Coupled lignin-first biorefining and hydrodeoxygenation for the production of aromatic sustainable aviation fuel blendstocks

by

Matthew S. Webber

Lignin, an abundant source of renewable aromatic carbon, has long been targeted for the generation of fuels owing to its high aromaticity and energy content relative to biomass carbohydrates. However, these efforts have been hindered by its inherent heterogeneity and reactivity, leading to it instead being combusted for the generation of process heat and electricity generation within conventional industrial biorefinery configurations. With this in mind, conventional sustainable aviation fuels (SAFs) consist primarily of *iso*- and *n*-alkanes and are limited to a 50 v% blend with petroleum-derived aviation fuels as they generally lack the cyclic components present in conventional fuels. This thesis centers on addressing this challenge through the development of lignin processing strategies with a final target of aromatic sustainable aviation fuel (SAF) blendstocks, which lend themselves well to the heterogeneous aromatic structure lignin provides.

To generate jet-range aromatic hydrocarbons from lignin, we initially adopt a multi-stage approach in which lignin is extracted and depolymerized in a process known as reductive catalytic fractionation (RCF). RCF functions by the initial solvolytic extraction and depolymerization of lignin using a polar protic solvent, followed by subsequent hydrogenolytic depolymerization and stabilization of reactive intermediates. In turn, the process results in a low molar mass, phenolic oil, as well as a solid holocellulose pulp. However, RCF oils typically have oxygen contents near 25 wt%, which must to be reduced below 0.5 wt% to meet the required specifications for use in SAF. Using a custom-built trickle bed reactor, we are able to deoxygenate the resulting phenolic oil over a molybdenum carbide (Mo_2C) catalyst using a two-pass approach, working to balance between oil and catalyst stability to produce aromatic hydrocarbon mixtures with aromatic selectivities >85%.

We subsequently scale our process to enable elevated production volumes, achieving carbon yields 93% of theoretical while enabling rigorous physical/combustion property testing. These measurements reveal that our hydrocarbon mixture, when blended with conventional SAFs derived from both triglyceride and ethanol feedstocks, enables 100% drop-in aviation fuel substitutes which satisfy all measured specifications for use as Jet A while achieving elastomer swell extents on par with petroleum-derived fuels. Our process also shows robust performance across an array of biomass streams, potentially enabling the processing of substrates such as mixed forestry residues.

Finally, we turn our focus to improving the economics of future RCF-oriented biorefineries by targeting a solvent-looping approach to eliminate the use of exogeneous organic solvents in RCF, wherein our deoxygenation reaction products are utilized as extraction co-solvents. We find that mixtures of 4-propylguaiacol, a representative model for depolymerized lignin oils, and water demonstrate promising RCF performance, achieving heightened monomer yields relative to methanol at the cost of decreased carbohydrate retention. Interestingly, these solvent mixtures phase-separate at ambient conditions, enabling a natural liquid-liquid fractionation akin to RCF utilizing n-butanol/water mixtures.

Taken together, this thesis describes a robust, sequential catalytic strategy for the depolymerization and deoxygenation of lignin to aromatic SAF blendstocks while subsequently describing a potential future process configuration to eliminate exogeneous organic solvents from RCF.

Thesis supervisor: Yuriy Román-Leshkov
Title: Robert T. Haslam (1911) Professor in Chemical Engineering