U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) 2017 Project Peer Review

A Hybrid Catalytic Route to Fuels from Biomass Syngas

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Biochemical Conversion

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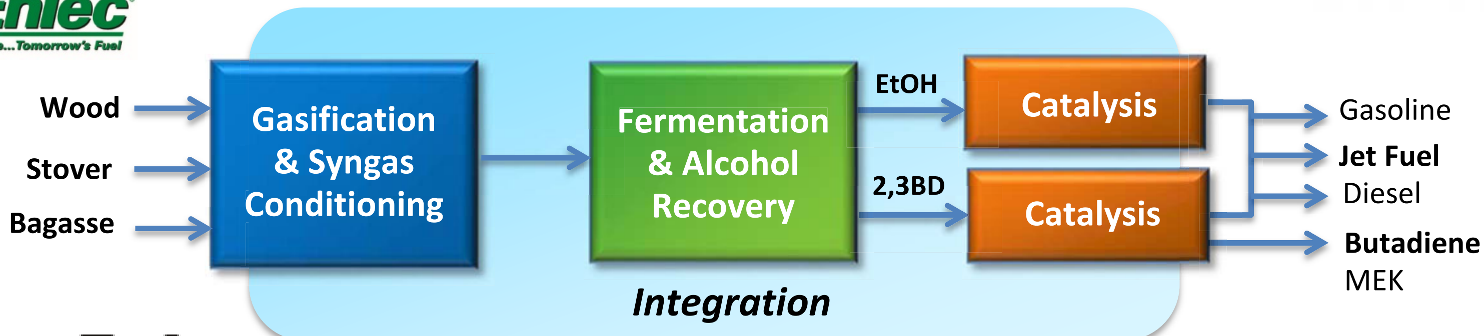
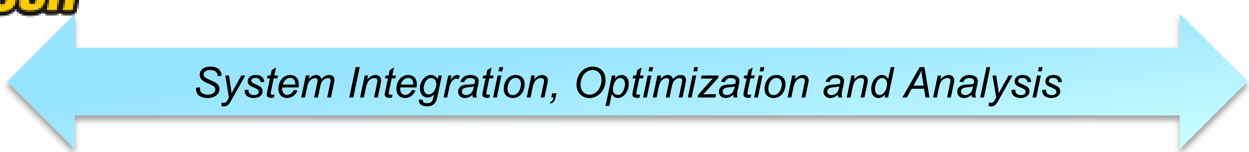
Project Goal

Develop a hybrid conversion technology for catalytic upgrading of biomass-derived syngas to produce Alcohol-to-Jet (ATJ) fuel and chemicals while meeting the cost, quality and environmental requirements of the aviation industry.





Cost-competitive sustainable alternative jet fuel

Quad Chart Overview

Timeline

- Project Start: April 2012
- Project End: September 2016
- Percent Complete: 100%

Budget

	Total Costs FY 12 –FY 14	FY 15 Costs *	FY 16 Costs	Total Project
DOE Funded				
LanzaTech and Partners	$921,624	$0	$559,139	$1,480,763
PNNL	$990,846	$0	$995,566	$1,986,412
NREL	$425,390	$0	$105,110	$546,146
Cost Share				
LanzaTech and Partners	$262,667	$0	$1,578,652	$1,841,319 (31.53%)

**FY 15 work was not invoiced until FY 16*

Barriers *(Specific to Gaseous Intermediates Pathway)*

- **Ct-F**. High Temperature Deconstruction to Intermediates: Gasification of multiple biomass types to produce syngas **Ct-G**. Intermediate Cleanup and Conditioning: investigate minimum necessary gas cleanup and conditioning requirements for syngas fermentation.
- **Ct-H**. Catalytic Upgrading of Gaseous Intermediates: Biocatalytic upgrading of syngas to Ethanol and 2,3-BDO and thermocatalytic upgrading to jet and butadiene.
- **Commercial barrier**: Sufficient fuel to support alternative jet fuel qualification: Produced large jet fuel samples from multiple ethanol sources and measured Fit-for-Purpose properties for OEM review.

Partners

LanzaTech: Project Lead, Project Management, Integrated TEA, Syngas Gasification and Fermentation Lead, Commercialization Partner, Analysis Support
PNNL: Catalytic Alcohol Conversion Lead, Catalyst-Fermentation Integration, TEA Modeling
Imperium Renewables: Commercialization, Market and Engineering Analysis
Orochem Technologies: Advanced Alcohol Recovery
Michigan Technological University: Life Cycle Assessment
University of Delaware: Alcohol Conversion Catalyst Fundamentals
InEnTec: Biomass Gasification
The Boeing Company: Commercialization Support and Aviation Industry Analysis

