



Catalytic Fast Pyrolysis with Bio-Oil Recycle to Enhance Yield of Aromatics

Cooperative Research and Development Final Report

**CRADA Number: CRD-18-00765 Project 16
(Mods 15-28-33)**

NREL Technical Contact: Calvin Mukarakate

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Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5100-88379
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Cooperative Research and Development Final Report

Report Date: December 15, 2023

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 Research and Engineering Company (EMRE)

CRADA Number: CRD-18-00765 (Project 16)

CRADA Title: Catalytic Fast Pyrolysis with Bio-Oil Recycle to Enhance Yield of Aromatics

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Sponsoring DOE Program Office(s):

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

Joint Work Statement Funding Table showing DOE commitment:

No NREL Shared Resources.

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	\$0.00
Year 2, Modification #1	\$0.00
Year 3, Modification #2	\$0.00
TOTALS	\$0.00

Executive Summary of CRADA Work:

The objective of this project is to pursue enhanced yields of benzene, toluene, and xylene (BTX) from catalytic fast pyrolysis (CFP) of biomass by recycling a portion of the bio-oil back to the pyrolyzer. Additionally, this work evaluated the impact of CFP process variables on the yields of BTX.

Summary of Research Results:

This CRADA Final Report addresses Modifications 13, 28 and 33 of this **Multi-Project CRADA Field of Study:**

Work performed under this CRADA may include research related to the *Petroleum and Petrochemical Field or PPC Field*. *Petroleum and Petrochemical Field or PPC Field* means the exploration, production, refining, supply, transport, formulation and/or blending, sales, including retail sales, and marketing of hydrocarbons, specifically including crude oil, petroleum fractions, petroleum refining fractions (including vacuum gas oil, heavy gas oil, biofuel, biofuel blends, vacuum resid, atmospheric resid, coking resid), power generation and associated transportation and marketing, petrochemicals and polymers, bitumen, heavy oil, water/oil emulsions, oil sands, shale oil, coal, coal gases and liquids, hydrocarbon gases either naturally occurring or synthesized and liquid forms or derivatives thereof, and petrochemicals (including polymers), or the products of any of the foregoing, together with methods of making same. The PPC Field shall also include geothermal, hydro, solar, wind and nuclear alternative energy sources, carbon capture and sequestration, separations and separation/storage materials, biobased fuels, chemicals and basestocks, as well as all catalysis and catalytic materials useful for the processing of petroleum or petrochemicals within the PPC Field as defined above.

This is a very unique CRADA that is designed to enable ExxonMobil to work with several DOE labs. For most labs, we subcontract to them via an MPO (memorandum purchase order) but to NETL they have unique requirements so they just joined as a party to the CRADA so EM can work with them directly instead of going through us. NETL will always be listed as a party in Osprey because they are a signatory to the overarching CRADA, though they are only participating on a subset of the projects. They do not sign mods for projects they are not participating in, and therefore they also do not need to approve CFRs for projects they are not participating in. See the attached file - Column D shows if there was another lab involved. It looks like Project 16 did not include NETL.

Purpose: This work will address knowledge gaps in the production of renewable chemicals (aromatics and olefins) from catalytic fast pyrolysis of biomass. One of these gaps is the impact of recycling a fraction of the bio-oil back to the pyrolyzer and co-feeding it with the biomass. This strategy decreases the oxygen content and increases the effective H/C ratio of the total feed going into the pyrolyzer, but the impact of this approach on the yield of benzene, toluene, and xylene is unclear. Experiments performed within this project will quantify the impact of bio-oil recycling on the yield of these monoaromatics.

Statement of Work - Task Descriptions:

Below is a list of tasks NREL will perform:

Task 1: Modification and Commissioning of NREL's Bench-Scale Integrated Catalytic Pyrolysis System

The experiments for this campaign require that (1) the catalytic upgrading reactor of NREL's bench-scale integrated catalytic pyrolysis system be operated in a fluidized bed configuration with zeolite-based catalysts and (2) a fraction of the liquid bio-oil be co-fed into the pyrolyzer with biomass.

NREL will (1) reconfigure the catalytic upgrading reactor from a fixed-bed configuration to an overflowing fluidized bed configuration, (2) design a liquid feeding system, perform a process hazard analysis, proceed through management of change, and modify the system for liquid co-feeding, (3) procure/prepare the zeolite catalyst, and (4) commission the system.

