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Catalyst Development to Overcome Barriers for Commercialization of Synthetic High-Octane Hydrocarbons

Cooperative Research and Development Final Report

CRADA Number: CRD-18-00757

NREL Technical Contact: Jesse Hensley

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated under Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5100-92988
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National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
303-275-3000 • www.nrel.gov

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Cooperative Research and Development Final Report

Report Date: January 22, 2025

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded 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: Regents of the University of California on behalf of the Berkeley campus

CRADA Number: CRD-18-00757

CRADA Title: Catalyst Development to Overcome Barriers for Commercialization of Synthetic High-Octane Hydrocarbons

Responsible Technical Contact at Alliance/National Renewable Energy Laboratory (NREL):

Jesse Hensley | jesse.hensley@nrel.gov

Name and Email Address of POC at Company:

Professor Enrique Iglesia | iglesia@berkeley.edu

Sponsoring DOE Program Office(s):

Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies Office

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$15,000.00
Year 2	$15,000.00
Year 3	$15,000.00
TOTALS	$45,000.00

Note: CRADA work proceeded for only a few months and then ceased. Estimated actual NREL contribution was $10,000, equivalent to about 16h of time each for a senior chemist and senior engineer and about 40h of time for a postdoctoral researcher. See below for explanation on the change.

Executive Summary of CRADA Work:

In recent years, researchers at the National Renewable Energy Laboratory (NREL) and the University of California Berkeley (UC Berkeley) have independently developed catalysts that convert methanol and dimethyl ether into alkylate-like hydrocarbons with a high-octane value, and both have developed intellectual property around these chemical transformations. Both UC Berkeley and NREL wish to see their technologies commercialized to address a number of domestic and international energy challenges. The technologies developed by NREL and UC Berkeley are complimentary but neither have moved beyond the laboratory scale due to remaining challenges with the catalyst activity and selectivity, and/or with the reaction engineering associated with maximizing the yield of the high-value product. NREL and UC Berkeley wish to collaboratively through a shared resources CRADA to solve issues related to the scale-up and process integration of their high-octane hydrocarbon technologies, thus enabling future licensing of the technology to an industry partner.

CRADA Benefit to DOE, Participant, and US Taxpayer:

This CRADA benefits DOE by using partner resources and expertise to accelerate the market adoption of a DOE-funded project to develop synthetic fuels from domestic biomass. The CRADA benefits the partner by using DOE (NREL) resources and expertise to accelerate the market adoption of a previously privately-funded effort to produce 2,3,3-trimethylbutane. The CRADA benefits the US Taxpayer by accelerating the commercialization of a technology that can increase the value of domestic resources (non-food biomass, biogenic waste gases, carbonaceous waste, flared gas, “fracked” petroleum light ends, and natural gas liquids), which can result in lower energy prices, improved environmental quality, and expanded national energy security.

Summary of Research Results:

CRADA CRD-18-00757 contained a single task description as follows:

NREL and UC Berkeley will leverage their unique facilities and human capital to resolve outstanding issues related to scale-up and process integration of their high-octane hydrocarbon technologies. These issues include, but are not limited to:

- Strategies to take advantage of commercial-scale forms (e.g., extrudates) and adjustments to operating conditions (e.g. temperature, pressure, phase) to maximize yield of the 2,3,3-trimethylbutane containing product*
- Strategies to manage high melting point coproducts, and to separate them continuously from the reaction product*
- Activation of low-value, highly-available hydrocarbons, (e.g. natural gasolines) for conversion to high-octane, high-value product*
- Industry engagement and feedback on process challenges*

It is common for just one or two activities to gain priority or importance as more information is gained, therefore, the above bullets should be understood as a list of possible activities that could translate to faster market adoption, and not as a “to do” list for the CRADA period of performance.

Task Descriptions and Estimated Completion Dates

All tasks will be performed by the Parties in their own facilities, using their own funds. Example tasks include, but are not limited to:

- Providing expert interpretation and analysis of data sets for the purpose of drawing conclusions and developing follow-on research plans
- Synthesizing catalysts using a variety of techniques*
- Computational modeling of catalyst/reactant interactions*
- Physical and chemical catalyst characterization (e.g. X-ray absorption spectroscopy*, inductively-coupled plasma spectroscopy*, X-ray diffraction*, surface area/pore volume measurements*, temperature programmed reduction*, pyridine diffuse reflectance*, infrared Fourier transform spectroscopy*, ultraviolet/visible light absorbance spectroscopy*, transmission electron microscopy*, thermogravimetric analysis*)
- Reaction screening (batch, continuous, gas-phase, liquid-phase)
- Reactant and product analysis (gas chromatography)
- Preparing records of invention and manuscripts on new learnings*

Items marked with a "" were never initiated in this CRADA due to activities stopping early in the period of performance.*

All work performed under this CRADA occurred between December 1, 2018, and March 30, 2019, or about 10% of the full period of performance. The reason for this short timeline is that a core objective was met quickly ("enabling future licensing of the technology to an industry partner") as NREL was approached by ExxonMobil with interest in working toward commercialization of the technology. Ultimately, ExxonMobil signed an ACT with NREL in late 2019 and has been working with NREL on this technology since that time.

