PNNL-30831

Improved Value of the Gasoline and Fuel Oil Co-Product Fractions Generated by the PNNL/LanzaTech Alcohol-to-Jet Process

CRADA 394 (Final Report)

December 2020

Robert A Dagle
Vanessa Dagle
Johnny Saavedra Lopez

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99354

Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: December 31, 2020

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Battelle Memorial Institute and LanzaTech

CRADA number: 394

CRADA Title: Improved Value of the Gasoline and Fuel Oil Co-Product Fractions Generated by the PNNL/LanzaTech Alcohol-to-Jet Process

Responsible Technical Contact at DOE Lab:

Name and Email Address of POC at Company: Robert Dagle, Robert.dagle@pnnl.gov

DOE Program Office: Bioenergy Technology Office (BETO)

Joint Work Statement Funding Table showing DOE funding commitment:

	Funding Table		
	FY18	**FY19**	**Total**
DOE-BETO Funding	$600*K*	$300*K*	$600*K*
LanzaTech Cost Share	$129k	$129*K*	$258*K*

Executive Summary of CRADA Work:

The BETO-funded PNNL collaboration with LanzaTech, Inc. utilizes patented technology to address the need for low aromatic jet fuel blendstocks. The PNNL/LanzaTech alcohol-to-jet (ATJ) process converts ethanol from LanzaTech's syngas fermentation process to jet-range isoparaffins. The aim of this Cooperative Research Development Agreement (CRADA) project was to improve the commercial viability of the LanzaTech/ PNNL ATJ process by developing two new co-product options. Two Focus Areas (FA) were explored: FA1) Increasing the RON of the lighter-than-jet gasoline fraction above 98; and FA2) Creating a synthetic lubricant base oil from the heavier-than-jet fraction.

For FA 1, multiple processing approaches were evaluated, and RONs ranging from 96-100 were obtained, each comprising different processing costs. The most cost effective approach identified was a single-step process and yielded a liquid product of 97. Thus, additional development is required to obtain a RON > 98. We will continue work on this focus area with separate Direct Funding Opportunity (DFO) funding within the DOE-BETO Co-Optima Consortium (expected to begin Q2-FY21). Experimental work will focus on i) increasing single pass conversion to > 50%, and ii) obtaining a > 98 RON product. Technoeconomic analysis performed in this project suggests cost competitiveness provided these technical targets can be met.

For FA2, multiple approaches were evaluated for increasing the viscosity index (VI) of the heavier-than-jet fraction to at least 120 in order to meet ASTM specifications for a Group III Base Oil (ASTM D6074). All other ASTM specifications are already met. A viscosity index of 115 was obtained, and with minimal undesirable cracking products. We believe a VI of 115 is about the highest possible from a catalytic approach, per review of the patent literature. In order to further increase the VI to > 120 we believe additives and/or liquid-liquid extraction is required. TEA performed earlier in the project suggests cost competitiveness with market prices assuming cracking byproducts are kept < 10 wt.%. If TEA updated with this additional processing still projects economic feasibility next steps could be taken in a subsequent effort.

Summary of Research Results:

This product contains Protected CRADA Information, which was produced on 3/29/2018 under CRADA No. 394 and is not to be further disclosed for a period of five (5) years from the date it was produced except as expressly provided for in the CRADA.

Scope

The BETO-funded PNNL collaboration with LanzaTech, Inc. utilizes patented technology to address the need for low aromatic jet fuel blendstocks. The PNNL/LanzaTech alcohol-to-jet (ATJ) process converts ethanol from LanzaTech's syngas fermentation process to jet-range isoparaffins. Compounds are generated across a wide boiling range by the process. The project performed here aimed to improve the commercial viability of the ATJ process through two Focus Areas (FA):

- Focus Area 1 (FA1): Increasing the RON of the lighter-than-jet gasoline fraction above 98
- Focus Area 2 (FA2): Creating a synthetic lubricant base oil from the heavier-than-jet fraction.

FA1 utilized a stream rich in linear butenes from the oligomerization reactor in the PNNL ATJ process. We investigated isomerization technology to convert the isoolefin mixture produced by oligomerization to more highly-branched compounds like isobutene, which increased the product RON. For example, isooctene exhibits a RON of 106, making the lighter-than-jet fraction a valuable gasoline blendstock. In FA2, we evaluated isoparaffins in the heavier-than-jet fraction produced by the ATJ process as a Group III synthetic motor oil base. We evaluated a hydroisomerization process to improve the viscosity index to > 120 to meet specification as Group III base oil.

