Catalytic oxidation of alcohol moieties in lignin and lignin model compounds

Justin K. Mobley1,2, Mark Crocker2, Tonya Morgan2, Yaying Ji2, Tian Li3
1University of Kentucky, Lexington, Kentucky 40506
2University of Kentucky, Center for Applied Energy Research, Lexington, Kentucky 40511
3Dalian Institute of Chemical Physics, Dalian, China 116023
*corresponding author: Mark.Crocker@uky.edu

Introduction
With world demand for liquid petroleum expected to increase by more than 25% in the next 30 years and reserves of readily accessible petroleum diminishing, there is a strong need to replace petro-derived fuels and chemicals with renewable and sustainable resources. Lignin (the polymer product of the three monolignols, namely, sinapyl-, coniferyl-, and p-coumaryl-alcohol) is the second most abundant biopolymer on Earth and the world’s largest renewable aromatic resource. These characteristics, coupled with its present underutilization, make lignin uniquely well-suited for replacement of petroleum in chemical and fuel production.

In the present work the focus was to develop a protocol for catalytic oxidative depolymerization of lignin. An oxidative pathway to lignin depolymerization is highly desirable given that highly corrosive alkali species, high pressures of petro-derived H2, or high temperatures (as in pyrolysis) are not required. Due to the irregular structure of lignin, its characterization remains a challenge. For this reason simple model systems were employed for the development of suitable reagents and reaction conditions. In this work, the benzylic alcohol moiety present in both the β-O-4 and β-1 linkages found in lignin was targeted for selective oxidation. In total, benzylic alcohols comprise as much as 67% of the linkages found in lignin. We show that the use of Layered Double Hydroxides (LDHs) in combination with molecular oxygen may be the key to unlocking the first step of an oxidative pathway to lignin depolymerization.

Materials and Methods
Catalysts were prepared from literature procedures via coprecipitation. In a typical synthesis two solutions, one containing the appropriate metal nitrates and one containing a mixture of NaOH and Na2CO3, were simultaneously added and mixed while maintaining a constant pH (usually 8-10). The resulting slurry was aged overnight, washed to neutral pH and dried in vacuo.

In a typical oxidation reaction a 3-neck reaction flask was charged with catalyst (0.5 g), 1-phenyl ethanol (2 mmol) and solvent (10 mL). The mixture was stirred at the desired temperature while O2 was continuously bubbled through it. Subsequently, the catalyst was removed by filtration and the products were analyzed using a HP6890 GC-FID equipped with a DB-Wax column (30 m x 530 μm x 0.5 μm).

Results and Discussion
Following the work of Choudary et al., LDHs were investigated as catalysts for the oxidation of a lignin model compound, 1-phenyl ethanol, using O2 as the oxidant. While Choudary’s Ni-Al LDH catalyst is active for benzylic alcohol oxidation in non-polar solvents such as toluene and hexane, for this catalyst to be successful in lignin oxidation a more polar solvent is required. Consequently, solvents were screened which are compatible with organosolv lignin. During initial work it was found that the only effective solvents for conversion of 1-phenylethanol were toluene, α,α,α-trifluorotoluene, and, to a limited extent, 1,4-dioxane. Of these solvents, only 1,4-dioxane partially dissolves lignin. Thus in order to exploit the properties of both toluene (an electron rich solvent) and 1,4-dioxane (an ether), phenyl ether was chosen as solvent. Notably, phenyl ether was found to be effective as a solvent for both the dissolution of organosolv lignin and for the conversion of 1-phenyl ethanol to acetophenone in 97% yield. Other LDH catalysts, containing copper and manganese, were also found to be active for the oxidation of 1-phenyl ethanol, as shown in Table 1.

Significance
Lignin utilization is a key component of the biorefinery concept. In this work, LDH catalysts were explored for oxidation of the benzylic alcohol moiety present in lignin in solvents suitable for lignin dissolution. This could be the first step in developing an inexpensive approach to lignin utilization.

References