



The Development of Catalysts for Upgrading of Pyrolysis Vapor for Refinery Feedstocks and Intermediates

Cooperative Research and Development Final Report

CRADA Number: CRD-12-00497

NREL Technical Contact: Mark Nimlos

**NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC**

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-2800-79862
April 2021



The Development of Catalysts for Upgrading of Pyrolysis Vapor for Refinery Feedstocks and Intermediates

Cooperative Research and Development Final Report

CRADA Number: CRD-12-00497

NREL Technical Contact: Mark Nimlos

Suggested Citation

Nimlos, Mark. 2021. *The Development of Catalysts for Upgrading of Pyrolysis Vapor for Refinery Feedstocks and Intermediates: Cooperative Research and Development Final Report, CRADA Number CRD-12-00497*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-2800-79862. <https://www.nrel.gov/docs/fy21osti/79862.pdf>.

**NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC**

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-2800-79862
April 2021

National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401
303-275-3000 • www.nrel.gov

NOTICE

This work was authored [in part] by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government.

This work was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, its contractors or subcontractors.

This report is available at no cost from the National Renewable Energy Laboratory (NREL) at www.nrel.gov/publications.

U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via www.OSTI.gov.

Cover Photos by Dennis Schroeder: (clockwise, left to right) NREL 51934, NREL 45897, NREL 42160, NREL 45891, NREL 48097, NREL 46526.

NREL prints on paper that contains recycled content.

Cooperative Research and Development Final Report

Report Date: April 26, 2021

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA 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: Johnson Matthey

CRADA Number: CRD-12-00497

CRADA Title: The Development of Catalysts for Upgrading of Pyrolysis Vapor for Refinery Feedstocks and Intermediates

Responsible Technical Contact at Alliance/NREL:

Mark Nimlos | mark.nimlos@nrel.gov

Name and Email Address of POC at Company:

Michael Watson | mike.watson@matthey.com

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	\$ 1,000,000.00
Year 2	\$ 1,000,000.00
Year 3	\$1,000,000.00
Year 4	\$1,000,000.00
Year 5	\$1,000,000.00
TOTALS	\$ 5,000,000.00

Executive Summary of CRADA Work:

Fast pyrolysis of biomass with vapor phase upgrading (VPU) can produce refinery feedstocks or intermediates that can meet the Department of Energy’s goal of cost-competitive hydrocarbon fuels by 2017. A key technical barrier for this technology is the lack of selective, cost effective catalysts that can produce high yields of fuel-appropriate hydrocarbons from the pyrolysis vapors. In overcoming this barrier, it will be important to engage leading catalyst development companies

to devote their resources and expertise to the development of these materials. Thus, we propose a Cooperative Research and Development Agreement (CRADA) between the National Renewable Energy Laboratory (NREL), a world leader in biomass pyrolysis research and Johnson Matthey (JM), a world leader in the production of advanced catalyst materials to develop and test novel catalysts for efficient VPU. Through its Intercat Inc. subsidiary in Savannah, Ga., Johnson Matthey is internationally recognized as a leader in zeolite-based vapor phase upgrading in refinery duties and an emerging developer of biomass conversion technologies.

The research and development efforts described in the proposed work will build upon existing collaborations between NREL and JM and play to the strengths of both institutions. NREL will analyze the composition of pyrolysis vapors as an input to catalyst design, screen and test catalysts, characterize the resulting oil and conduct techno-economic analysis. Catalyst samples will be produced and funded by JM. JM will design and synthesize catalysts, characterize fresh and used catalysts and develop catalyst supports needed to achieve commercially meaningful lifetimes. The project will span catalyst development and testing from the fundamental stage using quantum mechanical modeling and chemical reaction analysis to catalyst screening to integrated pilot studies.

The proposed work will occur over five years starting in FY2013 and culminating in pilot-scale demonstrations using the most promising catalyst in FY2017. At the start NREL and JM will develop new catalyst materials for increasing fuel range hydrocarbon yields. Optimization of the hydrogen requirement for the process is seen as a key requirement and the joint program will develop technologies to most effectively manage this critical process need. This will include utilizing added molecular hydrogen and hydrogen donor molecules, the use of multifunctional catalysis to maximize hydrogen production from the low value, light component of the vapor, and breaking of aromatic rings. The program will also develop technology to optimize the yields of valuable co-products (e.g. propylene) from the process. Optimization of light olefin yields from a refinery is an increasingly important factor in driving economic success and has not been the subject of significant research focus in pyrolysis upgrading. These catalysts will be screened using laboratory scale reactor systems at NREL and catalyst characterization tools at JM. Down-selected catalysts will be tested under more realistic conditions at laboratory scales to obtain kinetics for scale-up and economic analysis. Finally, pilot-scale experiments will be conducted to demonstrate the technology. All of the experimental data in this project will be used to help build credible process and techno-economic cost models, which will also help guide the research.

