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**Technical Report**  
NREL/TP-5100-58050  
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# Ex-Situ Catalytic Fast Pyrolysis

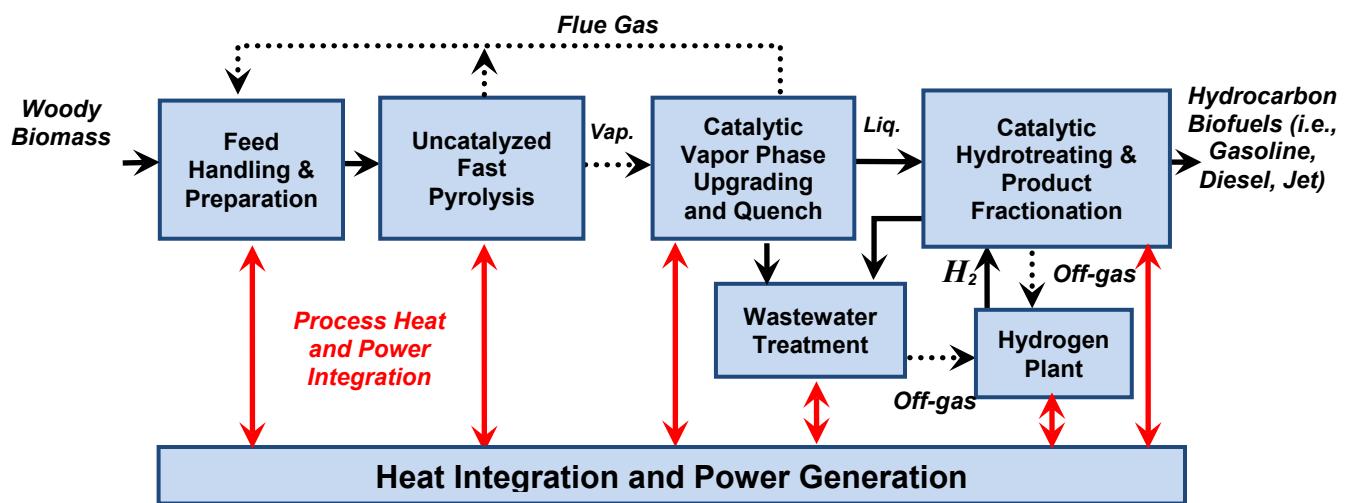
## Developing Technology Pathway Cases to Understand the Cost of Converting Biomass to Hydrocarbon Fuels

In support of the Bioenergy Technologies Office, the National Renewable Energy Laboratory (NREL) and the Pacific Northwest National Laboratory (PNNL) are undertaking studies of biomass conversion technologies to hydrocarbon fuels to identify barriers and target research toward reducing conversion costs.

Process designs and preliminary economic estimates for each of these pathway cases were developed using rigorous modeling tools (Aspen Plus and Chemcad). These analyses incorporated the best information available at the time of development, including data from recent pilot- and bench-scale demonstrations, collaborative industrial and academic partners, and published literature and patents. The economic results of these analyses are in the process of further refinement and will be published in FY13 and FY14 design reports. This report summarizes the preliminary technical data used for the models and identified data gaps.

This technology pathway case investigates converting woody biomass using ex-situ catalytic fast pyrolysis followed by upgrading to gasoline-, diesel-, and jet-range hydrocarbon blendstocks. Technical barriers and key research needs that should be pursued for this pathway to be competitive with petroleum-derived blendstocks have been identified.

## Process Block Diagram



## Key Highlights

- Catalytic vapor phase upgrading (VPU) of fast pyrolysis vapors has the potential to reduce costs associated with upgrading conventional fast pyrolysis oil to a hydrocarbon by producing a lower-oxygen-content intermediate with lower associated water. Hydrogen consumption during final upgrading to a hydrocarbon will also be reduced.

- The use of a vapor phase reactor separate from the pyrolyzer allows more control over the vapor phase reactions than if biomass pyrolysis and vapor phase upgrading occur in the same vessel (in-situ pyrolysis). This also allows the unreacted char and mineral components to be removed prior to exposing pyrolysis vapors to the upgrading catalyst.
- The upgraded vapor's lower reactivity may allow use of extended surface heat exchangers to recuperate heat and reduce the cooling water load when the vapors are condensed.
- Important research needs for this pathway include the development of catalysts with improved yields, stability, and lifetimes, maximizing overall conversion to the desired hydrocarbon product, optimizing VPU oil hydrotreating, and developing economic wastewater treatments.

## Process Design Details

**Feed handling:** Woody biomass is dried to approximately 10 wt% moisture and finely ground to 2–6 mm. Waste heat streams from the pyrolysis section are used to dry the biomass. Drying and grinding costs are included in the feedstock costs (Jones and Male 2012).

