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Syngas Upgrading to Hydrocarbon Fuels Technology Pathway

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Syngas Upgrading to Hydrocarbon Fuels

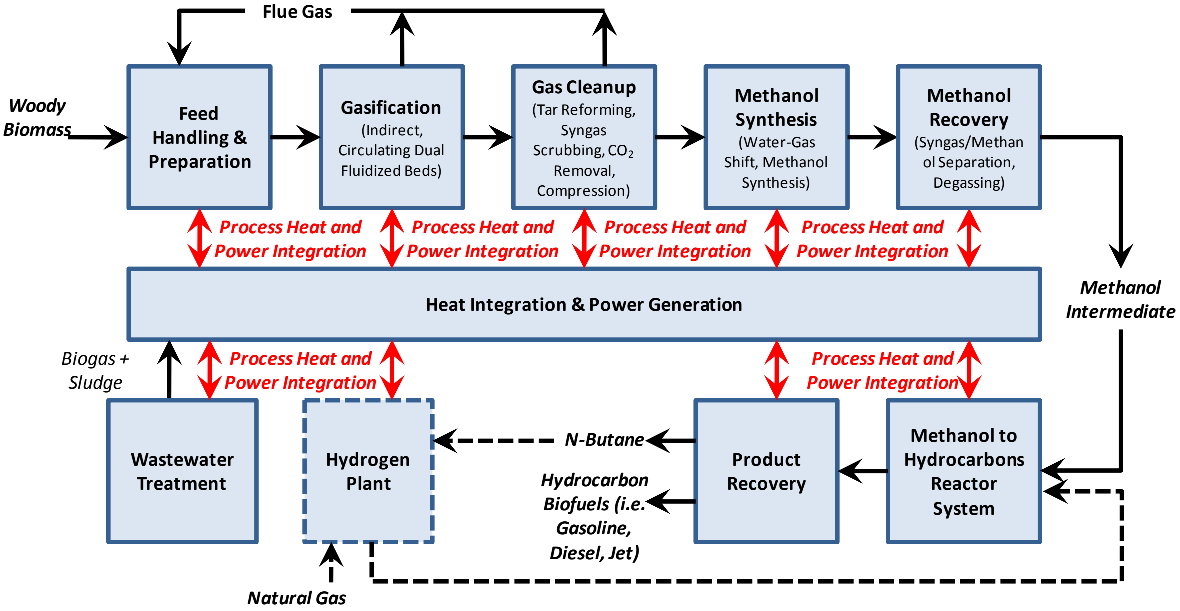
Developing Technology Pathway Cases to Understand the Cost of Converting Biomass to Hydrocarbon Fuels

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 the upgrading of woody biomass derived synthesis gas (syngas) to hydrocarbon biofuels. While this specific discussion focuses on the conversion of syngas via a methanol intermediate to hydrocarbon blendstocks, there are a number of alternative conversion routes for production of hydrocarbons through a wide array of intermediates from syngas. Future work will also consider the variations to this pathway to determine the most economically viable and lowest risk conversion route. Technical barriers and key research needs have been identified that should be pursued for the syngas-to-hydrocarbon pathway to be competitive with petroleum-derived gasoline-, diesel- and jet-range hydrocarbon blendstocks.

Process Block Diagram



Key Highlights

- This thermochemical conversion pathway for the production of hydrocarbon biofuels from synthesis gas and methanol intermediates leverages advances in syngas production and cleanup technologies developed for the thermochemical ethanol platform, specifically the gasification and tar reforming processes.
- Configuration from feed handling through methanol synthesis for the described design is consistent with the NREL methanol to gasoline (MTG) design report.
- The methanol-to-hydrocarbon conversion process utilizes less severe operating conditions relative to traditional MTG processes (< 100 psia / 400°F relative to 210 psia / 750°F for MTG). Homologation (-CH2- addition) and alkylation reactions take place in a single reactor system, which reduces the overall capital costs relative to traditional MTG processes.
- This pathway has the potential for targeting a large slate of hydrocarbon blending components ranging from gasoline-range to diesel-range hydrocarbon fuels through rational catalyst design and optimization.
- Important research needs for this pathway include improving the lifetime, stability, and maintenance of the catalysts, demonstrating high conversion yields at larger scales, maximizing overall product selectivity to the desired product slate, and reducing costs through process consolidation and integration.