The benefits of this CRADA for the Department of Energy are many. 1) The project will create a strong collaboration between NREL and JM in pyrolysis vapor upgrading, which will accelerate the development of catalysts. 2) JM and NREL will be involved in all of the steps of catalyst development and testing through pilot studies. 3) The work will result in a fundamental understanding of catalysis for upgrading biomass. 4) Novel catalytic materials will be produced that will benefit other OPB projects. 5) The catalysts and processes will be incorporated into realistic economic analysis models that will be validated with data from realistic experimental measurements.

Summary of Research Results:

Task 1. Catalyst design

Extensive molecular modeling was conducted on zeolite catalysts to determine reaction mechanisms and to help explain observed reactivities. For instance, isopropanol dehydration was used as a model reaction for the catalysis of biomass pyrolysis vapors. The hydroxyl groups found on the pyrolysis products from carbohydrates undergo similar dehydration reaction on zeolite catalysts. We have observed that gallium loaded zeolites undergo greater dehydration in when the catalyst is reduced, which results in high yields of olefins. To explain this, quantum molecular modeling of gallium loaded zeolites was conducted using isopropanol and typical results are shown in Figure 1. These calculations showed that the barriers for reaction were lower for the reduced gallium.

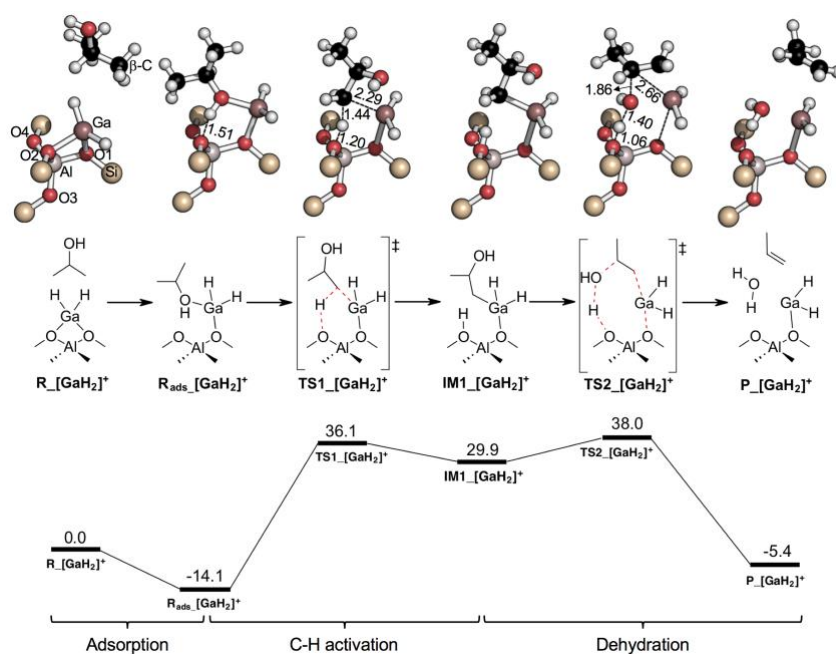


Figure 1. The potential energy surface for the dehydration of isopropanol on the gallium site in a zeolite catalyst.

Task 2. Catalyst synthesis

Johnson Matthey worked with NREL's CFP group to develop zeolite-based catalysts that increased 1) biomass-derived fast pyrolysis vapor conversion to upgradable hydrocarbons via VPU and 2) bio oils in the presence of petroleum feedstocks like vacuum gas oil (VGO) during co-processing to fuels and chemicals. Catalysts variations were tested at the micro scale for performance with the best materials scaled up to kg quantities for testing in NREL's pilot fluidized catalytic cracking (FCC) unit. The most active catalysts were an HZSM-5 based catalyst that produces aromatics and enhanced olefins along with reduced "other" species as shown in the Figure 2. An E-Cat mixture with MFI zeolite produced > 90wt% aromatics while La reduced olefin content. These catalysts will be scaled up for evaluation in NREL's FCC in late 2020. The ability to "tune" biogenic product compositions for fuels and chemicals production is a key output of this CRADA collaboration.

