A Hybrid Catalytic Route to Fuels from Biomass Syngas

Contract DE-EE0005356
Final Report

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FOREWORD

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Chemical and fuel producers are not immune to fluctuations in currency, oil prices, or raw materials costs. Smaller producers, such as today's biofuel and bioproducts enterprises, face the greatest level of risk. Addressing this requires fuel and chemical production flexibility.

Every five years, the Bioenergy Technologies Office (BETO) hosts a semi-integrated process demonstration of the most economically promising new fuel production technology. In 2017, BETO leveraged thousands of hours of lab and pilot scale experience to demonstrate production of hydrocarbon fuels at a mature modeled price of $3/gge. Much of that experience is detailed in the following report.

To achieve a profitable enterprise for BETO's 2017 goal, chemicals were assumed to be co-produced with fuel. Taking full advantage of the flexibility to make two different co-products, 1,3-Butadiene (BD) and Methyl Ethyl Ketone (MEK), and recognizing the fluctuations in the prices of these chemicals, the techno-economic analysis approach was to identify the ***ranges of product slate distributions between fuel, BD, and MEK*** for:

- Various price points that have occurred between 2011 and 2017 (shown in **Figure F1**, below, adjusted to constant 2014 dollars);
- Achieving a Minimum Fuel Selling Price (MFSP) of $3/gge; and,
- Achieving greenhouse gas (GHG) reductions appropriate for classifying the fuel as 'advanced' or 'cellulosic', e.g. 50% and 60%, respectively.

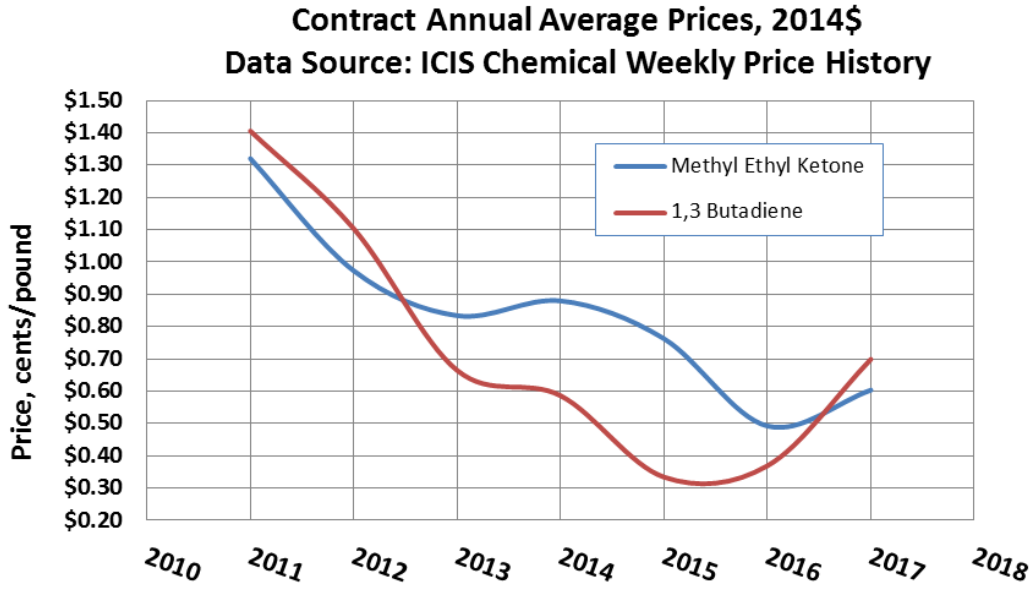

Figure F1. Published pricing for BD and MEK.

The basis for this analysis aligns with other State of Technology (SOT) and Design Case studies completed for BETO. The basis includes the following assumptions:

- N^{th} plant – meaning that all capital and operating risks have been overcome;
- Scale of the biorefinery is 2,000 dry tonnes of biomass per day;

- The woody biomass is delivered to the plant gate at $59.75/dry ton;
- Economic assumptions such as depreciation and IRR are from BETO's Multi-Year Program Plan (MYPP), Appendix C;
- The indirectly-heated gasifier, tar reformer, steam generation, and power production are based on the NREL model;
- Syngas fermentation to ethanol and 2,3-Butanediol is modeled after the LanzaTech process; and,
- The catalytic conversion of ethanol and 2,3-Butanediol to fuels and chemicals is modeled after the PNNL process.

A block flow diagram for the conceptual commercial-scale biorefinery used in the analysis isshown in **Figure F2**.

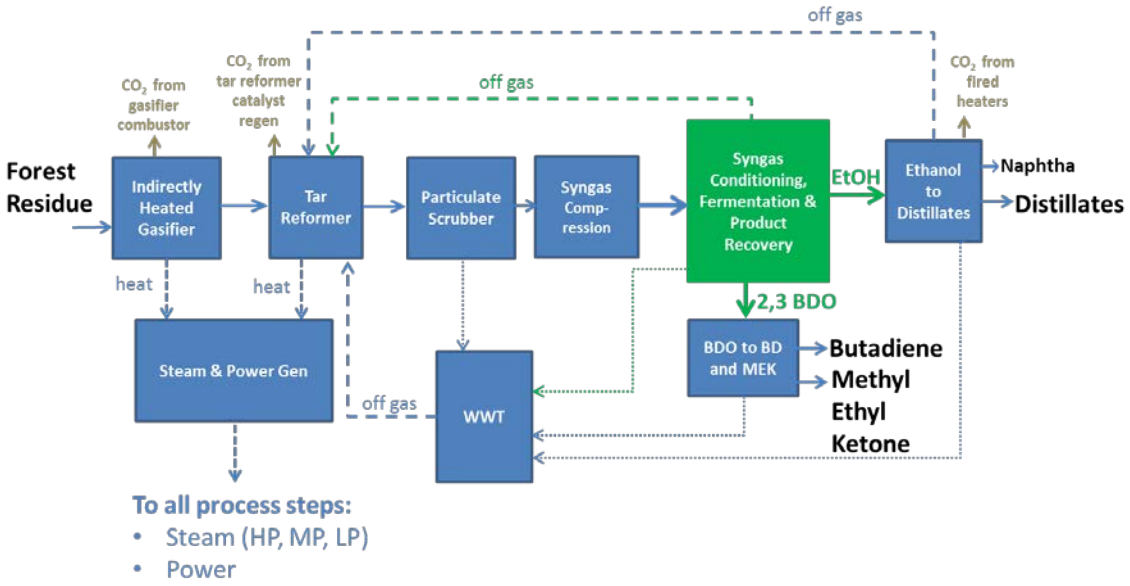

Figure F2. Block flow diagram for the 2017 SOT conceptual biorefinery.

The biorefinery concept provides multiple levels of flexibility. Both BD and MEK can be produced from this process, either together or separately, from a common intermediate: 2,3-Butanediol. Because BD and MEK prices fall and rise at different rates, this affords flexibility in terms of how much, and which chemical to produce at any given time. Another lever is the split between the fermentation products (ethanol and BDO), which in turn dictates the overall fuel/chemical split. **Figure F3** shows the combinations of fuel and chemicals, and the resulting fuel selling price.

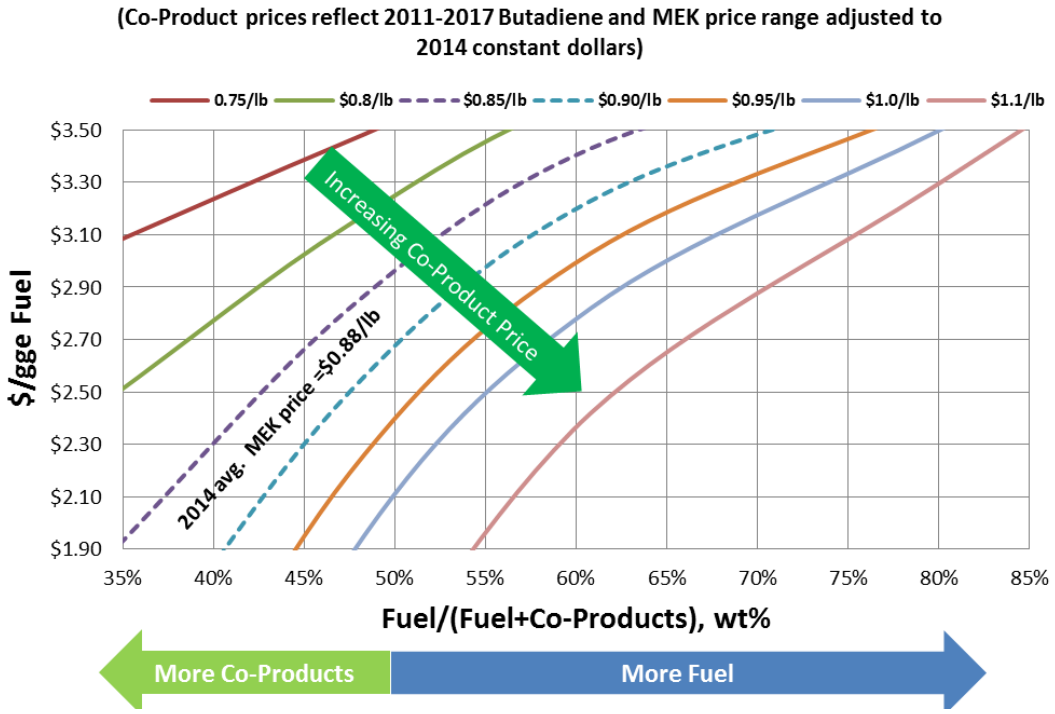

Figure F3. Combinations of fuel and chemicals that meet the 2017 target cost

Very low co-product prices and very high fuel-to-co-product ratios cause the MFSP to fall outside the desired range. However, numerous combinations that fall within historic co-product prices meet the cost target of $3/gge while still enabling fuel as the majority product.

Life-cycle inventories for the 60% fuel/40% co-product case were delivered to researchers at Argonne National Laboratory (ANL) in order to estimate the GHG impact for this process. Supporting information was also provided for raw material and utility consumption for the conventional petroleum-based production of BD and MEK using data from the PEP Yearbook (PEP 2014). ANL researchers, using the displacement method to account for the GHG emissions from field to fuel and co-product end use, concluded that GHG reduction for this case exceeds the 60% requirement for a cellulosic fuel.

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1 Executive Summary

1.1 Project Objectives

LanzaTech partnered with the Pacific Northwest National Laboratory (PNNL), Imperium Aviation Fuels (IAF)[1], InEnTec, Orochem Technologies, the University of Delaware (UD), Michigan Technological University (MTU), the National Renewable Energy Laboratory (NREL), and The Boeing Company, to develop a cost-effective hybrid conversion technology for catalytic upgrading of biomass-derived syngas to sustainable alternative jet fuel (SAJF) meeting the price, quality and environmental requirements of the aviation industry.

