BETO 2021 Peer Review: 3.4.3.304 Optimization of Carbon Efficiency for Catalytic Fast Pyrolysis (CFP) and Hydrotreating

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Systems Development and Integration

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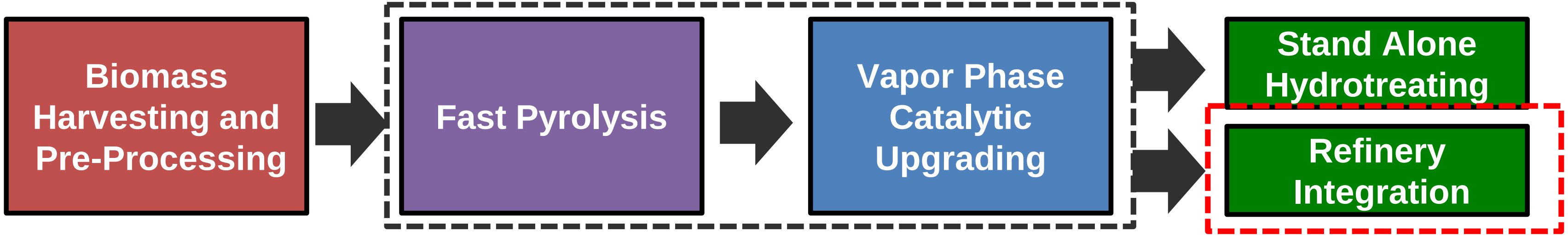
Project Overview

- Overall objective is to *support development of the catalytic fast pyrolysis (CFP) platform by addressing knowledge gaps in the integration of CFP and hydrotreating*
- Optimization of combination of CFP and hydrotreating required
  - Too much upgrading during CFP leads to low CFP oil yields
  - Too little upgrading during CFP leads to low hydrotreating yields and operational problems
- Initially goal was to optimize CFP + standalone hydrotreating
- With the pivot of CFP to production of application-specific bio-oils and refinery integration, emphasis is now on *co-hydrotreating.*



CFP = catalytic fast pyrolysis

HT = Hydrotreating

Project Overview: Co-Hydrotreating

Standalone hydrotreating of CFP oil

- Process, catalyst and conditions can be developed to optimize CFP oil hydrotreating
- Need to generate product suitable as blendstock or further processing
- High temperature: ~400°C
- High pressure: ~125 bar
- Low liquid hourly space velocity (LHSV): ~0.2 L/(L h)

Co-hydrotreating

- Need to be performed at petroleum operating conditions and with petroleum catalyst
- Cannot interfere with efficiency of petroleum operation or product quality
- Lower temperatures: ~325°C
- Lower pressures: ~60 bar
- Higher liquid hourly space velocity (LHSV): ~1-2 L/(L h)

Very limited information on co-hydrotreating

- CFP oil deoxygenation efficiency at co-hydrotreating conditions
- Impact of CFP oil addition on petroleum stream transformation and unit operation
- Quality requirements for CFP oil to enable co-processing

Market Trends

Product
- Gasoline/ethanol demand decreasing, diesel demand steady
- Increasing demand for aviation and marine fuel
- Demand for higher-performance products
- Increasing demand for renewable/recyclable materials

Feedstock
- Sustained low oil prices
- Decreasing cost of renewable electricity
- Sustainable waste management
- Expanding availability of green H_2
- Closing the carbon cycle

Capital
- Risk of greenfield investments
- Challenges and costs of biorefinery start-up
- Availability of depreciated and underutilized capital equipment

Social Responsibility
- Carbon intensity reduction
- Access to clean air and water
- Environmental equity

NREL's Bioenergy Program Is Enabling a Sustainable Energy Future by Responding to Key Market Needs

Value Proposition

- This **work addresses critical risks associated with co-hydrotreating** at the refinery, thereby facilitating adoption of the technology.