Task 1 Work Description:

The NREL's 2-inch fluidized bed reactor (2FBR) was modified to accommodate a downstream bubbling fluidized bed vapor phase upgrading (VPU) reactor and liquid recycle. The modification enabled completion of experiments using three configurations: (1) in-situ CFP, in which ZSM-5 catalyst was loaded in the pyrolysis reactor in place of an inert fluidized bed material (sand), (2) ex-situ CFP, in which pyrolysis was conducted in an inert fluidized sand bed and catalysis was conducted in a downstream fluidized bed reactor over a ZSM-5 catalyst, and (3) ex-situ CFP with liquid recycle, in which biomass plus bio-oil-derived liquid was fed to the pyrolyzer and the vapors were upgraded over a ZSM-5 catalyst in the downstream fluidized bed reactor. A schematic of the modified 2FBR system is provided in Figure 1. A detailed process hazard analysis was conducted prior to turning-on the system and all changes from the previous configurations were documented following NREL's management of change process.

During CFP experiments, biomass was introduced and pyrolyzed in a 5.2-cm inner-diameter bubbling fluidized bed reactor. Char and fine particulates were separated using a cyclone, after which, the pyrolysis vapors and gases were passed through the second reactor (see Figure 1). ZSM-5 catalyst was placed either in the pyrolyzer (in-situ CFP) or the second reactor (ex-situ CFP). The remaining particulates were captured by a hot gas filter (HGF) and the upgraded vapors were introduced into a fractional condensation system. Oil and aqueous phase yields were determined gravimetrically from the mass increase in the condensation train. Light gas compositions in the exit gases were measured by NDIR analyzers (CO, CO₂, and CH₄) and by a microGC (N₂, H₂, CO, CO₂, and C₁-C₄ hydrocarbons) and composition of light condensable compounds in the exit gas by an online GC-MS/Polyarc-FID, and the gas flow by a dry gas meter.