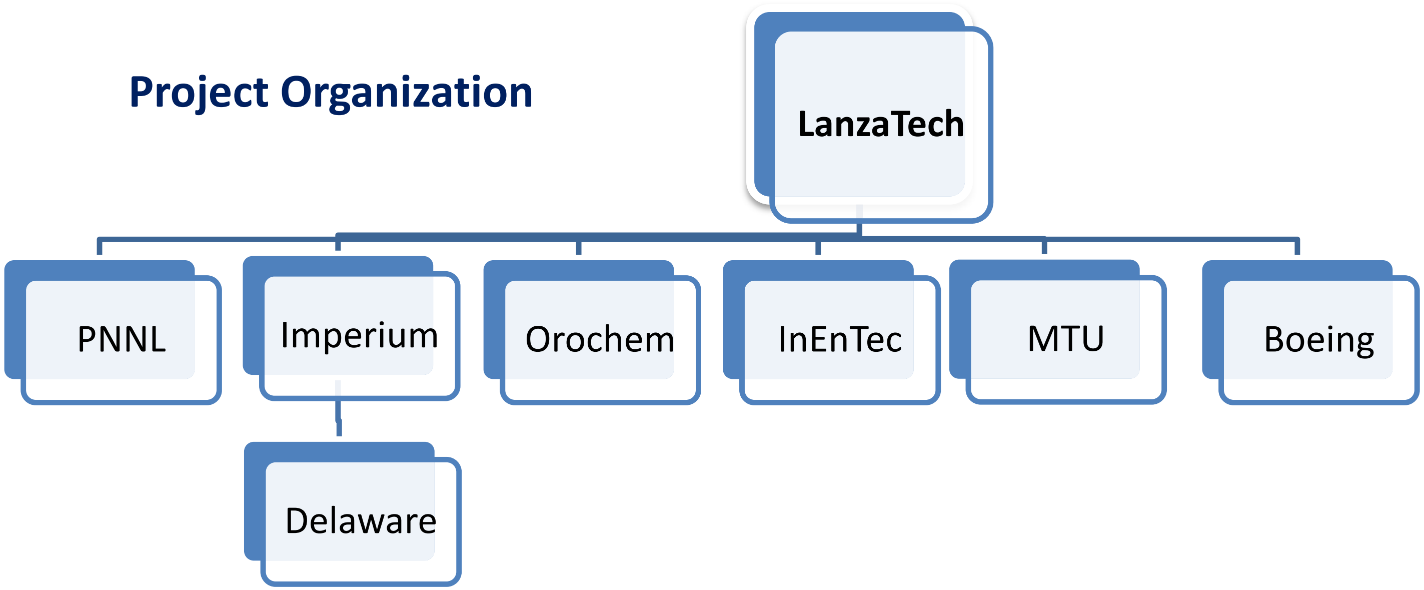
1 - Project Overview

- **Demonstrate that gasification of corn stover, woody biomass, and bagasse produces syngas suitable for gas fermentation**
- **Demonstrate that ethanol from gas fermentation is suitable for catalytic conversion to jet fuel blendstock**
- **Demonstrate Alcohol-to-Jet (ATJ) Synthetic Paraffinic Kerosene (SPK) process for converting ethanol to jet fuel with over 2000 hours of operation**
- **Show that the LanzaTech/PNNL ATJ SPK process produces high quality distillate**
- **Show that the LanzaTech/PNNL ATJ SPK process can be economic at commercial scale, with > 50% GHG reductions**
- **Supporting goals discussed in prior Peer Review Meetings**
  - Establish technical feasibility and economic benefits of chemical co-production, specifically 2,3-Butanediol for conversion to commodity chemicals such as Butadiene
  - Develop mechanistic and kinetic models of key catalytic steps in ATJ process

2 – Approach (Management)

Approach (Management)

Project Organization



- LanzaTech responsible for coordinating directly with the DOE on all project activities, including technical progress and financial reporting
- Project monitoring achieved through the tracking of key milestones that relate to each major project task and ensuring the actions associated are completed by the required party
- Effective integration of each sub contractor into the project is assured through regular project reviews and technical interactions

Approach (Management) - Task Organization

Task A: Gasification Fermentation Interface
LanzaTech
Develop and demonstrate an integrated gasification and fermentation process for commercial jet fuel production

Task B: Prepare Alcohol Intermediates
Production/EtOH Separations: *LanzaTech*
2,3 BDO Separations: *Orochem*
Produce 2,3BDO and ethanol samples for upgrading

Task C: Catalytic Upgrading
PNNL / Imperium Aviation Fuels (IAF)
Develop and demonstrate catalytic conversion of alcohols to chemicals and hydrocarbon fuels

Task D: Catalyst Fundamentals
Univ. of Delaware / PNNL
Develop mechanistic understanding of conversion catalysts to improve performance

Task E: Production of Hydrocarbon Fuels
PNNL / LanzaTech
Produce hydrocarbon fuels for analysis and fit-for-purpose testing

Task F: Product Evaluation
PNNL / Boeing / IAF / LanzaTech
Validate jet fuel properties from hybrid processing route

Task G: Techno-Economics & Life Cycle Analysis
LanzaTech / MTU / NREL / PNNL / Boeing
Identify additional integration opportunities. Estimate the input requirements, costs, and environmental impact of the integrated process.