Key Differentiators

- **Access to CFP oil production** with direct feedback
- **Identification of bad actors in CFP** oils via systematic co-hydrotreating evaluation and oil spiking
- Establishing **critical material attributes (CMA's)** for CFP oil

1. Management: Challenges and Goals

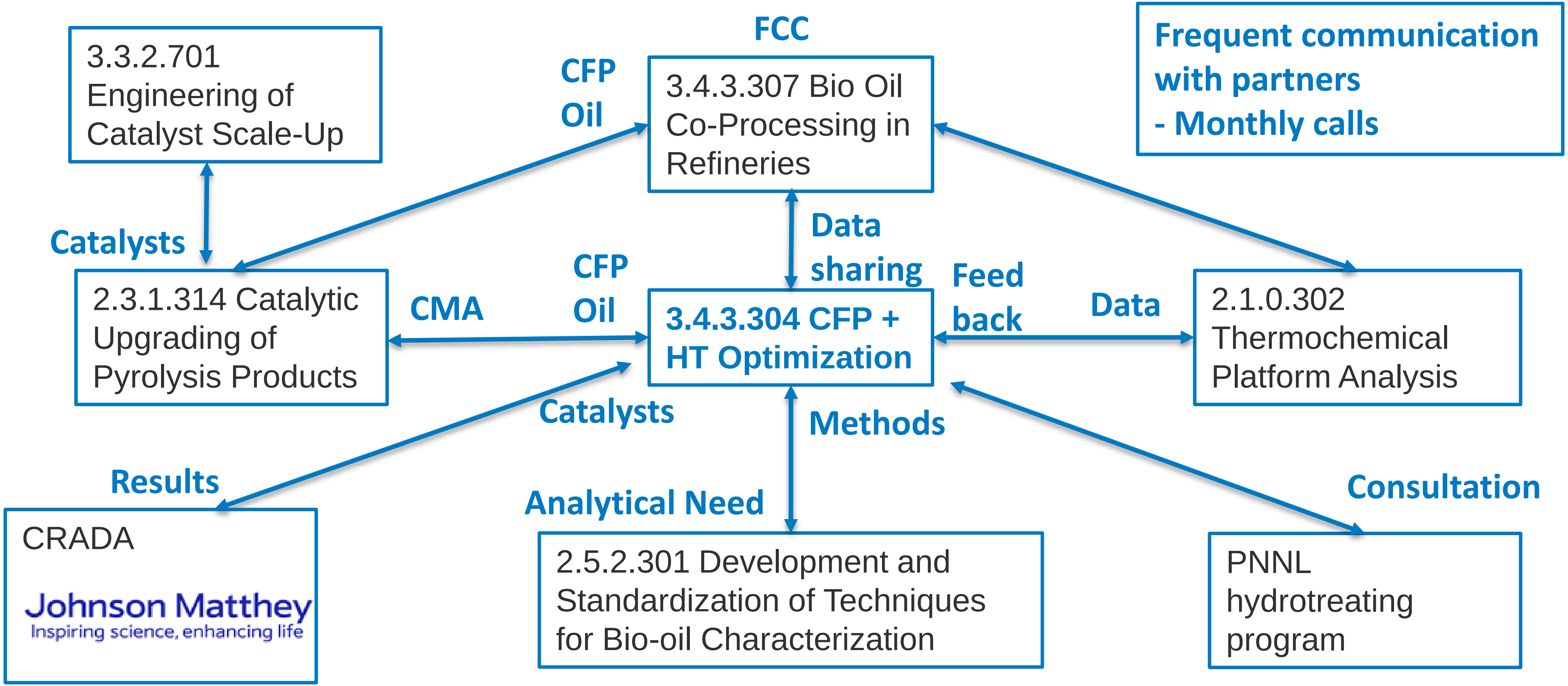
Co-hydrotreating

- **Reduces minimum fuel selling price (MFSP) for CFP-based biofuel**
- **Reduces biorefinery complexity**
- **Introduces biogenic carbon** into refinery and **reduces carbon intensity**, and opens possibility for **advanced molecules for e.g., jet**
- **Introduces risks at refinery**
  - Product quality
  - Catalyst deactivation
  - Plugging and fouling

Goals of this work

- Demonstrate **production of quality fuel via co-hydrotreating** of CFP oil and a petroleum stream
- **Identify compound groups in CFP oil that negatively impact co-hydrotreating**
- Within the constraints of the petroleum operation, find **optimum co-hydrotreating conditions** for the CFP oil.