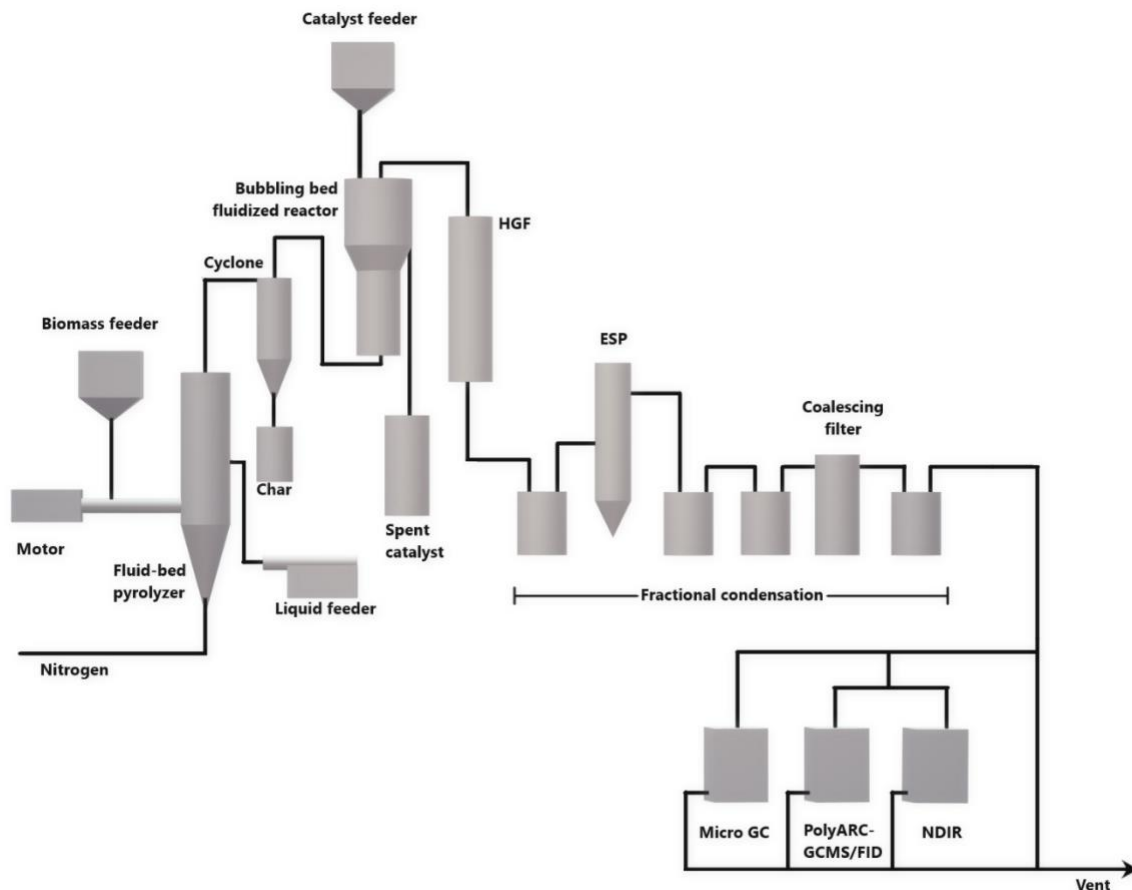


Figure 1. A schematic of the new 2FBR bubbling bed configuration comprising of (1) feeding, (2) fluid-bed pyrolysis, (3) char and fine particulate separations, (4) pyrolysis product catalytic upgrading, (5) hot gas filtering, (6) fractional condensation, and (7) on-line product analyses.

Three replicate biomass CFP experiments using the bubbling bed reactor with ZSM-5 catalyst demonstrated average mass and carbon balance closures of $99\% \pm 2\%$ and $97\% \pm 1\%$, respectively. Relative standard deviations (RDS) of CFP oil metrics (i.e., carbon yield, oxygen content, coke yield, gas yield) were $\leq 10\%$, indicating that the data generated on this new configuration was reproducible. In summary, data from the new 2FBR system bubbling bed VPU exhibited mass and carbon closures near 100% and good reproducibility (RSD < 10).

Task 2: Experimental Generation of Aromatic-rich Bio-oil

Task 2 will focus on investigating a recycling and co-feeding strategy of catalytic fast pyrolysis (CFP) liquid product to enhance yields of benzene, toluene, and xylene (BTX). This is one of the data gaps identified by CRADA Project 9 – Technology Evaluation of Biomass Pyrolysis and Catalytic Pyrolysis Strategies to Produce Renewable Chemicals (Olefins and Aromatics) and Stabilized Bio-oil.

Bio-oil will first be produced in NREL's bench-scale integrated catalytic pyrolysis reactor system using biomass feedstock and zeolite catalysts, followed by distillation to separate the CFP bio-oil into a light fraction and a heavy fraction. The heavy fraction will be hydrotreated in NREL's bench-scale continuous hydrotreater unit to partially reduce the oxygen content and increase effective H/C ratio of the oil. The obtained liquid will then be co-fed together with the biomass feedstock to NREL's integrated catalytic pyrolysis reactor system to generate BTX-enriched bio-oil. All liquid products will be fully characterized at NREL using a series of techniques including gas chromatography-mass spectrometry, elemental analysis, Karl Fischer, nuclear magnetic resonance spectroscopy, total acid number (TAN) and inductively coupled plasma (ICP). A sample of the liquid products (10-50 ml) will also be provided to ExxonMobil for further analysis (GC, NMR) and experimentation (ACE testing unit).

Task 2 Work Description:

Catalytic fast pyrolysis (CFP) had been identified in Project 9 as having a high potential for olefin and aromatics production. CFP can be performed in an in-situ configuration with pyrolysis and catalytic vapor upgrading taking place in the same reactor or in an ex-situ configuration with separate reactors for pyrolysis and catalytic upgrading of the pyrolysis vapors. In-situ pyrolysis offers a simpler design with a lower capital cost, but it exposes the upgrading catalyst directly to biomass and char, which can lead to irreversible catalyst deactivation and need for higher catalyst replacement rates.¹ Contaminant removal from biomass may be required to reduce catalyst deactivation for in-situ CFP. Ex-situ CFP has a more complex design with higher capital cost, but the catalyst is not directly exposed to biomass. In addition, ex-situ CFP allows separate optimization of conditions for pyrolysis and catalysis.

It is possible to separate a light fraction rich in BTX from the CFP oil by distillation. The residue can be hydroprocessed and recycled back to the pyrolysis reactor to enhance the yield of BTX and olefins during CFP by increasing the hydrogen to carbon ratio of the feed. Based on the previous findings, the goals for this task were to (1) compare in-situ and ex-situ CFP on the same basis, (2) evaluate the impact of operating conditions (temperature and biomass-to-catalyst mass ratio) on BTX yields for ex-situ CFP, and (3) evaluate the impact of recycling the hydrotreated stream back to CFP.

