figure 3: Adding HCl to Yield



Figure 4: Freeze-drying yield

3. Results and Discussion

Effect of Temperature on Yield

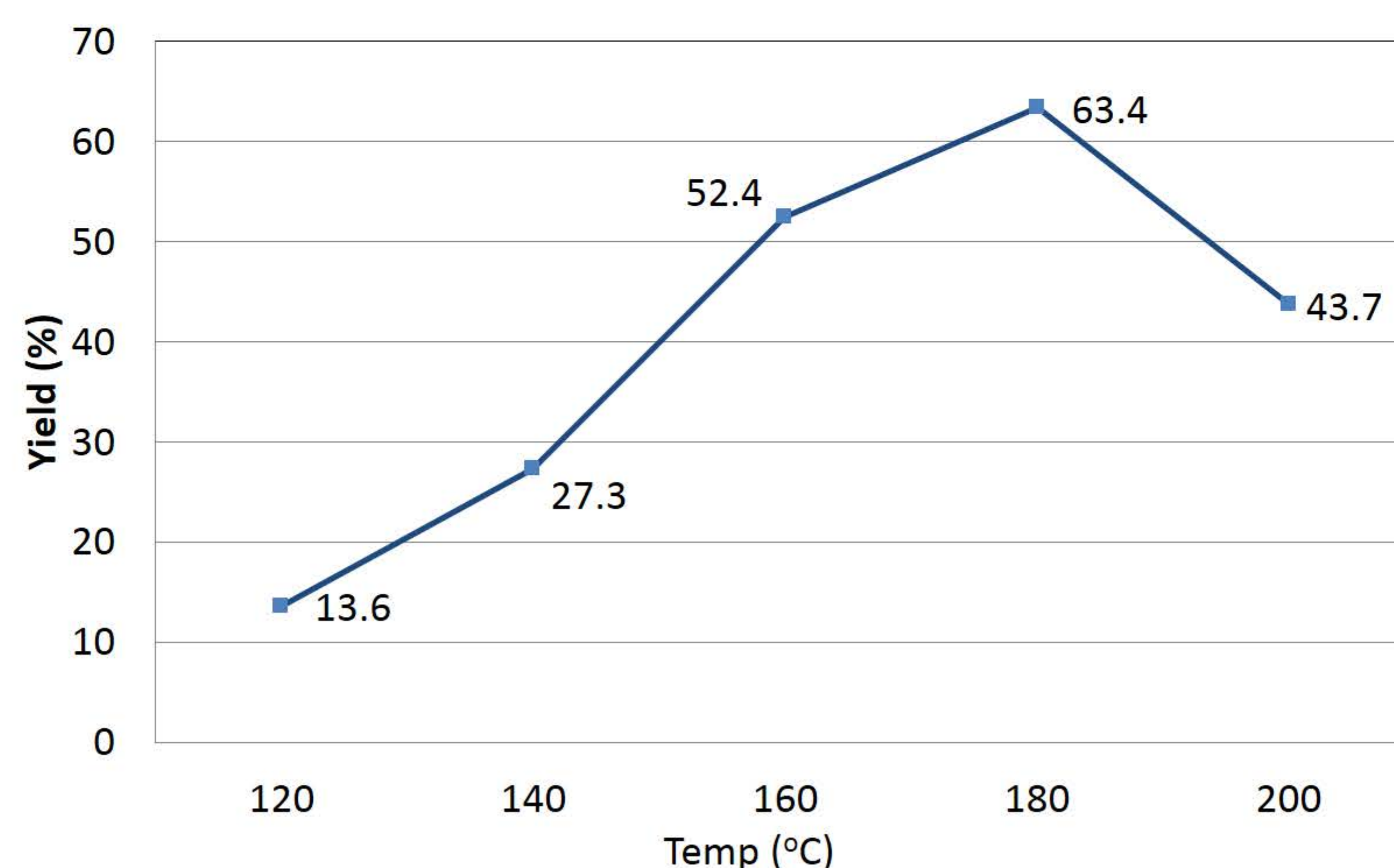


Figure 5: Effect of temperature on yield

- Figure 5 showed that 180 °C was the optimal temperature.
- The yield increased with temperatures from 120 to 180 °C. Decreased yield at higher temperatures (200 °C) was due to the formation of more gaseous chemicals (CO, CO₂, CH₄, etc.)

