NABC National Advanced Biofuels Consortium
Biofuels for Advancing America
Developing cost-competitive, sustainable biofuels for today's transportation infrastructure.

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Hydropyrolysis Catalyst Development: A Lab-Industry Partnership

A major research goal of the National Advanced Biofuels Consortium (NABC) is to develop improved methods for producing high value intermediates that can be transformed into hydrocarbon fuels. Hydropyrolysis (HYP) is one process strategy being employed within the NABC. Hydropyrolysis involves co-feeding biomass and hydrogen into a pressurized fluidized catalyst bed, as depicted in Figure 1, where the biomass undergoes fast-catalytic pyrolysis in the presence of hydrogen to produce bio-oil with reduced oxygen content over other pyrolysis methods.

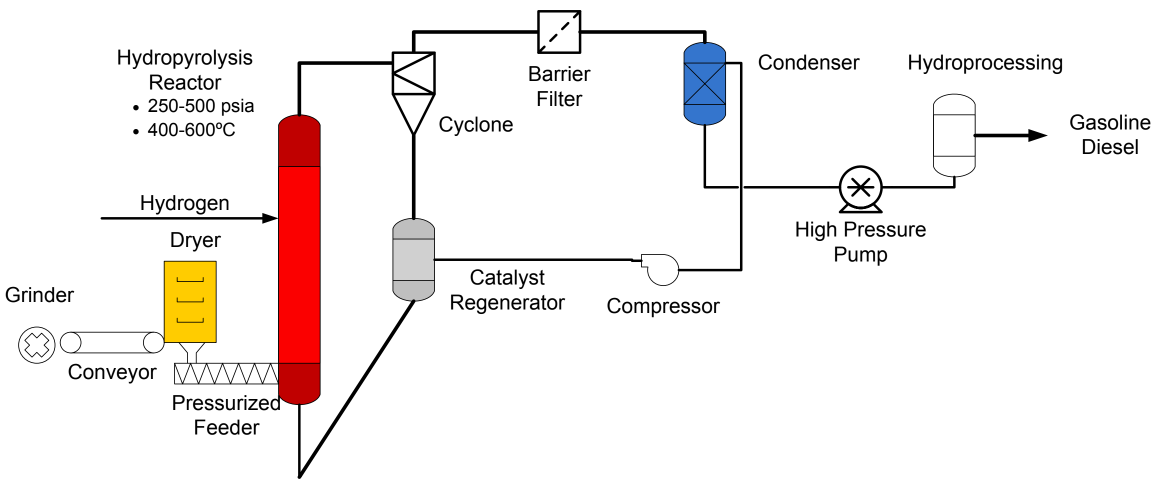

Figure 1. Major unit operations for hydropyrolysis of biomass

The development efforts focus on the following elements:

- Use of a reactive gas to cap the reactive intermediates formed in pyrolysis vapor to produce a quality bio-oil for refinery integration
- Catalytically enhanced hydrogen transfer within the pyrolysis zone to reduce the oxygen content in the hydrocarbon intermediate
- Use of process modeling to explore commercial concepts, evaluating the potential for integrating this technology into existing refineries or developing stand-alone processing and upgrading facilities.

One of the biggest challenges for hydropyrolysis is catalyst development for improving hydrogen transfer reactions to stabilize reactive intermediates within the pyrolysis zone. Catalyst screening in a bench-scale fluidized bed reactor is not practical due to high costs and turn-around times. To expedite catalyst development efforts, alternative means of analyzing catalytic activity, selectivity, and stability are necessary.

This issue of NABC Highlights focuses on how the interactions between partners are being used to accelerate catalyst research, where the Pacific Northwest National Laboratory (PNNL) is working closely with Albemarle on identifying low-cost, effective catalysts. Here's how the process works.

Initial catalyst down-selection and development is performed at Albemarle. Using a high throughput screening apparatus, Albemarle can rapidly evaluate a large number of catalysts. Albemarle's AutoCat unit pulses model compounds (such as guaiacol) over a small quantity of catalyst, and conversion, deoxygenation activity, deoxygenation mechanism, and resistance to coking is measured as a function of temperature and hydrogen concentration at 1 atmosphere. Based on initial screening results, the most promising catalysts showing improved deoxygenation activity and stability are selected for further testing at PNNL.