2 – Approach (Technical)

Approach (Technical)

Determine impacts of syngas contaminants on fermentation productivity and stability, with the goal of optimizing syngas cleanup costs

Optimize alcohol upgrading catalysts and process conditions by high throughput screening, mechanistic/kinetic studies and computation

Validate suitability of ethanol from gas fermentation as a feedstock for alcohol to jet conversion

Validate process stability through extended process operations and establish commercial formulation for new catalyst

Transfer ATJ technology from PNNL to LanzaTech for scale up to validate catalyst performance, operating conditions and fuel properties, leading to an integrated process design

Technical Challenges:

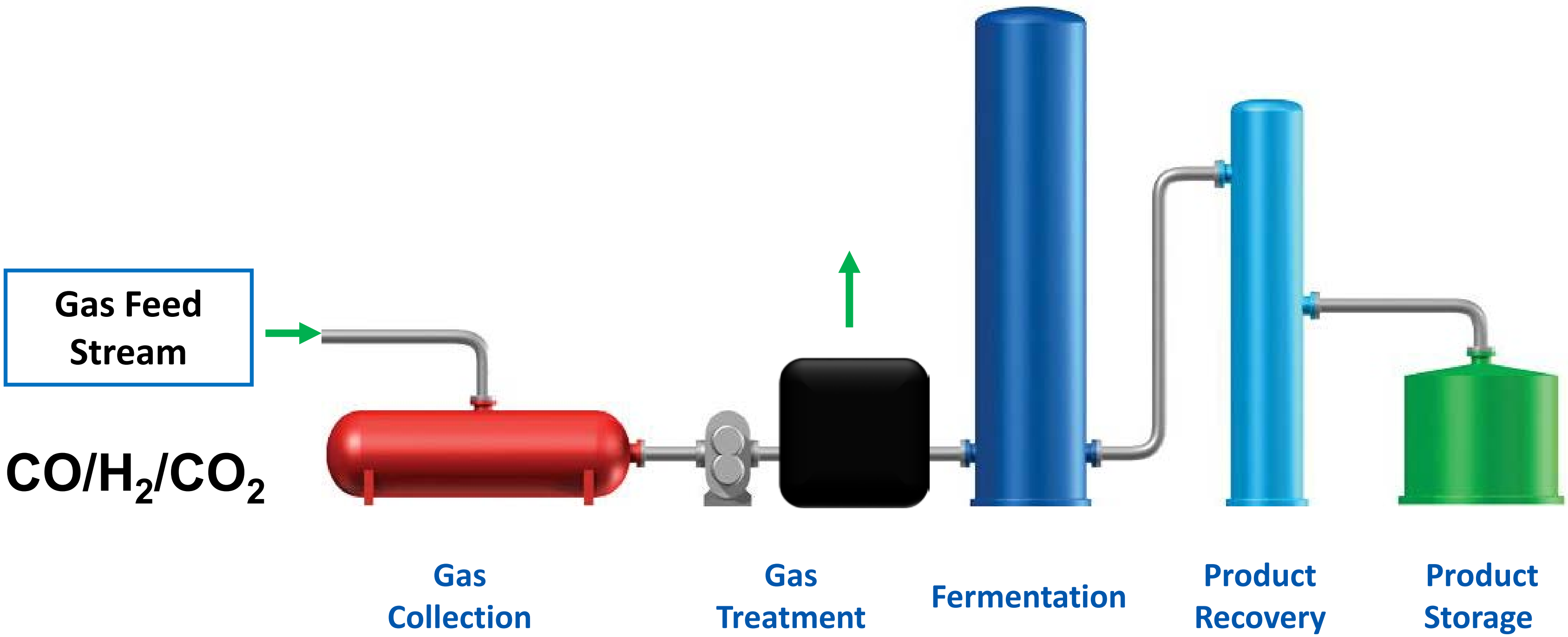
- Gasification commissioning and operation – addressed by InEnTec addition to team
- 2,3-BDO recovery – addressed by Orochem system design
- Catalyst development for ethanol to jet conversion – addressed by PNNL studies and LT scale up

Approach (Technical)

- **PNNL conducted AOP and commercialization projects during hiatus**
  - Validated ATJ SPK process on ethanol from steel mill offgas and grain
  - Produced ATJ SPK samples in support of Specification Properties and Fit for Purpose testing by AFRL, UDRI and SwRI
- **Final project period focused on**
  - Syngas-fermentation integration and validation
  - Alcohol to jet (ATJ) SPK catalyst/process scale up and fuel production
  - Demonstration of ATJ SPK feedstock flexibility
- **Approach for final project period**
  - InEnTec joined project team as gasification partner for integrated operation and syngas sample production
  - ATJ SPK process demonstrated at pilot scale
    - Catalyst for critical ATJ SPK step scaled up for custom production
    - Unit operations integrated at pilot scale
    - Fuel produced in support of ASTM fuel qualification process

3 – Technical Accomplishments/ Progress/Results

Gas Fermentation Overview



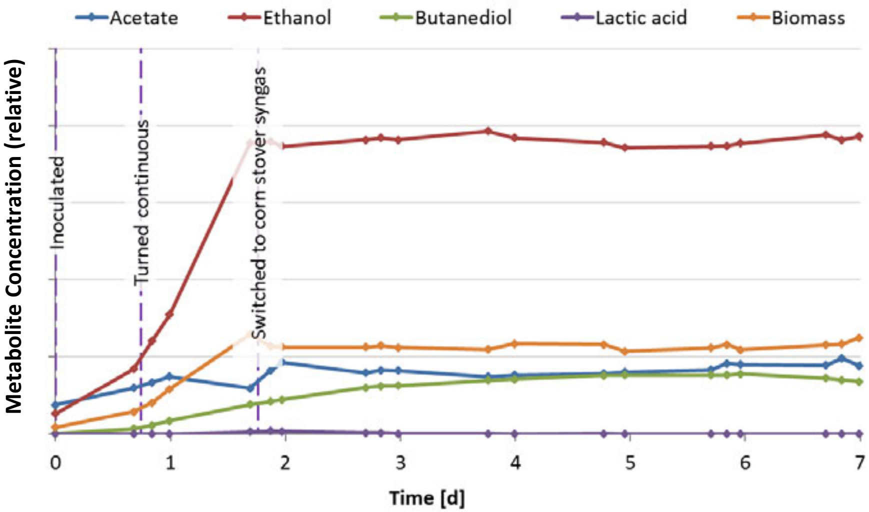
Continuous microbial fermentation –
gases are sole source of carbon and energy

