



Catalytic Fast Pyrolysis for Chemicals

Cooperative Research and Development Final Report

CRADA Number: CRD-16-00637

NREL Technical Contact: Joshua Schaidle

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Contract No. DE-AC36-08GO28308

**Technical Report
NREL/TP-5100-81201
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Cooperative Research and Development Final Report

Report Date: October 7, 2021

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: ExxonMobil Chemical Company

CRADA Number: CRD-16-00637

CRADA Title: Catalytic Fast Pyrolysis for Chemicals

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

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Sponsoring DOE Program Office(s): Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies Office (BETO)

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	\$250,000.00
Year 2	\$250,000.00
Year 3	\$250,000.00
TOTALS	\$750,000.00

Executive Summary of CRADA Work:

The purpose of this partnership between the ExxonMobil Chemical Company and NREL is to advance the state of the art for converting biomass to liquid hydrocarbons using catalytic fast pyrolysis (CFP), with particular emphasis on directing and improving yields of such liquid hydrocarbons for uses in commodity chemical markets. CFP of biomass is a promising route for the production of renewable fuels and chemicals, and the key driver for economic viability is carbon yield to valuable products. The majority of prior CFP work has been targeted at fuel production, but this CRADA seeks to pursue routes to chemical co-products, thereby enhancing the overall economic viability of CFP. This project is beneficial to the public because it advances a technology that could one day provide renewable fuels and chemicals to our economy, thus improving the sustainability of our transportation and chemical manufacturing sectors.

Summary of Research Results:

Over the last decade, NREL has worked extensively on catalyst fast pyrolysis of biomass to produce biofuels and chemicals. Through this CRADA project, NREL and the ExxonMobil Chemical Company engaged in joint activities to improve particular aspects of the CFP technology. These **joint activities** included:

1. Improving the yield of hydrocarbon liquids versus light hydrocarbon gases (e.g., methane) and carbonaceous solids (coke) through improvements in pretreatment, catalysis, reactor design, product recovery, or combinations thereof.
2. Identifying, in CFP hydrocarbon liquids, compounds of value in commodity chemical markets that are of sufficient concentration, ease of recovery, and market demand so that the overall value proposition of CFP is improved.
3. Improving selectivities within CFP hydrocarbon liquids to compounds of value in commodity chemical markets through improvements in pretreatment, catalysis, reactor design, product recovery, or combinations thereof.
4. Identifying typical purity targets for compounds of value in commodity chemical markets.
5. Identifying downstream upgrading processes for compounds of value in commodity chemical markets and define their integration with the CFP process.
6. Develop a generic facilities basis, including specification of key offsite facilities and utilities. Identify key gaps in supporting technology for facilities.

In all of these activities, the ExxonMobil Chemical Company served solely in a consulting role so as to provide an industrial perspective on our research activities. This consultation was provided via annual face-to-face meetings as well as periodic teleconferences on specific topics. No publications or subject matter inventions were co-authored, but ExxonMobil provided consultation on specific areas of active DOE research. Research within these areas resulted in follow-on publications which will be noted below.

Regarding joint activity 1, NREL advanced the state of the art of bifunctional metal-acid catalysts for CFP to achieve an improvement in overall bio-oil carbon yield. The two primary catalysts of interest were Pt/TiO₂ and Mo₂C. In the presence of hydrogen and operated in a fixed-bed reactor configuration, these catalysts exhibited an improvement in bio-oil yield as compared to a H-ZSM-5 catalyst (Fig. 1).¹ This work was captured in a recent article in *Energy & Environmental Science*,¹ with additional articles forthcoming. This improvement in carbon yield results in a cost reduction of approximately \$1/gasoline gallon equivalent for the overall process.

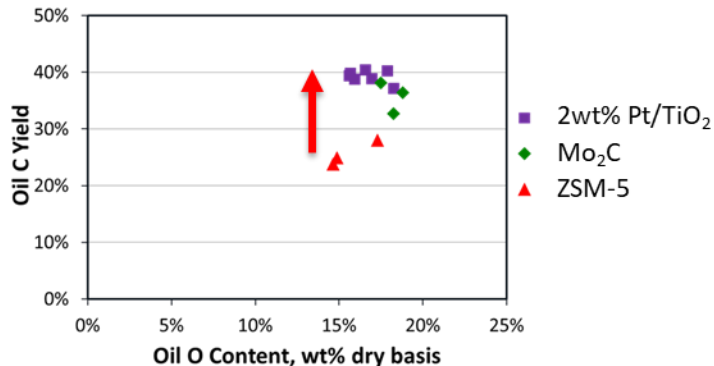


Fig 1. Carbon yield to bio-oil from CFP of pine over 2wt% Pt/TiO₂, Mo₂C, and ZSM-5.