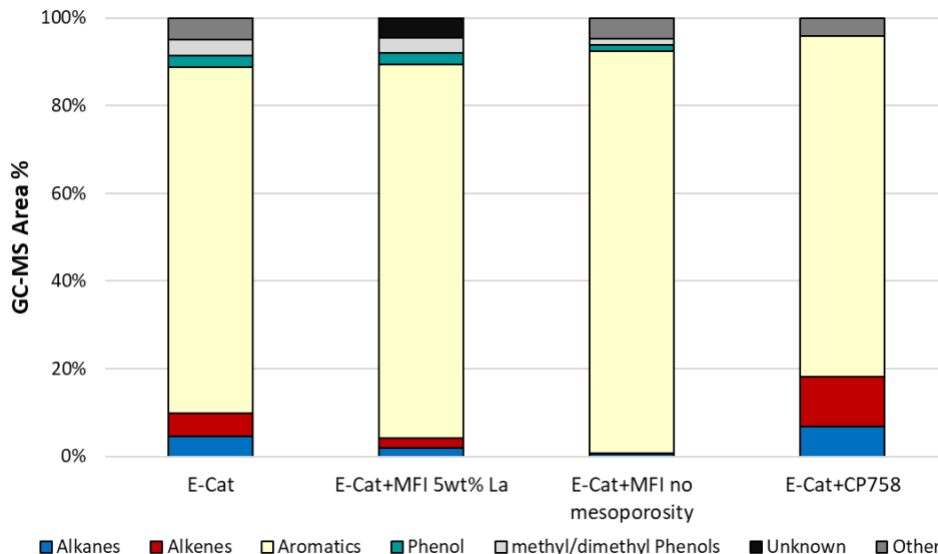


Figure 2. Compound classes determined by GCMS analysis of condensed fuel product produced with JM catalyst mixtures (10wt% JM/90wt% E-Cat) and 10wt% mixtures of pine CFP oil in VGO using a micro scale reactor system.

Task 3. Catalyst characterization

Comprehensive material characterization performed at JM and NREL has provided insight into the properties of multiple classes of VPU catalysts (e.g., zeolites, supported metals, metal carbides). The CRADA allowed our research team to leverage capabilities at each institution, which streamlined access to techniques such as ICP-OES, XRD, TPD, TEM, SEM, Raman and IR spectroscopy, chemisorption, and physisorption. The data from these measurements, coupled with multi-scale reaction testing, informed significant improvements in catalyst design and enabled a >60% relative increase in carbon efficiency. Typical experimental results for conversion of pyrolysis vapors to aromatic hydrocarbons and coke as a function of catalyst are shown in Figure 3. Likewise, extended catalyst lifetime has been achieved by using post-reaction characterization to identify and mitigate deactivation mechanisms. Collectively, these improvements have played an important role in reducing the modelled median fuel selling prices (MFSP) from \$6.25 to \$3.50/gallon gasoline equivalent (GGE) from 2014-2018.

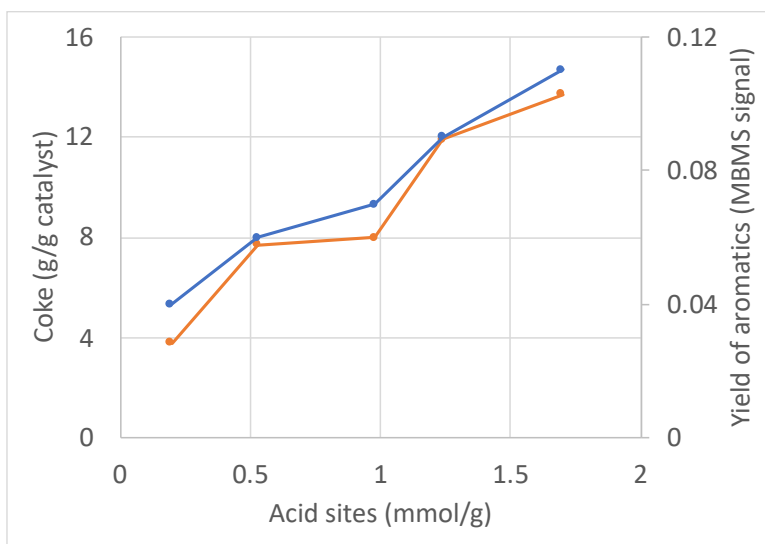


Figure 3. Yield of aromatics and coke as a function of catalyst acid sites. Although the yields of the desired aromatic hydrocarbons increase with the number of acid sites in a catalyst, the amount of coke also increases with acid sites. This information helps select catalyst properties for pyrolysis vapors conversion.

Task 4. Catalyst screening with laboratory reactors

Several zeolite-based catalysts were evaluated on NREL's micro- and bench-scale reactors for their performance towards upgrading biomass pyrolysis vapors into fuel and chemical intermediates. Figure 4 shows a schematic diagram of the bench scale reactor used for screening JM catalysts. The materials tested included ZSM-5, mordenite, γ -zeolite, β -zeolite, including meso- or metal-modified zeolites, silica alumina and hydrotalcite catalysts. Some of the results were published in high impact factor journals¹⁻⁸ highlighted below and three were selected for the back-cover of Green Chemistry journal^{2, 5, 7} and one was selected for the cover of ACS Sustainable Chemistry and Engineering journal⁶. Hydrodeoxygenation catalysts and the impacts of support for bifunctional metal-acid catalysts were also evaluated for biomass pyrolysis vapor upgrading and hydrodeoxygenation catalysts for hydroprocessing of upgraded pyrolysis oils.