Alternative "synthetic paraffinic kerosene" (SPK) blendstock produced from syngas via "Fischer-Tropsch" (F-T) or from lipids via "hydroprocessing of esters and fatty acids" (HEFA) are currently being used in commercial jet fuel blends containing at least 50% petroleum-based fuel. This project developed an alternative route to SAJF from ethanol, a type of "alcohol to jet" (ATJ) SPK.

The specific objective of this project was to demonstrate a pathway that combines syngas fermentation to ethanol with catalytic upgrading of ethanol to sustainable alternative jet fuel and shows attractive overall system economics to drive down the price of biomass-derived jet fuel. The hybrid pathway (**Figure 1**) was to be demonstrated on three biomass feedstocks: corn stover, woody biomass, and third biomass feedstock, for which LanzaTech selected cellulosic residues, or "bagasse", from a U.S. crop with commercial potential. The objectives also included the co-production of chemicals, exemplified by 2,3-Butanediol (2,3-BDO), which can be converted to key chemical intermediates.

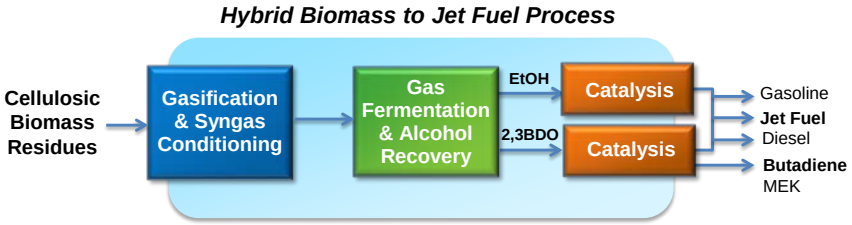

Figure 1. Hybrid conversion of biomass to fuels and chemicals.

1.2 Summary of Major Findings

The LanzaTech-led team successfully demonstrated that biomass syngas fermentation followed by catalytic conversion is a viable alternative to the capital- and energy-intensive Fischer-Tropsch process and produces a fuel with properties comparable to F-T and HEFA SPKs. Specific findings from the project include:

- Plasma gasification produces a clean, consistent, syngas suitable for gas fermentation.
- Plasma gasification and gas fermentation were successfully integrated and demonstrated in at least 7-day continuous fermentations on waste wood, corn stover, and cellulosic bagasse.
- Gas fermentation was demonstrated to produce ethanol suitable for catalytic upgrading, isolating the upgrading from variations in biomass feed, syngas composition, and impurities.

[1] Acquired by Renewable Energy Group during the course of the project.

- Ethanol feedstocks from all three types of biomass were demonstrated to be comparable to grain derived ethanol and suitable for the LT-PNNL ATJ process.
- The LT-PNNL ATJ catalytic upgrading process was demonstrated at lab scale for over 2000 hours of continuous operation on a single catalyst load.
- LanzaTech scaled up the ATJ process, producing 4000 gallons of jet and 600 gallons of diesel for testing and a future proving flight.
- The LT-PNNL ATJ process, at lab and pilot scale, from commercial grain-based ethanol and steel mill waste gas-based ethanol ("Lanzanol"), produces high-quality fuel-range distillates containing primarily normal paraffins and isoparaffins.
- The LT-PNNL ATJ fuel has equivalent properties to previously-approved SPKs such as F-T, HEFA, and ATJ from isobutanol, and conforms with critical properties needed to blend with conventional jet fuel.
- The 2,3-BDO fermentation co-product can be separated economically utilizing Simulated Moving Bed (SMB) technology.
- 2,3-BDO can be catalytically converted to 1,3-butadiene (BD) in a two-step process with at least 70% yield, producing a chemical intermediate suitable for downstream applications.

Technoeconomic and life cycle analyses of the biomass to jet process with and without 2,3-BDO production showed that:

- Capital costs increase as the proportion of the 2,3-BDO co-product increases due to additional separation and conversion requirements.
- Capital cost is also sensitive to biomass feedstock, with costs for using corn stover somewhat higher than woody biomass.
- Roughly 30% of total cash cost of production is due to biomass feedstock costs.
- The co-product 2,3-BDO, converted through to BD, significantly reduces the cash cost of production of the hydrocarbon fuels.
- There is significant opportunity to reduce capital costs, through optimization of individual units, and operating costs, particularly utility costs, through fully integrated system designs.
- Life cycle GHG emissions of ATJ SPK produced from biomass using a steam gasification system are projected to be significantly lower than those of conventional jet fuel.
- Plasma gasification reduces GHG savings of jet from biomass due to increased utility costs.
- Integration of utilities will be important in designing commercial biomass to jet systems using plasma gasification.

1.3 Project Impact

This project successfully demonstrated that a high quality ATJ SPK, can be produced from biomass via a hybrid gas fermentation/catalytic route. Validation of the LT-PNNL ATJ process using a variety of ethanol feedstocks demonstrates the viability of a future model of distributed ATJ production, in which ethanol may be produced at multiple facilities from local feedstocks and shipped to a central facility for conversion. The project demonstrated that co-production of chemicals has the potential to reduce jet cost of production, thereby accelerating commercial production of SAJF from biomass. This project also enabled the production of key data for the early stages of the Original Equipment Manufacturer (OEM) review process that was required to add ethanol as a qualified ATJ feedstock in D7566 Annex A5, *Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ SPK).*

2 Summary of Project Accomplishments

The LanzaTech-led team successfully demonstrated that biomass syngas fermentation followed by catalytic conversion is a viable alternative to replace the capital- and energy-intensive Fischer-Tropsch process and produces an ATJ SPK based fuel with properties comparable to F-T and HEFA SPKs. This hybrid fermentation process exploits the natural advantages of biochemical and thermochemical processing. Gasification efficiently transforms cellulosic biomass into syngas, primarily composed of carbon monoxide (CO) and hydrogen (H_2). Gas fermentation utilizes a robust microbial catalyst to consume the CO and H_2, and produce ethanol with high selectivity in a continuous process. The robust fermentation and alcohol recovery process provides a clean and consistent alcohol product for catalytic upgrading, which isolates the upgrading from any variations in biomass feed, syngas composition, and impurities. The PNNL catalytic upgrading process leverages standard refinery unit operations to remove oxygen from the alcohols and to extend the carbon chain lengths, creating the desired distribution of hydrocarbons for jet blendstocks and for other fuels.

Production of Ethanol Intermediate. In the first major step, syngas was converted to ethanol using a biochemical catalyst through a gas fermentation process. **Figure 2** provides an overview of a generalized biomass to ethanol process for production of ATJ feedstock. Syngas from biomass gasification is piped into a holding tank (1) to ensure constant supply to the fermentation. The collected gas is compressed and passed through clean up steps specific to the gas feed stream (2). The treated gas is introduced into a purpose-built gas fermentation bioreactor containing microbial biomass suspended in a nutrient broth (3). The bioreactor is designed to dissolve the gas in the nutrient broth, in which the CO, H_2 and CO_2 components of the gas are converted to ethanol using bacteria. The ethanol product is continuously produced and secreted by the bacteria and accumulates in the nutrient broth. The bioreactor broth, containing both bacterial biomass and ethanol, is continuously distilled for ethanol recovery (4). The ethanol product (Lanzanol) is stored awaiting distribution to the ethanol to jet conversion site. As discussed below, the fermentation can also produce 2,3-BDO as a co-product, which requires a different approach to separation.

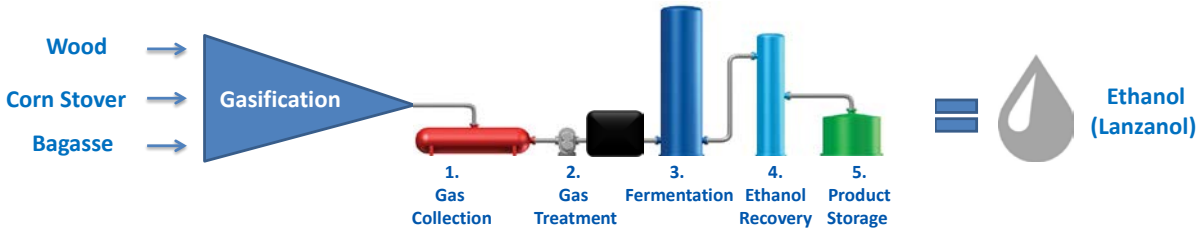

Figure 2: Overview of syngas fermentation process

For this project, each of the three types of cellulosic biomass was gasified in an InEnTec pilot-scale gasifier, producing syngas. To demonstrate the integration of gasification with fermentation, the syngas from each biomass feedstock was fed into LanzaTech's portable gas fermentation unit for at least 7 days of continuous fermentation. Additional quantities of each type of syngas were shipped to LanzaTech's laboratories, where they were converted into ethanol and supplied to PNNL for conversion into jet- and diesel-range hydrocarbons. Detailed analysis of the ethanol samples showed no components that would impact catalysts in the upgrading process.

Production of Jet from Ethanol. In the second step, ethanol was upgraded to jet in a thermochemical catalytic process developed by PNNL. PNNL developed and demonstrated a

process to produce ATJ SPK from ethanol, with optional diesel and gasoline co-products. As shown in **Figure 3**, the PNNL ATJ process consists of a sequence of catalytic conversions, in which ethanol is first dehydrated to produce ethylene. Ethylene is then oligomerized to produce longer-chain olefins, which are saturated via hydrogenation and fractionated into the desired product slate.

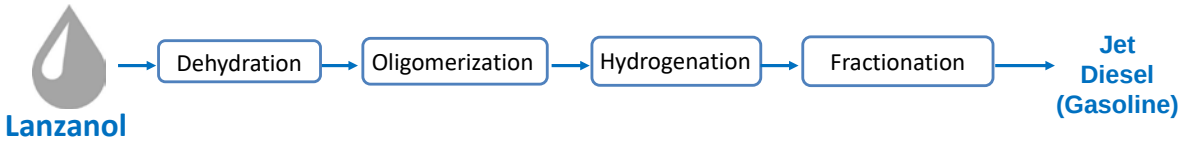

Figure 3: Overview of ethanol to jet process

PNNL developed an oligomerization process which uses commercially viable catalysts and an overall conversion system for controlled catalytic conversion of ethylene to produce fuel-range hydrocarbons containing primarily normal paraffins and isoparaffins. PNNL demonstrated oligomerization catalyst lifetime and regeneration for over 2,000 hours on stream with a single catalyst loading, meeting the FOA objective for operating history. All other steps are practiced commercially.

In order to provide larger quantities of ATJ SPK for property testing and a proving flight, LanzaTech scaled up the ATJ process developed by PNNL to pilot scale. Commercially derived catalysts were employed for all steps except the oligomerization catalyst, which was scaled up and produced using a commercially available support.

Two sources of ethanol were used for the pilot-scale production: Lanzanol produced from steel mill waste gas in one of LanzaTech's gas fermentation demonstration plants and grain-based ethanol purchased commercially. As part of the scale up, the integration of ethanol dehydration and ethylene oligomerization was further optimized and an in-situ catalyst regeneration procedure was developed. In total, over 4000 gal of jet fuel range product was produced, with 600 gallons of diesel co-product. The specification properties from the two ethanol sources were the same and comparable to ATJ SPKs produced from ethanol at the smaller scale.