Actual Accomplishments

Focus Area 1 Accomplishments: 98+ RON Gasoline Blendstock via Olefin Isomerization and Controlled Oligomerization. For producing high octane (RON) gasoline the challenge is to selectivity produce a highly branched isoparaffinic product in the gasoline-range, with minimal formation of undesirable formation of cracking, cycloalkane, paraffin, aromatic, and coking byproducts. While aromatics contribute to increased octane rating, their production is undesirable due to environmental and regulatory concerns. Dozens of experiments were performed, primarily evaluating the use of different catalysts (e.g., solid acid resin, zeolites, and promoted zeolites) and at various operating temperatures and pressures. Catalytic materials known to exhibit low activity in cracking and disproportionation, high activity in isomerization and alkylation, and good anticokability were evaluated. Two approaches were evaluated for producing a high RON gasoline.

First, a 2-step process was explored whereby skeletal isomerization is first performed at high temperature (e.g., 400°C) followed by controlled dimerization at lower temperature (e.g., 60-150°C). **Our best results for this approach produced a gasoline-range hydrocarbon with a RON of 96, as measured using engine testing via ASTM D2699.** By comparison, the gasoline cut of the oligomerization product, from the current ATJ process, has a RON of only ~85. Drawbacks to this approach include the production of undesired byproducts, including aromatics, paraffins, and cycloalkanes, formed primarily in the skeletal isomerization. By comparison, dimerization of isobutene alone, without inclusion of the other intermediates obtained in the skeletal isomerization, results in a liquid product with a RON of 100. This meets the RON target of > 98, however, in practice this would require separation of isobutene from the intermediate mixture, and this incurs additional processing cost. Additional TEA is required to definitively assess commercial viability for this approach; however, we believe the requirement for this additional processing would not warrant feasibility.

Second, a single-step, low temperature dimerization approach was also evaluated, with the goal to achieve both skeletal isomerization and dimerization in the same step. **This resulted in a liquid product with a RON of 97, also measured using engine testing via ASTM D2699.** A primary advantage to this approach is that the production of other undesirable byproducts such as cracking products (<1 wt.%), aromatics (0 wt.%), paraffins (<1 wt.%), cycloalkanes (< 1 wt.%), and coking are minimal. We note that in order to reduce (low RON) cycloalkane content a uniquely promoted zeolite catalyst was developed thereby producing < 1 wt. % cycloalkanes content (without promotion yielding > 10 wt.% cycloalkanes). Taken together, the process is carbon efficient: when operating at 60°C and with 30% single pass conversion approximately 2/3 of the carbon yields high RON gasoline-range hydrocarbons, with the balance to the distillate-range, the latter which can be used for jet blendstock. The primary drawback to *this* approach includes the fact that branching of the isoolefin product is limited, thereby limiting the production of quaternary carbons (high RON constituents). This approach was the most favorable, of the two approaches investigated, producing the highest RON content of 97 (excluding the route from pure isobutene intermediate). However, this did not meet the > 98 high RON target, required in order to obtain premium fuel pricing. Evaluation of market pricing for a lower RON product of 97 will dictate market feasibility. We will continue work on this focus area with a separate Direct Funding Opportunity (DFO) project funded within the Co-Optima Consortium (expected to begin Q2-FY21).

Focus Area 2 Accomplishments: Group III Base Oil Production via Fuel Oil Fraction Hydroisomerization. For producing lubricant, heavier-than-jet feedstocks were used. In order to qualify as Group III base oil lubricant a viscosity index of 120 is required. All other properties including saturates, aromatics, and polar contents were found to be favorable for lubricant qualification (ASTM D6074). Different zeolite catalysts, with various pore structures and acidities, and process conditions were evaluated. Results indicate how with just a modest increase in viscosity index, hydrocracking is dramatically increased from ~ 5 to 20 wt.%. Thus, an increase in viscosity index occurs at the expense of significant hydrocracking (which lowers carbon efficiency and increases cost). This is in line with reports for commercial hydrotreating processes where relatively severe conditions are required to activate highly branched and slower to diffuse isomers. However, these severe conditions also facilitate the formation of undesirable hydrocracking products. We note that in commercial practice, hydrotreatment produces multiple hydrocarbon streams (e.g. gasoline, naphtha) that are integrated back into downstream reactor units. Thus, producing a single specific product with high selectivity is not as critical as in a biorefiney with fewer product offerings. Other approaches were evaluated that resulted in minimal formation of cracking products (< 10 wt.%). Best results produced a VI of up to 115, and with < 10 wt.% cracking byproduct formation. In order to further increase the VI to > 120 additional processing is required. If updated TEA to be performed in the future suggests the process could still be cost competitive, even with this additional processing, next steps could be further pursued in a subsequent effort.

Project Output: The following list of invention reports, presentations, and reports were delivered in this project:

- Quarterly reports to BETO
- CRADA Final Report (this report, open distribution, published on osit.gov)
- ChemCatBio DFO Final Report (closed distribution, submitted to BETO)
- Final Report (~ 30 page comprehensive report with data and analysis, submitted to LanzaTech)
- Invention Report (submitted internally to PNNL Commercialization Manager, Alan Tuan)

Pacific Northwest
National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354
1-888-375-PNNL (7665)

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