1. Management: Collaboration w. Related Projects



FCC = Fuid Catalytic Cracking
CMA = Critical Material Attribute

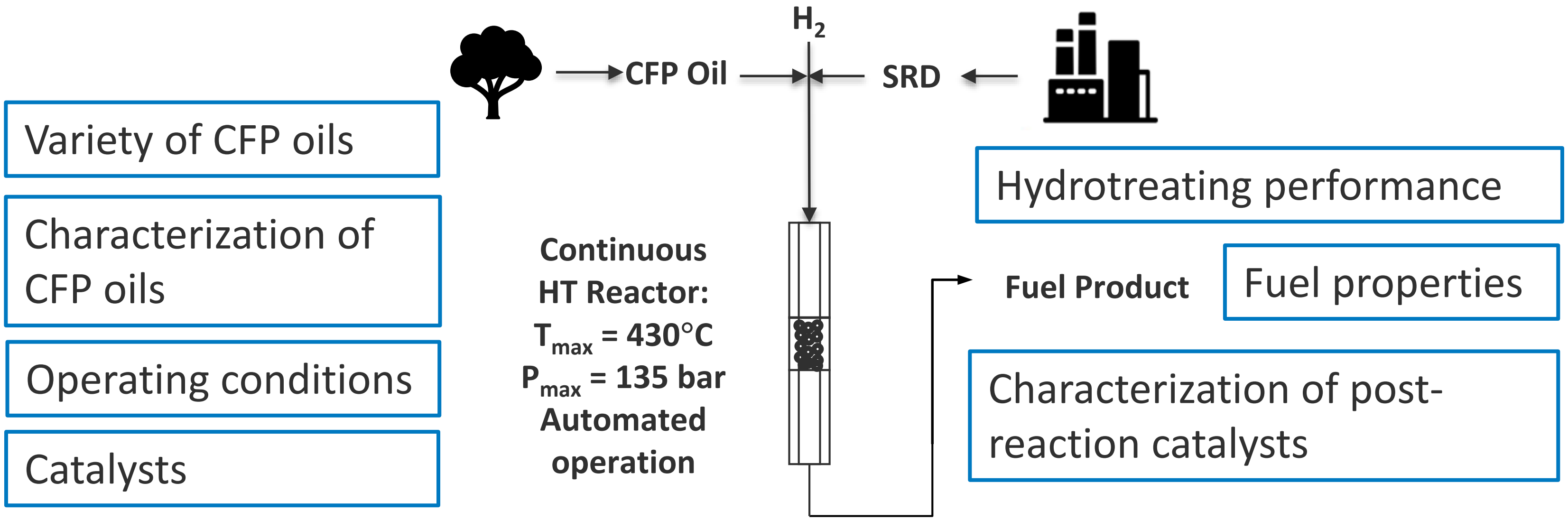
CRADA = Collaborative Research and Development Agreement

1. Management: Risk Mitigation

Risk	Mitigation
Availability of CFP oils	• Secured 6 CFP oils (3 Pt/TiO_2 and 3 ZSM-5) • Collaboration with project 2.3.1.314 for production of oils
Co-hydrotreating not successful (poor fuel quality or plugging)	• Develop pretreatment methods • Fractionate CFP oil • Identify different petroleum hydrotreating process
No negative impacts observed	• Spike CFP oils with suspected detrimental compounds • Increase time on stream
Failure to identify functional group by spiking	• Test combinations of functional groups • Test different subgroups within functional groups
Problematic compound group not identified	• Additional analyses • Collaboration with 2.5.2.301 for method development • Elimination of compound groups from oil

2. Approach

- **Reduce risk of co-hydrotreating at refineries** by
  - Demonstrating that CFP oil can be co-hydrotreated for good-quality fuel product
  - Identifying risk factors in CFP oil
  - Enhanced understanding → Mitigation strategies
- Co-hydrotreating of **CFP oils produced over Pt/TiO_2 and ZSM-5 catalysts** together with **refinery diesel fraction** (straight-run diesel = SRD)



2. Approach: Timetable

Milestone	Deadline
Characterize variety of CFP oils	March 2020
Hydrotreating catalyst comparison	Dec. 2020
Impact of co-hydrotreating conditions on CFP oil deoxygenation	March 2021
Production of cycloalkanes for jet	June 2021
Identification of detrimental compound groups in CFP oil	Sept. 2021