PNNL validated the ethanol-to-jet process on the biomass syngas-derived ethanol samples supplied by LanzaTech. PNNL conducted an extended run in which each sample of ethanol from gas fermentation was fed to the dehydration reactor for an interval, followed by a period of grain ethanol feed, diluted to emulate the concentration of the biomass-derived ethanol. The Lanzanol produced from steel mill waste gas was included in the run for comparison. When the change in catalyst with time on stream was taken into account, the data from all ethanol sources was within the expected range from start to finish.

Jet Fuel Property Testing. Jet fuel produced from ethanol falls into the class designated as "Alcohol to Jet Synthetic Paraffinic Kerosene" (ATJ-SPK) in ASTM D7566, *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*, which specifies requirements for alternative jet fuels. Isobutanol is a qualified feedstock under D7566 Annex A5, the specification annex for ATJ-SPKs. As of the close of the project, ATJ produced from ethanol using the LanzaTech-PNNL hybrid process developed here was in the ASTM balloting and review process with the goal of adding ethanol as a qualified ATJ feedstock in D7566 Annex A5.

Testing by the Air Force Research Laboratory (AFRL), University of Dayton Research Institute (UDRI), and Southwest Research Institute (SwRI) demonstrated that the SPK produced from

ethanol feedstocks (LT/PNNL ATJ) has equivalent properties to SPKs previously approved such as F-T, HEFA and ATJ from isobutanol as well as conforming with critical properties needed to blend with conventional jet fuel. The comparisons were made using the same methodology and measurement equipment, and plotted or tabulated together when possible. The tests showed that the SPK produced from the LT-PNNL process developed in this project is a wide-boiling primarily isoparaffinic kerosene, closely resembling HEFA in composition and properties. Both Specification Property and Fit for Purpose Property data from multiple LT/PNNL ATJ samples were provided as input to the OEM review process during the project period.

Co-Production of 2,3-Butanediol. As illustrated in **Figure 1**, above, 2,3-BDO is an optional co-product of ethanol in the syngas fermentation process. This project addressed the two key challenges to incorporating this chemical co-product in a future commercial process: cost-effective separation of 2,3-BDO and upgrading of 2,3-BDO to butadiene or other standard chemical intermediates.

Distillation of 2,3-BDO from fermentation broth incurs a large energy cost because its high boiling point (177 °C) means that, in effect, the majority water component must be distilled away from the low concentration alcohol. Orochem Technologies, Inc., adapted its Simulated Moving Bed (SMB) continuous chromatographic process to 2,3-BDO and ethanol separation. Utilizing samples of fermentation broth containing 2,3-BDO and ethanol, Orochem developed a recovery scheme with a regenerable guard bed, proprietary adsorbent, extraction solvent and process design parameters.

In parallel, PNNL investigated options for conversion of 2,3-BDO, produced as a fermentation co-product, to value-added chemical products. PNNL demonstrated pathways to the chemical intermediates 1,3-Butadiene (BD) and methyl ethyl ketone (MEK). In addition, PNNL identified pathways from 2,3-BDO to butanol, which can serve fuel markets as a gasoline additive or be dehydrated to butene and used in the alcohol to jet process.

Technoeconomics and Life Cycle. LanzaTech conducted technoeconomic analyses (TEA) of the project technology for multiple cases, using public data sources for plasma gasification, LanzaTech internal gas fermentation process models, an ATJ process model developed by PNNL, and LanzaTech internal process models for 2,3-BDO separation and conversion to BD. The TEA emphasized capital and operating costs for producing jet and other hydrocarbon fuels, including impacts of feedstock and the ratio of 2,3-BDO to ethanol. The TEA considered six base cases: two primary biomass feedstocks (waste pine wood and corn stover) and three fermentation options (ethanol only and BDO:ethanol mass ratios of 0.5:1 and 1:1). Co-production of 2,3-BDO and conversion to BD was the most significant factor distinguishing the capital costs (CAPEX) of the 6 cases, with CAPEX increasing with higher 2,3-BDO production. CAPEX is also higher in the corn stover cases, due to its lower quality. Co-production of 2,3-BDO reduced the cash cost of jet fuel production by providing another source of revenue, offsetting the increased CAPEX in the overall process economics.

Michigan Technological University developed a full life cycle assessment (LCA) of the biomass-to-jet system. LCA based on the use of a steam gasifier showed very large GHG reductions for biomass-based jet fuel. Estimates of GHG reductions from LCA assuming a plasma gasifier, using public information regarding operating parameters, combined with syngas compositions from pilot-scale gasifier operations during the project, were less favorable due to high external electricity requirements and the current U.S. grid intensity; recommendations for future enhancements were developed.

3 Summary of Project Activities

The goal of this project was to drive down the cost of biomass-derived SAJF by optimizing overall system economics. This was addressed in the project by integrating each of the interfaces between unit operations in the hybrid biomass to jet process, leading to a process design which was used to assess both technoeconomics and life cycle impacts of future commercial-scale implementation, including co-production of chemicals and other fuels.

The production of ethanol intermediates from biomass syngas is discussed in **Section 3.1** followed by the ethanol to jet technology development in **Section 3.2**. The properties of the resulting ATJ SPK are described in **Section 3.3**. **Section 3.4** discusses work done to support co-production of 2,3-BDO. The TEA and LCA of the biomass to jet system, with and without 2,3-BDO co-product, are summarized in **Section 3.5**.

Overview of Project Activities

The project was designed to support a distributed model of jet fuel production, in which a standard intermediate – ethanol – can be produced at smaller scale and at lower cost in regional facilities using conversion technologies appropriate to locally-available resources. Ethanol from all sources can then be processed at a centralized ATJ unit, which can ultimately be integrated directly with refinery infrastructure and fuel distribution systems. This combination of distributed ethanol production with centralized ATJ processing will enable each to be implemented at its optimum scale. In general, ATJ unit operations, which are standard refinery processes, experience greater economies of scale than do biological gas fermentation or other methods to produce ethanol from cellulosic biomass and other residues. Gas fermentation scale is based on gasifier capacity and the bioreactor size. Gasifiers and bioreactors are typically optimized at certain sizes so that increasing ethanol capacity involves installing additional trains. To increase ATJ production capacity simply involves increasing the sizes or numbers of standard reactors and columns, etc., all of which are already implemented at vastly larger scales in petroleum refineries.

With a distributed model, the key technical elements to be demonstrated were:

- Integration of syngas production (gasification) and ethanol production (gas fermentation), with validation of ethanol quality
- Ability of the ATJ SPK upgrading process to accommodate ethanol from a variety of sources
- Continuous operation and stability of the ATJ SPK upgrading process
- Quality of the ATJ SPK jet fuel product
- Ability to produce and upgrade a fermentation co-product with potential to improve economics

3.1 Production of Ethanol Intermediates from Biomass

This section discusses work performed to demonstrate the integration of gasification and fermentation, the production of ethanol samples from biomass syngas, and the quality of the ethanol produced from biomass.

3.1.1 Demonstration of Gasifier-Fermentation Integration

In the original project plan, a LanzaTech fermentation pilot unit was to be installed at the NREL Thermochemical Process Demonstration Unit (TCPDU). A 100L fermentation pilot (designated

"Columbo") was transported to NREL, upgraded for continuous operation and syngas processing, and commissioned using simulated syngas. The unit was then integrated with the NREL TCPDU syngas output and initial tests were performed using wood chip (pine) feedstock. Due to events external to the project, the TCPDU was shut down for an indefinite duration. Alternative sites were investigated to identify suitable gasifiers at an appropriate scale for integration with Columbo but no site was found that would be available within the timeline and budget of the project. Therefore, the Columbo pilot unit was moved to LanzaTech's Freedom Pines Biorefinery in Soperton, Georgia. The Columbo unit was recommissioned and testing continued on simulated biomass syngas. LanzaTech procured a 0.5 ton/day biomass gasifier outside of the project. Construction and installation was initiated in parallel with on-going gas fermentation studies in Columbo, including co-production of 2,3-BDO and ethanol. Ultimately, based on timing and the opportunity to utilize Freedom Pines resources for ATJ scale up, it was agreed that the integration of gasification with gas fermentation would be accomplished with a new partner, InEnTec, utilizing a different, portable fermentation unit, the "Gas Testing Station" or GTS.

The GTS was installed at InEnTec's facility in Richland, Washington, and integrated with a slipstream of InEnTec's 0.5 ton/day pilot gasifier to demonstrate integrated operation of gas fermentation with syngas production. The specific goals of the GTS installation and integration at InEnTec were threefold: 1) Optimize operation of the InEnTec Plasma Enhanced Melter (PEM®) to obtain high quality syngas with gas compositions suitable for gas fermentation; 2) Demonstrate the compatibility of three gasified biomass feedstocks (corn stover, pine, and bagasse) with the LanzaTech fermentation process to demonstrate the production of ethanol from live syngas; and 3) Identify any gas clean-up unit operations required to prevent fermentation inhibition.

Samples of the corn stover and pine feedstocks are shown in **Figure 4**. Both were purchased in pellet form with moisture levels of 13% and 6%, respectively. The bagasse feedstock was supplied by an industrial partner in the form of dried powder.

Corn Stover **Pine**

Figure 4. Photographs of corn stover and pine feedstocks.

Biomass Gasification

InEnTec's proprietary PEM gasification process has multiple configurations that can be optimized for economical operation with particular feedstocks and a desired throughput. For this demonstration, InEnTec's gasifier included a high-temperature plasma chamber and a Thermal Residence Chamber (TRC). The plasma chamber uses electrically powered graphite electrodes to create a high-temperature plasma that provides intense energy to rapidly gasify volatile materials and convert them to syngas. Syngas from the plasma chamber flows to the TRC, which provides additional residence time at high temperature to allow gasification reactions to reach equilibrium.

The plasma vessel has a molten glass bath in the bottom of the processing chamber. Non-volatile components of the feed material that do not become syngas melt into and become part of the liquid glass.

Syngas exiting the TRC flows through a series of process units to cool it and remove undesired constituents such as particulates and acid gases before the syngas is fed to the GTS (**Figure 5)**. The conditioning system may vary depending on the feedstock. The system used in this demonstration included a partial quench to rapidly cool the syngas, a bag filter to remove particulates, a pH controlled acid gas scrubbing system to remove acid gasses, and an activated carbon filter to remove any trace organic compounds.

Figure 5. Syngas clean-up.

During processing, LanzaTech filled canisters with produced syngas from a point located after the conditioning process and sent samples from some of the canisters to a third-party laboratory for analysis. The syngas contained CO concentrations above 35% (vol %, dry basis), approximately 25% H_2, and 20-25% CO_2, which are all the primary molecules expected in high quality syngas. The H_2:CO ratios in the syngas varied from 0.5:1 to 0.65:1.