Regarding joint activities 2, 4, and 5, NREL advanced the state of the art for separations targeted at extracting chemical co-products from the aqueous waste stream generated by CFP. These aqueous waste streams can contain on the order of 3% – 8% of the carbon in the biomass feedstock. We demonstrated the separation of phenol and catechol at 97% purity using a liquid-liquid extraction process followed by distillation and crystallization (Fig. 2).² This work was captured in a recent article in Green Chemistry,² and highlights an approach to improve the overall economic viability of CFP by turning a waste stream into a revenue generating stream. Using techno-economic analysis, it was estimated that a mixed phenolics stream could be produced from the aqueous waste stream at a minimum selling price of \$1.06/kg.

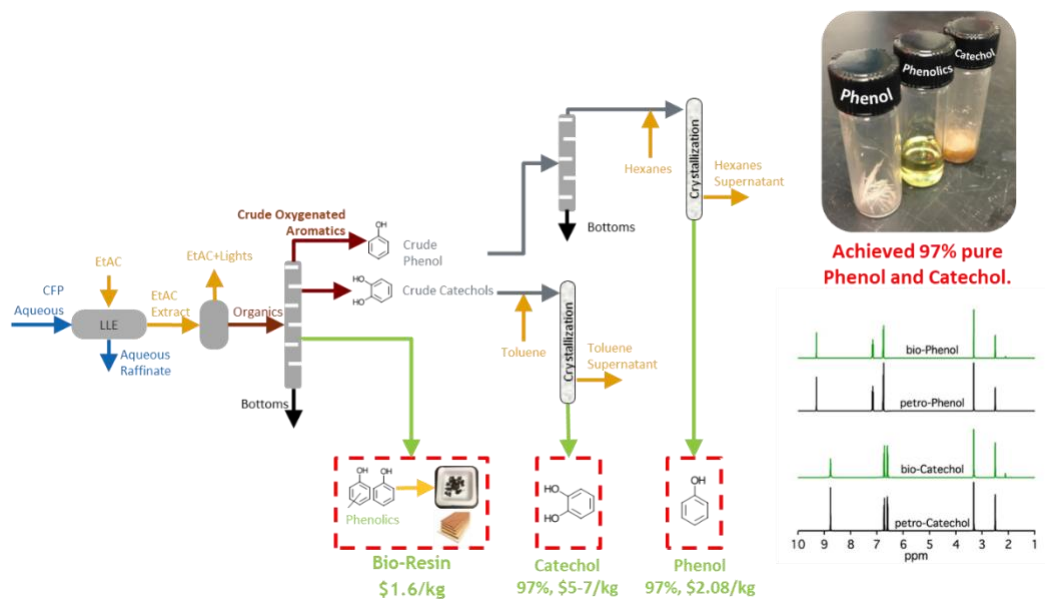


Fig. 2. Separations strategy for capturing and purifying catechol and phenol from the CFP aqueous waste stream. The collected products are shown in the top right along with their Nuclear Magnetic Resonance spectrums in the bottom right.

Regarding joint activity 3, NREL advanced the state of the art for directly producing light olefins from CFP. Ethylene and propylene are large-market commodity chemicals used as polymer precursors and are important intermediates in several product families produced by the ExxonMobil Chemical Company. By modifying a HZSM-5 catalyst with Ga and operating the catalyst in the presence of hydrogen (following activation in hydrogen), an approximately 3x increase in olefin carbon yield was observed as compared to a HZSM-5 benchmark catalyst (Fig. 3).³ This work was recently published in *Green Chemistry*,³ and it included catalyst characterization, model compound studies, and supporting computational modeling to identify the most likely Ga species responsible for this improvement in olefin yield: $[\text{Ga}(\text{OH})_2]^+$ and $[\text{GaH}(\text{OH})]^+$. This fundamental insight can be leveraged to guide development of next-generation catalytic materials.

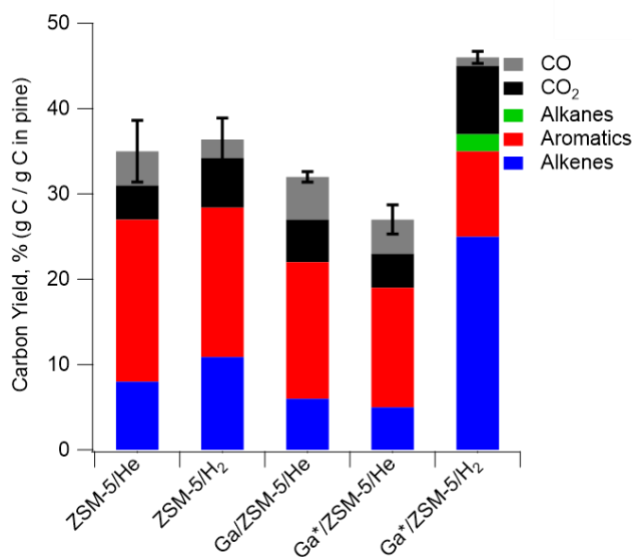


Fig. 3. Carbon yield to alkenes, aromatics, alkanes, CO₂, and CO during catalytic pyrolysis of pine using a micro-scale py-GCMS system. Ga* indicates a Ga/ZSM5 catalyst that was reduced in H₂ prior to the experiment.