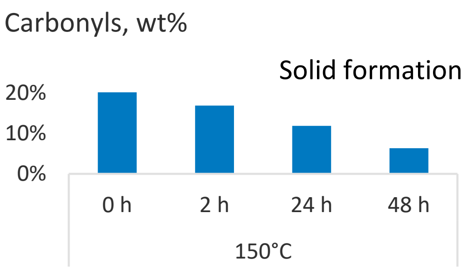
Go/No-Go	Deadline
Viability of proposed work for identifying detrimental functional groups	March 2021

3. Impact: Risk Reduction for Industrial Adoption

- Co-hydrotreating of CFP oil in a petroleum refinery offers several potential advantages
- **Introduces significant risk to refineries**
- This work **aims to reduce risks** by
  - Filling knowledge gaps
  - Identifying bad actors in CFP oils
  - Providing critical material attributes (CMA's) for CFP oils
  - Suggesting mitigation strategies

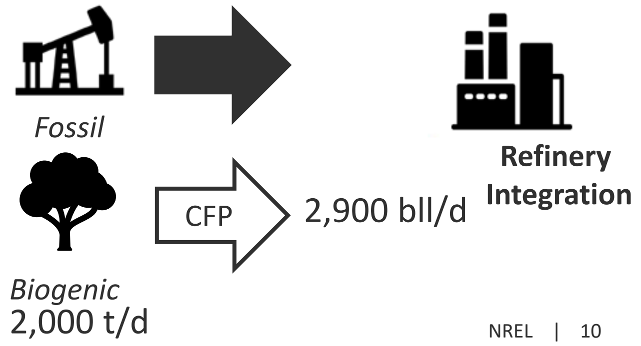
US:
- 131 operating refineries (2020)
- Each with several hydrotreaters
- Total hydrotreating capacity: 18 million bll/day

Data from EIA 2020



Example Result:
- *Carbonyls correlated with polymerization and solid formation*
- *→ Mitigation strategy*

US average refinery size 140,000 bll/d



3. Impact: BETO Goals Support

The project addresses BETO barriers

- Process Integration
- Co-Processing with Petroleum Refineries
- Cost of Production

Part of closely related projects in BETO Conversion and Systems Development and Integration portfolio

- 2.1.0.302 Thermochemical Platform Analysis
- 2.3.1.314 Upgrading of Pyrolysis Products
- 2.5.2.301 Development and Standardization of Techniques for Bio-oil Characterization
- 3.3.2.701 Engineering of Catalyst Scale-Up
- 3.4.2.302 Process Scale-up to Production Environments
- 3.4.3.307 Bio Oil Co-Processing in Refineries

Industry Engagement

- CRADA with Johnson Matthey
- Close collaboration with projects with Industry Advisory Boards
  - ChemCatBio
  - Bio-Oil Co-Processing in Refineries

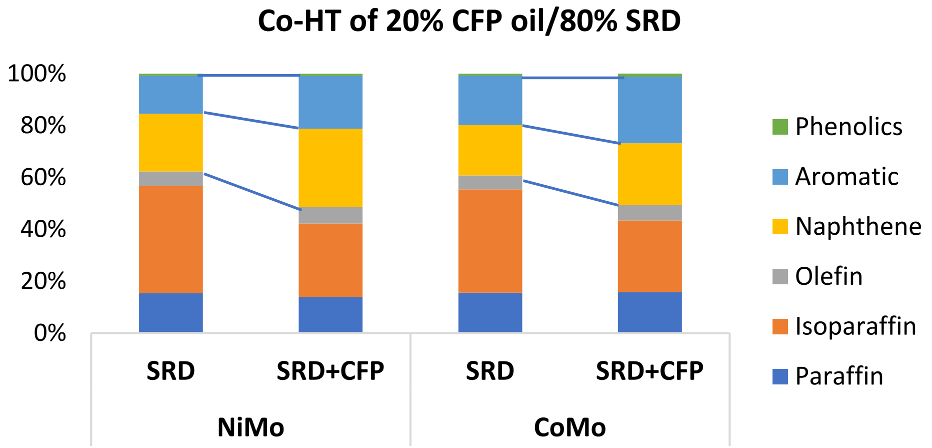
Public dissemination of results

- Peer-reviewed publications
- Conference presentations

CRADA = Collaborative Research and Development Agreement

4. Progress and Outcomes: Co-Hydrotreating Success

- Successfully co-hydrotreated Pt/TiO_2 CFP oil at SRD operating conditions (325°C, 55 bar, 1 h^{-1})
- Produced good-quality products
  - ≤0.3% O
  - Cetane numbers >40 (US lower limit)
- High biogenic carbon incorporation
  - CFP oil C efficiency: 94-95%
- *NiMo more desirable catalyst for co-hydrotreating than CoMo*
  - Improved aromatics saturation
  - Better cetane number

