

Reactions Responsible for Aging in Wood-Based Pyrolysis Oil: Coniferyl Alcohol, Variants and the Role of Protonated Quinone Methides

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Our dependence on fossil fuels can be alarming not only because they are a non-renewable source, but also due to the concerns surrounding increasing carbon dioxide levels in the atmosphere. As fossil fuel resources become scarce and continue to damage our atmosphere, developing alternative fuel sources is becoming increasingly important. In the process of developing alternative resources, the conversion of biomass to a fuel is one possibility. Given that the state of Maine has a significant industry related to wood products, wood-wastes, such as sawdust or unusable branches, have the potential to be used as a feedstock to generate an oil. Specifically, the wood can be converted to “pyrolysis oil” by intensely heating for seconds in a reactor.ⁱ While wood-based pyrolysis oil has the potential of becoming an alternative for the consumption of fossil fuels, it is currently highly unstable in that it reacts at room temperature to form a viscous liquid making it difficult to manage.ⁱⁱ

In collaboration with faculty and students at University of Maine, Orono, Professor Stemmler and other Bowdoin students have researched the production and chemical composition of pyrolysis oil.ⁱⁱⁱ This previous research concluded that coniferyl alcohol and small aldehydes, such as formaldehyde, react in the presence of acid to form a dimer (see Fig.1) which then continues to polymerize to form larger molecules, which would explain the increase in viscosity.

Last summer formation of the dimer using a synthetic oil that simulated reactions in the authentic oil was studied. By varying the concentration of formic acid (an acid naturally found in wood-based pyrolysis oil) in the synthetic oil to conform to realistic acid concentrations found in authentic oils, we simulated reaction conditions and found clear evidence of the dimer at six hours of simulated aging, which can be translated to 1.5 months of aging at room temperature.^{iv}

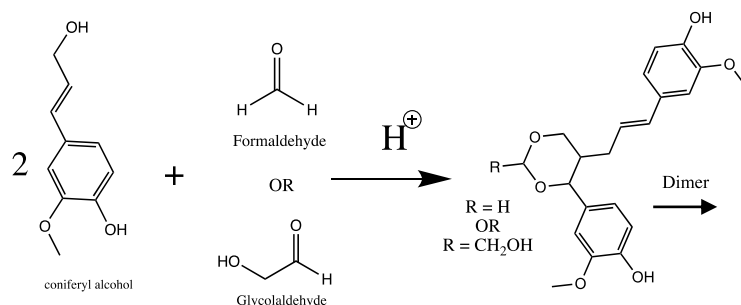


Figure 1: The dimer produced by the reaction with coniferyl alcohol and formaldehyde or glycolaldehyde in the presence of acid

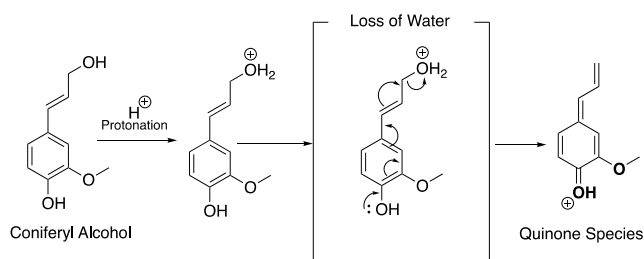


Figure 2: Coniferyl alcohol to quinone methide mechanism

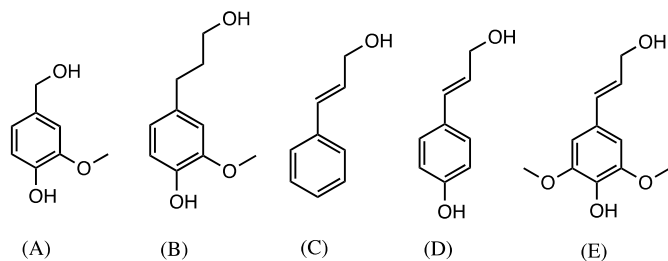


Figure 3: Coniferyl alcohol's structural variants

This summer we set out to test the hypothesis that quinone methides, highly reactive conjugated cation species, are important for reactivity (Figure 2). By varying the substituents on coniferyl alcohol we can identify what attributes of the molecule are essential to promoting the quinone species into existence.

We worked on developing a method to track the reaction progress via GC/MS. By adding biphenyl, a compound that does not participate in the chemistry, we were able to ratio the integrated peak values of the analytes to that of biphenyl. Each analyte, or structural variants, with the exception of (B; Figure 3), was individually reacted with formaldehyde in the presence of formic acid to assess their ability to dimerize. Structural variants (C) – (E) showed evidence of dimerization. Although structural variant (A) did not show dimerization, it may react to form other products. Now that we have established data for the individual compounds, future work points towards performing competitive experiments, in which more than one analyte will

be reacted with formaldehyde in the same vial. This will help us gain insight into the relative reactivity of structural variants (C) - (E). Furthermore, kinetic analysis will be performed to determine the rate constant and half-lives and to directly compare the reactivity of the analytes to each other. In understanding the role of each of substituents, we can devise ways in how to treat the oil before the reaction occurs.

While the chemistry that takes place in authentic oils is still poorly understood due to the complexity of the oil, and continued and extensive research is called for, hopefully this research will be as stepping stone for the further work towards the end goal of stabilizing oils.

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ⁱ Bridgwater, A. V. *Biomass Bioenergy* **2012**, *38*, 68-94.

ⁱⁱ Czernik, S.; Johnson, D. K.; Black, S. *Biomass Bioenergy* **1994**, *7*, 187-192.

ⁱⁱⁱ DeSisto, W. J.; Hill, N.; Beis, S. H.; Mukkamala, S.; Joseph, J.; Baker, C.; Ong, T. H.; Stemmler, E. A.; Wheeler, M. C.; Frederick, B. G.; van Heiningen, A. *Energy Fuels* **2010**, *24*, 2642-2651.

^{iv} Joseph, J.; Rasmussen, M. J.; Fecteau, J. P.; Kim, S.; Lee, H.; Tracy, K. A.; Jensen, B. L.; Frederick, B. G.; Stemmler, E. A. *Energy and Fuels*, **2016**, *30*, 4825-4840.