Gasification-Fermentation Integration

Validated integrated operations and gas cleanup requirements

Continuous operation of mobile fermentation unit integrated with InEnTec pilot gasifier in Richland, WA

Continuous lab-scale ethanol production from corn stover syngas*

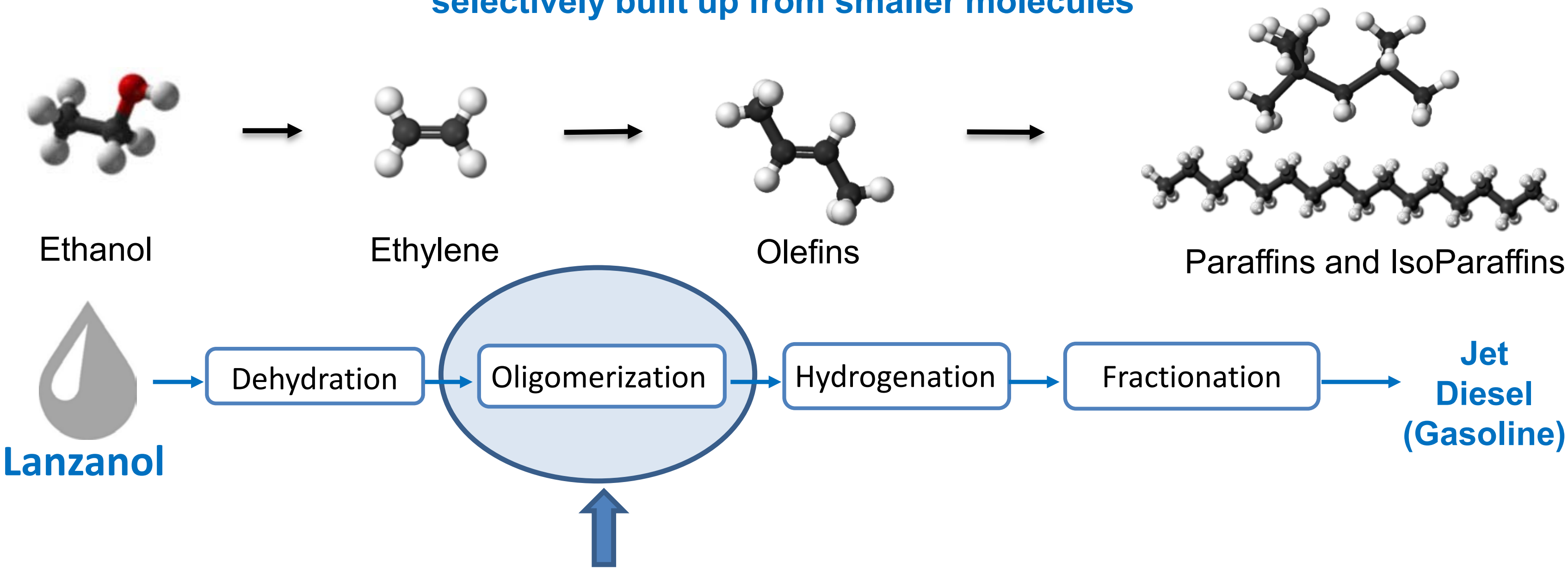


Produced ethanol samples in lab from corn stover, pine & bagasse syngas to validate upgrading.