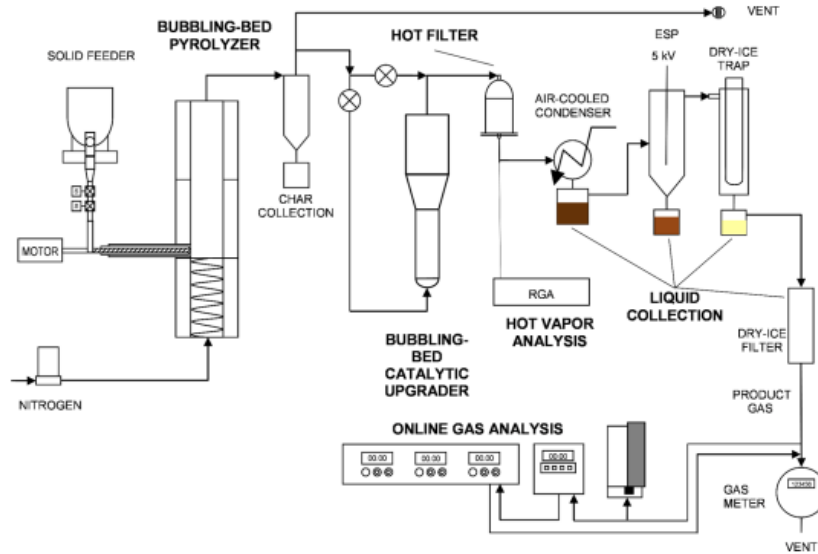


Figure 4. Schematic diagram of 2-inch fluidized bed reactor (2FBR) used to screen catalysts developed as part of the JM/NREL CRADA.

Task 5. Upgrading kinetics

A combined experimental and modelling protocol was used to extract intrinsic kinetics for describing the upgrading of biomass pyrolysis vapors and deactivation of the ZSM-5 based materials (Figure 5). These models have been used in combination with transport models to predict the performance of VPU reactors.

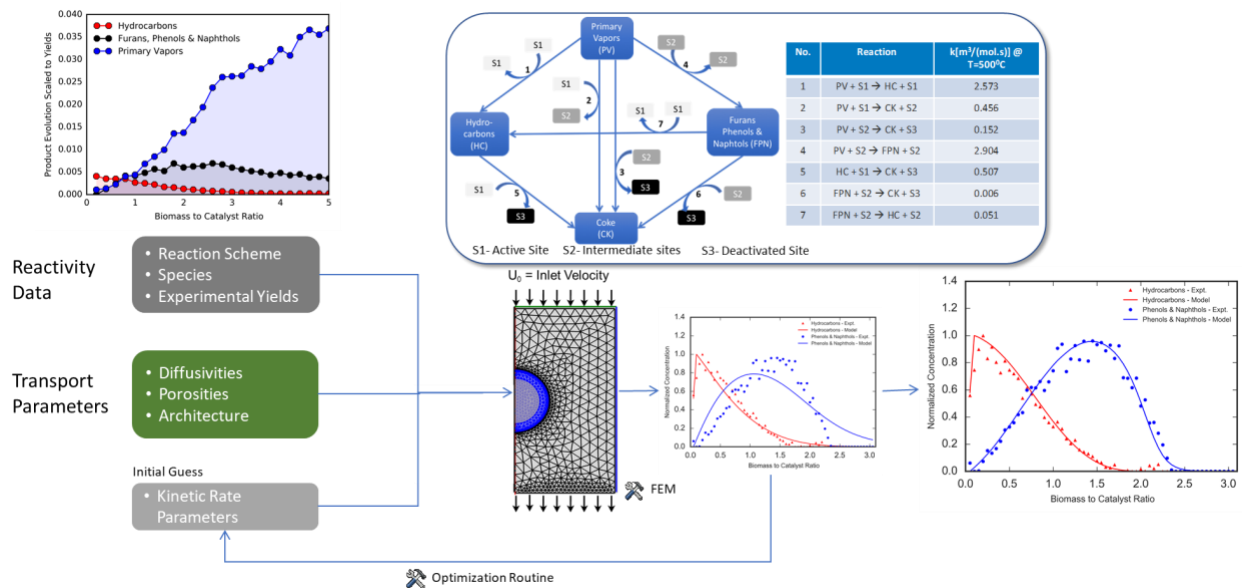


Figure 5. Process for developing a kinetic model of the upgrading of biomass pyrolysis vapors using a ZSM-5 catalyst. Experimental data from NREL’s MBMS (upper left) is used to develop a chemistry model (upper right) which is combined with a transport model (bottom).

Task 6. Pyrolysis vapor filtration

Pyrolysis vapor filtration using commercially available ceramic filters (Pall) removed > 99% of char and alkali particulates that can catalyze undesirable polymerization reactions in both vapors and condensed liquids. Filtered condensed pyrolysis liquids were shown to be stable with storage with periodic samples taken at 6-month intervals showing little or no change in oil composition. Adding a catalyst to the interior of the annular filter provides additional vapor conditioning prior to catalytic upgrading. Mo-heteropolyacid supported catalysts alkylated particulate free vapors before catalytic upgrading via zeolites to fungible hydrocarbon liquids. Typical results are shown in Figure 6. The added alkylation improved product fuel octane numbers. Future work will assess Johnson Matthey modified zeolites in the filter to assess impact on vapor composition prior to FCC upgrading in a Davison Circulating Riser reactor system. This work is published in ACS Sustainable Chemistry and Engineering.

