NREL
Transforming ENERGY

BETO 2021 Peer Review: Process Monitoring and Predictions of Biorefinery Performance

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System Development and Integration
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Project Overview

Goal: Accelerate the commercialization of biomass-derived fuels and chemicals through the development of **online process monitoring and prediction tools to enable real-time adjustments during plant operation**

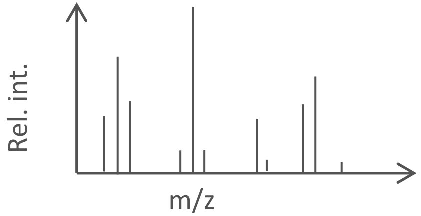
Impact: Enabling quick process optimization responses and reducing costs associated with process downtime, off-specification product distributions, and misdirected resources

Outcome:

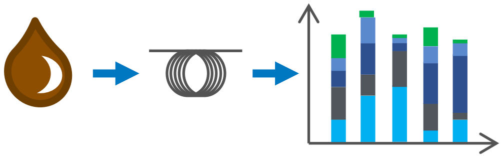
- De-risked pathway for the generation of predictive tools from on-line mass spectral analysis that will be integrated into a refinery's distributed control system
- Predictive tool specific to co-processing bio-oil and vacuum gas oil (VGO) in a Davison Circulating Riser (DCR) reactor

Project Overview

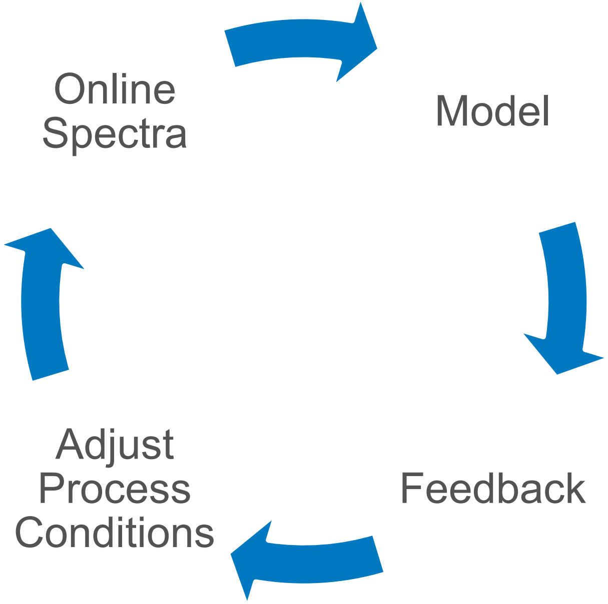
Analytical Tool: On-line, slip stream vapor phase **mass spectrometry**



Benchmark: **gas chromatography-based** analysis of condensed product



Opportunity to obtain faster (seconds to minutes vs. hours) feedback on product composition that is desired by refiners

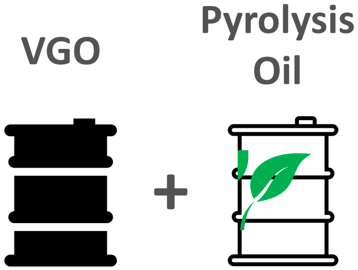


Based on NREL/PNNL model for a large, complex, Gulf Coast refinery, the team estimates the risk of off-spec penalties on order of $10,000 to $100,000 per 3-hour event

Project Overview: Pivot of Initial Starting Point

Catalytic pyrolysis of pine with Pt/TiO_2

Co-processing of pyrolysis oils and vacuum gas oil (VGO) with a fluid catalytic cracking (FCC) catalyst



Market Trends

Product
- Anticipated decrease in gasoline/ethanol demand; 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

- Online process monitoring coupled with rapid predictive tools will provide real-time feedback and process control on comparatively new feeds, processes, and products

