

A Hybrid Catalytic Route to Fuels from Biomass Syngas

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Hybrid Catalytic Route to Fuels from Biomass Syngas

A Bioenergy Technology Office (BETO) Project

Project Objective: develop a hybrid conversion technology for catalytic upgrading of biomassderived syngas to jet fuel and chemicals while ensure the cost, quality and environmental requirements of the aviation industry are met



Improve Economics and Process Sustainability





Quad Chart Overview

Timeline					Barriers (Specific to Gaseous Intermediates Pathway)	
Project Start: April 2012 Project End: June 2016 Percent Complete: 50% Total Budget:					 Tt-E. Deconstruction of Biomass Feedstock to Form Gaseous Intermediates: Construction and integration of a gasification technology for evaluation of varying biomass feedstock to produce syngas for fermentation Tt-G. Gaseous Intermediate Cleanup and Conditioning: LanzaTech investigating minimum necessary gas cleanup and conditioning requirements for syngas fermentation Tt-I. Catalytic Upgrading of Gaseous Intermediates to fuels and Chemicals: Ethanol and 2,3-BDO upgraded to jet fuel and butadiene. PNNL and Imperium developing catalyst technologies for upgrading alcohols to high value chemicals and hydrocarbon fuels. Tt-K. Product Finishing: Production of large jet fuel sample by PNNL and subjected to fit-for-purpose testing in collaboration with Boeing and IAF. 	
Budget TOTAL: \$7.1M, DOE: \$4M, Cost Share: \$3.1M			IM, Cost Sha	re: \$3.1M	Current Partners	
WBS 2.3.1.403	FY 12	FY 13	FY 14	FY 15	LanzaTech: Project Lead, Project Management, Integrated TEA, Syngas Gasification and Fermentation Lead, Commercialization Partner, Analysis Support	
Peer Review Costs	\$0.00	\$299,331	\$622,293	\$559,139	PNNL: Catalytic Alcohol Conversion Lead, Catalyst-Fermentation Integration, TEA Modeling, Fuel Quality Measurements	
Project Budge	t FY 1	2 FY 13	FY 14	FY 15	Imperium Renewables: Commercialization, Market and Engineering Analysis	
PNNL	\$445	5K \$787K	\$296K	\$456K	Orochem Technologies: Advanced Alcohol Recovery	
NREL	\$0K	\$465K	\$64K	\$0K	Michigan Technological University: Life Cycle Assessment	
LT DOE \$2		ЭК \$292К	\$330K	\$560K	University of Delaware: Alcohol Conversion Catalyst Fundamentals	
Cost Share \$98K		K \$164K	\$48K	\$2.8MM	The Boeing Company: Fuel Quality and Aviation Industry Analysis	





Technical Approach

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

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

Determine the impact of fermentation broth components on catalyst stability and product yield, with the goal of optimizing alcohol recovery cost

Validate process stability through extended process operations and detailed catalyst characterization

Design an integrated process that optimizes the performance of each process step (including material and energy integration between steps) and produce a globally optimized process design

Identified Project Challenges:

- Gasification commissioning and operation with varying feedstock
- Recovery of 2,3 butanediol and ethanol to required catalytic quality
- Delivering an economically favorable integrated process using preliminary research costs





Management Approach



- LanzaTech is responsible for coordinating directly with the DOE on all project activities, including technical progress and finance reporting
- Project monitoring will be 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





Task A: Gasification Fermentation Interface

LanzaTech

Develop and demonstrate an integrated gasification and fermentation process for commercial jet fuel production

Task C: Catalytic Upgrading

PNNL / Imperium Aviation Fuels (IAF) Develop and demonstrate catalytic conversion of alcohols to chemicals and hydrocarbon fuels

Task E: Production of Hydrocarbon Fuels

PNNL / LanzaTech

Produce hydrocarbon fuels for analysis and fit-for-purpose testing

Task B: Prepare Alcohol Intermediates

Production/EtOH Separations: LanzaTech 2,3 BDO Separations: Orochem Produce 2,3BDO and ethanol samples for upgrading

Task D: Catalyst Fundamentals

Univ. of Delaware / PNNL Develop mechanistic understanding of conversion catalysts to improve performance

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.