Regarding joint activity 6, NREL published a design report in 2015 for the CFP process, which includes a comprehensive Aspen Plus process model and associated cost estimates.⁴ On a yearly basis, we provide state-of-technology updates for this initial process based on experimental progress and advancements. The ExxonMobil Chemical Company was consulted on various aspects of these state-of-technology updates, especially from an equipment, hydrogen utilization, separations, and facilities/infrastructure perspective, and we have published these recent reports.^{5,6} Of particular interest is the 2019 state-of-technology update which included the co-production of acetone and methyl-ethyl ketone alongside the liquid hydrocarbon fuel blendstock. The analysis indicated that co-production of these chemicals could reduce the minimum fuel selling price for fuel blendstocks by ca. \$0.5/gasoline gallon equivalent,⁶ highlighting the underlying premise of this CRADA that generating commodity chemicals from CFP represents a path to improve the overall economic viability of the process.

Lastly, due to our strong working relationship and the exposure of ExxonMobil to NREL's experimental capabilities, this CRADA project resulted in two other follow-on projects between NREL and ExxonMobil in the areas of (1) plastics pyrolysis and (2) technology evaluation of biomass pyrolysis and catalytic pyrolysis strategies to produce renewable chemicals (olefins and aromatics) and stabilized bio-oil.

References:

- [1] Michael Griffin, Kristiina Iisa, Huamin Wang, Abhijit Dutta, Kellene Orton, Richard French, Daniel Santosa, Nolan Wilson, Earl Christensen, Connor Nash, Kurt Van Allsburg, Frederick Baddour, Daniel Ruddy, Eric Tan, Hao Cai, Calvin Mukarakate, and Joshua Schaidle, "Driving towards cost-competitive biofuels through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration," *Energy & Environmental Science* 11, (2018): 2904-2918, <https://pubs.rsc.org/fa/content/articlehtml/2018/ee/c8ee01872c>.
- [2] A. Nolan Wilson, Abhijit Dutta, Brenna Black, Calvin Mukarakate, Kim Magrini, Joshua Schaidle, William Michener, Gregg Beckham, Mark Nimlos, "Valorization of aqueous waste streams from thermochemical biorefineries," *Green Chemistry* 21 (2019): 4217-4230, <https://pubs.rsc.org/lv/content/articlehtml/2019/gc/c9gc00902g>.
- [3] Kristiina Iisa, Yeonjoon Kim, Kellene Orton, David Robichaud, Rui Katahira, Michael Watson, Evan Wegener, Mark Nimlos, Joshua Schaidle, Calvin Mukarakate, Seonah Kim, "Ga/ZSM5 catalyst improves hydrocarbon yields and increases alkene selectivity during catalytic fast pyrolysis of biomass with co-fed hydrogen," *Green Chemistry* 22 (2020): 2403-2418, <https://pubs.rsc.org/en/content/articlehtml/2020/gc/c9gc03408k>.
- [4] Abhijit Dutta, Asad Sahir, Eric Tan, David Humbird, Lesley Snowden-Swan, Pimphan Meyer, Jeff Ross, Danielle Sexton, Raymond Yap, and John Lukas, "Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: thermochemical research pathways with in situ and ex situ upgrading of fast pyrolysis vapors," NREL Technical Report, March 2015, NREL/TP-5100-62455, <https://www.nrel.gov/docs/fy15osti/62455.pdf>.
- [5] Abhijit Dutta, Kristiina Iisa, Calvin Mukarakate, Michael Griffin, Eric Tan, Joshua Schaidle, David Humbird, Huamin Wang, Damon Hartley, David Thompson, Hao Cai, "Ex situ catalytic fast pyrolysis of lignocellulosic biomass to hydrocarbon fuels: 2018 state of technology and future research," NREL Technical Report, October 2018, NREL/TP-5100-71954, <https://www.nrel.gov/docs/fy19osti/71954.pdf>.
- [6] Abhijit Dutta, Kristiina Iisa, Michael Talmadge, Calvin Mukarakate, Michael Griffin, Eric Tan, Nolan Wilson, Matt Yung, Mark Nimlos, Joshua Schaidle, Huamin Wang, Michael Thorson, Damon Hartley, Jordan Klinger, Hao Cai, "Ex situ catalytic fast pyrolysis of lignocellulosic biomass to hydrocarbon fuels: 2019 state of technology and future research," NREL Technical Report, March 2020, NREL/TP-5100-76269, <https://www.nrel.gov/docs/fy20osti/76269.pdf>.

Subject Inventions Listing:

None

ROI #:

None