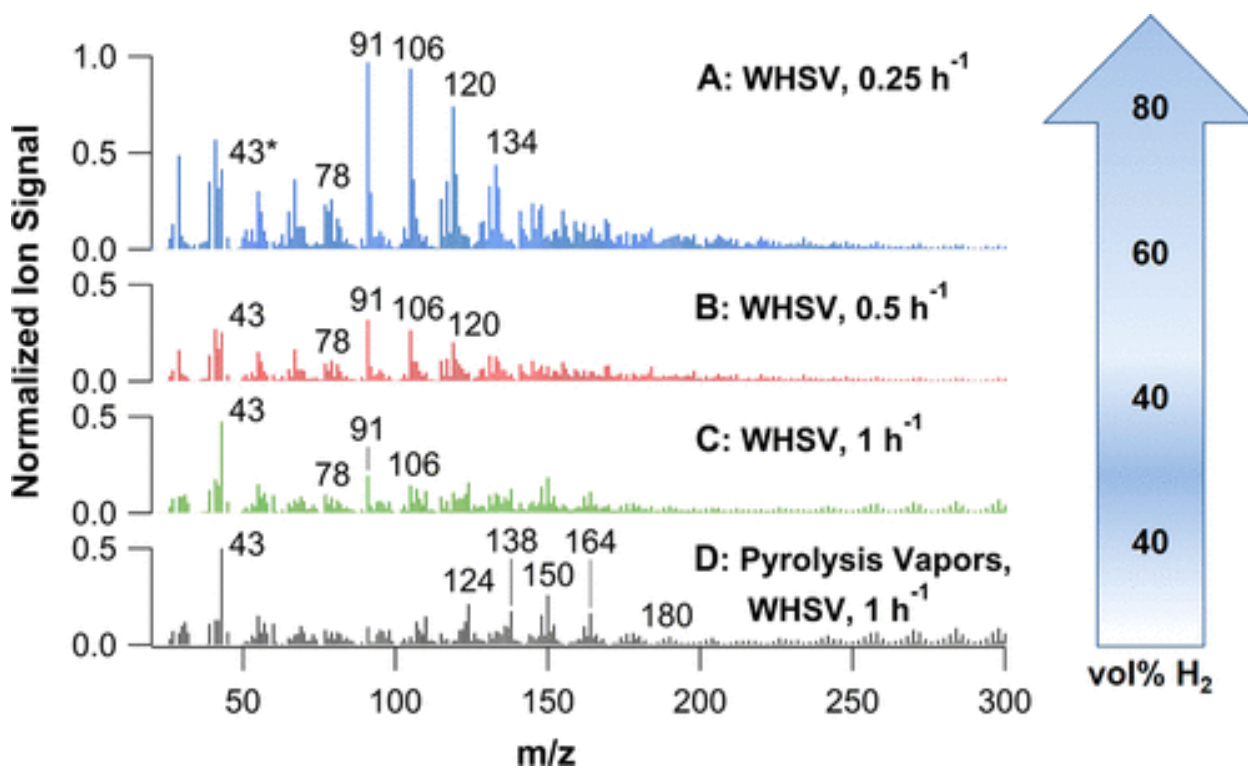


Figure 6. Comparison of molecular beam mass spectra for pyrolysis vapors over a molybdenum heteropolyacid on titania with increasing weight hourly space velocity (WHSV) (A – C) compared to the raw pyrolysis spectra (D). [Peterson 2019, ACS Sustainable Chemistry and Engineering]

Task 7. Integrated testing with a riser reactor

Johnson Matthey is developing and providing modified zeolite catalysts for upgrading of the gas phase arising from fast pyrolysis of biomass to produce liquid hydrocarbon fuel intermediates that can either be hydrotreated and fractionated into gasoline and diesel fuel or co-processed with petroleum feedstocks to produce biogenic carbon containing gasoline. Both processes use a Davison Circulating Riser reactor for fluid catalyst cracking of pyrolysis vapors, bio oils, or bio oil petroleum feedstock mixtures. Zeolite modifications include adding metals, mesoporosity, and varied additives to HZSM-5 based catalysts. These modifications target increased biomass

oxygenate conversion to hydrocarbons with specific additives producing varied hydrocarbons of interest to refineries for either fuels or chemicals production. Figure 7 shows JM catalyst impact on liquid products obtained from DCR processing. The CP758 proprietary catalyst reduces oxygenate (phenol) conversion while increasing toluene and xylene in the hydrocarbon product.