CFP experiments were conducted in both in-situ and ex-situ configurations. The mass balance closures in the CFP experiments ranged from 98 to 101%. Three liquid products were formed: a top oil, an aqueous fraction, and a bottom oil. In addition, there were condensable vapors that exited with the light gases and whose concentrations were measured by a GC-MS-Polyarc-FID analyzer. In the dilute system utilized here, these compounds, which consisted of C₅₊ hydrocarbons and light oxygenates, such as acetone, were not collected in the condensation train,

though in principle they could be condensed. The in-situ and ex-situ CFP yields were in very good agreement with those in publications from the same reactor system, shown below.²

Table 1. Total mass balance on the basis of feed pine. 2

Mass balance g/g feed	Catalyst A in situ	Catalyst B in situ	Catalyst B ex situ	No catalyst
Liquids	40.6%	41.9%	37.2%	66.9%
Organic	17.3%	16.9%	14.1%	
Aqueous	23.4%	25.0%	23.1%	
Gas	31.8%	34.4%	33.7%	17.9%
Light gases	25.8%	28.1%	28.4%	17.9%
Condensables	2.9%	3.1%	2.1%	
Water	3.1%	3.2%	3.1%	
Solids	18.1%	16.0%	16.7%	12.0%
Char	9.6%	8.8%	8.8%	12.0%
Coke	8.5%	7.2%	7.9%	-
Total	90.3%	92.3%	87.5%	96.8%

The CFP oils were analyzed using TGA-simdist, ¹³C NMR, acid, phenolics, and carbonyl titrations, ICP-OES analysis, and GCMS. The characterization data were in very good agreement with those from published literature using the same system.³