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

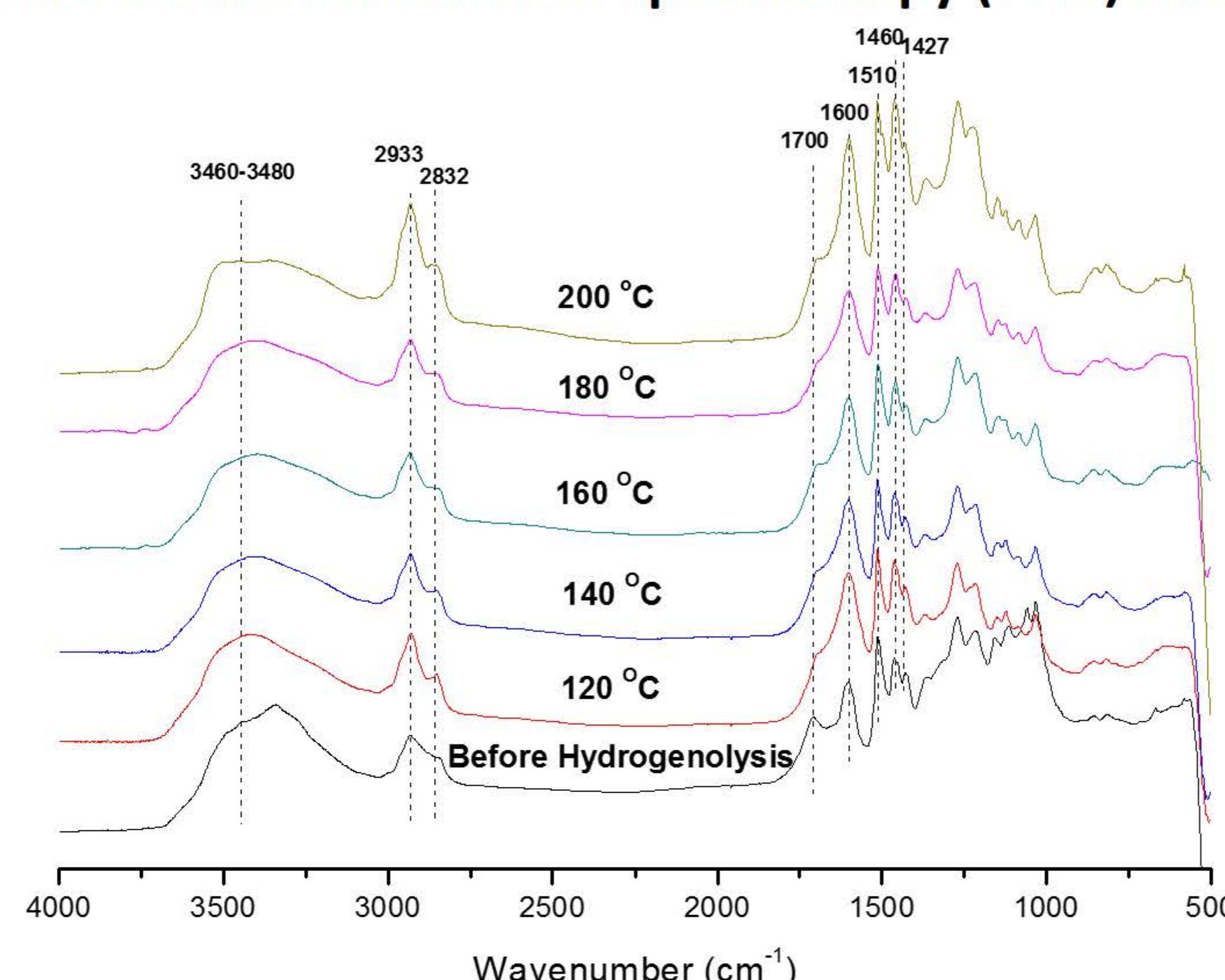


Figure 6: FTIR of hydrogenated lignin obtained from different temperatures. The dotted lines signify peaks of interest.

- The broad peak at 3460-3480 cm⁻¹ was attributed to the absorption of phenolic and aliphatic hydroxyl groups.
- The absorption of carbonyl groups at 1700 cm⁻¹ was strong in the original lignin but was weak in the hydrogenated samples because the O=C-C- linkages were hydrogenated to form HO-C-C-. The C-H of the aromatic ring at 1600 and 1510 cm⁻¹ and methoxyl groups at 1460 and 1427 cm⁻¹ were also observed.