**Proof of concept data, not representative of at-scale production*

LanzaTech/PNNL Alcohol to Jet Process

Jet range hydrocarbons (C8-C16)
selectively built up from smaller molecules



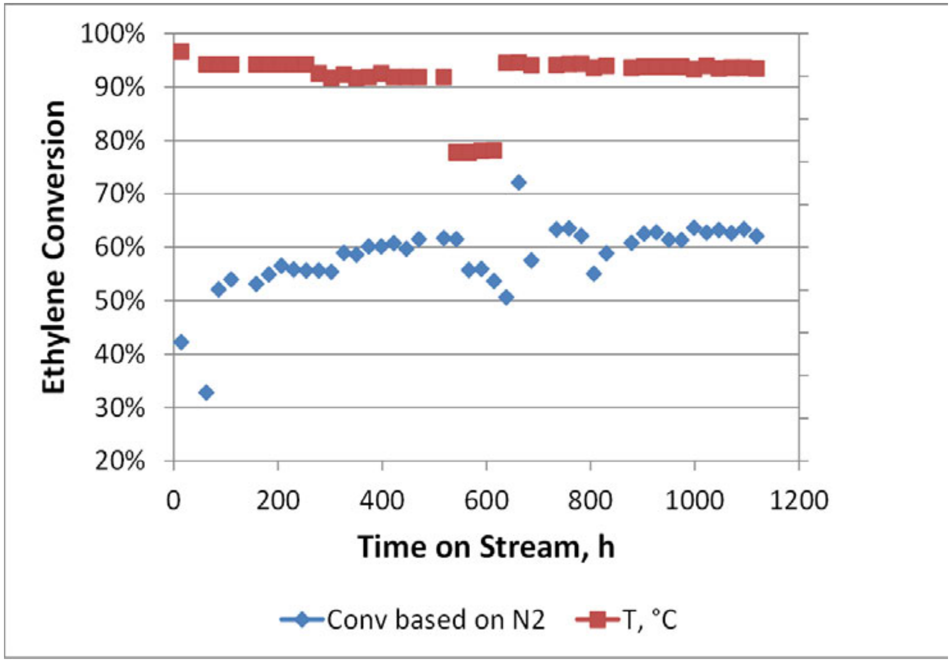
Requirements for Synthetic Paraffinic Kerosene (SPK)

- Control oligomerization to desired chain lengths, avoiding polymerization
- Produce targeted branched hydrocarbons, without aromatics

Primary Technical Challenge:
Oligomerization of ethylene to olefins

Demonstration of Ethylene Oligomerization

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



Laboratory development:

- PNNL accumulated over 2000 hours operation with single catalyst

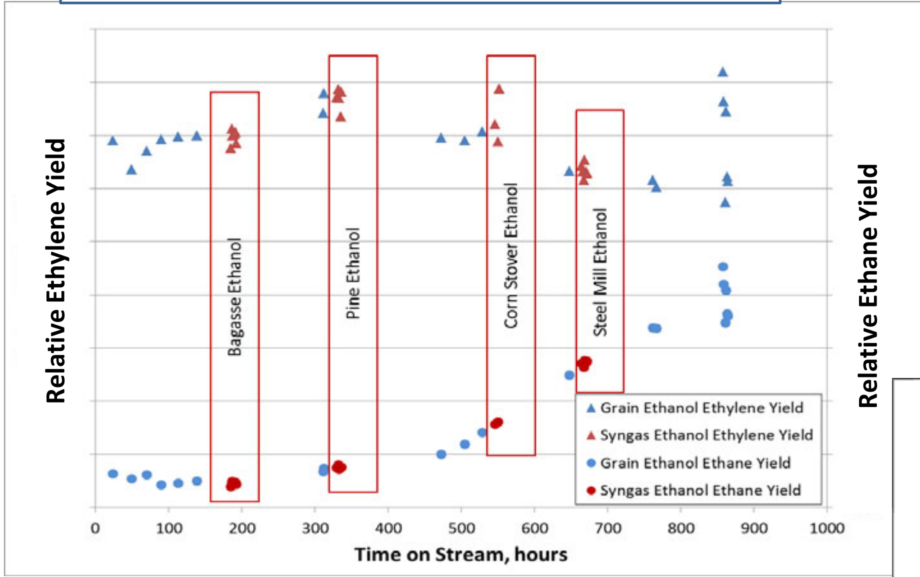
Pilot operations:

- LT developed and implemented ethylene clean up process
- LT scaled up novel ethylene oligomerization catalyst
- > 90% of input carbon in hydrocarbon product

Project demonstrated 2000 hours time on stream with single catalyst meeting FOA objective

ATJ SPK Feedstock Flexibility

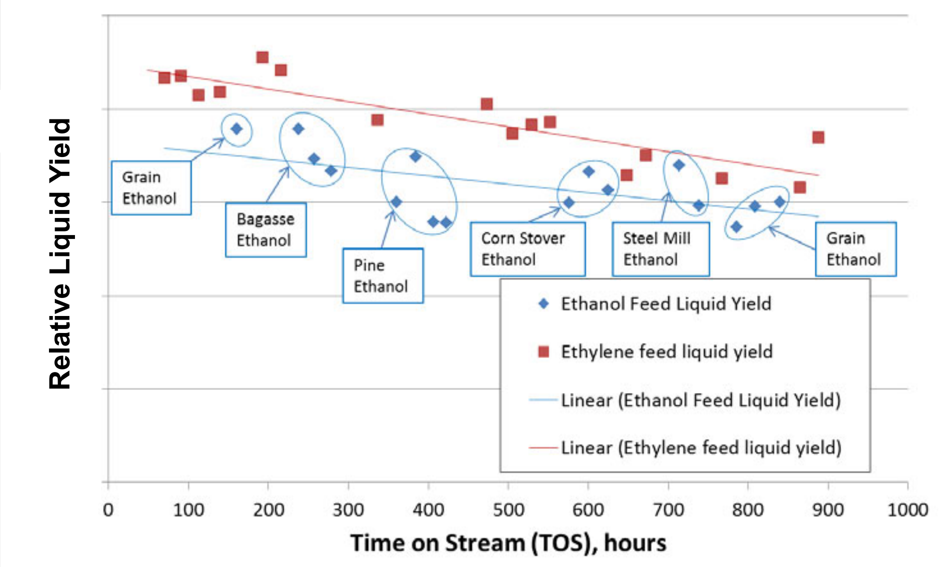
Ethanol Dehydration*



- Continuous bench-scale run with ethanol from different feedstocks
- Grain ethanol as reference feed