The syngas also contained about 10-15% N_2, which is used as a purge gas in the pilot scale gasification system. The concentration of N_2 would be lower in a commercial scale system where the quantity of purges would be relatively lower (compared to the quantity of syngas produced). Oxygen (O_2) at too high levels in syngas is toxic to anaerobic organisms and anaerobic processes, but any oxygen present in InEnTec's syngas was below toxic levels. Methane (CH_4) is inert in LanzaTech's process. However, it can sometimes serve as an indicator for reformed inhibitory contaminants that could be in syngas, but InEnTec's syngas was not toxic to LanzaTech's process so such compounds either did not exist or were below levels of concern.

Integrated Testing on Biomass Syngas

The Gas Testing Station (GTS) is a LanzaTech portable gas fermentation apparatus, as described in US Patent Application No. 20160115517. It is designed as a tool for testing the compatibility of LanzaTech gas fermentation technology with raw or treated process gas at the sites of potential customers. The GTS contains core components of LanzaTech's technology – two gas fermentation bioreactors, LanzaTech's proprietary microbe and media, with associated process control and analytics – in a mobile package designed for ease of shipping. This allows a comparative analysis of two fermentations operated in parallel: one operated using a live feed of a customer feed gas, the other using a synthetic blend of gases to mimic the customer gas composition. The main GTS function is an extended exposure test, performed on-site, of raw process gas to the LanzaTech proprietary microbe to assess technology compatibility.

In order to operate continuously, the GTS requires synthetic process gas, untreated pressurized process gas, liquid media, dosing chemicals, microbes, and for analytics: nitrogen, hydrogen, argon, instrument air as well as a continuous power supply. The GTS was installed at InEnTec and bacterial cultures (control and experimental) were inoculated in each bioreactor using a synthetic gas blend and tap water for media make-up.

Proof-of-Concept Fermentation Results

While the GTS was continuously operating, the experimental culture was switched first to corn stover syngas, then to pine, and finally to bagasse after stabilizing on synthetic syngas between feedstocks. The fermentation was operated without interruption for at least seven days on each feedstock, showing no adverse effects on key performance measures such as gas consumption rate and ethanol selectivity. These results demonstrated that ethanol can be produced from live syngas feeds, and that the gas clean-up operations used were sufficient to remove fermentation inhibitors.

The control culture was run on a synthetic bottled gas mixture (~19% H_2, 32% CO, balance CO_2 and N_2, purchased and clean). Experimental cultures were stabilized on the same synthetic bottled gas mixture, and then switched to live syngas from corn stover, pine, or bagasse. While running on live syngas, the feed gas flow to the experimental cultures was consistently increased to enhance carbon uptake, thereby increasing ethanol production and microbe exposure to gas. Analytics consisted of automated hourly gas chromatography (GC) samples to measure the input and output gas compositions, and manual liquid high performance liquid chromatography (HPLC) samples to measure the metabolite concentrations in the fermentation broth. Experiments were performed at atmospheric pressure.

Typical culture parameters such as gas consumption, metabolite production, product specificity, as well as pH/ORP profiles showed positive trends while running the process gas. Ethanol selectivity remained at standard levels for the fermenter configuration used in the GTS. Although some fermentations showed fluctuating gas uptake due to mechanical (pump) issues, no fermentation runs encountered early termination due to contaminant build up.

It is important to note that the operation of the GTS is designed to investigate possible contaminant effects and is not intended to achieve or duplicate the performance thresholds seen in laboratory, pilot, demonstration, or commercial fermentations. The tests conducted on site at InEnTec confirmed that InEnTec's plasma gasification technology is capable of gasifying various biomass feedstocks to produce a high-quality syngas that can be directly integrated with LanzaTech's gas fermentation process. Although the GTS fermentation cannot be directly compared to commercial scale operation, long term growth behaviour and product profiles fell within standard ranges observed on synthetic gas at LanzaTech laboratories as well as GTS control cultures on synthetic, clean, gas blends. When combined with LanzaTech's over 20,000 hours of pilot operations on MSW syngas (outside of this project), the GTS data confirm the potential for future commercial production of ethanol for ATJ production using a variety of biomass feedstocks.

3.1.2 Production of Ethanol Samples for Upgrading

Ethanol samples from the three types of biomass were produced in LanzaTech's laboratory for upgrading to jet at PNNL, using syngas produced in the InEnTec gasifier, as described in **Section 3.1.1**. Certified empty and cleaned gas cylinders were filled with syngas from each feedstock, and sent to LanzaTech's headquarters in Skokie, Illinois, for additional testing and analysis in bench scale fermenters. The goals of bench scale fermentation were to produce adequate amounts of ethanol for further processing and identify any special product recovery and separation operations needed to yield the quality of ethanol required as an ATJ feedstock. Before feeding to the laboratory fermentation system, the gas was passed through an additional clean-up system, shown in **Figure 6**. A hot copper bed was operated at 350 °C, followed by an activated carbon bed to remove organic impurities. The gas was then cooled to ambient temperature before feeding into the fermentation system.

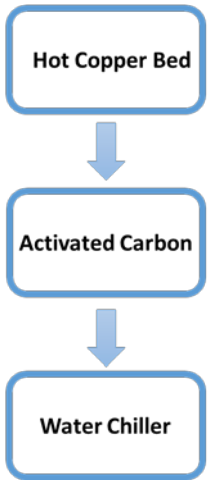

Figure 6. Gas clean up for ethanol sample production.

Before switching cultures to syngas, each fermentation was stabilized on a synthetic gas blend with a similar composition to the average of the selected syngas feed, and fermentation was operated to produce ethanol as the main product. Analytics consisted of hourly automated online GC samples to measure the input and output gas composition, and liquid HPLC samples to measure the metabolite profile. Experiments were performed at atmospheric pressure.

Fermentation performance on the syngas was varied with corn stover derived syngas being the best feedstock using the baseline clean up system (**Figure 7**). For corn stover, the culture was switched to syngas on day two, and uninterrupted fermentation ran for five days. Pine and bagasse feedstocks showed a decline in fermentation performance over time, which may be attributed to the presence of contaminants that could accumulate in the bioreactor under laboratory fermentation conditions. As a consequence, the latter two fermentations were run for longer periods in order to generate the desired quantity of ethanol.

From the laboratory fermentation runs, it was concluded that additional gas clean up was required for the pine and bagasse feedstocks. This work led to the design of a gas clean up system that will be investigated in post-project work by LanzaTech.

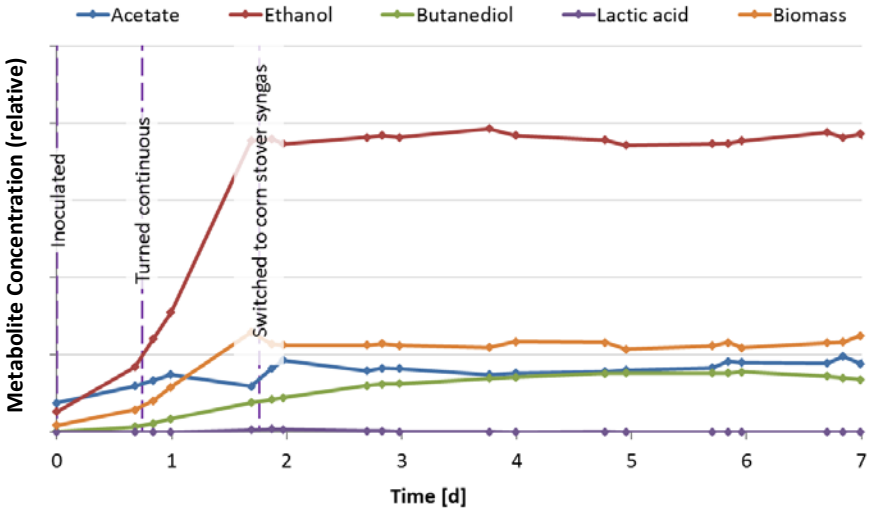

Figure 7. Metabolite profile (relative) in a bench scale fermenter running on corn stover syngas.

Broth and permeate were collected from each fermentation experiment and distilled to separate ethanol for further processing. The first 25 – 50 mL fraction of distillate is collected separately and set aside as a lights fraction since it mostly contains impurities such as hydrocarbons; the bottoms, containing heavier components, are also collected separately. Approximately 1 liter of ethanol was recovered from each syngas-derived product.

3.1.3 Ethanol Quality

The ethanol samples were analyzed in detail using both in-house equipment and an external commercial analytical laboratory. In addition to the primary metabolites of fermentation, the analyses looked for trace components that may have remained in the ethanol product after distillation. The primary fermentation metabolites were analyzed using HPLC with refractive index (RI) detection. Other organics were analysed using gas chromatography with flame ionization detection (GC-FID). Organic acids were detected using gas chromatography mass spectrometry (GCMS). Trace metals, heteroatom compounds, and total non volatiles were analysed by external analytical laboratories. Each of the ethanol samples was laboratory distilled to roughly 90% by volume to meet the contaminant requirements of ASTM D4806 “Denatured Fuel Ethanol for Blending with Gasolines”. All ethanol samples met the requirements of less than 0.5% methanol by volume, less than 5 ppmw inorganic chloride, less than 30 ppmw total sulfur, less than 4 ppmw existent sulfate, and less 0.1 ppmw copper. From the analyses and subsequent conversion at PNNL, it was concluded that standard distillation methods are sufficient to recover ethanol feedstock from fermentation broth to feed the ethanol to jet process.

3.2 Production of Jet from Ethanol

3.2.1 Process Development and Laboratory Validation

PNNL began work in 2010 to demonstrate that ethanol could be used as a feedstock for preparing an all-hydrocarbon fuel blendstock that meets standardized international specifications for jet fuel. That work was continued in the project reported here, with the specific goal of demonstrating a process to produce “synthetic paraffinic kerosene” (SPK) from ethanol that meets the requirements of ASTM D7566 Annex A5, *Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ SPK)*. PNNL

implemented the ethanol to jet process at bench scale and demonstrated that the product from upgrading to hydrocarbon met an initial set of jet specifications. Samples were prepared for internal fuel property evaluation and for off-site specification testing conducted by the AFRL, UDRI and SwRI. This testing provided key aviation stakeholders, including engine original equipment manufacturers, airlines, Federal Aviation Administration and rig manufacturers with valuable data which supported the incorporation of alcohol derived synthetic blending components into the ASTM specification for synthetic fuels, ASTM D7566 Annex A5. Fuel property data are discussed in **Section 3.3**, below.

A review of pathways to produce jet fuel from alcohols has been published by the project team [Brooks, et al. 2016]. The route pursued by PNNL and LanzaTech converts ethanol to SPK jet fuel via production of ethylene as an intermediate. Other chemistries for ethanol to SPK conversion proceed via propylene, higher alcohols, or carbonyl intermediates.

PNNL's approach to production of a highly valued isoparaffinic hydrocarbon product from ethanol was to decouple the ethanol dehydration and oligomerization reactions so the reaction conditions could be optimized for production of the isoparaffins and to control the boiling point range to maximize jet and/or diesel production without the formation of aromatic or cyclic hydrocarbons, while minimizing hydrogen requirements.

