Investigating the Polymerization of Coniferyl Alcohol in Pyrolysis Oil
Paige Speight, Class of 2016

For the past six years, Professor Stemmler and students have collaborated with scientists at the University of Maine, Orono, on the production and chemical characterization of a new bio-oil, known as pyrolysis oil. Pyrolysis oil has the potential to be used as an alternative fuel and a source of non-petroleum based polymers. Generated by the rapid burning of sawdust and wood waste, pyrolysis oil represents an attractive replacement for petroleum, because it is both renewable and carbon neutral. However, currently the oil is unstable, and it reacts with itself over the course of several months. During this time, compounds within the oil polymerize, reacting together to form larger chains. The polymerization of these compounds makes the oil highly viscous and unfit for use.

The reactions that cause this increased viscosity and polymerization are still largely unknown. My project examined the polymerization of coniferyl alcohol, one of pyrolysis oil’s most reactive compounds. Previous work on this project determined that coniferyl alcohol reacts with itself, small aldehydes, and acid within the oil to form a dimer.¹

![Figure 1: Coniferyl Alcohol reacts with itself, formaldehyde, and acid to form a dimer within the oil.](image1)

I synthetically replicated this reaction, reacting coniferyl alcohol, formaldehyde and hydrochloric acid at 80˚C for 5 minutes to mimic the conditions of an aged old oil sample that has undergone some polymerization. I identified the products of my synthetic reaction by observing chromatograms of my reaction generated by the Liquid Chromatography Mass Spectrometer (LC-MS) and Gas Chromatography Mass Spectrometer (GC-MS). These two instruments separate the compounds within my reaction mixture, and then determine the mass and fragmentation pattern associated with each compound for the determination of structure and relative concentrations.

By using this synthetic approach and the information provided by the LC-MS and the GC-MS, I identified three intermediate species that were previously too small in concentration to observe in the samples of the whole oil.

![Figure 2: Intermediate species. In the leftmost intermediate species, coniferyl alcohol adds to formaldehyde, and forms a six-membered ring. In the second intermediate species, coniferyl alcohol adds to formaldehyde, and as it forms a six membered ring, also adds to a water molecule. In the third and rightmost intermediate, coniferyl alcohol adds to formaldehyde twice.](image2)

These three intermediate species indicate that in the presence of formaldehyde and acid, coniferyl
alcohol reacts through a consistent mechanism. Although coniferyl alcohol may have different reaction partners, the same part of the coniferyl alcohol molecule is reacting, and in the same way each time. The presence of these intermediates supports a previous hypothesis for the mechanism of formation of the coniferyl alcohol dimer. Understanding the mechanism provides a basis from which to predict the polymerization of related compounds present in the oil. Once the aging reactions are known, the oil may be treated to prevent polymerization and optimized for use.

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1. Rasmussen, Matthew J.; Joseph, Jincy; Frederick, Brian E.; Stemmler, Elizabeth A. Pyrolysis oil aging reactions: An LC/MS/MS investigation of reactive components and reaction products. 39th Northeast Regional Meeting of the American Chemical Society, New Haven, CT, October 23 2013; Paper 220.