**Proof of concept data; not representative of at-scale production*

Ethylene Oligomerization



- Continuous bench-scale run with ethylene from different ethanol feedstocks
- Bottled ethylene as reference feed

Performance governed by time on stream and independent of ethanol source

ATJ SPK Process Scale Up and Production

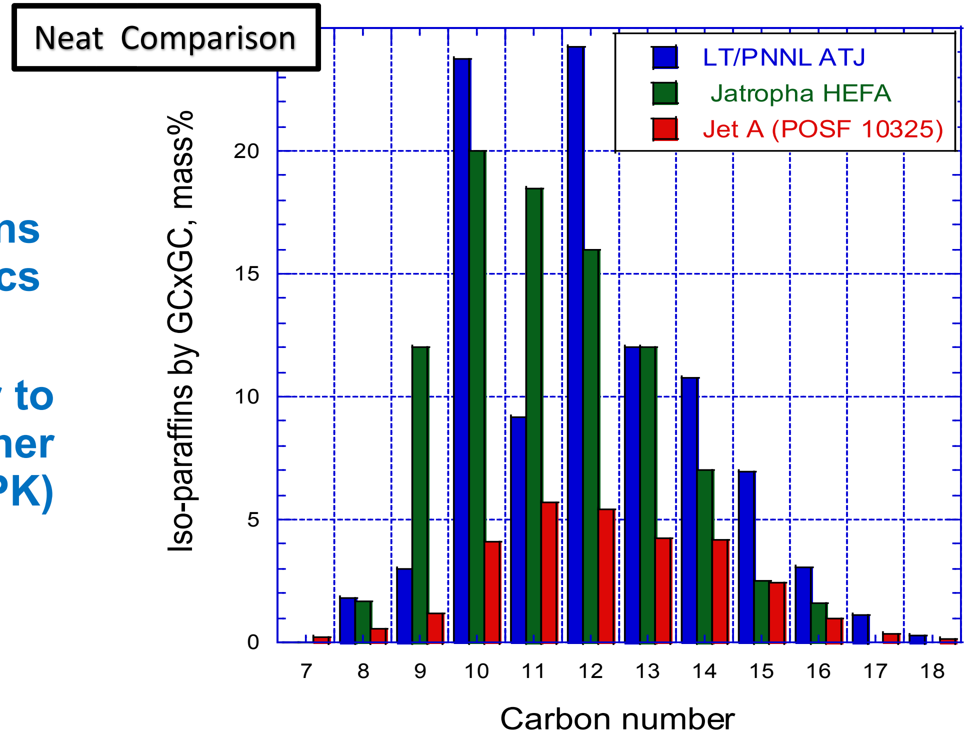
✓**4000 gallons Jet**

✓**600 gallons Diesel**

- **Demonstrated feedstock flexibility**
  - 1,500 gal from Lanzanol
  - 2,500 gal from Grain Ethanol
- **Lanzanol produced in an RSB-certified facility**
- **Specification & Fit for Purpose Properties measured by AFRL, SwRI and UDRI**
- **Both Grain Ethanol and Lanzanol neat match ATJ-SPK specifications**
- **Both Grain Ethanol and Lanzanol blended with 50% Jet A match D7566 specifications**

Both Grain Ethanol and Lanzanol Neat Match ATJ-SPK Specifications

ATJ SPK Jet Properties



Neat fuel primarily isoparaffins with <0.2% aromatics

Carbon number range similar to conventional jet fuel and other Synthetic Paraffinic Kerosenes (SPK)

Meets or Exceeds Critical Jet Fuel Specifications

- Flash Point, Freeze Point
- Stability, Heat of Combustion

Excellent Cetane

- 47.9 Neat ATJ SPK
- 47.7 50/50 Blend with Jet A

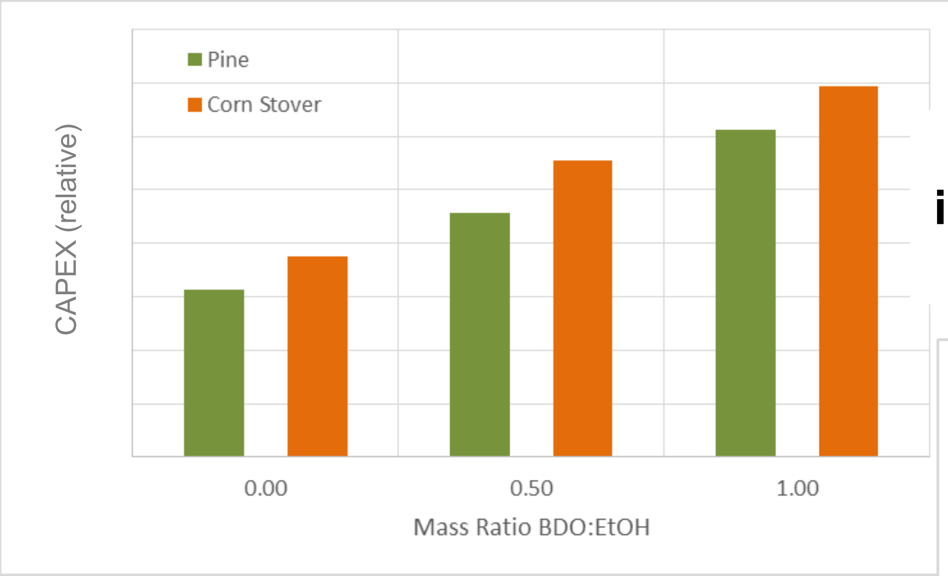
Produces wide boiling range material with excellent properties