Project Overview

Project Timeline

- 2012- Project kick-off
 - LanzaTech's fermentation installed at NREL (Denver, CO), integration with NREL's gasifier
 - Lab scale reactors operated, preliminary gas contaminant evaluation achieved
- 2013- Project suspension due to gasifier complications
 - Project fermenters relocated to LanzaTech's Freedom Pines facility (Soperton, GA)
 - Alternative gasification unit purchased for installation at Freedom Pines

• 2014:

- Lab and pilot scale reactors commissioned at Freedom Pines on bottled gas
- Begin assembly of gasifier at Freedom Pines
- Preliminary TEA and LCA completed and presented at AIChE
- catalyst development and kinetic modelling completed
- **2015-** Project technical tasks to recommence: gasification and fermentation integration for fuel sample production





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Technical Accomplishments- Fermentation

Relevant Project Task:

 Task A.1: Syngas Screening to Optimize Alcohol Production Gas Contaminant Analysis

 Task A.2: Commissioning Pilot Scale Fermentation System

LAB SCALE FERMENTATION

- fermentation on biomass syngas- preliminary runs achieved prior to leaving NREL
- Gas analysis performed and undesired contaminants identified
- Gas clean up design modified

PILOT SCALE FERMENTATION

- Relocated from NREL to Freedom Pines
- Batch pharmaceutical bioreactor converted to a continuous syngas fermentation unit
- Successfully commissioned on bottled syngas
- Robust and stable fermentation repeatable achieved









Technical Accomplishments- Catalyst Development

Relevant Project Task:

Task C.1: Ethanol to Fuels- Catalyst Development Task C.3: Catalyst Lifetime/Regeneration Testing







- Transition from small lab to larger bench-scale catalyst reactor systems (5cc to 50 cc)
- 2000+ hour catalyst lifetime study at lab-scale
- Produced multiple liter samples for fuel testing





Technical Accomplishments- Fuel Sample Generation

Relevant Project Task:



Task F.1: Preliminary Product Testing

- Jet fuel sample prepared with syngas fermentation-derived ethanol
- sample tested by Air Force Research Laboratories (AFRL)
- Results adhere to ASTM standards and are aligned with typical Jet A-1 properties

Method	Test	D7566	Jet A-1	PNNL ETJ
ASTM D 86	Distillation			
	Initial Boiling Point (°C)			164
	10% Recovered (°C)	<205	<205	177
	End Point (°C)	<300	<300	272
	Residue (% vol)		<1.5	1.6
	Loss (% vol)		<1.5	0.7
	T90-T10	>22	>40	77
	T50-T10		>15	28
ASTM D 93	Flash Point (°C)	38	38	52
ASTM D 3241	Thermal Stability JFTOT @ 325°C	325°C	260°C	325°C
	Tube Deposit Rating, Visual	<3	<3	1
	Change in Pressure (mmHg)	<25	<25	0
ASTM D 4809	Net Heat of Combustion (MJ/kg)		>42.8	43.7
ASTM D 5972	Freeze Point (°C)	<-40	<-47	< -70
ASTM D 4052	Density (kg/L, 15 °C)	0.730 to 0.770	0.775 to 0.840	0.775





Technical Accomplishments- Catalyst Kinetics Modelling

Relevant Project Tasks:

Task D: Catalyst Fundamentals and Mechanistic Understanding of Reaction Branch Points

- Modelling performed by University of Delaware and PNNL
- Completed kinetic assessment of jet fuel catalyst process
- It was determined that reactor scale-up can be achieved through empirical modeling

based on apparent reaction rate



Example of test data used for the development of a kinetic model

Demonstrates PNNL olefin oligomerization catalyst is more active and deactivates slower than "traditional" catalysts





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Relevant Project Tasks:

Task G.1: Process Analysis- Identify Additional Opportunities for Process Integration and Synergy Task G.2: Life Cycle and Cost Analysis

- LanzaTech and MTU collaboration
- Preliminary TEA and LCA developed, benchmark economics established
- Three cases evaluated for three different biomass feedstocks
- Data Presented at AIChE annual meeting, Atlanta GA





Preliminary Results- Carbon Displacement Allocation

Create the Future

	GHG Emissions (g CO2eq / MJ Jet)			
Item	Corn Stover	Forest Residue	Switchgrass	
Biomass Carbon Sequestration	-310.1	-310.1	-310.1	
Biomass Procurement	18.6	11.9	25.4	
EtOH Production	192.1	191.9	192.1	
Electricity Credit	-14.7	-14.7	-14.7	
EtOH Transport	1.2	1.2	1.2	
Fuel Upgrading	17.6	17.6	17.6	
Gasoline co-product credit	-7.1	-7.1	-7.1	
(avoided production)				
Gasoline Transport	0.17	0.17	0.17	
Jet Transport	0.45	0.45	0.45	
Gasoline co-product combustion	27.7	27.7	27.7	
Jet combustion	72.9	72.9	72.9	
Total GHG Emissions	-1.23	-8.23	5.55	
Percent Reduction (%)	101.4%	109.5%	93.6%	
(petroleum jet)				