The three months of activity included:

1. A kickoff meeting between NREL an UC Berkeley where NREL presented its catalyst state of the art on 12/3/18
2. Some simple experiments recommended by UC Berkeley and conducted by NREL
3. A second meeting between NREL and UC Berkeley where NREL presented the results of a few experiments on 1/29/19
4. A third meeting between NREL and UC Berkeley where NREL presented a few more results of experiments on 3/19/19

In the joint work statement activities, the only ones started included:

A. Expert interpretation and analysis of NREL *pre-CRADA* data sets by UC Berkeley
B. Chemical catalyst characterization using solvent extraction followed by gas chromatography and ^{13}C nuclear magnetic resonance spectroscopy (NMR)
C. Reaction screening using liquid phase batch reactions and gas phase continuous reactions and analysis of products using gas chromatography

No other activities were started, and no publications or records of invention were prepared. Only tasks A-C were started, and task A was successfully accomplished via activities (meetings) 1, 3, and 4 above. Tasks B and C were completed in parallel and the results from that effort follow.

The focus of discussions was to understand some low-productivity results obtained from a pilot study NREL conducted for the high-octane hydrocarbon process. Specifically, we wanted to understand why the catalyst, when operated in a pilot reactor, would produce 10 times less product than then same catalyst operated in a bench scale reactor at the same conditions.

Our hypothesis was that the hydrodynamic conditions in the pilot reactor, which approached plug flow, prevented the back-diffusion of reaction products, which are needed to "seed" the reaction, i.e., to establish an inventory of reactive carbon on the catalyst surface. Stated differently, we suspected that a substantial fraction of the catalyst bed never activated and never participated in high-octane hydrocarbon production. The hydrodynamic conditions in the bench scale reactor were more conducive to back-mixing of product gases due to the lower linear velocity of reactant gases as they travel in the channels between catalyst particles. We tested this hypothesis by conducting an experiment where the same mass of catalyst was diluted in different ratios with an inert sand, thereby increasing the distance between catalyst particles and decreasing the probability that reaction products would diffuse in the opposite direction of reactant flow to seed catalyst particles upstream.

The ratio of the length of the catalyst bed (L) to the diameter of the bed (D) are shown in relative scale in Figure 1. The concentration of 2,3,3-trimethylbutane for each test is shown in Figure 2 as a function of time on stream. While there is slight variation in the concentration of 2,3,3-trimethylbutane after about 5h on stream, the difference is negligible, and not clear evidence of a partially-activated catalyst bed. We noted that we could only achieve L/D of 4.9, while the pilot reactor had an L/D of 152. The results of this experiment were *inconclusive*.

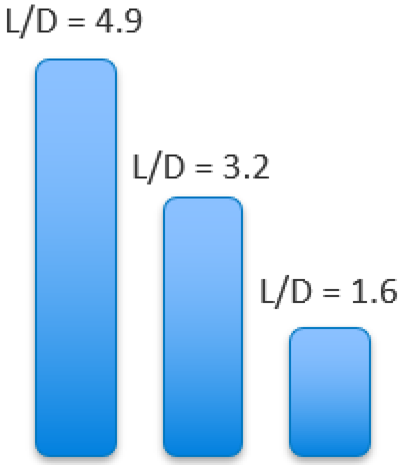

Figure 1: relative scale of catalyst bed lengths of the same gravimetric load (diluted with inert sand)