**Fast pyrolysis:** The model is based on a circulating fluidized bed consisting of a pyrolysis reactor, cyclones, and combustor. Biomass is contacted with hot sand and fluidizing gas in a short residence time (<2 seconds) pyrolysis reactor at ~500°C and atmospheric pressure in the absence of air. Biomass is converted to predominately condensable vapors, non-condensable gas, and some char. Char and sand are separated from the vapor in cyclones and subsequently sent to a combustor to burn the char and reheat the sand, which is returned to the pyrolysis reactor. The pyrolysis vapors leaving the cyclone are passed to the vapor phase upgrading reactor.

Conventional non-catalyzed fast pyrolysis is already commercialized (Envergent 2009–2011). The n<sup>th</sup> plant model assumes two parallel pyrolyzers processing 1,000 dry metric tonnes per day (tpd) of dry biomass.

**Vapor phase upgrading:** Pyrolysis vapors that have been separated in a cyclone from sand and char are fed to a reactor where the vapors are catalytically upgraded to less reactive compounds. Coke deposits on the catalyst can be significant, and the catalyst is regenerated by burning off accumulated coke. The resultant oxygen content is dependent upon catalyst type, residence time, and temperature, and can range from very low (~4 wt%) to quite high (35 wt% or more on a wet basis). Very low oxygen content typically means very low yields. Reported yields range from 0.1 to 0.2 mass dry oil/mass dry biomass (Dayton 2011; Mante and Agblevor 2011; Zacher et al. 2011; Czernik 2011; Diebold et al. 1994; Stefanidis et al. 2011). The primary objective is to retain as much carbon in the liquid product as possible while removing the highly reactive oxygen species.

Unlike uncatalyzed fast pyrolysis, where use of extended surface heat exchangers is not possible because of excessive fouling, heat recovery from condensing the vapors may be possible, which will in turn decrease the cooling water demand. Upon cooling, non-condensable gases are removed and two liquid phases are formed. The predominately organic phase is sent to hydrodeoxygenation and the predominately aqueous phase goes to water treatment. The carbon content of each liquid phase is dependent upon the oxygen content of the vapors leaving the VPU reactor. The VPU reactor is likely to be a circulating fluidized bed with external catalyst

regeneration, similar to a petroleum refining fluidized catalytic cracking unit. Two base cases were modeled. The first case used a complete dataset (Mante and Agblevor 2011) with detailed reporting for pyrolysis and VPU. The second case used typical fast pyrolysis yields, followed by VPU results from various sources and with varying oxygen contents (Dayton 2011; Mante and Agblevor 2011; Zacher et al. 2011; Czernik 2011; Diebold et al. 1994; Stefanidis et al. 2011).

**Catalytic hydrodeoxygenation:** VPU oil is combined with hydrogen at 255°–410°C and ~2,000 psig and is converted to hydrocarbons, water, and gases over a fixed bed reactor. Depending upon the reactivity of the VPU oil, two beds may be needed. The first bed is operated at the lower end of the temperature range to further reduce any remaining highly reactive compounds. The second bed is operated at the higher end of the temperature range, and possibly at a lower space velocity to allow complete deoxygenation. The ideal goal is that the VPU oil is of high enough quality so that only a single hydrotreater is needed. After cooling, the products are separated and the hydrocarbon product is distilled into C<sub>4</sub> minus, gasoline range, diesel range, and heavy oil (if any) range material. Experimental results suggest that there may be little or no heavy oil produced, thus the distillate fraction may not need a final boiling point correction (Zacher et al. 2011). The cost model assumes that the product quality of the gasoline- and diesel-range streams is sufficiently suitable for use as blendstocks. The targeted oxygen content of the upgraded product is <1 wt%. Wastewater is assumed to have <1 wt% carbon. The process model is based on experimental conditions and hydrodeoxygenation conversion for catalytic pyrolysis oil (Dayton 2011; Zacher et al. 2011) and conventional pyrolysis oil (Elliott et al. 2009). The flow scheme is based on Jones et al. 2009.

**Hydrogen plant:** Off-gases from the VPU section, and from the hydrodeoxygenation section are sent to a conventional hydrogen plant consisting of a steam reformer, water gas shift reactor, pressure swing adsorption unit, and heat recovery. Supplemental natural gas to satisfy the hydrogen demand is not needed based on the modeled results at the assumed level of VPU deoxygenation. No processing penalty is assumed for using off-gas in place of natural gas as feed to the reformer; this may be optimistic. The hydrogen plant size is within typical commercial scale. Design conditions are based on commercial-type systems using natural gas (SRI Consulting 2007). Alternately, the fluidized bed reformer system developed for steam reforming of biomass syngas for the 2012 ethanol demonstration (Dutta et al. 2011) can be used as the reformer for this process.

**Wastewater treatment:** The VPU aqueous phase contains acids, aldehydes, and phenolics and is assumed to be digestible in a process similar to the one described in NREL's biochemical ethanol design report (Humbird et al. 2011). Off-gas from the digester is routed to the hydrogen plant. As no data yet exist for this treatment, the model was based on the biochemical ethanol design case. The process was modeled as a stoichiometric reactor with complete conversion to CO<sub>2</sub> and CH<sub>4</sub>.