The PNNL route, at a high level, comprises three basic catalytic processes, followed by a final fractionation step to select the desired jet product cut:

- Production of the ethylene intermediate
- Oligomerization of ethylene to jet-range olefins
- Hydrogenation of olefins to paraffins

Production of Ethylene. Ethylene is produced by ethanol dehydration, which is a well-developed and commercially practiced process, recently reviewed by Zhang and Yu [2013] and Jernberg [2015]. Renewable, high purity, polymer grade ethylene has been produced commercially from fermentation-derived ethanol. Aluminum oxide, specifically gamma alumina, is the most industrially common catalyst and has been historically used due to its low cost and high stability. 99.6% conversion of ethanol to ethylene with 99.9% selectivity over silica-alumina was reported as early as the 1970s (Tsao and Zasloff, 1979).

Ethylene Oligomerization. The PNNL technology employs an oligomerization process, in which ethylene is first converted to a mixture of primarily C_4–C_6 olefins followed by further oligomerization to longer-chain olefins. Ethylene can be converted to a range of commercial chemical products such as HDPE and long chain olefins. However, activation and conversion of ethylene via conventional acid catalysts, such as zeolites, is problematic, difficult to control, and can lead to large quantities of coke, and extensive formation of aromatic compounds (up to 70 wt%). Controlled ethylene oligomerization generally uses homogeneous catalysis and selectively produces normal, linear olefins often desired as alpha olefins. Homogeneous catalysts are generally difficult to separate from the product and reuse and generally considered too expensive for producing lower value hydrocarbon products such as fuels. The literature contains reports of limited success by Heveling et al. [1998] utilizing heterogeneous Ni/Si-Al catalysts to produce open-chain hydrocarbons at high ethylene conversions, but the selectivities to ≥ C10 (jet and diesel range) of only ca 40% and to ≥ C8 of about 60%.

Others have looked at different oligomerization catalysts and processes but conversions to date are relatively low and significant quantities of aromatic compounds are produced. For example,

Synfuels International reports an oligomerization process using Ni catalysts at process temperatures from 220 °C to 240 °C that produces a product composition containing between 4% to 90% aromatics. At the reported maximum selectivity of 70% middle distillate products and an ethylene conversion of only 26%, the maximum possible product yield in the middle distillate range is only about 18%. The Synfuels International process does not improve upon and, in fact, gives a lower distillate yield than the Heveling oligomerization process

PNNL developed an oligomerization process which uses commercially derived and scaled catalysts and an overall conversion system for controlled catalytic conversion of ethylene to produce fuel-range hydrocarbon distillates containing primarily open-chain oligomers including, e.g., normal paraffins and isoparaffins. Jet range olefins can be produced with high conversion and selectivity depending on process conditions.

Hydrogenation and Fractionation. The product is fractionated using conventional technologies. PNNL has demonstrated that a fraction of the lighter olefins can be recovered from the distillate range olefins for recycling back to the inlet of the oligomerization to further increase the yield of distillate range olefins. The C8 and greater olefins are hydrotreated to produce distillate range hydrocarbons which are separated into jet and diesel range components. The oligomerization chemistry produces primarily mono-olefins which are easily hydrogenated at mild conditions with conventional hydrotreating technology and hydrogen usage is very low.

Catalyst Lifetime. PNNL demonstrated oligomerization catalyst lifetime and regeneration in bench-scale equipment. All other steps are practiced commercially. The oligomerization was operated for over 2,000 hours on stream at 85 C with a single catalyst loading, meeting the FOA objective for operating history. Two regenerations under mild conditions were carried out during the 2000 hour period. In addition, feed was interrupted during the interval when the reactor was offline and the catalyst recovered well, demonstrating robustness. After further work on oligomerization operating conditions, PNNL again demonstrated extended operations (**Figure 8**).

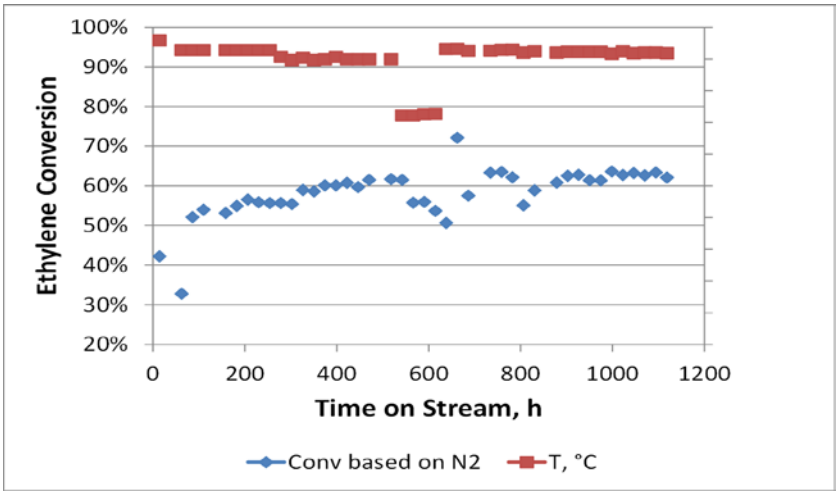

Figure 8. Follow on stability testing at bench scale using improved process conditions identified during development

PNNL also demonstrated that if aromatic content is desired for a full synthetic jet fuel, containing greater than 8% aromatic content, a different process using direct ethanol conversion could be used. Controlled ethanol conversion over an acidic zeolite catalyst, such as HZSM-5, at higher

temperatures, can undergo a number of reactions (e.g., oligomerization, dehydrocyclization, hydrogenation, and cracking) to form a complex mixture of hydrocarbon products that can be high in aromatic content. The blended combination of the tightly controlled olefin oligomerization mentioned previously with the direct ethanol conversion products would provide normal paraffins, isoparaffins, cycloparaffins, indans, tetralins, and alkylated aromatics that are needed to produce full synthetic jet fuel and/or diesel fuel. Composition of the final fuel can be controlled by the blended quantities of each product.

3.2.2 ATJ Scale Up and Production

In order to provide larger quantities of fuel for property testing and a proving flight, LanzaTech scaled up the ATJ process developed by PNNL. Commercially derived catalysts were employed for ethanol dehydration, as well as the oligomerization and hydrogenation unit operations. A commercially derived support was used to scale up the oligomerization catalyst formulation selected by PNNL.

Two sources of ethanol were used for the larger production: Lanzanol produced in one of LanzaTech's gas fermentation demonstration plants, which had been certified by the Roundtable on Sustainable Biomaterials; and, grain-based ethanol purchased commercially. As part of the scale up, the integration of ethanol dehydration and ethylene oligomerization was further optimized. A number of in-situ catalyst regenerations were performed, and optimized large scale recyle operations were developed for oligomerization. In total, over 4000 gallons of jet fuel range product was produced, with 600 gallons of diesel as a deliberate co-product. As discussed in **Section 3.3**, the jet fuel properties from the two ethanol sources were the same and comparable to SPK produced at the smaller laboratory scale.

3.3 ATJ –SPK Property Testing

ASTM D7566, the *Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons*, is accompanied by an Annex for each type of alternative aviation fuel that has been defined for use. The ASTM Aviation Fuel subcommittee defining each Annex works closely with the FAA under a consensus-based process to ensure that aviation fuel specifications meet the FAA's airworthiness requirements. In the case of significant changes to aviation fuel specifications, such as the use of synthetic blending components in jet fuel, the FAA collaborates with the aviation original equipment manufacturers (OEMs), such as aircraft, engine and aviation electronic and mechanical equipment manufacturers, to review the technical data compiled and evaluate the proposed changes.

In April 2016, ASTM D7566 Annex A5 *Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ SPK)*, defined the pathway for ATJ, however isobutanol was the only alcohol with sufficient supporting conformance data. The Annex stated that "It is the ultimate objective of this committee to permit use of all C2 to C5 alcohols for the production of ATJ-SPK once sufficient test data is available for these other alcohols".

Laboratory samples produced by PNNL were submitted to AFRL for Tier 1 Specification Properties testing. The LT/PNNL ATJ SPK product demonstrated conformance with the required product specifications set out in ASTM D7566 Annex A5. The data showed that the LT/PNNL ATJ SPK is a wide-boiling isoparaffinic kerosene, closely resembling HEFA and having a similar carbon number distribution to conventional Jet A, as shown in **Figure 9**, GCXGC of the isoparaffinic fraction. **Figure 10** compares the GC X GC of two other neat ATJ SPKs with LT PNNL ATJ SPK, clearly showing the LT PNNL SPK advantage in carbon number distribution.

Fuels made at larger scale from both Lanzanol- and grain-derived ethanol were also evaluated as neat fuels and as blended with petroleum Jet A and found to have equivalent properties.

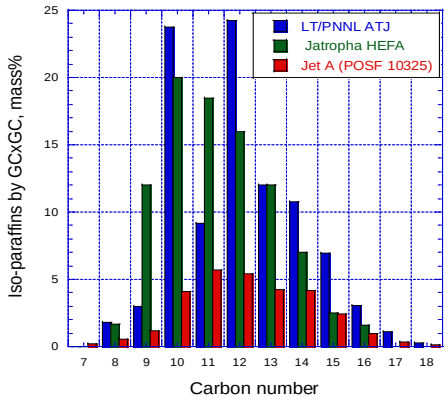

Figure 9. GC X GC Comparison of isoparaffinic carbon number distributions.

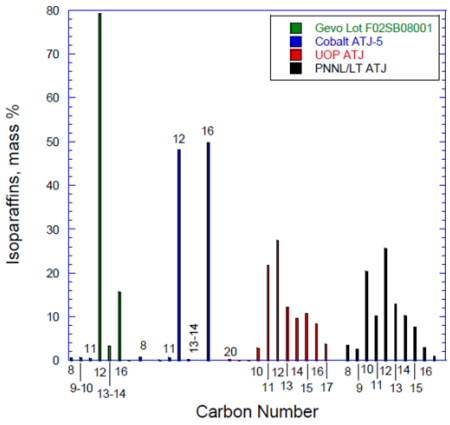

Figure 10. GC X GC for various ATJ SPKs

Key properties of the LT/PNNL ATJ fuel include:

- The LT/PNNL ATJ SPK is wide-boiling kerosene fuel with distillation results similar to HEFA and typical jet fuels.
- The aromatic content is very low and the hydrogen content quite high, consistent with the predominance of isoparaffins.
- Low freeze point indicating excellent low temperature performance.
- The thermal stability of the neat LT/PNNL ATJ SPK exceeds the ASTM D7566 Annex A5 criterion of 325 °C (passing at > 340 °C), indicating low levels of contaminants (also low existent gum).