Key Properties of LanzaTech/PNNL ATJ SPK

- **The LanzaTech/PNNL ATJ SPK is wide-boiling kerosene fuel blendstock 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 iso-paraffins.**
- **Low freeze point indicating excellent low temperature performance**
- **The thermal stability of the neat LanzaTech/PNNL ATJ SPK exceeds ASTM D7566 criteria (pass at 340°C), indicating low levels of contaminants (also low existent gum).**

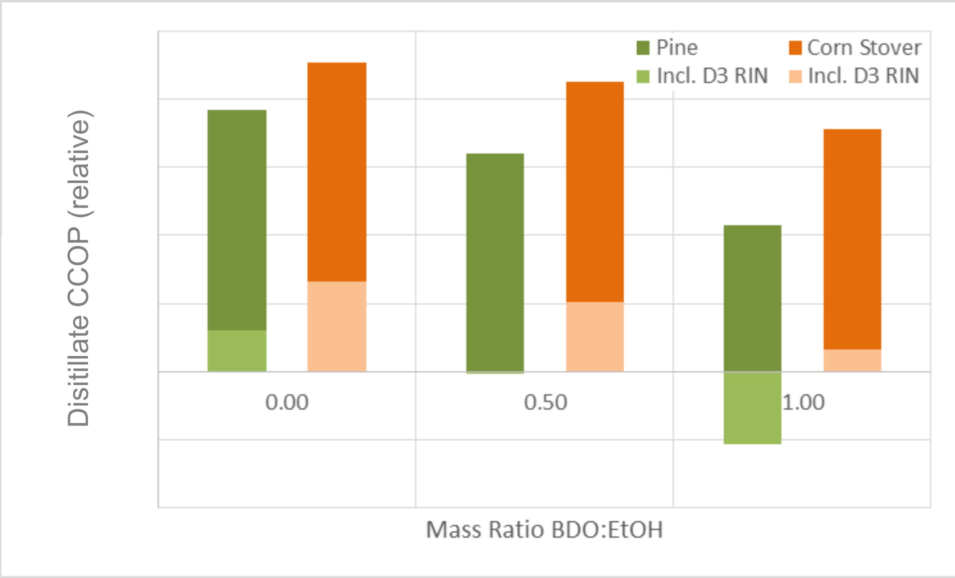
Techno economics: Jet and 2,3-BDO

Results based on DOE assumptions with national lab-based models.



Production of co-product 2,3-BDO increases CAPEX for 2,3-BDO separation and upgrading to Butadiene