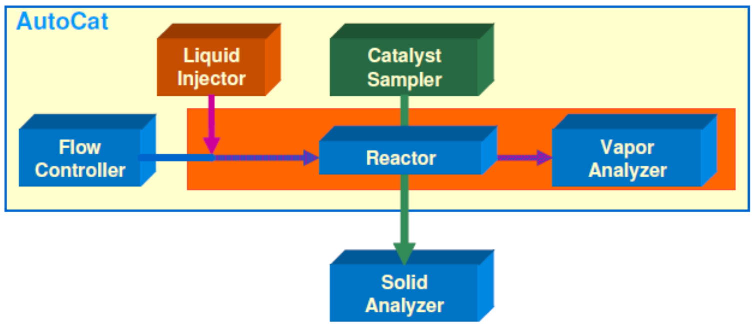

Figure 2. Initial catalyst screening process performed at Albemarle

A new capability at PNNL is a high-pressure reactor pyrolysis probe (CDS Analytical) that is coupled with a GCxGC-TOFMS (LECO). Catalysts and biomass are physically admixed, and milligram quantities are inserted into the high-pressure reactor pyrolysis probe where the mixture is rapidly heated under high pressure reactive gas atmosphere. Catalytic effects on the bio-oil composition are analyzed as a function of reaction temperature (300°–1,200°C), reactive gas pressure (15–500 psi), heating rate (1°C/min – 999°C/s), and final hold time at temperature. To analyze the bio-oil composition the pyrolysates from the pyrolysis probe are injected, through a heated transfer line, into a GCxGC-TOFMS where the composition of the bio-derived oil is analyzed in detail. Unlike conventional 1-dimensional GC where product separation occurs only on one column, the GCxGC uses a cryogenic modulator to concentrate fractions evolving from the primary column, which are then separated on a second column to generate a 2-dimensional chromatogram, as demonstrated in Figure 3. As a result of the 2-D separation, the components of the bio-oil are separated based on boiling range and polarity, enabling detailed deconvolution of individual compounds. Various catalysts are screened and down-selected based on catalytic impact on the final bio-oil quality as defined compositionally.

Information obtained by Albemarle and PNNL is shared among other partners of the hydropyrolysis team. Through sharing information between partners, the limitations—experimental or analytical—of PNNL's and Albemarle's screening approaches can be correlated to improve developmental efforts through a more thorough understanding of catalyst performance with model compounds and real biomass.

As catalyst and process variables are down-selected, RTI International will then evaluate top-performing and baseline catalysts at the bench-scale (kilogram-scale) in their entrained flow reactor for final demonstrations. RTI's laboratory-scale hydropyrolysis studies and final product collection will be conducted in a 1 kilogram per hour transport reactor system. Operating conditions in the transport reactor can achieve reaction temperatures up to 1,800°F and pressures up to 600 psig. Biomass is pneumatically conveyed into the reactor system at the selected operating pressure. The entrainment gas and input biomass are injected into a circulating bed of hot solids and rapidly heated to system temperature in the mixing zone. The solids/biomass mixture is transported through the riser section at high velocity such that the residence time is about 2–3 seconds. The solids mixture is recycled through the standpipe. Any solids that escape the reactor are collected in a downstream cyclone and the bio-crude product is collected in a solvent-filled quench vessel.

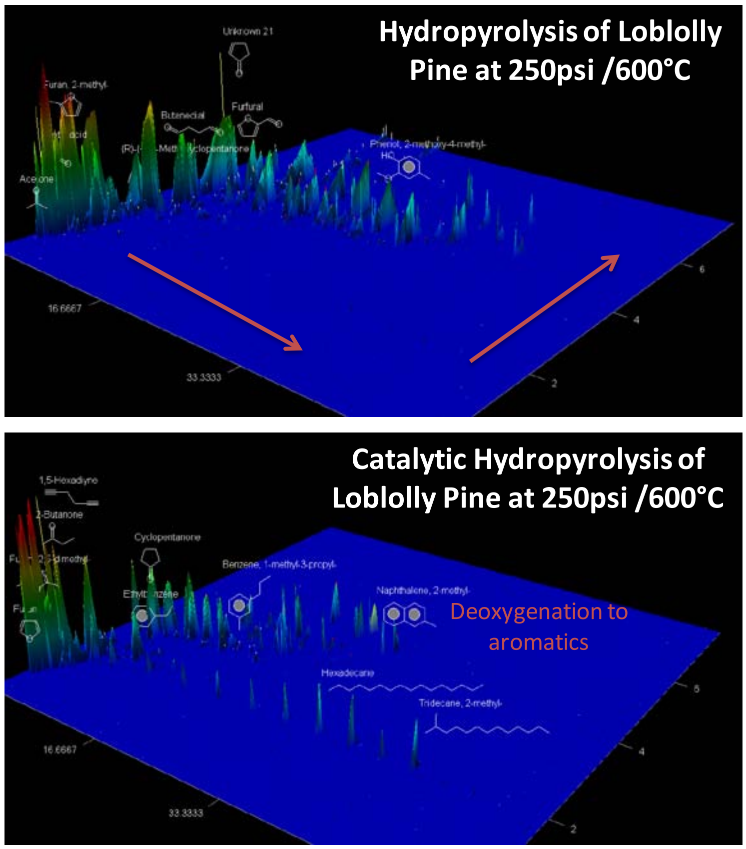

Figure 3. Effect of catalyst during hydropyrolysis on the 2-D resolved composition of the bio-oil generated during hydropyrolysis. Catalytic hydropyrolysis generates a compositionally-improved bio-oil that is more likely to be compatible for refinery integration, based on increased non-oxygenated hydrocarbons, reduced acids, and increased hydrogen content of the final oil.

Gas phase products are analyzed with an on-line micro-GC that samples the products every 3.5 minutes. The elemental composition of the solids collected in the cyclone and recovered from the bed are analyzed offline in a CHONS analyzer. The elemental composition of the liquid products is also determined with the CHONS analyzer. GC/MS analysis of the products provides the chemical composition of the liquid bio-crude and the water content of the liquid product is determined by Karl-Fischer titration. Mass balances in the system are routinely greater than 90%.

By combining expertise, knowledge, and facilities, the hydropyrolysis team members are working together to identify low-cost, effective catalysts for hydropyrolysis.