Process Design Details

The current state of technology process design configuration is outlined below and includes feedstock handling and preparation, syngas production by gasification, syngas cleanup, methanol synthesis, methanol recovery and storage, methanol to hydrocarbons, product recovery, heat integration and power generation, and utilities. The process configuration may also include a hydrogen plant to supply process hydrogen from purchased natural gas or light ends (C_{4-} hydrocarbons) generated and recovered in the process. The front-end of this process through tar reforming is based on the 2011 NREL thermochemical mixed alcohol design (Dutta et al. 2011) and amine scrubbing through methanol production is based on the 2011 methanol-to-gasoline design report (Phillips et al. 2011).

Feed handling and preparation: The woody biomass feedstock, with an average particle size of 2 inches, is fed to the plant at a rate of 2,000 dry metric tonnes per day. The woody biomass is further dried to the target of 10 wt% required for proper feeding into the gasifier. Drying is accomplished using flue gases from the char combustor and tar reformer catalyst regenerator. Conveyors and hoppers feed biomass to the low-pressure entrained flow gasifier.

Syngas production by gasification: Indirect gasification serves as the basis for syngas production. Heat for the gasification reactions is supplied by circulating synthetic olivine (sand) that is pre-heated in a char combustor and fed to the gasifier. Steam is injected into the gasifier to stabilize the flow of biomass and olivine through the gasifier. Within the gasifier, biomass thermally deconstructs to a mixture of syngas components (CO, H_2, CO_2, CH_4, etc.), tars, and solid char containing residual carbon from the biomass and coke deposited on the olivine. Cyclones at the exit of the gasifier separate the char and olivine from the syngas. The solids flow to the char combustor where the char is burned in air in a fluidized bed, resulting in olivine temperatures greater than 1,800°F (980°C). The hot olivine and residual ash is carried out of the combustor by the combustion gases and separated using a pair of cyclones. The first cyclone recovers the bulk of the olivine while the second cyclone captures ash and olivine fines. Hot olivine flows back into the gasifier, completing the gasification loop. The hot flue gas from the char combustor is utilized for heat recovery and feedstock drying. Ash and olivine fines are cooled, moistened to minimize dust, and removed as waste.

Syngas cleanup: This process area consists of multiple operations including reforming of tars to CO and H_2, syngas quench and scrubbing, and acid gas (CO_2 and H_2S) removal. In the tar reforming step tars, methane, and light hydrocarbons are reformed to syngas in a circulating, fluidized, solid catalyst system that resembles a small-scale fluid catalytic cracker (FCC), complete with reforming and regeneration operations in separate beds. The syngas is reacted with tar reforming catalyst in an entrained flow reactor at a gas hourly space velocity of approximately 2,500 h^{-1}. The catalyst is then separated from the effluent syngas in a cyclone. From the cyclone, the spent catalyst flows to the catalyst regenerator vessel where residual coke from the reforming reactions is removed from the catalyst by mild oxidation. The hot catalyst is separated from the combustion flue gas in the regenerator cyclone and flows back to the tar reformer reactor to provide the energy necessary for the reforming reactions. Additional syngas and unreacted gases from the methanol synthesis reactor may also be combusted to provide all the heat necessary for the endothermic reforming reactions. A similar approach is documented in a patent application by Rentech (Apanel and Wright 2010). The hot reformed syngas is cooled through heat exchange with other process streams and scrubbed with water to remove persistent impurities such as particulates, ammonia, halides, and recalcitrant tars. Scrubber water is purged and treated continuously in an on-site wastewater treatment facility. After heat recovery, the remaining low-quality heat in the flue gas from the catalyst regenerator is utilized for feedstock drying. Although water-gas-shift reaction occurs in the tar reformer reactor, it may be necessary to include a water-gas shift reactor to adjust the syngas H_2:CO ratio after scrubbing in order to optimize methanol production. After leaving the shift reactor, the syngas enters an amine system for removal of the CO_2 and H_2S and subsequently enters the methanol synthesis reactor. The H_2S is reduced to elemental sulfur and stockpiled for disposal. The CO_2 is vented to the atmosphere in the current design configuration.