Revenue from 2,3-BDO co-product decreases CCOP of jet fuel

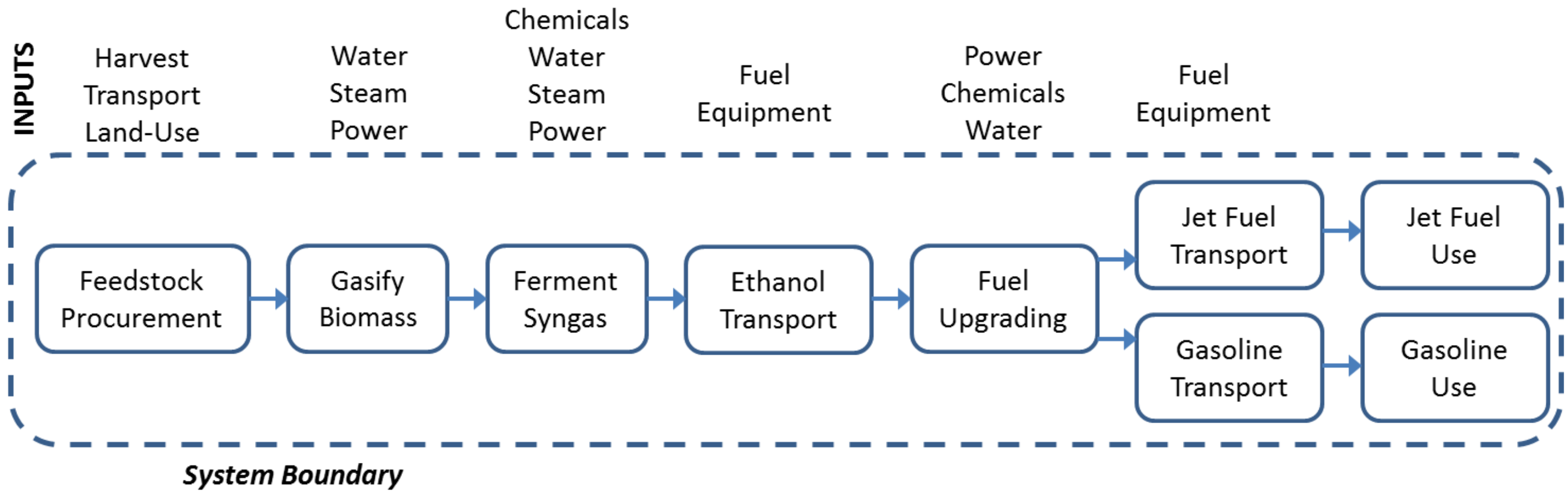


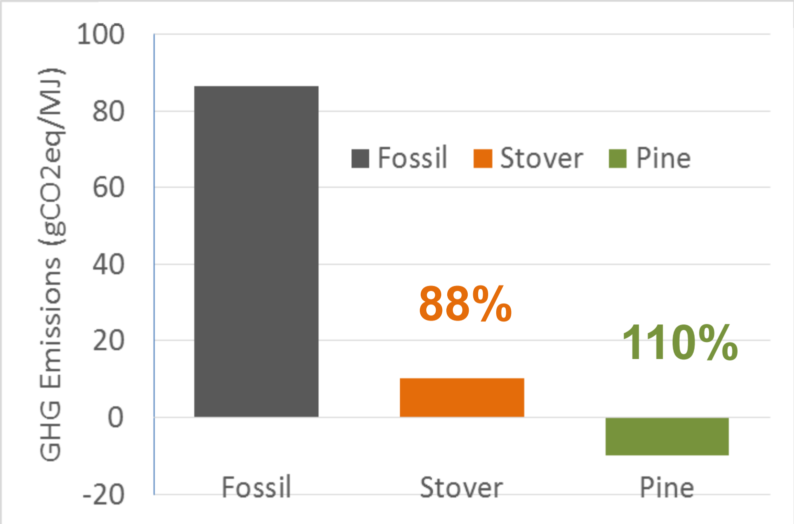
D3 RIN at average 2016 value ($1.93/gal, EV = 1.67)

Chemical co-product enables cost-competitive production of jet fuel from biomass in the LanzaTech – PNNL process

LanzaTech
capturing carbon. fueling growth.

Jet Fuel Life Cycle Assessment





- **Steam gasifier highly integrated with fermentation process.**
- **Gasoline co-product displacement credit contributes to large GHG reductions**

Results based on DOE assumptions with national lab-based models.

Significant reduction in GHG emissions

4 – Relevance (DOE)

- **Goal – develop a hybrid technology to convert biomass syngas to jet fuel and chemicals while meeting commercial cost, quality and environmental requirements of the aviation industry**

- **Contributions to BETO MYPP:**
  - Addressed BETO strategic goal to develop an advanced drop-in jet fuel with GHG reductions > 50%
  - Addressed BETO goal to achieve a $3/gge modeled cost of hydrocarbon fuels
  - Addressed Conversion R&D goal to develop commercially viable technologies for converting feedstocks via biological and chemical routes into energy-dense, fungible, finished liquid transportation fuels

4 – Relevance (Industry)

- **Relevance to LanzaTech and commercialization of ATJ SPK:**
  - Established feasibility of ATJ SPK production from ethanol using a wide range of feedstocks
  - Developed catalysts and process parameters required for next-scale implementation
  - Developed data to support addition of ethanol as a qualified ATJ SPK feedstock in ASTM D7566, which will apply to any ethanol source

- **Relevance to bioenergy industry:**
  - Aviation is a growing, long term, market for sustainable alternative jet fuel
  - Project demonstrated a feedstock-independent pathway from ethanol to jet fuel
  - Provides a new outlet for sustainably-produced ethanol, independent of blend wall or electrification of road transport

5 – Future Work

- The project is complete and in closeout

Summary

- **Established the viability of the hybrid biomass to jet pathway**
  - Demonstrated integration of gasification and syngas fermentation
  - Demonstrated ethanol from gas fermentation is suitable for ATJ SPK production and independent of feedstock
  - Demonstrated high quality of the jet fuel blendstock
  - Demonstrated production and upgrading of 2,3-BDO co-product
  - Cost of jet fuel production projected to be competitive with fossil jet with additional revenues from co-product
  - Over 80% GHG reductions projected using biomass feeds and integrated steam gasification
- **Capital cost of gasification remains a challenge**
  - Cost-competitive with fossil, when supported by co-product and/or RINs
- **ATJ SPK technology is ready for implementation at demonstration scale**

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

Publications and Presentations

Review chapter on ATJ processes, 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 CoProducts Made from LanzaTech Biomass-Based Ethanol. in *AIChE National Meeting* (2014).

Patents

M.A. Lilga, et al. (Battelle Memorial Institute), US 9,434,659. *Conversion of 2,3-Butanediol to Butadiene*. Issued 2016.

M.A. Lilga, et al. (Battelle Memorial Institute), WO 2016067032. *Systems and Processes For Conversion Of Ethylene Feedstocks To Hydrocarbon Fuels*. Published 2016.

M.A. Lilga, et al. (Battelle Memorial Institute), WO 2016067033. *Systems and Processes For Conversion Of Ethylene Feedstocks To Hydrocarbon Fuels*. Published 2016.

Commercialization Activities At Project Close

- PNNL and LanzaTech in licensing discussions
- Process selected for demonstration scale project under PD2B3 (Award DE-EE0007966)
- Data from demonstration fuel provided to engine and aircraft OEMs for review with goal of adding ethanol to ASTM D7566, Annex 5
- Demonstration fuel to be used in proving flight