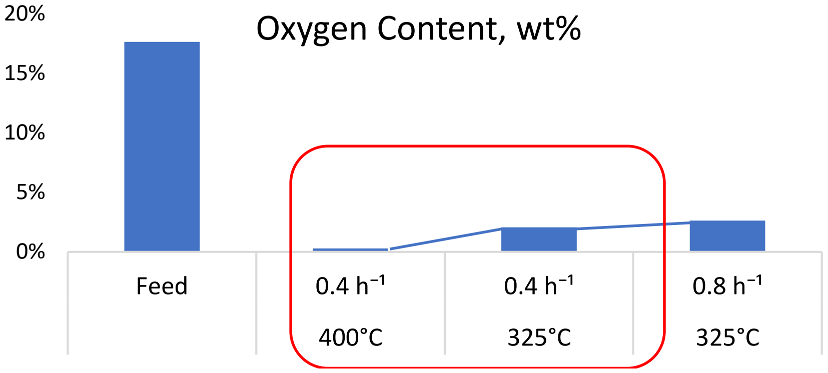


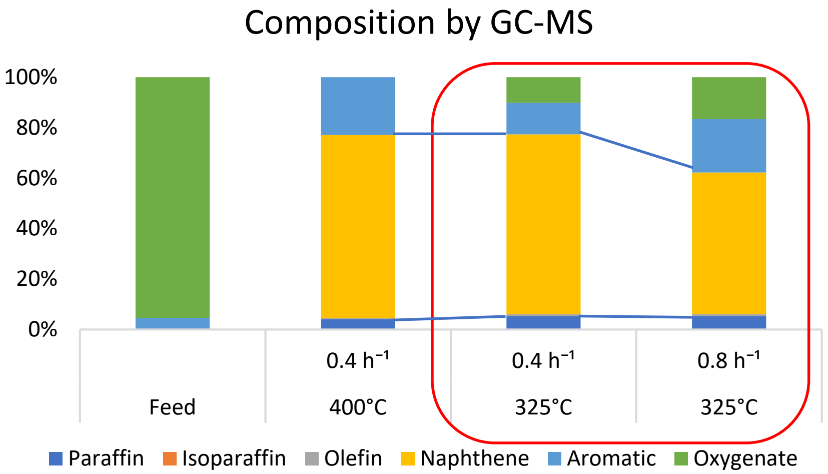
Feed	Catal.	O, wt%	N, wt%	S, wt%	ICN	H_2 Cons %
SRD	-	0.2	0.03	0.21		
CFP Oil	-	17.5	0.18	0.01		
SRD	NiMo	0.3	0.03	0.01	50	0.1
SRD+CFP	NiMo	0.2	0.04	0.03	45	1.4
SRD	CoMo	0.2	0.02	0.02	48	0.0
SRD+CFP	CoMo	0.3	0.04	0.04	42	1.1

CFP = catalytic fast pyrolysis, SRD = straight run diesel, HT = hydrotreating, ICN = Indicated Cetane Number

4. Progress and Outcomes: Operating Conditions Impact

- Evaluated impact of temperature and WHSV on CFP model oil over NiMo
    - 10 compounds representing different oxygen functional groups typical for Pt/TiO_2 CFP oils
- Temperature has a large impact on oxygen content
- WHSV impacts aromatics saturation (formation of naphthenes) and, hence, cetane number
- Can be used as guidance to combat negative impacts of CFP oil addition
- Next step: Confirm impacts with real CFP oil