Methanol synthesis: The cleaned and conditioned syngas is converted to methanol in a tubular, fixed-bed reactor containing a copper / zinc oxide / alumina catalyst. The mixture of methanol and unconverted syngas is cooled through heat exchange with the steam cycle and other process streams. The methanol is recovered by condensing the product and separating it from unconverted syngas and light product vapors in a vapor / liquid disengaging vessel. The unconverted syngas is recycled back to the methanol synthesis reactor inlet. The basis and conditions for the methanol synthesis reactor design are consistent with the basis utilized in the NREL MTG design report (Phillips et al. 2011) from Bartholomew and Farrauto (2006). Temperature control and heat removal from the exothermic reactor is accomplished by steam production on the shell-side of the tubular reactor. The reactor operating conditions assumed for this analysis are 572°F, 735 psia, space velocity of 8,000 h^{-1}, and single-pass CO conversion of 41.8%. Methanol production from clean, natural gas-derived syngas is deemed a commercially available process with relatively low level of uncertainty.

Methanol recovery and storage: The synthesis reactor effluent is condensed at elevated pressure and then degassed to remove dissolved light products from the methanol product. The conditioned methanol intermediate is sent to a storage tank for upgrading to hydrocarbon products including gasoline and diesel range blendstocks.

Methanol to hydrocarbons: From intermediate storage, the methanol is sent to a fixed-bed reactor of approximately 4,000 ft^3 in volume to convert the methanol to dimethyl ether (DME) at 572°F and 95 psia. After mild temperature adjustment to optimal conditions, the effluent from the methanol-to-DME reactor feeds the parallel catalytic fixed-bed tubular reactors. The number of reactors specified for a specific scenario depends on the predicted coke production rate. It is assumed that while two reactors are in methanol-to-hydrocarbon service, the other reactor(s) are in coke-burn/catalyst regeneration service. The reactors are rotated through conversion and regeneration services with a lead-lag strategy (lead reactor to coke-burn, regenerated reactor to lag, lag to lead). Direct conversion to gasoline- and diesel-range hydrocarbons is achieved in the fixed-bed reactor. The light intermediates are recycled to the methanol-to-hydrocarbon reactor(s) for conversion to improve overall product yield to the desired hydrocarbon blend stock. It is assumed that the catalyst replacement rate will be equivalent to a single reactor volume per year. As discussed later in the report, the hydrocarbon production reactor system represents the area of the highest level of uncertainty in the process. Details on the design assumptions, conversion, and yields associated with this example reactor system are based on published data from Ahn et al. (2009) and Simonetti et al. (2011). Temperature control and heat removal from the hydrocarbon reactor is accomplished by steam production on the shell-side of the tubular reactor. The reactor operating conditions assumed for this analysis are 400°F and 95 psia. The sizing of the reactor for each scenario (state of technology or target) is calculated based on the C_7 production rate. Ahn et al. (2009) specifies a C_7 production rate of 16 μmol $(\text{second-mol Al})^{-1}$ over a β-zeolite catalyst possessing Si / Al molar ratio of 12.5.

Although it is expected that hydrogen addition to the DME-to-hydrocarbons reactor could impact aromatic content of the product, no supplemental hydrogen is considered for the state of technology analysis. Hydrogen addition is considered for the target process assessment for purposes of yield improvement and reduced coke formation. However, the hypothesized yield benefit must be confirmed through experiment.

Product recovery: The separation of the hydrocarbon products is similar to the processing steps used in a petroleum refinery. For the current case, the configuration utilized in this model consists of three separation steps. The first step is a deethanizer/ absorber system that removes the light ends. This is followed by a debutanizer column that removes the C_3 and C_4 material from the gasoline-range material. From the debutanizer, the product stream is sent to storage. The overhead stream from the debutanizer, primarily C_4, is sent to the third separation step, the butane splitter, where iso-butane and butenes (olefins) are recovered from the normal-butane and recycled to the hydrocarbon conversion reactor. The normal-butane, recovered from the bottoms of the butane splitter, is stored for sales or sent to the hydrogen plant for production of hydrogen in the target scenario. The product recovery scenario will need to be modified/optimized if the hydrocarbon component slate is changed.