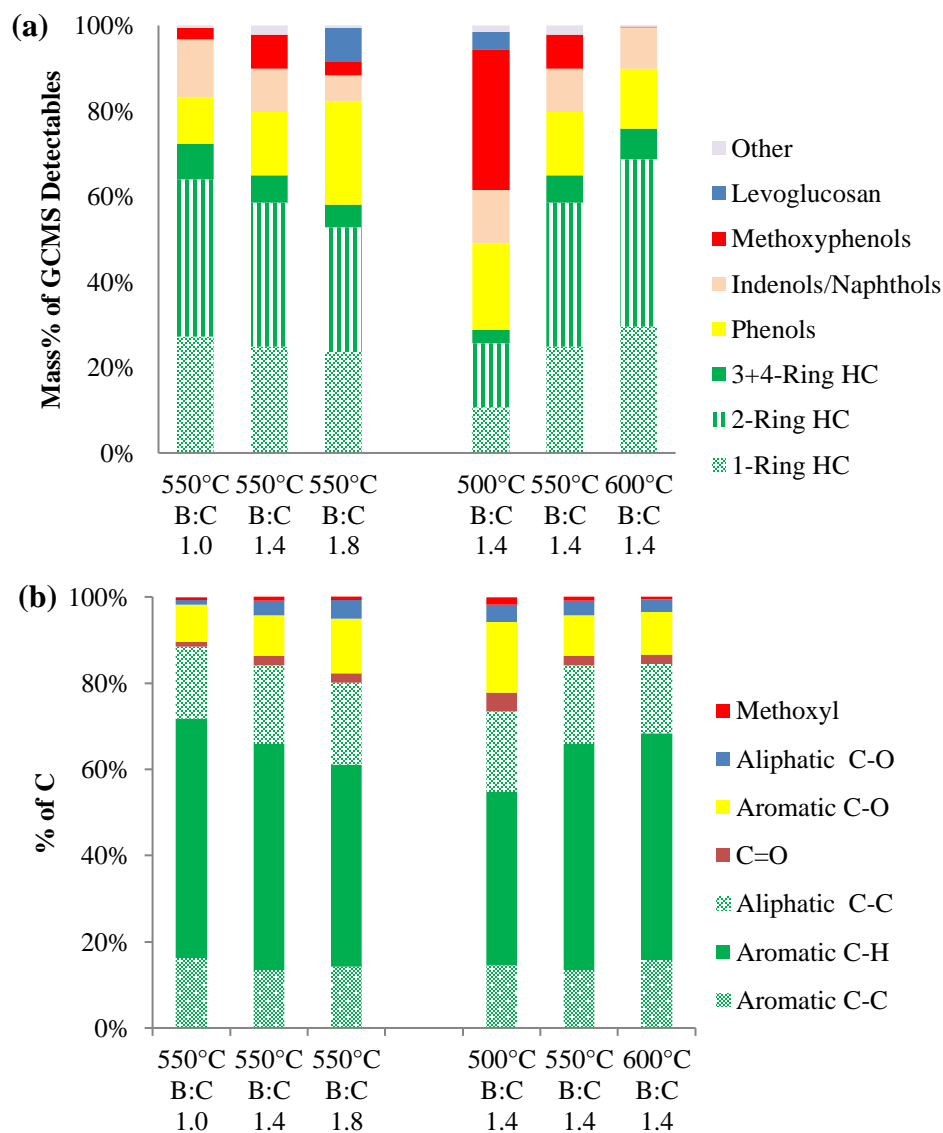


Figure 2. a) GC-MS analysis and b) ¹³C NMR analysis of CFP oils. The values are weight-averaged results of analyses of bottom and top oils. The GC-MS analysis shows the mass selectivity of the identified fraction, and the identified compounds constituted 25-43% of the oil.³

The experiments of the impact of operating conditions during ex-situ CFP were consistent with previous literature results obtained in a similar reactor system.⁴

CFP oil was hydrotreated in NREL's continuous trickle-bed reactor. CFP oil was fed into the system via an ISCO syringe pump and hydrogen with 60 ppm H₂S was compressed into storage tanks from which it was fed together with the oil to the top of the trickle bed reactor. The liquid products were condensed in chilled condensation vessels and collected every 12 h. The outlet gas flow was measured with a Coriolis flow meter and the exit gas concentrations were measured with a microGC for H₂, CO₂, CO, and C₁-C₅ hydrocarbons. The pressure during hydrotreating was 1800 psi (125 bar) and the temperature was 385°C. The catalyst was NiMo/Al₂O₃, which was presulfided in the reactor at the beginning of the experiment. GC x GC-TOFMS-FID analysis showed that the hydrotreated product consisted of cycloalkanes and aromatic hydrocarbons, and non-GC detectable (high-molecular weight) material.

The hydrotreated product was fed into the 2FBR pyrolysis reactor together with biomass in an ex-situ CFP configuration. The organic liquid yield and the yield of BTX were enhanced by the recycle of the hydrotreated product stream, compared to biomass feed only, as reported previously.⁴

Task 3: Final Report

Preparation and submission of a final report in accordance with Article X of the CRADA.

Facilities: For this project, NREL has allocated time on its integrated bench-scale (2 inch) catalytic pyrolysis system, hydrotreater, distillation system and characterization equipment for all required experiments including reactor system reconfiguration, modification, commissioning, bio-oil generation, separation, hydrotreating, liquid co-feeding and bio-oil characterization. The catalyst synthesis, preparation and characterization are also included.

Subject Inventions Listing: None

ROI #: None

References:

1. Eschenbacher, A.; Fennell, P.; Jensen, A. D., A Review of Recent Research on Catalytic Biomass Pyrolysis and Low-Pressure Hydrolysis. *Energy Fuels* **2021**.
2. 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. *Energ. Fuel* **2016**, *30* (3), 2144-2157.
3. Patel, H.; Hao, N.; Iisa, K.; French, R. J.; Orton, K. A.; Mukarakate, C.; Ragauskas, A. J.; Nimlos, M. R., Detailed Oil Compositional Analysis Enables Evaluation of Impact of Temperature and Biomass-to-Catalyst Ratio on ex Situ Catalytic Fast Pyrolysis of Pine Vapors over ZSM-5. *ACS Sustainable Chemistry and Engineering* **2020**, *8* (4), 1762-1773.
4. Patel, H.; Hao, N.; Iisa, K.; French, R. J.; Orton, K. A.; Mukarakate, C.; Ragauskas, A. J.; Nimlos, M. R., Detailed Oil Compositional Analysis Enables Evaluation of Impact of Temperature and Biomass-to-Catalyst Ratio on ex Situ Catalytic Fast Pyrolysis of Pine Vapors over ZSM-5. *ACS Sustain. Chem. Eng.* **2020**, *8*, 1762-1773.