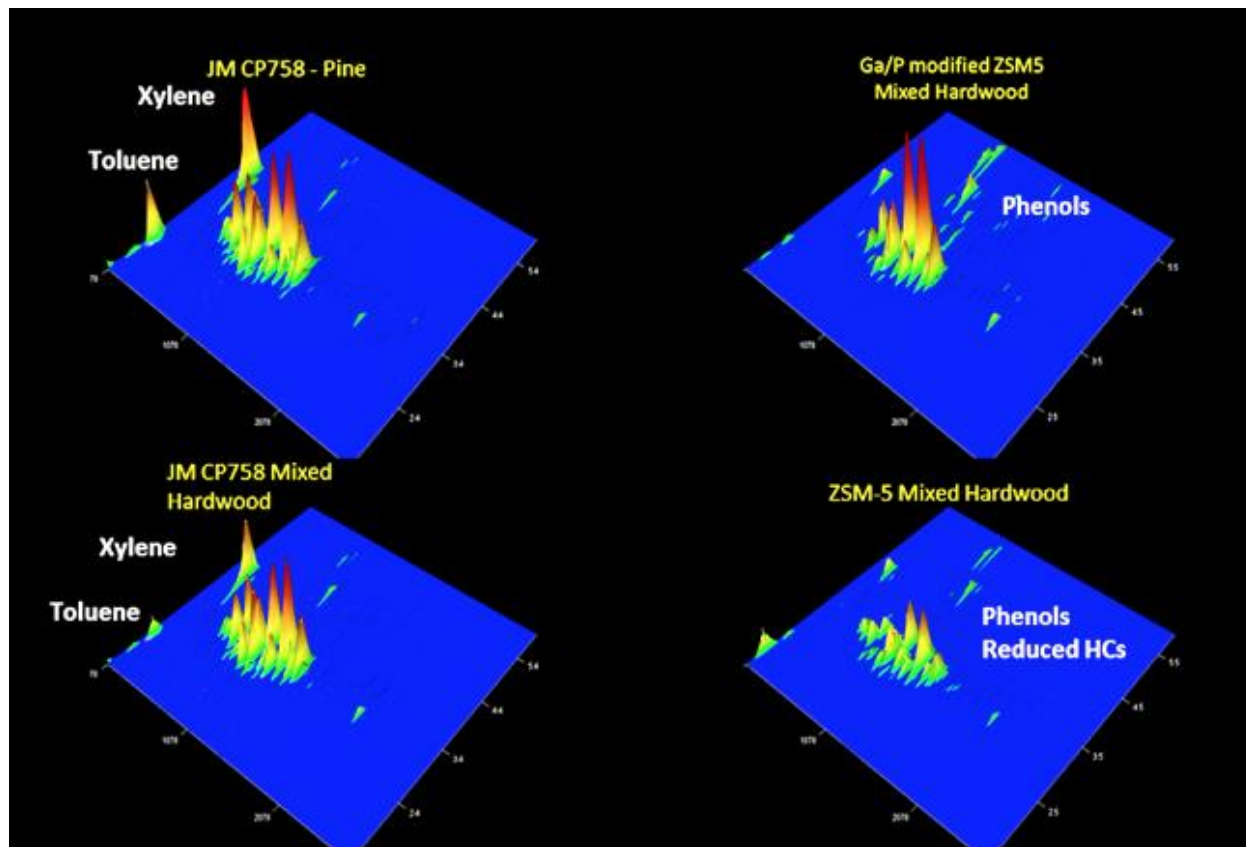


Figure 7. Two dimensional GC x GC/TOFMS chromatograms of upgraded oils using pyrolysis vapors and catalysts.

Task 8. Testing of pyrolysis oil

Fast pyrolysis with vapor phase upgrading (VPU) oils were found to have dramatically different chemical properties than fast pyrolysis (FP) oils. To start, VPU oils have much lower oxygen content, typically ~15-20 wt%, while FP oils have oxygen content ~35 wt%; these oxygen contents do not include water, which is typically 5-10 wt% for VPU oils and 15-20 wt% for FP oils. Correspondingly, VPU oils have much higher carbon content (~75 wt%) as compared to FP oils (~58 wt%). Beyond lower oxygen content, VPU oils have lower acidity, lower viscosity, and higher energy density than FP oils. It is well known that FP oils change significantly (age) upon storage at room temperature. This is evidenced as a rise in viscosity, or a decrease in carbonyl content upon aging. VPU oils, however, do not age nearly as rapidly as FP oils. FP oils see significant changes upon storage at room temperature for several months. VPU oils, however, do not see appreciable changes on these timescales.

Detailed chemical composition was characterized by both GC-MS and ^{13}C NMR. From ^{13}C NMR analysis it was apparent that the reduction in oxygen content upon catalytic upgrading was

due mostly to a reduction in carbonyl (C=O) and aliphatic C-O functionality, while aromatic C-O and methoxyl oxygen contents were similar between VPU and FP. Figure 8 shows the results of detailed chemical analysis of VPU and FP biocrude. Aliphatic and aromatic C-C functionality was similar for VPU and FP, but the VPU sample had a significantly higher aromatic C-H content than the FP sample. The GC-MS results largely corroborated the ^{13}C NMR results, even though GC-MS is only capable of analyzing < 50% of the samples due to volatility limitations. Less FP oils was able to be analyzed than VPU oil, due to a larger amount of acids (which would require derivatization for GC-MS analysis) and the presence of higher molecular weight species in the FP sample. Also, the VPU sample showed a higher amount of upgraded aromatic species (1, 2, and 3-ring aromatics, e.g., benzene, naphthalene). Further, VPU samples still contained large amounts of phenolics (including methoxyphenols and alkylphenols) and furan species which survived the upgrading process. However, VPU oils had less abundances of sugars than did FP oils.

