

October 22, 2012

Hydrothermal Liquefaction—Mid-Stage 2 Developments

The Hydrothermal Liquefaction (HTL) Strategy, led by Pacific Northwest National Laboratory (PNNL), has just completed the first year of Stage 2 in the NABC as a Tier 2 strategy. Under Tier 2 status, efforts are focused on addressing the technical and economic barriers identified in Stage 1: reactor plugging, reactor scalability, bio-oil quality (upgradability), and process operability (including improved process separations). In this highlight, project priorities and progress made to address the technical challenges in the first half of Stage 2 are described.

Stage 2 Priorities. The techno-economic analysis (TEA) for the HTL strategy was updated based on results from the Stage 1 extension and is being used to guide process development priorities. Figure 1 summarizes the major process advancements that must be accomplished to move the process from its current state of technology (SOT) to a goal case (nth plant). In this figure, the aggregate cost per gallon gasoline equivalent is expressed as a percentage of the SOT case. The overall process yield has the most significant impact on the process economics (i.e., goal: recover 20% of the carbon from the aqueous phase into the bio-oil).

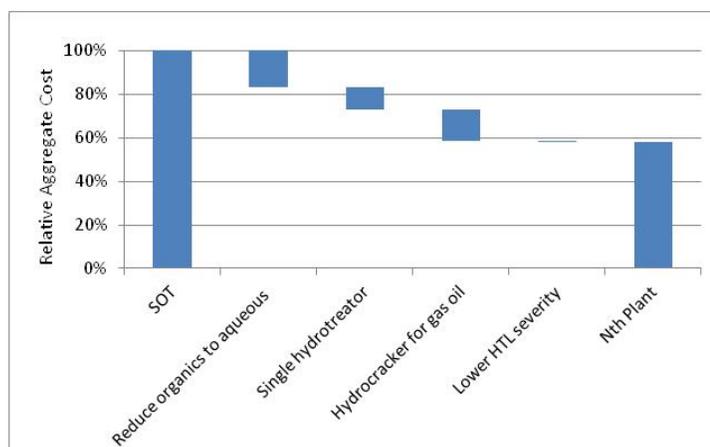


Figure 1. Moving HTL from SOT to target case

In Stage 1, a conservative approach was used to demonstrate the hydrotreatment step and a two-stage reactor was used. Based on the relatively low oxygen content of the HTL bio-oil, use of a single stage hydrotreating reactor appears technically feasible, and if confirmed in Stage 2, will have an appreciable beneficial impact on the economics. For the SOT case, the gas oil fraction was treated as a co-product and monetized as a bunker fuel. Conversion of the gas oil to transportation fuel via hydrocracking has a substantial effect on the economics and will be evaluated in Stage 2. Reduction of the process severity, evaluated as a 20% reduction in the HTL reactor pressure (pressure reduced from 2,930 to 2,400 psig, with a corresponding drop in reaction temperature), has only a minor impact. Further sensitivity analyses were performed to evaluate the HTL reactor space velocity (e.g., residence time) and the use of a small continuous stirred tank reactor (for slurry heating and conditioning); the aggregate cost of production was found to be relatively insensitive to these parameters. During the second half of Stage 2, more detailed sensitivity evaluations are planned and a contract has been placed with an engineering firm to confirm HTL reactor cost assumptions.

Stage 2 Progress. For Stage 1, all HTL testing was conducted in a 1-L continuous stirred tank reactor (CSTR). The CSTR is not readily scalable to a production facility; hence, significant project emphasis has been placed on the minimization or elimination of the CSTR component. A pure plug flow reactor (PFR) system was investigated during the Stage 1 extension, but the system was only partially successful due to frequent plug formation during the tests (Figure 2, top).



To better understand the processing conditions that contributed to plugging, rheology testing was performed using a rheometer equipped with a high-pressure test cell. The viscosity data are presented in Figure 2 (bottom) for slurries of pine forest product residue, corn stover, and a corn stover lignin-rich test material. After initial decreases, the viscosity increases to peak values in the range of 130°C to 160°C. The magnitude of the changes appears to be more pronounced in the slurries with higher lignin concentrations.

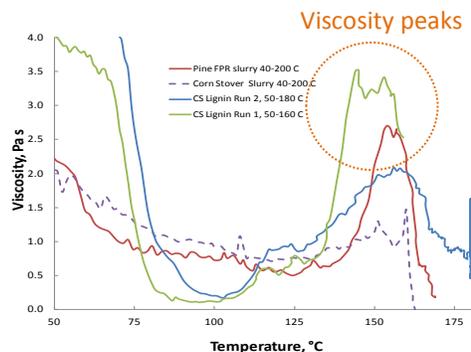


Figure 2. Plug removed from HTL preheater (top) and viscosity of feed slurry as a function of temperature (bottom)

Based on the slurry behavior observed in the rheology testing and the plugging occurrences in the Stage 1 extension, a hybrid reactor system has evolved that combines the robustness of a stirred reactor with the efficiency of a plug flow reactor (Figure 3). The feed preheater temperature is now set to minimize the impact of feed slurry viscosity increases. After exiting the preheater, the slurry is rapidly heated to 300°–350°C in the CSTR, with additional reaction time being provided in the PFR. Use of a small volume CSTR to heat and liquefy the slurry in the temperature range at which viscosity undergoes a dramatic increase has resulted in a reactor system that has been operated for many hours without plugging.