Gel Permeation Chromatography (GPC) Analysis

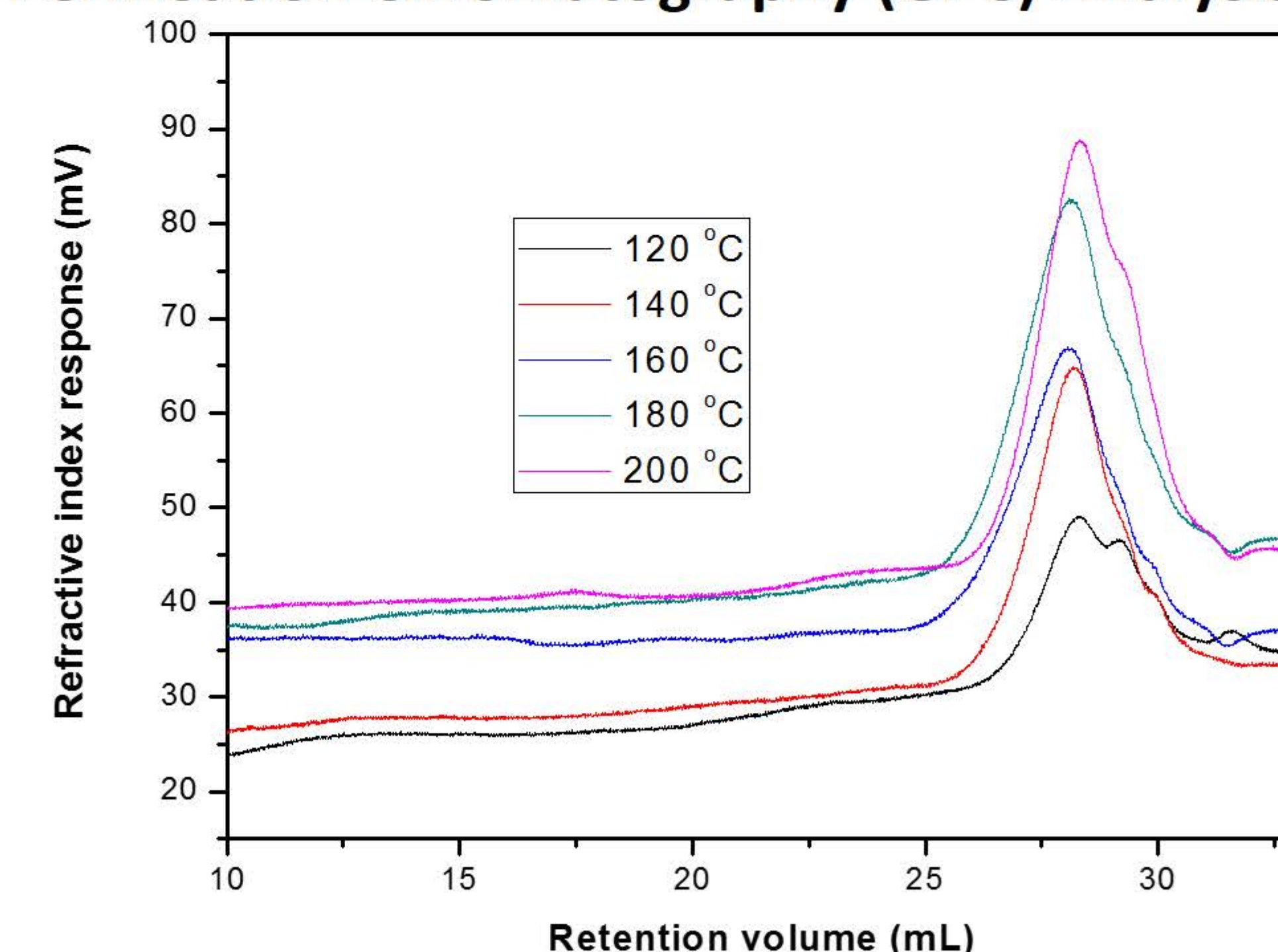


Figure 7: GPC Analysis of hydrogenated lignin obtained from different temperatures.

- The sample hydrogenated at 120 °C exhibited several peaks because only the lignin of low molecular weights was depolymerized at this temperature.
- At higher reaction temperatures, the resulting products exhibit similar molecular weight distributions.

Molecular Weight Analysis

Table 1: Results of molecular weight analysis of the depolymerized lignins.

Hydrogenolysis Temp.	MW (g/mol)	MN (g/mol)	MW/MN (polydispersity)
120 °C	1388	166	-
140 °C	2199	523	4.20
160 °C	3242	891	3.64
180 °C	2681	610	4.40
200 °C	1662	458	3.63

- Molecule weight and Molecule number first increased from 120 to 160 °C and then decreased from 160 to 200 °C. MW/MN (3.6-4.4) was relatively low (Table 1).
- Further hydrogenolysis was successfully performed with improving solubility of lignin at high temperatures. Hydrogenolysis under mild conditions effectively broke the bulky structure of lignin into oligomer units with low MW.

4. Conclusion and Future Work

- Hydrogenolysis with Raney Ni was an effective method to partially depolymerize lignin.
- Hydroxyl content was increased by hydrogenolysis and the optimal reaction temperature is 180 °C.
- The partially depolymerized lignin with narrow molecular distribution and increased hydroxyl value is potential feedstock in the preparations of epoxies and polyurethanes.
- Future work could involve using the yield of hydrogenolysis reactions as feedstock for epoxies and polyurethanes.

References

1. Nagy, Máté, Kasi David, George J.P. Britovsek, and Arthur J. Ragauskas. "Catalytic Hydrogenolysis of Ethanol Organosolv Lignin." *Holzforchung* 63.5 (2009): 513-20.
2. Yan, Ning, Chen Zhao, Paul J. Dyson, and Chen Wang. "Selective Degradation of Organosolv Lignin over Noble Metal Catalyst in a Two-Step Process." *Chemsuschem*, n.d. Web. 22 July 2013.

Acknowledgements

This work was supported by the Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30416 from the USDA National Institute of Food and Agriculture. I would also like to thank the members of CMEC.