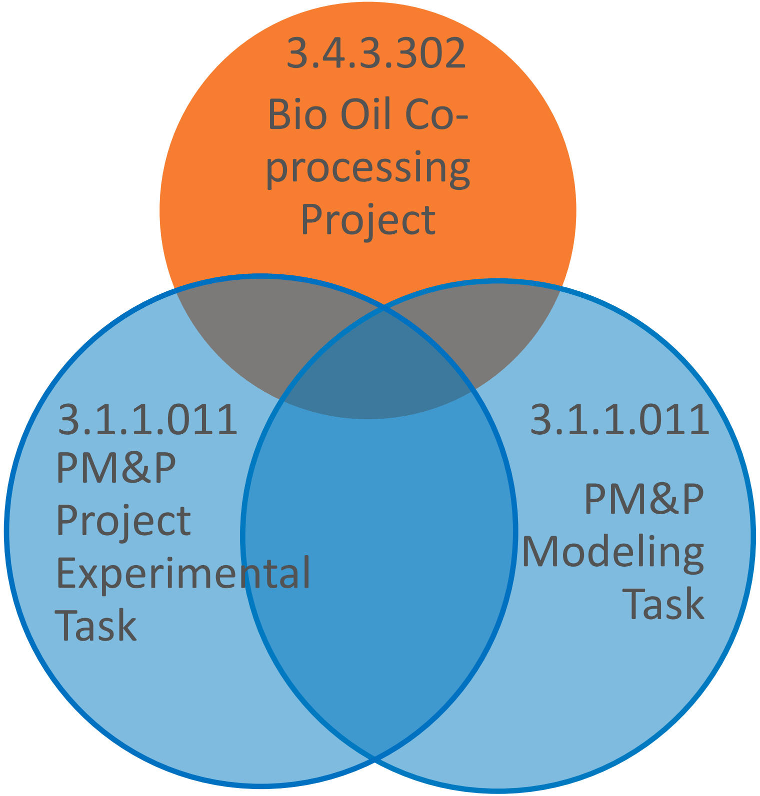
Key Differentiators

- Online mass spectrometry of hot vapors is a capability that can directly track intermediates and products, rather than tracking process conditions like temperature and pressure
- Leader in developing hot vapor mass spectral analysis as a high-throughput analytical technique
- Access to pilot-scale Davison Circulating Riser reactor with online mass spectrometry

1. Management: Risk Mitigation

Risks:

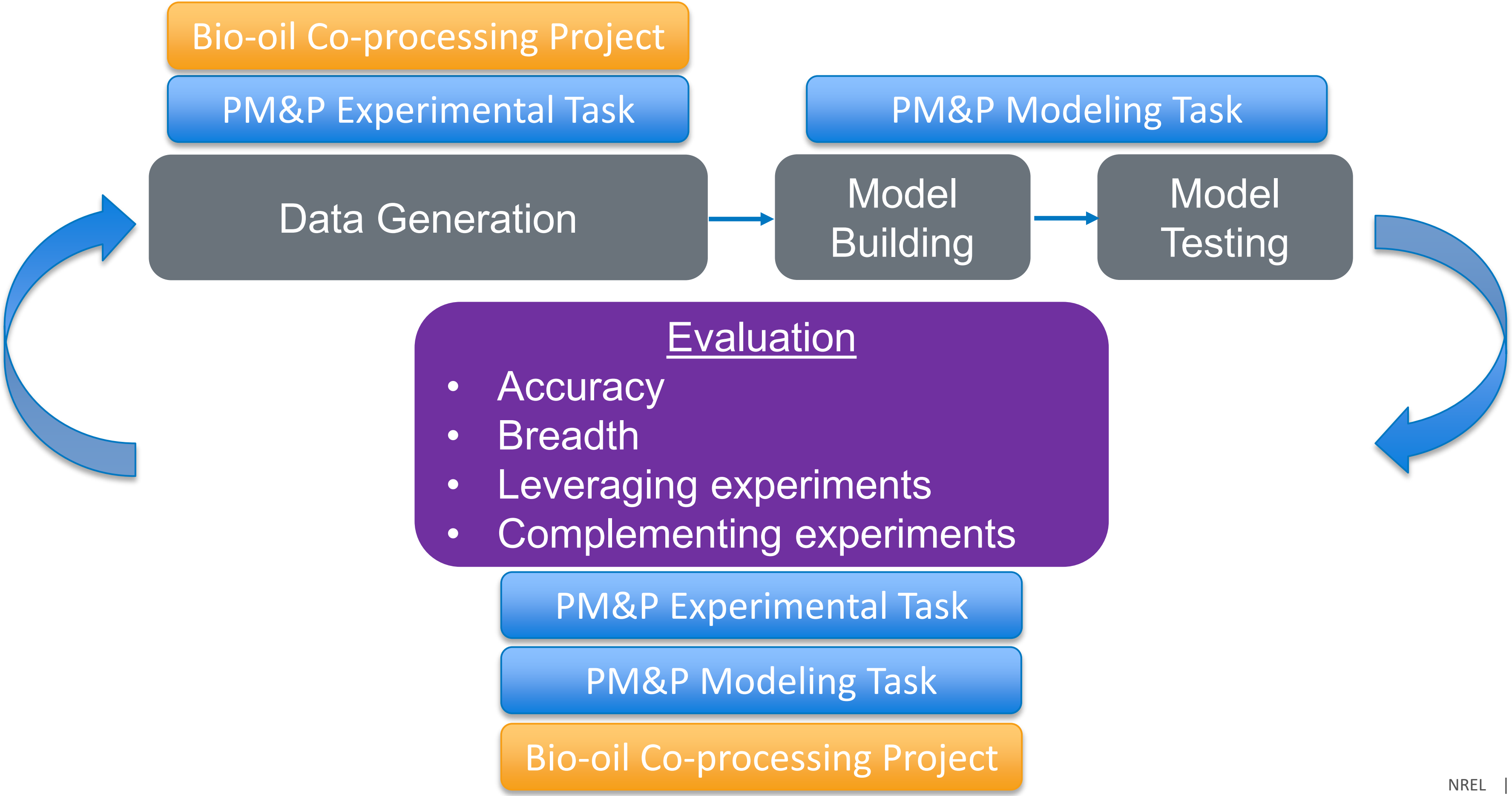
- Many points of data handoff
- Difficulty maintaining industrial relevancy



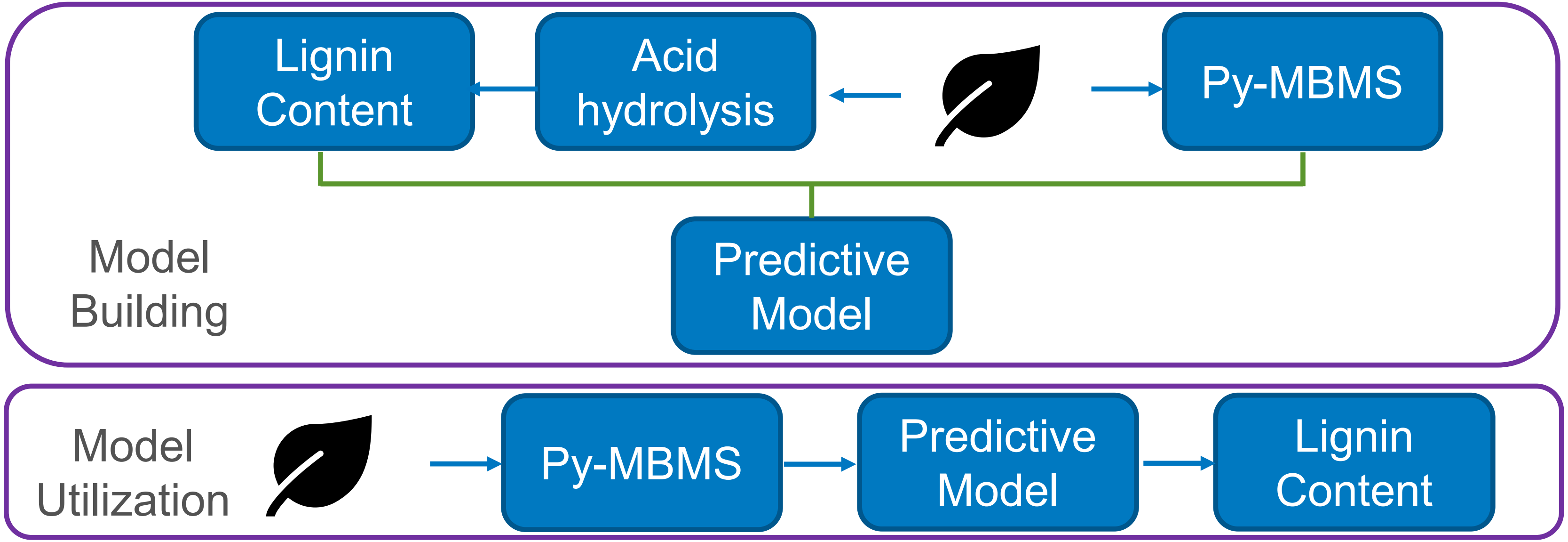
Mitigations:

- Bi-weekly meetings between team members
- Data and metadata posted same-day on internally shared platform
- Formatted data shared on LabKey LabKey
- Request input from industrial advisor at Phillips 66 and industrial review board for Bio Oil Co-processing task

1. Management: Processes and Coordination



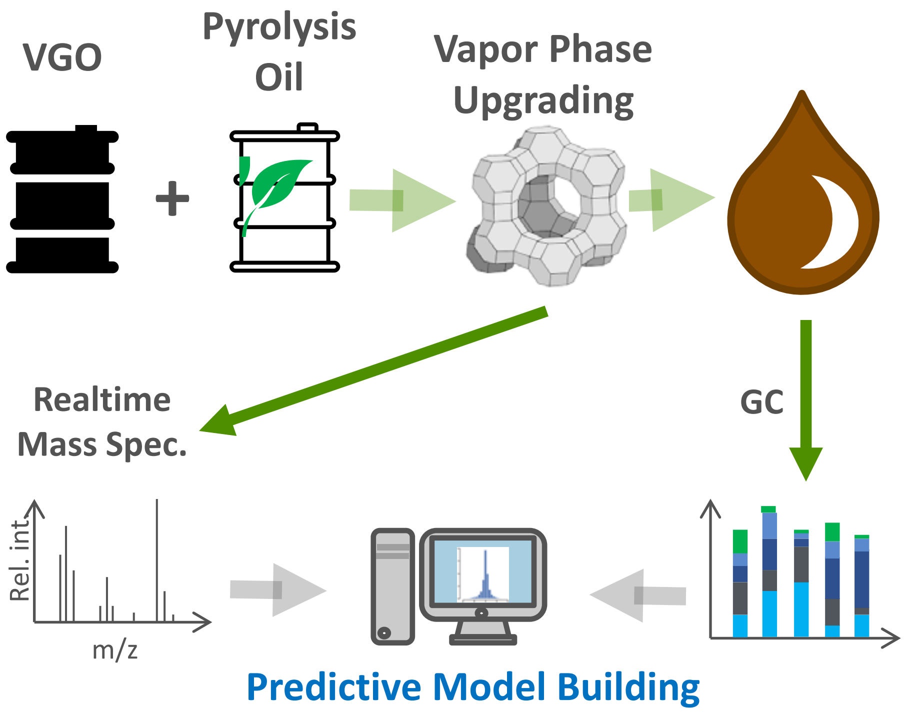
2. Approach: Building on Past Success



Successfully rapidly predicted lignin content and S:G lignin ratio using predictive models coupled with py-MBMS – **reduced analysis time from days to minutes**