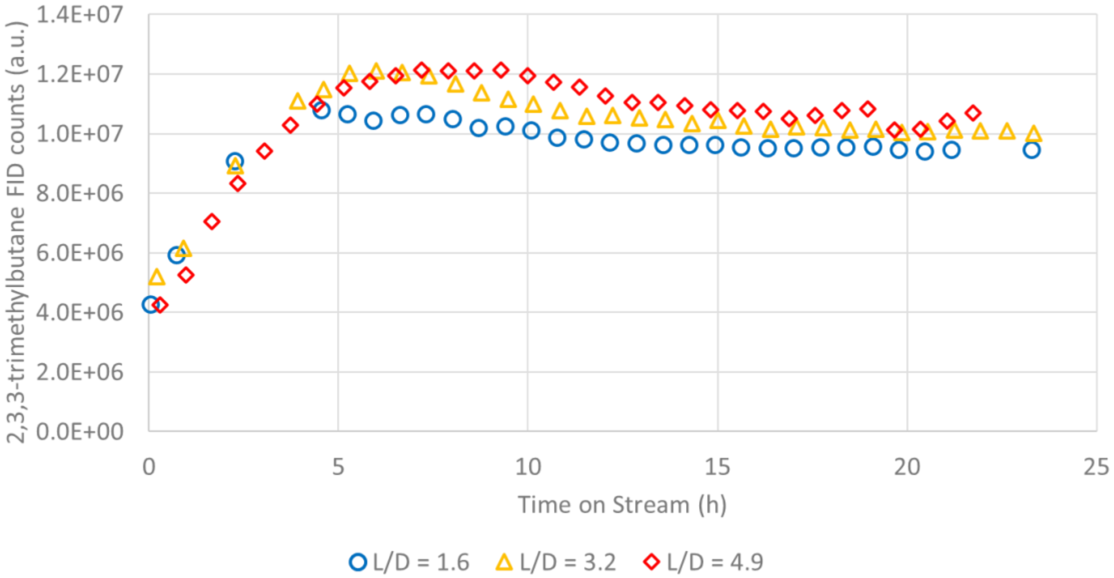

Figure 2: concentration of 2,3,3-trimethylbutane in reaction product gas as measured by gas chromatography as a function of reaction time. Reaction conditions were 200 °C, 21 psia, 1:1 H2:DME, 2.5 mole% argon, 1.8 gDME-gcat-1-h-1

Next, we took samples of catalyst unloaded from the pilot reactor tube, from among the samples shown in the photograph in Figure 3. Catalyst was soaked in chloroform to extract soluble hydrocarbons and the solvent/extract were analyzed via gas chromatography, with results shown in Figure 4. Catalyst was then analyzed using ^{13}C NMR, with results shown in Figure 5.

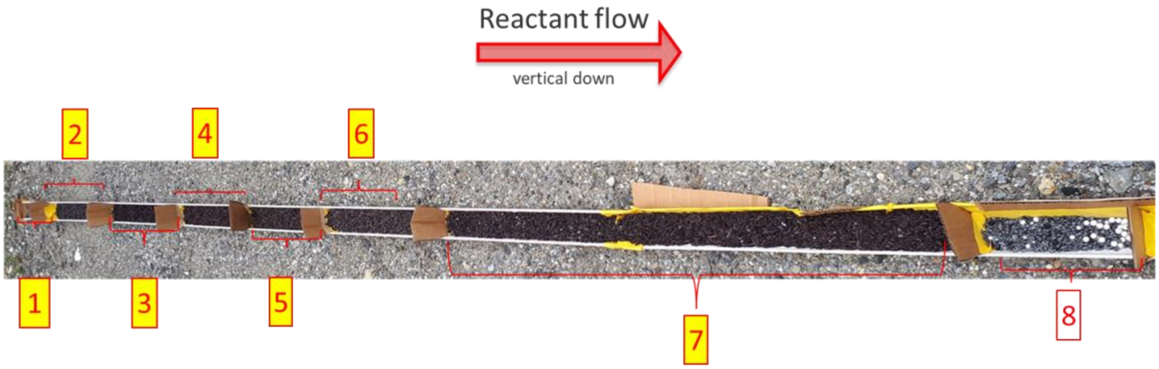

Figure 3: catalyst sections unloaded from Enerkem pilot reactor tube (separate project). Samples from sections 1 through 7 were used for chemical analysis