Petroleum Jet 86.4 g CO_{2eq} / MJ (GREET 2014)





Technical Achievement- TEA/LCA Development

Create the Future



Preliminary Results- Carbon Displacement Allocation





Relevance

Current Project Achievements and their Relationship to the BETO Multi-Year Project Plan

Task	Accomplishment	Relevant Barrier	
A- Gasification/ Fermentation	Preliminary evaluation of syngas components of fermentation	Tt-G. Gaseous Intermediate Cleanup and Conditioning	
Interface	Commissioning of pilot scale fermenter	Tt-G. Gaseous Intermediate Cleanup and Conditioning	
A- Gasification/Fermentation Interface	Progression with gasification construction/installation for integration with fermentation	Tt-E. Deconstruction of Biomass Feedstocks to Form Gaseous Intermediates	
C- Catalytic Upgrading	Completion of development and lifetime testing on ethanol to jet fuel catalysts. >2000hrs testing	Tt-I. Catalytic Upgrading of Gaseous Intermediates to Fuels and Chemicals	
C- Catalytic Upgrading	Successful AFRL analysis on jet fuel sample using fermentation derived ethanol. Shows equivalency	Tt.K. Product Finishing	
D- Catalyst Kinetics Modelling	Completion of mechanistic kinetics modelling for jet fuel catalysts	Tt-I. Catalytic Upgrading of Gaseous Intermediates to Fuels and Chemicals	

Establishment of a preliminary TEA and LCA also contributes to the project's objectives by providing a benchmark for the expected commercial economics and carbon life cycle emissions for this hybrid bioprocessing platform





Relevance

By the completion of this BETO project, demonstration of commercial viability is anticipated through further optimization and validation of each stage of the hybrid platform:

- Integration of Gasification with Fermentation- Reduction in fuel production cost through elimination of required gas clean-up steps; attributed to high contaminant tolerance of the fermentation process
- Alcohol Separation- Minimized separation requirements while still producing catalystquality product
- **Optimized Catalytic Conversion-** Reduced catalytic conversion costs through improved catalyst lifetime and viability, as well as the application of economically viable catalyst material
- Integration of Unit Operations- Reduce energy demands through heat integration between gasification, fermentation, separation and catalytic conversion.

Through the participation of aviation partners (IAF and Boeing) the advancement of this technology from demonstration to a commercial platform can be facilitated





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Future Work

- Integration of bioreactor and gasifer, operation of 3 different biomass feedstocks- 2015 LanzaTech, Task A
 - ML: Validation of integrated operations
 - *ML:* Demonstration of industrially relevant productivity
- Recovery and purification of fermentation derived alcohol products- 2015 LanzaTech, Task B
 - ML: Production of adequate alcohol for jet fuel upgrade
- Catalytic upgrade of ethanol to jet fuel- 2016 PNNL, Task E
 - ML: Delivery of fuel samples for product evaluation
- Fuel validation- 2016 LanzaTech/PNNL/Boeing/IAF, Task F
 - ML: Defining pathway for fuel certification
- Economic and carbon life cycle update- 2016 LanzaTech/MTU, Task G
 - ML: achieve projected GHG reduction > 60% compared to gasoline equivalent

Key achievements required for project progression:

- Successful integration of fermentation with biomass syngas at pilot scale
- Purification and conversion of biomass derived ethanol to jet fuel
- Final jet fuel product demonstrates adherence to fuel certification requirements





Summary

- LanzaTech and partners are working together to establish a hybrid catalytic production platform that demonstrates:
 - 1. Gasification of various biomass feedstocks
 - 2. Production and purification of alcohols from syngas fermentation
 - 3. Catalytic upgrade of alcohols to fuels and chemicals (jet fuel and 1,3 butadiene)
 - 4. Fuel certification and demonstration of commercial viability
- Initial gas clean-up requirements are identified
- Catalytic development and fundamental modelling has been completed
- Fermentation derived jet fuel demonstrated desired properties; data submitted to ASTM
- Preliminary TEA and LCA completed, commercial viability observed
- Gasification/Fermentation integration and fuel production delayed due to location change, recommencing 2015

The completion of this project will result in a hybrid biorefinery design that will demonstrate an economically favourable platform with significant reductions in greenhouse gas emissions compared to current fuel production processes





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Project Publications

 R. Handler et al (2014) Life Cycle Assessment of LanzaTech Waste Gas Conversion to Ethanol and Co-Products. PowerPoint Presentation. LanzaTech/Michigan Tech/PNNL. 2014 AIChE Annual Meeting, Atlanta GA. Session: Life Cycle Assessment of Advanced Biofuels.