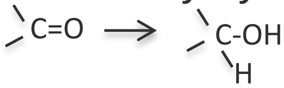


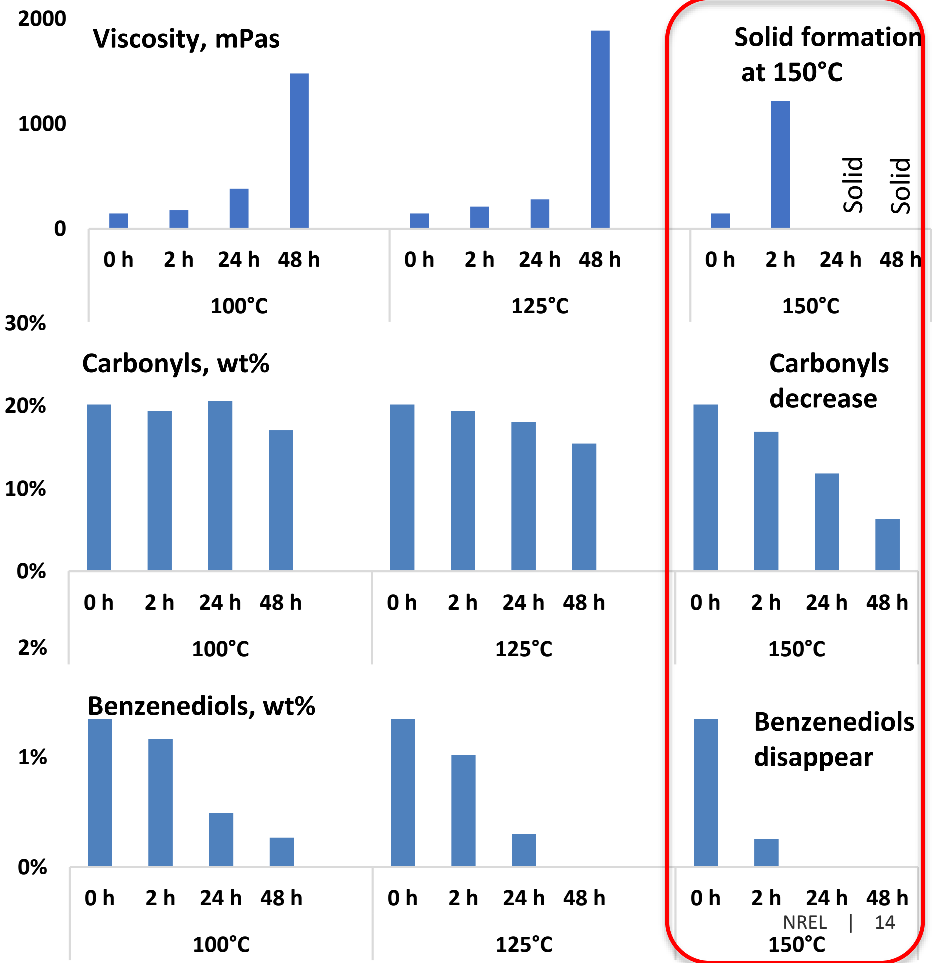


WHSV = weight hourly space velocity

4. Progress and Outcomes: Plugging and Fouling Mitigation

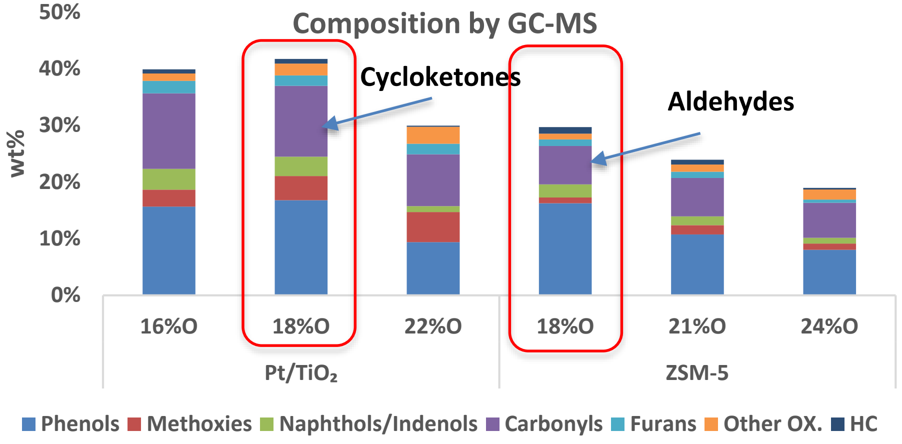
- Components in CFP oil may cause plugging and fouling on top of hydrotreating bed due to polymerization reactions
- Identified potential compound groups responsible for plugging
  - Heating of Pt/TiO_2 CFP oil to 150°C leads to rapid viscosity increase and solid formation
  - Correlates with decrease in carbonyls and benzenediol disappearance
    - Phenol-aldehyde resin formation
- Possible **mitigation strategies** if plugging a problem:
  – Pretreatment by hydrogenation