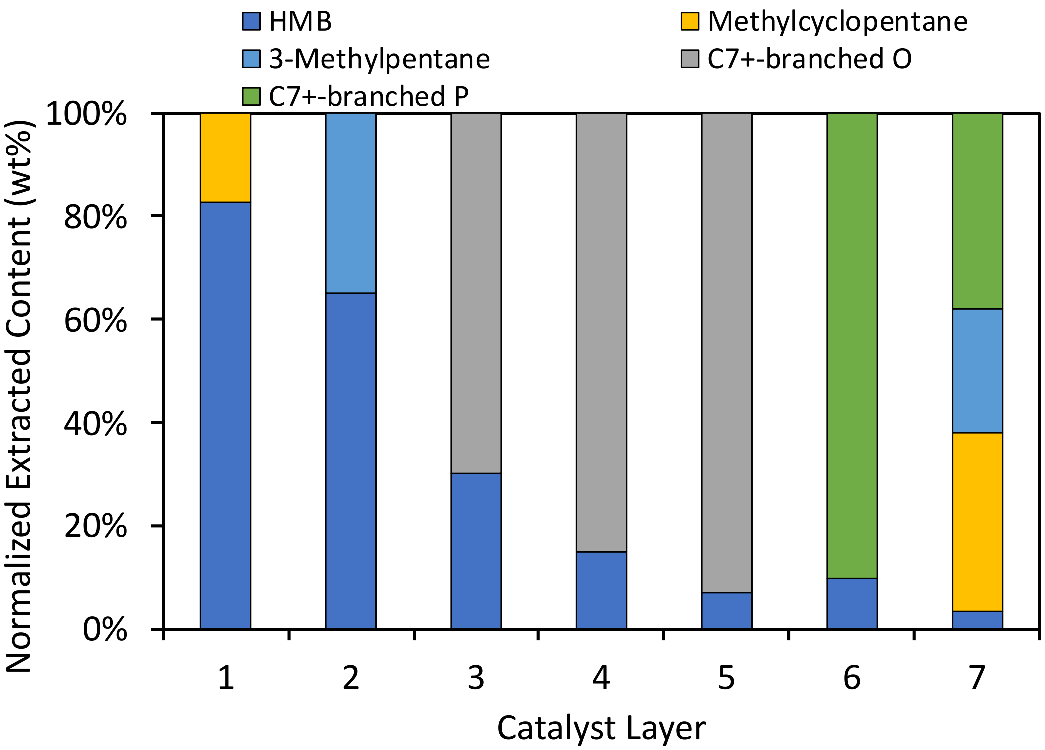

Figure 4: composition of hydrocarbons extracted from used catalyst, samples taken from bed positions as indicated in Figure 3. “HMB” is hexamethylbenzene, “P” is paraffins (alkanes), and “O” is olefins (mono-alkenes).

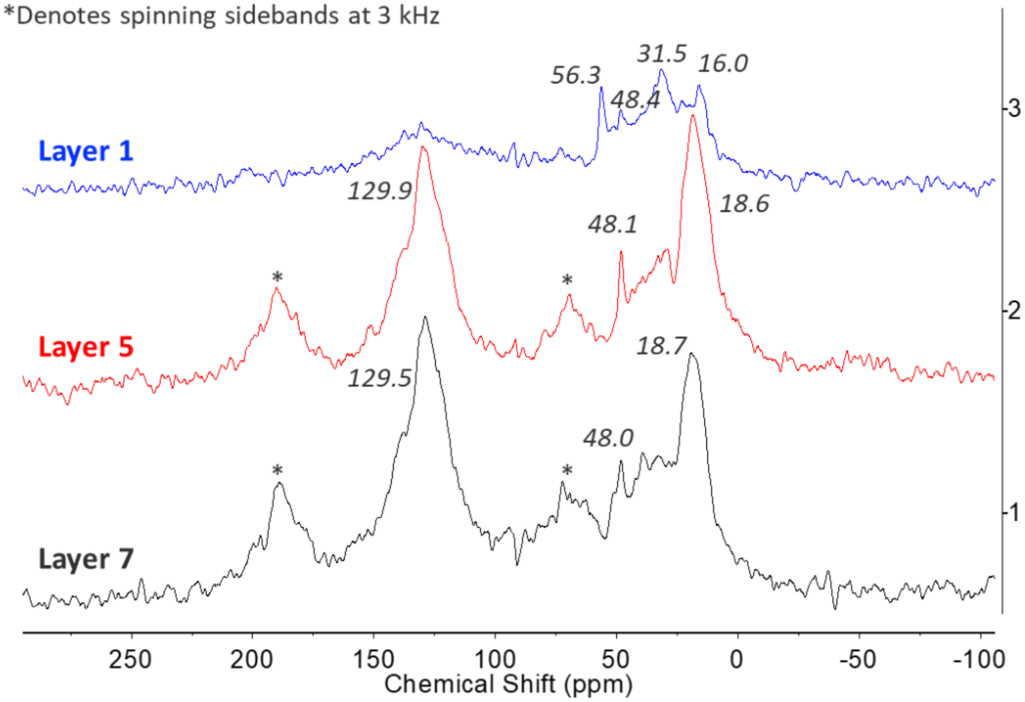

Figure 5: 13C NMR analysis of hydrocarbons trapped in catalyst pores of used catalyst, samples taken from bed positions as indicated in Figure 3

Data in Figures 3-5 suggest that a greater hydrocarbon inventory had established within the catalyst pores at the bottom of the bed than at the top, with very little hydrocarbon present at the top (inlet) of the bed. These results support the hypothesis that much of the pilot reactor bed was at lower activity than a fully activated catalyst and supports the observation of lower-than-expected catalyst activity. Further experimentation is required to determine how best to activate a pilot or larger scale reactor so that the full bed participates in high-octane hydrocarbon production.