Heat integration and power: A conventional steam cycle produces heat (as steam) for the gasifier and reformer operations and electricity for internal power requirements with the possibility to export excess electricity as a co-product. The steam cycle is integrated with the biomass conversion and methanol-to-hydrocarbon processes.

Previous analyses of gasification processes have shown the importance of properly utilizing the heat from the high temperature streams to improve efficiency of the overall plant design. A correlation developed from Aspen Icarus Process Evaluator 2006.5 was used to estimate the costs of the heat exchanger network. The correlation is based on the total heat transfer duty and pinch delta temperature (estimated from Aspen Plus model data).

Utilities: A cooling water system is included in the Aspen Plus model to determine the requirements of each cooling water heat exchanger as well as makeup water and power requirements. Wastewater treatment and tankage for product storage is also included in the process configuration.

Data Gaps, Uncertainties, and Research Needs

While the pathway for the upgrading of syngas to hydrocarbon blendstocks is based on a thermochemical process configuration that has been rigorously developed, including biomass gasification, syngas cleanup, and methanol synthesis, other aspects of the configuration possess a higher degree of uncertainty. The goal of this pathway is to achieve 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:

- **Develop catalysts that maximize carbon selectivity to desired hydrocarbon products.** Catalysts should be developed that have increased selectivity to gasoline- and diesel-range products and that minimize unwanted side-products such as light gases and coke. Improved catalysts will show selectivity toward specific products and reduce the formation of aromatics. The rational design and development of catalysts could be accomplished using a combination of computational and experimental techniques.
- **Maximize catalyst life and stability.** The catalyst lifetime, maintenance, stability, and optimal regeneration protocols are unknown. Testing with the upgrading intermediate (methanol in this case) and a detailed characterization of catalyst performance and deactivation modes are needed. A better fundamental understanding of both chemical conversion and poisoning mechanisms may lead to better catalysts that are resistant to contaminants and poisons.
- **Investigate alternative intermediates for hydrocarbon production.** While the current design utilizes methanol as the intermediate for hydrocarbon production, future research should investigate the economic feasibility and design impacts of alternative intermediate routes to hydrocarbons. Intermediates such as light olefins, mixed alcohols, or mixed oxygenates may be economically viable and improve overall yields of hydrocarbon fuel. A variety of potential routes for the production of these intermediates should be considered, including both catalytic and fermentative processes.
- **Consolidate and optimize process configuration.** Identifying opportunities to further integrate the process design will lower the overall conversion costs. Areas of potential consolidation include the removal of the intermediate upgrading reactors, such as the methanol-to-DME step. There is also potential to develop catalysts that can directly

convert synthesis gas to the gasoline- and diesel-range products. Demonstration of impacts on product yields and catalyst lifetimes will need to be investigated to understand the economic viability of these process changes. Design of the upstream synthesis gas conditioning steps will also be evaluated for further cost reduction and improved heat integration. Off-gas conditioning may be required to feed light hydrocarbon co-products from the process to the hydrogen plant. There is a need to better characterize the gas composition and any required cleanup or design modifications to the hydrogen plant (i.e., the addition of pre-conditioning or hydrogenation steps prior to reforming).

- **Demonstrate current design assumptions on larger scale systems.** The data utilized in this example study are based on bench-scale information (Ahn et al. 2009; Simonetti et al. 2011). There is significant uncertainty in assuming that comparable yields can be achieved on a commercial scale with similar operating conditions. The design basis for sizing the reactor and associated catalyst volume must be confirmed by further bench- and pilot-scale demonstrations.

Summary and Next Steps

This literature-based techno-economic analysis of syngas upgrading to hydrocarbon biofuels was performed to identify technology gaps, uncertainties, and research needed to achieve a targeted minimum fuel selling price of $3/gallon of gasoline equivalent. Current experimental efforts are focused on demonstration of product yields. Research is on-going to design and develop catalysts with improved yields toward desired products and lifetimes. A design case detailing this pathway and utilizing research experimental results will be developed in FY14.

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