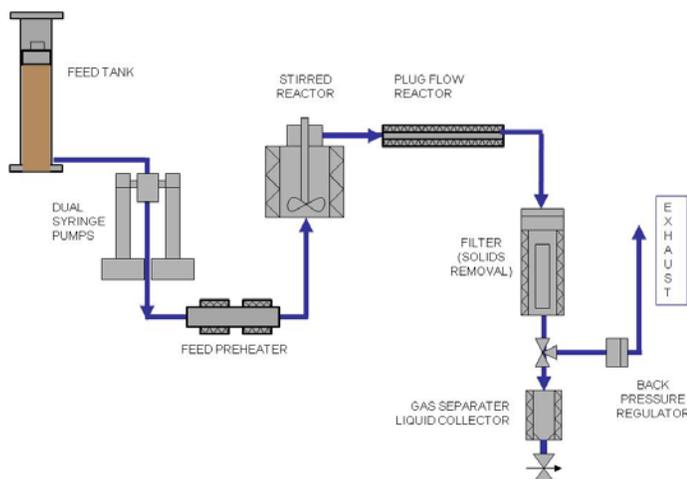


Figure 3. Schematic of hybrid continuous HTL reactor system

Three longer duration HTL runs have now been conducted with NABC feedstocks using the hybrid reactor system. No operational disruptions or difficulties have been encountered, and the resulting bio-oil has been provided to the HTL upgrading partner, UOP, LLC. These improvements in HTL reactor operations are allowing the team to provide greater emphasis on the upgrading tests. Bio-oil from both pine forest residual and corn stover have been evaluated by UOP. Figure 4 shows results from simulated distillations for HTL bio-oil and upgraded products (with a quality control diesel sample provided for comparison). These initial results suggest that a higher percentage of the hydrotreated product can be moved to the distillate range (in comparison to Stage 1 results). In support of the upgrading, detailed characterizations of the upgraded products are being conducted. Table 1 shows the distribution by compound class of hydrotreated corn stover bio-oil, based on GCxCG analysis.

During the second half of Stage 2, longer duration HTL tests will continue and will include recycle of aqueous product to generate more prototypic bio-oil for upgrading. Near term activities are also planned for testing and demonstration of improvements to oil recovery and to evaluate concentration of the organic carbon in the aqueous stream.

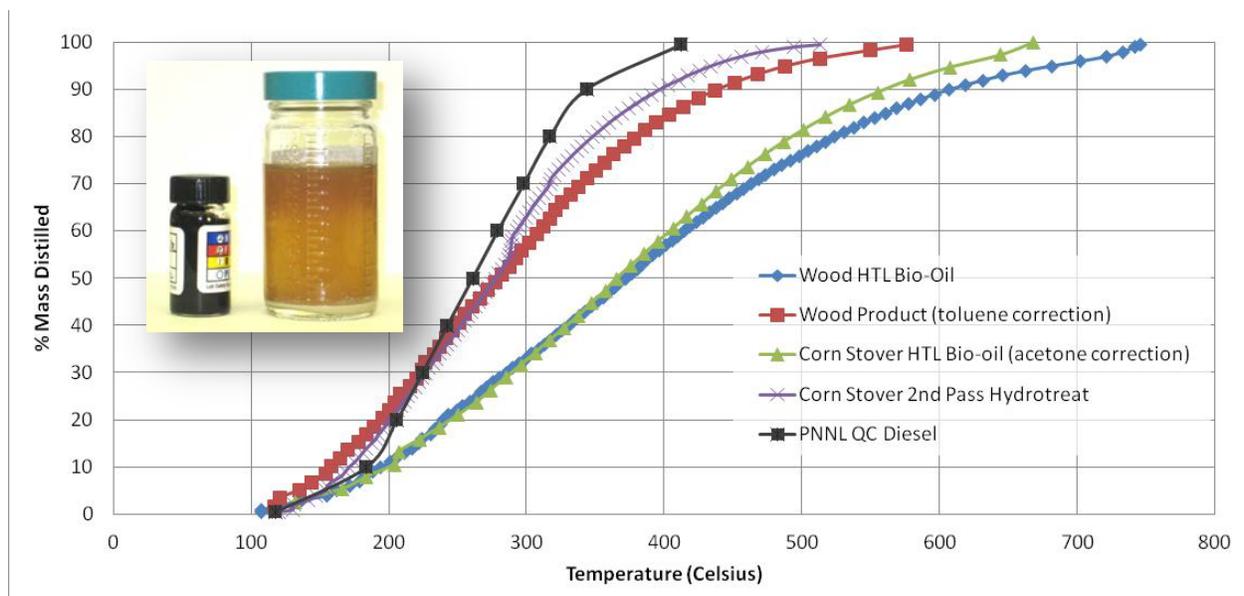


Figure 4. Simulated distillations between HTL bio-oil and upgraded products. Insert picture shows HTL corn stover bio-oil and upgraded product.

Table 1. Distribution by Compound Class in Corn Stover Bio-Oil after 2nd Pass Hydrotreatment

Class	Wt %
n-paraffins	8.0
iso-paraffins	4.8
Naphthenes	39.0
Alkylbenzenes	12.8
Indanes and tetralins	24.2
Naphthalenes	4.5
Other diaromatics	3.5
3-ring aromatics	1.3
4-ring aromatics	1.9
Polar unknowns	0.1