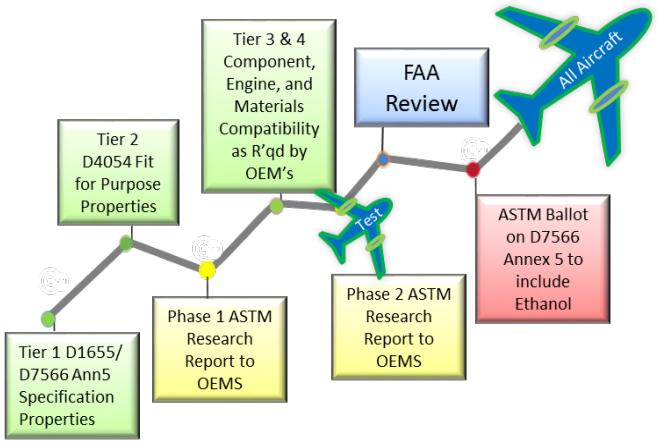

Figure 11: Illustration of OEM review process.

The additional data available on the LanzaTech/PNNL Alcohol to Jet SPK produced from ethanol were compiled into a Research Report summarizing the properties for LT/PNNL ATJ with the intent to demonstrate that a conforming SPK can be produced from ethanol (C_2 alcohol). The report follows the guidelines and methodology outlined in the current version of ASTM D4054 (D4054-16), "Standard Practice for the Qualification and Approval of New Aviation Turbine Fuels and Fuels Additives" also known as Fit for Purpose (FFP) testing. The qualification of alternative jet fuel for commercial use follows an OEM-defined testing and review process, as illustrated in **Figure 11**.

The specification and FFP test data from LT/PNNL ATJ SPK and blended fuels were compiled into a Research Report and submitted to the ASTM coordinators, the FAA and the OEMs. At the conclusion of the project, the report was in the step-by-step ASTM process, which begins with the review of FFP data by engine and aircraft OEMs (see **Figure 11**) to determine any required Tier 3 and 4 component, engine and materials compatibility testing. The ethanol based ATJ-SPK proceeded through the process and the OEM and FAA review was successfully completed.

3.4 Validation of PNNL Process Using Ethanol from Biomass Syngas.

Three one-liter samples of ethanol were produced from biomass, as described in **Section 3.1**, and sent to PNNL to validate their suitability as feedstock for the ethanol to jet process. The goal of the validation testing was to show that the biomass syngas-derived ethanol samples behaved similarly to grain-based ethanol and ethanol produced from steel-mill offgas when introduced into the ATJ process.

Ethanol Dehydration. Differences among ethanol sources would be expected to be most prominent in the first step of the ATJ process, when ethanol is converted to ethylene. To investigate the impact of ethanol source on the ethanol dehydration process, PNNL conducted an extended run in which each sample of ethanol from gas fermentation was fed to the dehydration reactor for an interval, followed by a period of grain ethanol as a reference feed, shown in **Figure 12**. The grain ethanol reference feed was 200 proof commercial ethanol diluted to 88% to emulate the concentration of the biomass-derived samples. Shaded regions represent periods when gas-derived ethanol samples were being fed; white areas represent grain ethanol. Time on stream is a factor in catalytic reactions, so for this experiment, ethane production (red squares) is used to track catalyst performance. Increasing ethane production, starting around 500 hours, reflects a chance in the dehydration catalyst that affects selectivity. When the change in catalyst with time on stream is taken into account, **Figure 12** shows that all data from all ethanol sources are within the expected range from start to finish; catalyst performance was unaffected during each transition from the reference (grain ethanol) to ethanol from syngas. Note that these data are not typical of commercial dehydration operation because the reaction was operated at >300 psig due to limitations in equipment, accelerating catalyst deactivation.

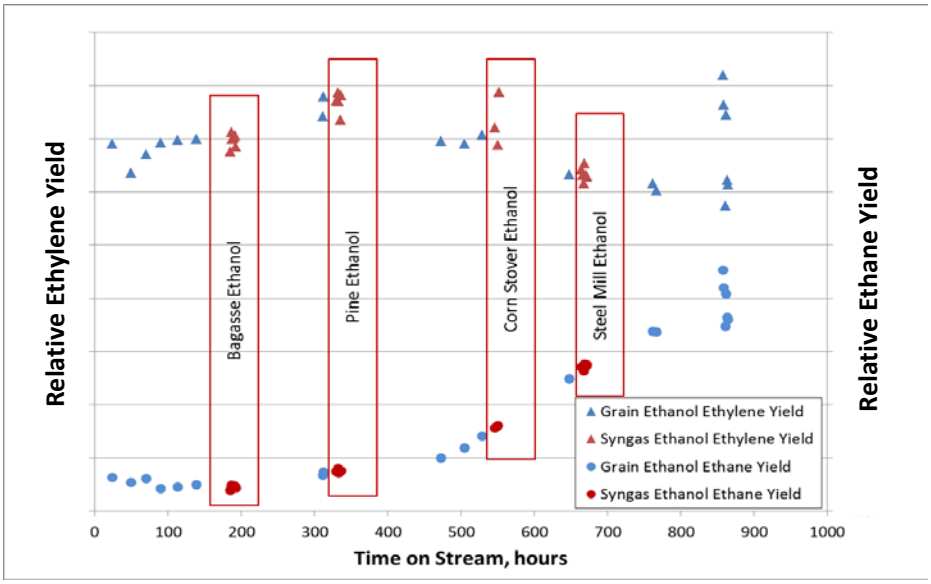

Figure 12. Impact of ethanol source on ethanol dehydration at bench scale. From left to right, the gray regions represent ethanol produced from: bagasse, pine, corn stover, and steel mill offgas.

Figure 13 shows the impact of ethanol source on oligomerization performance, clearly demonstrating that the effect is independent of ethanol source.

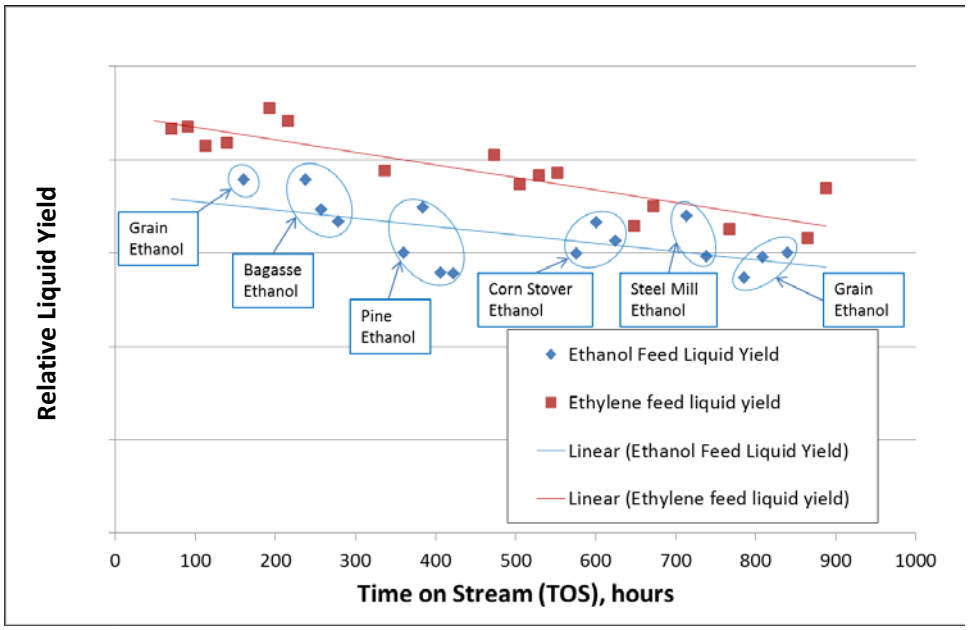

Figure 13. Impact of ethanol source on oligomerization.

3.5 Co-Production of 2,3-Butanediol

Fermentation process development for enhanced 2,3-BDO production was outside of the scope of the project and pursued in parallel. The two areas addressed within the project were:

- Development of an alternative to distillation for separating 2,3-BDO from fermentation broth
- Development of a catalytic method to upgrade 2,3-BDO to butadiene or other chemical intermediates

3.5.1 2,3-BDO Separation

Separation of 2,3-BDO from fermentation broth presents an economic challenge because its boiling point (177 °C) is well above that of water. This means that traditional methods would incur a significant energy cost to effectively distill water, the majority component in fermentation broth, from 2,3-BDO. Orochem Technologies, Inc., has over the last decade developed various chromatographic tools, in particular a Simulated Moving Bed (SMB) continuous chromatographic process, targeted towards the purification and separation of various pharmaceutical intermediates, fatty acids, sugars and petrochemicals.

Samples of fermentation broth containing ethanol and 2,3-BDO were sent to Orochem to support development of a cost-effective 2,3-BDO separations scheme using the SMB technology. The fermentation broth contained a dilute mixture (< 8% by weight) of alcohols such as ethanol and 2,3-BDO in water along with various salts and nutrients. Orochem developed a recovery scheme employing the SMB process, which combined proprietary adsorbents and novel process schemes to provide an economical route to the production of these alcohols.

The primary task in developing an SMB process for this application was to study the various adsorbents for the chromatographic process. Both commercial and proprietary adsorbents were tested using simulated broth, leading to selection of an Orochem proprietary adsorbent. Based on experiments with both simulated and real fermentation broth, a guard bed was designed to eliminate soluble proteins from the SMB feed. A method for regenerating the guard bed was designed and validated by demonstrating that similar adsorption profiles were obtained after regeneration of the bed. The SMB development continued with lab-scale investigations of extraction solvents and process design options to reduce capital and operating costs of desorbing the alcohol products. This work was continued at the pilot scale outside the scope of the project, leading to a full SMB system design for separation of 2,3-BDO co-produced with ethanol.

3.5.2 2,3-BDO Conversion (PNNL)

The catalysts and process developed by PNNL to convert 2,3-BDO to BD are the basis for a patent issued to PNNL (US9434659). The conversion of 2,3-BDO to BD is a dehydration reaction requiring the step-wise elimination of two equivalents of water **(Figure 14).** Dehydrations are catalyzed by acid catalysts; the nature of the catalyst determines the selectivity of the reaction. With normal Brønsted acid catalysts, such as alumina, alumino-silicates, and sulfuric acid, water is eliminated across C2-C3 via a carbonium ion intermediate, forming a reactive enol that rapidly isomerizes to undesired methyl ethyl ketone (MEK), itself a valuable product. Certain metal oxide catalysts, however, dehydrate via a different mechanism to eliminate across C1-C2 forming the olefin-alcohol (methyl vinyl carbinol, MVC). MVC can be dehydrated with high selectivity and yield to BD. Therefore, catalyst discovery in this project focused on metal oxides with a goal of forming either MVC or BD while minimizing or eliminating MEK.