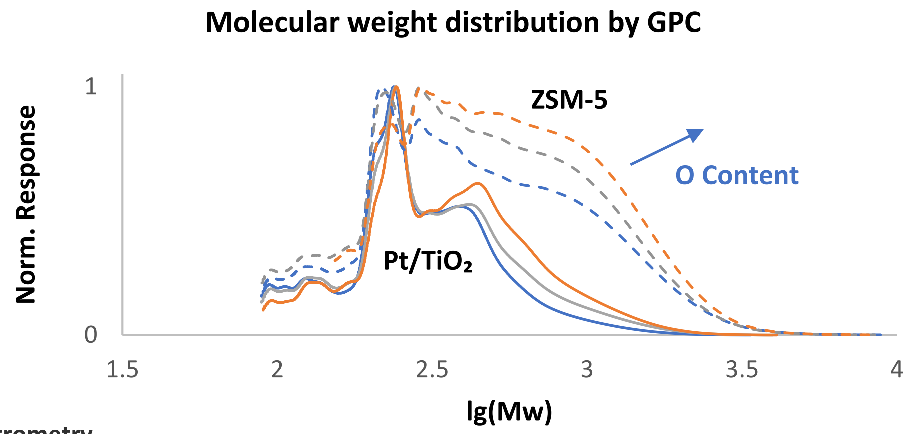




4. Progress and Outcomes: CFP Oil Composition Impacts

- Beyond oxygen concentration, **significant differences in CFP oils**
  - Volatility, compound groups, molecular weight distribution
- **Investigation of impact on co-hydrotreating on-going**
  - Preliminary results suggest faster deactivation with ZSM-5 than Pt/TiO_2 oil
  - Consistent with plugging evaluation
    - Higher aldehydes, benzenediols in ZSM-5
    - Also, more high molecular weight compounds





GPC = Gel Permeation Chromatography, GC-MS = Gas Chromatography – Mass Spectrometry

Summary

Value Proposition

- Co-hydrotreating of CFP oil in petroleum refineries will lead to **biogenic carbon incorporation at the refinery** and **reduced MFSP for CFP-based fuel**. This project **addresses risk to refineries** by filling knowledge gaps and determining critical material attributes.

Milestone	Deadline	
Characterize variety of CFP oils	March 2020	v
Catalyst comparison	Dec. 2020	v
Impact of co-HT conditions on CFP	March 2021	Progress
Cycloalkanes for jet	June 2021	On track
Identification of detrimental compound groups in CFP oil	Sept. 2021	Progress
Go/No-Go	**Deadline**	
Viability of proposed work for identifying detrimental functional groups.	March 2021	Progress

Key Accomplishments

- Showed production of **good-quality product** with **high CFP oil carbon incorporation**
- **Identified compounds responsible for possible plugging problems**
- Preliminarily **identified impact of operating variables on CFP oil hydrotreating**

Quad Chart Overview

Timeline
- Project start date: 10/1/2019
- Project end date: 9/30/2021

	FY20	Active Project
DOE Funding	(10/01/2019 – 9/30/2020) $500,000	$1,000,000

Project Partners
- Johnson Matthey

Barriers addressed
- ADO-A Process Integration
- ADO-G
- Ot-B Cost of Production

Project Goal
Support development of the catalytic fast pyrolysis (CFP) platform by addressing knowledge gaps in the integration of CFP and co-hydrotreating with refinery streams.
- Demonstrate production of quality fuel via co-hydrotreating of CFP oil and straight run diesel
- Identify compound groups in CFP oil that negatively impact co-hydrotreating
- Find optimum co-hydrotreating conditions for the CFP oil within the constraints of the petroleum operation.

End of Project Milestone
Identify CFP oil compound groups detrimental to hydrotreating performance.

Funding Mechanism
AOP 2020

Thank You

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