**Steam and power:** Off-gases that are not needed for hydrogen generation are sent to a boiler for combustion to generate superheated steam for a turbine. The turbine design is based on the power generation system in the NREL thermochemical mixed alcohols design report (Dutta et al. 2011).

## Data Gaps, Uncertainties, and Research Needs

The majority of the model is literature based. Experimental results from FY13 and FY14 tasks will be used to update the VPU and hydrotreating portions of the model. The goal of this pathway is to reach a minimum fuel selling price of \$3/gallon of gasoline equivalent (in 2011 U.S. dollars). To reach this targeted product price, the key bottlenecks, uncertainties, and areas for further development are summarized as follows:

- **Demonstrate and optimize VPU yield.** There is a wide range of literature data for yield and product quality (oxygen content) without a clear understanding of the effects on processing costs, organic losses to the aqueous phase, and severity of upgrading. The primary objective for optimization of this process is to retain as much carbon in the liquid product as possible while removing the highly reactive oxygen species.
- **Develop VPU reactor design data.** Careful design of the product recovery scheme is needed to ensure product stability and mitigate fouling. Handling of large amounts of solids will also need attention. Effective removal of solids prior to the VPU step may help improve VPU catalyst life and stability. Removal of solids after the VPU is necessary to ensure no negative effects on downstream integration. Design of the VPU catalyst regeneration system will be important to maximize catalyst life and productivity.
- **Develop and optimize VPU catalysts.** VPU catalyst maintenance and stability are unknown, as are regeneration protocols and lifetime. Testing with bio-oils and detailed characterization of catalyst performance and deactivation modes are needed. Catalysts developed for this process need to be both mechanically and thermally stable and robust to improve overall lifetimes. These catalysts must produce a VPU oil product that is an improvement over conventional pyrolysis oil, and that oil must be produced in good yield. A fundamental understanding of the detailed reaction mechanisms and kinetics can enable the design of catalysts with optimal productivity rates and yields toward desired product slates. Investigating the solid/vapor interface chemistry and increasing the catalytic conversion are key areas for realizing VPU catalysts improvements. Rational design and development of catalysts could be accomplished using a combination of computational and experimental techniques.
- **Optimize hydrotreating.** Hydrodeoxygenation upgrading may be performed in a single bed if the catalytic pyrolysis oil is of sufficiently low oxygen content or if the oxygen content is contained within unreactive species that do not readily polymerize. Parameter testing and development of compounds' structure-reactivity relationships are needed. Hydrodeoxygenation catalyst maintenance issues are unknown but should be better than processing raw fast pyrolysis oil. A preliminary short term test suggested few problems (Zacher et al. 2011); however, this test used two catalyst beds. Ideally, a single upgrading reactor is needed in order to reduce costs, as is reduced hydrogen consumption. Long term catalyst testing, upgraded bio-oil speciation, and fuel quality tests are needed. Understanding the speciation of olefins, aromatics, and oxygenates will assist in optimizing hydrogen usage.
- **Characterize fuels and intermediates.** The final hydrocarbon product may not be of sufficient quality to use as a blendstock, which was assumed in the economics. Key properties such as cetane and octane, as well as flash points, smoke points, cloud or pour

points, and distillation curves must be verified against gasoline and diesel specifications. Consideration should be given to production of refinery intermediates instead of finished fuels, and as such, better characterization of the VPU oil is needed. The off-gas composition should also be better understood to verify its suitability as a hydrogen plant feedstock.

- **Establish optimum VPU oil properties.** A key element to the process design will be developing an understanding of effective process integration—specifically, the trade-offs between the amount and quality of oil produced via VPU and the impact this has on downstream hydrodeoxygenation. Higher quality oil requires less hydrodeoxygenation but the yield may be reduced from the VPU step. Lower quality oil will require higher severity hydrodeoxygenation but also may have higher yields.
- **Determine optimum wastewater treatment.** Wastewater treatment is largely unexplored, and anaerobic digestion may not be appropriate for the types of species present. There is a need to understand the impact of organic compounds on wastewater treatment, to understand the toxicity of trace compounds, and to minimize carbon loss to wastewater treatment. Research is needed to understand the conversion of organics in the aqueous phase to hydrogen, bio-products, and species that can rejoin the predominately organic phase. Consideration should also be given to alternate wastewater treatment methods such as catalytic hydrothermal gasification.

## **Summary and Next Steps**

This study assessed the processing of woody biomass conversion via ex-situ catalytic fast pyrolysis followed by upgrading and finishing to gasoline-, diesel-, and jet-range hydrocarbon blendstocks. A mainly literature-based techno-economic analysis was performed to identify technology gaps, uncertainties, and research needed to achieve a minimum fuel selling price of \$3/gallon of gasoline equivalent. A design case detailing this pathway will be developed in FY14.

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