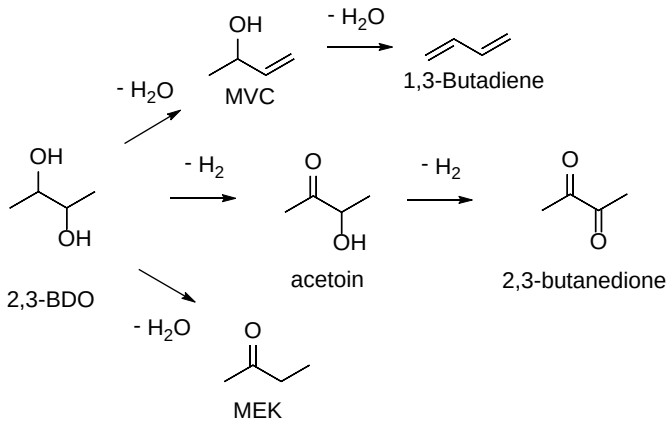

Figure 14. Competing reactions for conversion of 2,3-BDO to products.

Seven catalysts identified by PNNL in a previous CRADA formed the starting point for development, and suggested additional compositions for screening. Approximately 40 catalysts were synthesized and screened in a high-throughput Flowrence® system. This system is an Avantium® unit, consisting of 4 units of 4 parallel fixed bed flow micro-reactors or 16 total reactors capable of autonomous operation with computer control over temperature, flow, pressure and on-line analysis for high-throughput catalyst discovery. The best catalysts from the high-throughput testing were down-selected and then validated in a 1-5cc fixed bed flow reactor. One catalyst in particular vastly outperformed the others, showing high selectivity for MVC (70%) with low selectivities to MEK (1%) and BD (<1%) at 50% conversion.

Catalyst testing was conducted using commercial 2,3-BDO. For validation and BD sample production, LanzaTech provided 2,3-BDO samples produced in its laboratories and in the Columbo pilot unit at Freedom Pines.

To produce a 50cc sample of BD, PNNL set up two separate flow reactors. In the first reactor, MVC was produced from 2,3-BDO using PNNL's proprietary catalyst. This reactor was operated for approximately 10 days in order to produce a sufficient volume of MVC to be further upgraded to BD. As the MVC was produced and collected, it was stored in a freezer unit as a precaution against product degradation. The collected MVC was then passed through the second reactor containing a solid acid catalyst. The second reactor was operated for approximately 60 – 70 hrs. The final BD product was distilled and cryogenically transferred into a transport bomb.

During stage one, conversion of 2,3-BDO was up to 80% and the yield to MVC was up to 70 mole%, with 2 – 3 % MEK, < 1 % BD (approx.) and the remainder acetoin and 2,3-Butanedione (10 – 15% combined yield). Nearly 100% yield of BD from MVC was observed in the second

reaction. This exceptional yield was the result of optimizing process conditions such as feed flowrate and reactor temperature profile.

The final BD product was analyzed by an outside vendor and found to be approximately 98% BD, with the primary side-products being butenes which are relatively easy to remove in any future commercial process. The BD product was evaluated by a commercial partner outside of the project and found to be suitable for downstream polymerization.

This work validated that 2,3-BDO from gas fermentation can be successfully upgraded to BD using PNNL's proprietary catalyst platform at 70% yield, producing a high quality product for use as a chemical intermediate.

3.6 Technoeconomic and Lifecycle Analysis

3.6.1 Summary of Technoeconomics

LanzaTech conducted technoeconomic analyses (TEA) of the project technology for multiple cases. The TEA was based on public data sources for plasma gasification, LanzaTech internal gas fermentation process models, an ATJ process model developed by PNNL, and LanzaTech internal process models for 2,3-BDO separation and conversion to BD. Because the goal of the project is to produce hydrocarbon fuels, the capital and cash costs of distillate production are emphasized here.

Gasification. Transformation of solid waste biomass to syngas ($CO + H_2$). Inputs for feedstock handling were from an NREL study (Worley and Yale, 2012). The gasifier model is based on public sources of information (Dutta, 2011) for the operation of a commercial sized gasifier regarding syngas yield and utility usage. The syngas composition is taken from the actual pilot gasifier runs for each biomass feedstock. Commercial scale is set at 2,000 tonnes per day of dry biomass, although smaller units could be considered, even down to 500 tpd. Biomass to syngas yield is somewhat dependent on the type of biomass used, with values varying between 1.8 Nm^3 syngas per kg dry biomass (corn stover) and 2.2 Nm^3 syngas per kg biomass (waste pine wood) for the analyzed types (LanzaTech analysis).

Fermentation. Syngas fermentation via the LanzaTech process to produce alcohols (ethanol and 2,3-BDO). The modeled process includes product recovery, either ethanol or ethanol + BDO, as well as waste water treatment.

Ethanol-only. Ethanol is the main product of the LanzaTech fermentation. In the ethanol-only case, the rest of metabolites produced are not recovered and simply treated as by-products in the wastewater treatment system. Ethanol is recovered via distillation for use as transportation fuel or, as assumed in this project, to be further transformed to hydrocarbon fuels such as jet blendstock and diesel fuel.

Ethanol + BDO. The main fermentation co-product of the LanzaTech process is 2,3-BDO. The fermentation process can be run under conditions that either inhibit or promote the formation of BDO. For the techno-economic analysis we looked at three distinct cases: ethanol-only, and ethanol to BDO mass ratios of 2:1 and 1:1. 2,3-BDO is not a commercial product, in that there is no current commercial market for it[2], therefore this analysis included its conversion to BD.

[2] It is important to distinguish between the 2,3-BDO product discussed here and other isomers, such as 1,4-BDO, that are sold commercially.

BDO to BD. BDO is selectively dehydrated to 1,3-butadiene (BD). This process has been modeled with a 90% BDO conversion and a 94% selectivity to BD. Considering the difference in MW between BDO and BD, the mass yield of BD from BDO is about 0.54. Note that this analysis differs from that presented in the Foreword, which treated MEK as the main product, and BD as the by-product, since MEK was more valuable in the basis year of the GPRA analysis.

ATJ. Product ethanol is further processed to distillate-range hydrocarbon fuels, via the LanzaTech-PNNL ATJ process. The ATJ process consists of the dehydration of alcohol into ethylene, ethylene oligomerization into longer olefins, olefin saturation via hydrogenation into paraffins, and final distillation into commercial fuels (gasoline, jet blendstock, diesel). Due to the reduction in mass from water generation (dehydration step) and process efficiencies, the mass yield from ethanol to distillate is modelled at 0.56.

Capital Costs. Capital costs are a large driver for the profitability of the overall process, as well as of its individual sections (gasification + fermentation + recovery + BDO to BD + ATJ.)

Figure 15 illustrates the dependency of total CAPEX (gasification + fermentation + recovery + alcohol transformation) on biomass type and the BDO:ethanol mass ratio in the fermentation products. Clearly, the effects of BDO/BD co-production on CAPEX are significant, adding a burden to the overall production process.

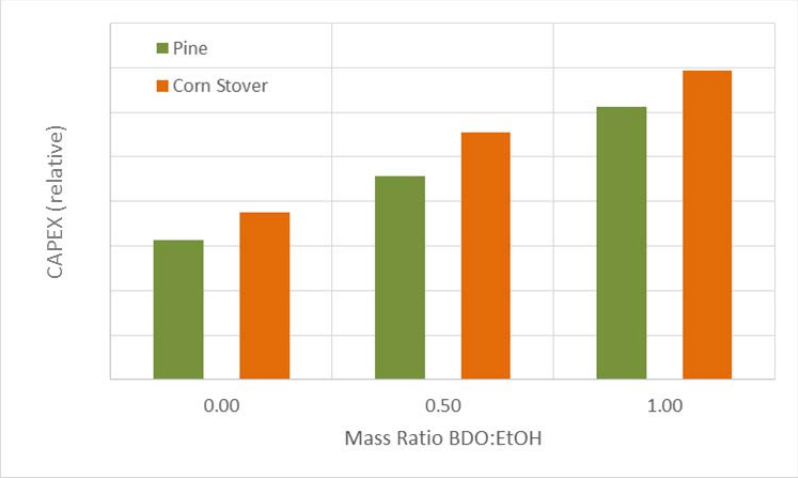

Figure 15. Impact of co-product ratio on CAPEX apportioned per KMTA of final distillate product.

Sensitivities. Feed biomass cost is the largest single component in the final cash cost of production (CCOP) of the distillate fuel, contributing 30% of total OPEX. **Figure 16** shows the effect of biomass cost on the CCOP of distillate for the six cases considered. As expected, the distillate CCOP is lower in cases of co-production of BDO/BD because BD credit lowers the total operational expense. However, it is also worth noting that increasing the co-product ratio increases dependency on the cost of feed biomass.

The distribution of fermentation products (ethanol vs. ethanol + BDO) is also another important variable affecting the final cash cost of the distillate fuel.

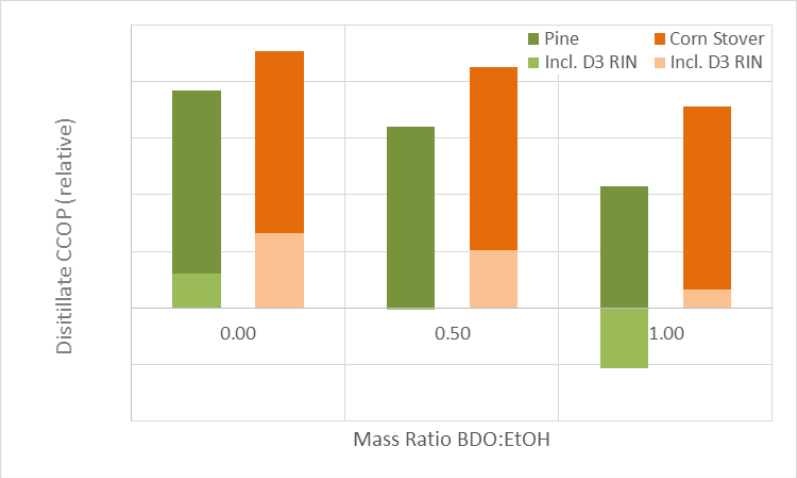

Figure 16. Impact of co-product ratio on distillate CCOP.

Conclusions. The effects on cost for the co-production of ethanol + BDO vs. ethanol alone are relatively complex. The primary cost impact of the co-product is to lower the CCOP of the main product by providing a credit towards its costs. This credit can be quite large, even turning the CCOP of the main product negative with sufficiently low biomass feed costs, as illustrated in **Figure 16** for the 1:1 EtOH:BDO case from free ($)/MT) pine biomass. A second major impact on the cost is the reduction of primary product volumes due to production of the co-product; the production of BDO reduces the amount of ethanol product and therefore the quantity of distillate produced from biomass.

Capital costs for the overall process are distributed into 3 areas: gasification, gas fermentation, and ATJ. Of the three major process sections, the ATJ (ethanol to jet) conversion is the smallest contributor to CAPEX. Process integration, both within and between units, represents a major opportunity to reduce both CAPEX and OPEX. For example, as modeled here, gasification utility usage is quite high, but there is significant potential for reduction through design modifications that integrate utility use and maximize heat recovery between gasification and fermentation.