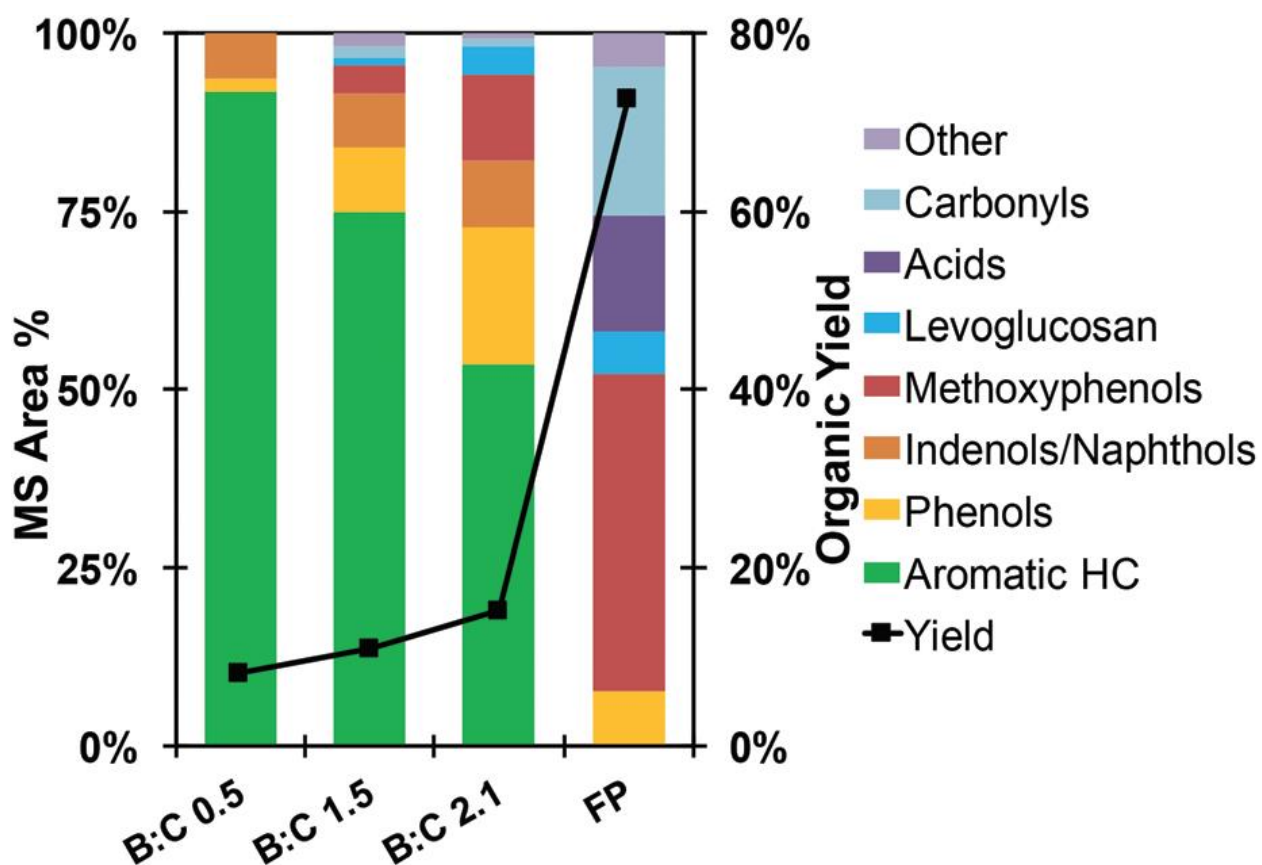


Figure 8. Measured composition of fast pyrolysis (FP) oil and the organic oils from VPU of pine pyrolysis vapors over HZSM-5 at different biomass-to-catalyst ratios (B : C) [Iisa 2018, Green Chem]

Task 9. Techno-economic analysis

In 2015 a design report was published^a that focused on *in-situ* and *ex-situ* catalytic fast pyrolysis. The baseline techno-economic modeling that was conducted for this report was based upon literature data and some preliminary data collected at NREL and the report focused on technology improvements that could lead to a MFSP of \$3.31/ GGE. In 2015 a journal article was published^b that investigated TEA models with a fixed bed reactor configuration compared to a circulating fluidized bed reactor for the catalyst vapor phase upgrading. In a journal article published³ in 2018 that was jointly published with JM scientists, the economics of oxygen removal in the catalytic upgrading step was compared to oxygen removal during a subsequent hydrotreating step. In the most recent published^c techno-economic study, a fuel price of \$3.91/GGE was obtained from a TEA model based upon the most recent experimental measurements.

