Hydrodeoxygenation of Lignin Model Compounds via Thermal Catalytic Reactions

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Abstract
The production of renewable specialty chemicals and fuel additives is of major importance as the economies of the world continue to grow while fossil resource production declines. At present, roughly one third to one half of biomass entering paper mills is used as low grade boiler fuel. The majority of this fuel is lignin which is a branched phenolic polymer with high molecular weight near that of gasoline. In this work, I will attempt to hydrodeoxygenate lignin model compounds with 5% P/C catalysts in organic and aqueous solvents under hydrogen atmosphere to compare solvent hydrogen solubility effects. In later work, depolymerization of lignin will be assessed to determine operating parameters necessary for the development of a biorefinery.

Methods & Materials
A batch Parr reactor, model 4593 with insertable glass liner, was used for all reactions at 250±5°C using the standard three blade stirrer. Heptane or water, guaiacol, and catalyst were weighed into the glass liner and sealed in the reactor. Hydrogen was used to purge air from the reactor and pressurize as desired. The reactor heating rate was on average 18°C min⁻¹ after delay of 2 minutes. Time to reach desired temperature was about 15 minutes for each run, and then held for the specified time at temperature. Once complete, the reactor was quenched in cool water to reduce temperature below 50°C within 5 minutes. Reactor was cooled to below 30°C, gases vented, and transfer contents from reactor to sample tubes in fringe. An AutoSpec M mass spectrometer equipped with a HP 6890 gas chromatograph was used for separation of complex, volatile samples. An Agilent 8453 UV-Vis will be used to detect aromatic ring at 178 nm.

Experimental Variables
Solvent (Heptane or Water)
Hydrogen pressure (Up to 200 bar, use 17.5 bar initially)
Reactor Temperature (Up to 350°C, varying)
Reactor Time
Catalyst loading (10 wt% used)
Model compound loading (1.0 wt% used)

Results
From experiments performed at high temperature, pressure, concentration, and catalyst loading, guaiacol was converted to 1-Methoxycyclohexane, Cylohexanol, and 1-Methyl-1,2-Cyclohexanediol. Further experiments have reduced the mass percent of guaiacol to 1.0 as well as decreasing the reaction temperature, pressure, and time. The solvents will be compared at the same weight fractions and their products analyzed against each other as well as conversion from the modeling compound.

Further work may include using Kraft lignin in the reactor to determine conditions necessary for depolymerization. By using a combination of one or both steps, valuable specialty chemicals or fuels could be derived.

Dulong’s Formula
This formula can be applied to estimate the higher heating value of an organic molecule based upon the weight percent of its components.

\[ \text{C.V. (MJ/kg)} = 0.3312 \times \%C + 1.4428 \times \%H - (\%O/8) \]

By applying this formula to the fossil and renewable resources above, it can be shown that wood and pyrolysis oils have an energy density in the 17 MJ/kg range while lignin is closer to 23 MJ/kg and crude oil up to 50 MJ/kg.

References