3.6.2 Life Cycle Assessment Summary

Life cycle assessment summary

MTU conducted life cycle assessments (LCA) studies in several stages based on data availability, ultimately developing a full life LCA of the biomass-to-jet system. In this summary, we summarize the sources of data for the LCA study, describe initial results, describe second-iteration results including data from pilot scale experiments and additional modeling, and discuss implications of the study and recommendations for future work. More information on the LCA work from this project was described in two national presentations for the American Institute of Chemical Engineering, as well as one journal publication (Handler et al. 2015) and one book chapter (Brooks et al., 2016), which can be referenced for additional detail.

A simple system schematic can be seen below (**Figure 17**), which details the key unit operations and inputs of materials and energy at each stage of the process. The goal of the LCA modeling effort was to characterize the greenhouse gas (GHG) emissions and global warming potential, measured in CO_2-equivalents (CO_{2eq}) for each megajoule of jet fuel produced. The study was cradle-to-grave in nature, beginning with inputs and consequences of biomass procurement, and

proceeding until fuel use and combustion. As a default assessment, a system expansion and displacement allocation was performed to account for the impact of co-product development and use, consistent with the approach favored by the US EPA, but other co-product allocation systems were also evaluated.

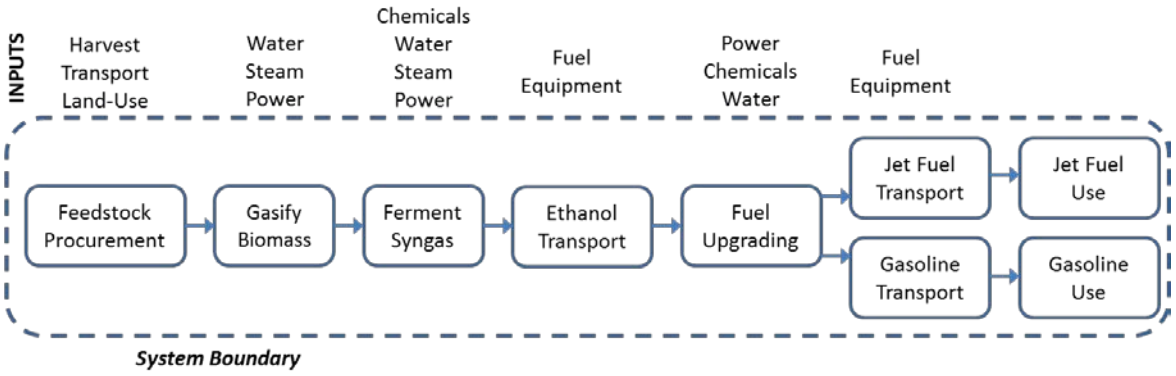

Figure 17. Schematic of biomass to jet system used for life cycle assessments.

LCA input data summary

Biomass procurement: Data on the inputs required for biomass procurement came from Johnson et al. (2012) for forest biomass, which characterized impacts of harvesting and collecting forest thinnings in different regions of the US. The Argonne National Lab GREET LCA model (ANL 2014) was the source of biomass procurement data for corn stover. Each of these data sources also characterized GHG emissions impacts due to land use change for these feedstocks, which involved detailed assumptions about direct and indirect effects of increased biomass procurement, and those impacts are included in the study as well. Carbon is sequestered in the biomass when the biomass is grown, and this carbon sequestration was taken as a credit in the initial stage of the LCA. Carbon emissions from this system into the environment during all later stages of the process were also counted towards the cumulative GHG emissions of the system.

Biomass gasification: Data were developed by MTU from consultation with LanzaTech process engineers. Gasification data from two different sources and gasifier types have been used: 1) a steam gasification system similar to the process described in Dutta (2011), and 2) a plasma gasification system modelled at commercial scale.

Syngas fermentation: Data on inputs of materials and energy for syngas fermentation also came from consultation with LanzaTech process engineers. Process data for this stage was initially based on lab scale performance, which was then updated to reflect the performance of a larger pilot scale reactor, extrapolated to commercial scale.

Ethanol transport: Ethanol was assumed to be transported 100 km using a large transport truck, as characterized within the Ecoinvent database (Weidema et al., 2013)

Ethanol upgrading: Data to characterize production of gasoline and a distillate jet/diesel fuel fraction from ethanol was provided by PNNL researchers, based on their experience with this catalytic upgrading process.

Fuel transport: Jet fuel and the gasoline co-product were each assumed to be transported 100 km using a large transport truck as characterized within the Ecoinvent database (Weidema et al., 2013).

Fuel combustion: GHG emissions from fuel combustion were estimated according to stoichiometry. In the displacement allocation scheme, a credit is given for the gasoline product due to avoided production of gasoline, but the gasoline was still combusted, so emissions for the proportional amount of gasoline combustion are included in this life cycle.

LCA: Modeling for the LCA study was performed in SimaPro. Inventory items for materials and energy in the system were represented by analogous items in the Ecoinvent database (Weidema et al., 2013) to characterize the full life cycle inventory of the system, except for the use of electricity. Data from the US EPA (US EPA, 2015) was used to represent the nationwide mix of US electricity generation sources as it existed in 2012, which was the most current data available, and provides a more realistic assessment of the environmental impacts of electricity production and use than the Ecoinvent database.

LCA Results

Early results indicated that GHG emissions from jet fuel production and use in this production system would be quite favorable compared to fossil fuel alternatives. As reported in Handler et al (2015), ethanol production for the forest biomass-based system and the corn stover-based system would be 1.5 g CO_{2eq} / MJ and 8.0 g CO_{2eq} / MJ, respectively, which represent over 90% GHG emissions savings compared to fossil gasoline (94 g CO_{2eq} / MJ) (Elgowainy et al., 2015). Considering the full system including jet fuel production and use, the GHG emission results were still quite favorable. Life cycle GHG emissions for forest residue and stover-based jet fuel would be -8.2 g CO_{2eq} / MJ and -1.2 g CO_{2eq} / MJ, respectively. When using forest biomass, a large quantity of carbon is sequestered in the growing biomass, which counteracts the emissions of carbon later in the process. Emissions due to land-use change for both of these feedstocks are anticipated to be minimal. Under the assumptions of a steam-based gasification system, all of the utilities for biomass gasification and fermentation could be generated from the latent heat of the hot syngas stream, with even an excess of power produced and exported as a co-product, which is an important benefit to the process. Impacts due to jet fuel production are small, as are the product transport stages.

The base case scenario is an update also involving a similar steam gasification system, but coupled to updated fermentation results. Utilities can be provided by using latent heat from the gasified syngas stream, and a small electricity credit is even awarded for excess electricity that is produced in the system and exported to offset electricity use elsewhere. The ethanol yield per unit of biomass input is quite high, reflecting syngas properties with an ideal steam gasification system, where less of the carbon-containing syngas is present as CO_2 and more CO is produced. Life cycle GHG emissions for jet fuel in this case would be -10.0 g CO_{2eq} / MJ jet fuel (forest residue feedstock) or 10.1 g CO_{2eq} / MJ jet fuel (corn stover feedstock). Significant GHG reductions (of 110% and 88% respectively) compared to the reference emissions standard for fossil petroleum jet fuel (86.4 g CO_{2eq} / MJ) (Elgowainy et al., 2015), are therefore achievable. If the system was focused only on ethanol production and combustion, life cycle GHG emissions results for ethanol in this case would be -0.4 g CO_{2eq} / MJ ethanol (forest residue feedstock) or 11.5 g CO_{2eq} / MJ ethanol (corn stover feedstock).

A second scenario was modeled using a commercial plasma-based gasification system, which requires a large quantity of electrical power (for the plasma system) as well as an input of enriched-air. Overall utility requirements are therefore higher than for the steam gasification baseline due to external electricity. Plasma gasifiers have been demonstrated successfully at commercial scale

and therefore offer a more robust near-term gasification platform than do steam gasifiers. Plasma gasifiers are designed to tackle difficult solid feedstocks (such as MSW or other types of mixed solid wastes) and could be streamlined for biomass feedstocks. In the future, three options to reduce GHG burdens of final fuel while using plasma gasifiers are recommended:

a) Use of complex waste feedstocks. In these cases extra emissions credits can be claimed for utilizing these materials for manufacturing instead of disposal without any benefits. The extra avoided emissions (from lack of landfilling, etc.) can compensate for some or all of the extra emissions from higher utility use.
b) Changes in gasifier configuration and operation for “easier” biomass feedstocks, lowering utility consumption as well as improving syngas composition.
c) Use of renewable power for the external electricity, reducing fossil CO_2 emissions from the grid.

The wide range of LCA results for GHG emissions for different configurations of the system, especially gasifier types, highlight the importance of validating system performance at large scales, to test assumptions surrounding inputs of materials and energy. The integration of unit operations to yield system benefits, such as the use of latent heat to provide utilities for downstream unit operations, is also important to consider in a system-wide view, which is easy to minimize when focusing on the technical performance of individual unit operations in isolation. Serious consideration should be given to the tradeoffs of technical performance, economic considerations, and environmental impact in this system, especially when evaluating different gasification systems.

4 Publications and Technology Transfer Activities

4.1 Publications and Presentations

The following publications and presentations were prepared under this project:

Review chapter on ATJ process, including LCA:

K.P. Brooks, L.J. Snowden-Swan, S.B. Jones, M.G. Butcher, G.-S.J. Lee, D.M. Anderson, J.G. Frye, J.E. Holladay, J. Owen, L. Harmon, F. Burton, I. Palou-Rivera, J. Plaza, R. Handler, D. Shonnard . "Chapter 6: Low-Carbon Aviation Fuel Through the Alcohol to Jet Pathway". Appears in *Biofuels for Aviation: Feedstocks, Technology and Implementation*. Editor: Christopher Chuck. Academic Press, 2016. 390p.

University of Delaware publication on catalyst modeling:

Wulfers, M. J and Lobo, R. F. Assessment of mass transfer limitations in oligomerization of butane at high pressure on H-beta. *Applied Catalysis A: General* 505 (2015) 394–401.

Life cycle assessment of ethanol production:

Handler, RM, Shonnard, DR, Griffing, EM, Lai, A, and Palou-Rivera, I. "Life Cycle Assessments of ethanol production via gas fermentation: anticipated greenhouse gas emissions for cellulosic and waste gas feedstocks." *Industrial & Engineering Chemistry Research* 55, no. 12 (2015): 3253-3261.

Presentation on life cycle assessment of jet fuel from ethanol:

Handler, R. M. *et al.* Life Cycle Assessments of Jet Fuel and Co-Products Made from Lanzatech Biomass-Based Ethanol. in *AIChE National Meeting* (2014).

4.2 Technology Transfer and Commercialization Activities

Patent Applications and Licensing Agreements

As a result of this work, four PNNL patents were in progress at the time the project closed.

Collaborations

Work conducted in this project contributed to the development of industrial collaborations with Invista and SKI on utilization of 2,3-Butanediol and with Virgin Atlantic, Boeing and HSBC for ATJ scale up and fuel production.

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