NREL/JM CRADA Joint Publications

1. Iisa, K.; French, R. J.; Orton, K. A.; Yung, M. M.; Johnson, D. K.; ten Dam, J.; Watson, M. J.; Nimlos, M. R., In Situ and ex Situ Catalytic Pyrolysis of Pine in a Bench-Scale Fluidized Bed Reactor System. *Energy Fuels* 2016, 30 (3), 2144-2157, [10.1021/acs.energyfuels.5b02165](https://doi.org/10.1021/acs.energyfuels.5b02165).
2. Iisa, K.; Kim, Y.; Orton, K. A.; Robichaud, D. J.; Katahira, R.; Watson, M. J.; Wegener, E. C.; Nimlos, M. R.; Schaidle, J. A.; Mukarakate, C.; Kim, S., Ga/ZSM-5 catalyst improves hydrocarbon yields and increases alkene selectivity during catalytic fast pyrolysis of biomass with co-fed hydrogen. *Green Chem.* 2020, [10.1039/C9GC03408K](https://doi.org/10.1039/C9GC03408K).
3. Iisa, K.; Robichaud, D. J.; Watson, M. J.; ten Dam, J.; Dutta, A.; Mukarakate, C.; Kim, S.; Nimlos, M. R.; Baldwin, R. M., Improving biomass pyrolysis economics by integrating vapor and liquid phase upgrading. *Green Chem.* 2018, 20 (3), 567-582, [10.1039/C7GC02947K](https://doi.org/10.1039/C7GC02947K).
4. Mukarakate, C.; Evans, R. J.; Deutch, S.; Evans, T.; Starace, A. K.; ten Dam, J.; Watson, M. J.; Magrini, K., Reforming Biomass Derived Pyrolysis Bio-oil Aqueous Phase to Fuels. *Energy Fuels* 2017, 31 (2), 1600-1607, [10.1021/acs.energyfuels.6b02463](https://doi.org/10.1021/acs.energyfuels.6b02463).
5. Mukarakate, C.; McBrayer, J. D.; Evans, T. J.; Budhi, S.; Robichaud, D. J.; Iisa, K.; Ten Dam, J.; Watson, M. J.; Baldwin, R. M.; Nimlos, M. R., Catalytic fast pyrolysis of biomass: the reactions of water and aromatic intermediates produces phenols. *Green Chem.* 2015, 17 (8), 4217-4227, DOI: [10.1039/c5gc00805k](https://doi.org/10.1039/c5gc00805k).
6. Mukarakate, C.; Orton, K.; Kim, Y.; Dell'Orco, S.; Farberow, C. A.; Kim, S.; Watson, M. J.; Baldwin, R. M.; Magrini, K. A., Isotopic Studies for Tracking Biogenic Carbon during Co-processing of Biomass and Vacuum Gas Oil. *ACS Sustain. Chem. Eng.* 2020, [10.1021/acssuschemeng.9b05762](https://doi.org/10.1021/acssuschemeng.9b05762).

^a Dutta *et al.*, Technical Report, NREL/TP-5100-62455, PNNL-23823, March 2015

^b Dutta, et al. *Topics in Catalysis* **2015**, 59, 2-18.

^c Griffin, et al. *Energy Envir. Sci.* **2018**, 11, 2904-2918.

7. Mukarakate, C.; Watson, M. J.; Ten Dam, J.; Baucherel, X.; Budhi, S.; Yung, M. M.; Ben, H.; Iisa, K.; Baldwin, R. M.; Nimlos, M. R., Upgrading biomass pyrolysis vapors over β -zeolites: Role of silica-to-alumina ratio. *Green Chem.* 2014, 16 (12), 4891-4905, [DOI: 10.1039/c4gc01425a](https://doi.org/10.1039/c4gc01425a).
8. Starace, A. K.; Black, B. A.; Lee, D. D.; Palmiotti, E. C.; Orton, K. A.; Michener, W. E.; ten Dam, J.; Watson, M. J.; Beckham, G. T.; Magrini, K. A.; Mukarakate, C., Characterization and Catalytic Upgrading of Aqueous Stream Carbon from Catalytic Fast Pyrolysis of Biomass. *ACS Sustain. Chem. Eng.* 2017, 5 (12), 11761-11769, [10.1021/acssuschemeng.7b03344](https://doi.org/10.1021/acssuschemeng.7b03344).
9. Peterson, B.; Engtrakul, C.; Wilson, A. N.; Dell'Orco, S.; Orton, K. A.; Deutch, S.; Yung, M. W.; Starace, A. K.; Parent, Y.; Chiaramonti, D.; Magrini, K. A., Catalytic Hot-Gas Filtration with a Supported Heteropolyacid Catalyst for Preconditioning Biomass Pyrolysis Vapors, *ACS Sustain. Chem. Eng.* 2019, 7 (17), 14941 – 14952, [10.1021/acssuschemeng.9b03188](https://doi.org/10.1021/acssuschemeng.9b03188).

Subject Inventions Listing:

None

ROI #:

An NREL/JM joint ROI was submitted based on the work that was published in report 2 above. The joint ROI was titled “ROI-18-124: Catalysts and conditions for producing higher olefins from biomass vapors”.