A second activity involved determining the reactivity of methanol in producing hydrocarbons from NREL's Cu/BEA catalyst. The reaction chemistry most-studied is the conversion of DME to hydrocarbons, however, DME is the product of methanol dehydration, and the Cu/BEA catalyst performs DME hydration to methanol readily. If methanol could be fed to the catalyst instead of DME, it would remove a conversion step in a biomass to high-octane hydrocarbons process. To test, we flowed gas phase methanol to the catalyst in place of DME, and observed methanol dehydration to DME, but did not observe any hydrocarbons.

We next charged batch reactors with DME or methanol, catalyst, hydrogen, and a molecule known to participate as a reaction intermediate (propene). We hypothesized that methanol should participate in the methylation of reaction products, and that a long batch reaction would produce some hydrocarbons. Results of the test are shown in Figure 6 in the form of a gas chromatography trace overlaid for each experiment. Regardless of the presence of reactive propene, methanol produced little to no detectable hydrocarbons on the Cu/BEA catalyst, while DME produced hydrocarbons with or without propene added. This result gave us the opinion that the use of methanol as a feed for high-octane hydrocarbon synthesis would be a major troubleshooting exercise and perhaps impossible, and we decided to not pursue this matrix further.

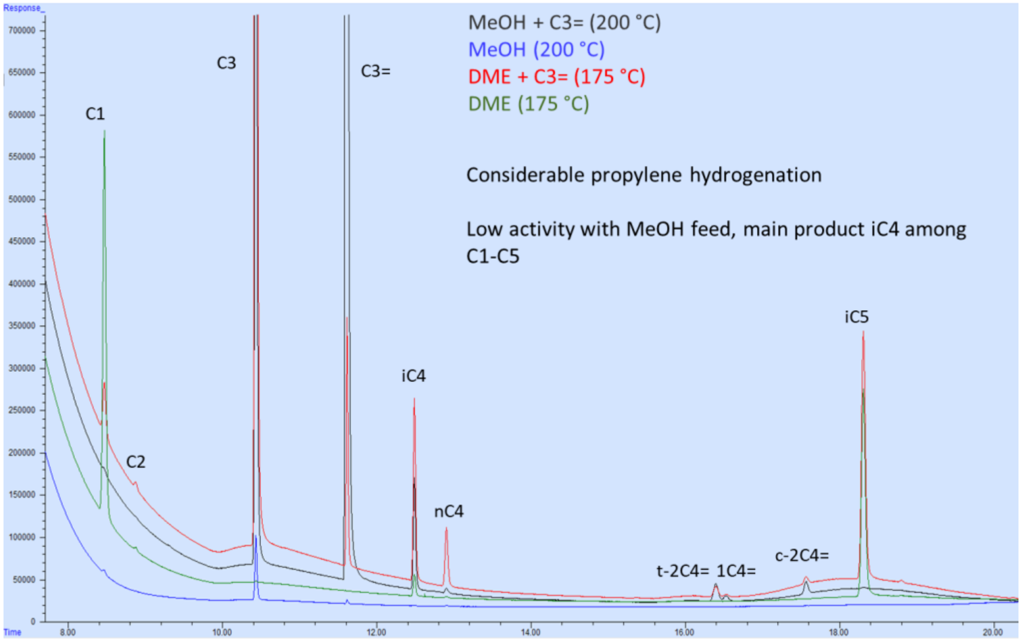

Figure 6: gas chromatograph of head space gases produced in a 20h batch reaction of methanol or DME, with or without added propene, over 0.5g of Cu/BEA catalyst with an initial H2 headspace. Reactors were operated at the temperatures indicated with a stir rate of 500 rpm.

Finally, we investigated the impact of propene gas on catalyst bed activation rate. Results were unrepeatable, ambiguous, and non-conclusive. Because the data is inconsistent, it is not shown here so as not to misinform.

No further experiments or discussions followed the above data collection and interpretation.

This work fostered an Agreement to Commercialize Technology (ACT) between NREL and ExxonMobil.

Subject Inventions Listing: None

ROI #: None