Biofuels Methods and Protocols **2009**, 581, 12
Bioenergy Research **2014,** 7, 899–908

2. Approach: Building Data Sets to Enable Modeling



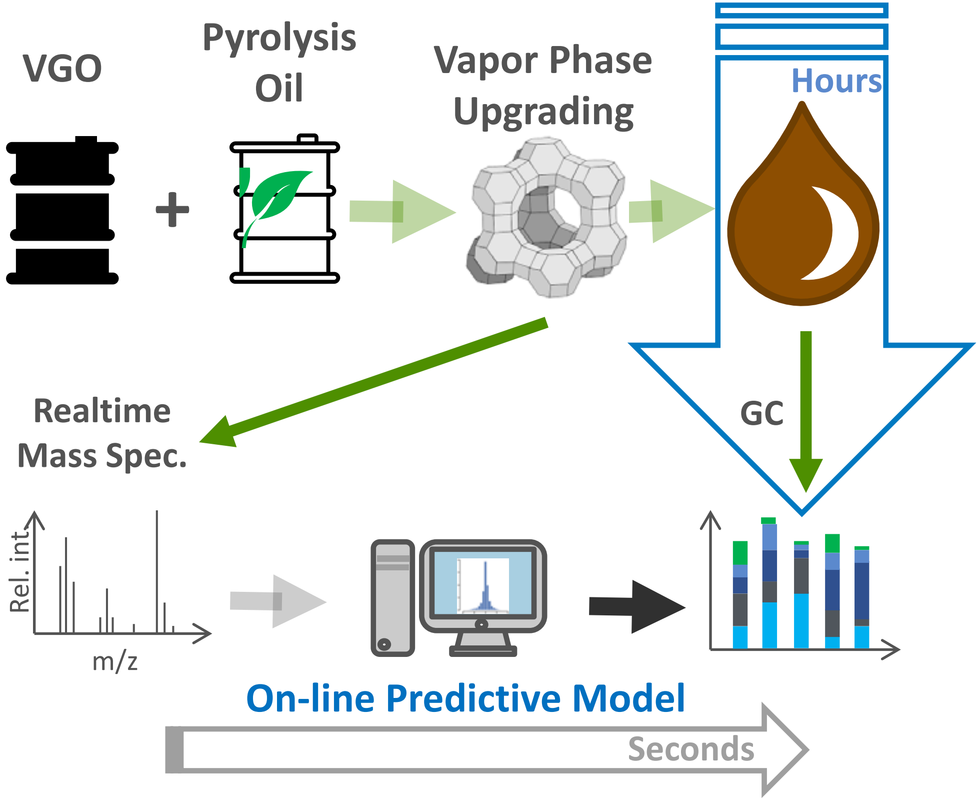
Model building with:

- Process conditions
- Real-time vapor phase mass spectra
- Gas-chromatography-based characterization of condensed product

Span relevant variables for model building

Add knowledge of reaction mechanisms through additional model compound work

2. Approach: Using Model for Faster Feedback



Model used to obtain rapid feedback from online mass spectra alone – reduce time from hours to seconds

2. Approach: Data Generation Across Scales

Experiments:

Micro-scale:

Model Compounds Studies

Innovation opportunity

Bench-scale:

Sweep Experimental Space with Real Vapors

Opportunity for optimization not feasible on pilot scale

Pilot Scale:

Davison Circulating Riser (DCR)

Most reliable for model-building

Most directly-translatable to industry

Modeling:

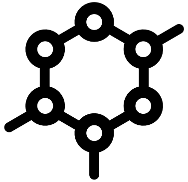
Semi-empirical: use model compound experiments, historical data, and literature to identify reactions. Improves accuracy over fully empirical model.

Validation: Set aside subset of experimental data at each scale as test set to validate model built with remaining data

2. Approach : Uses of Data Sets in Model Development and Training

Model compounds and VGO upgraded over FCC catalysts on microscale with MS analysis

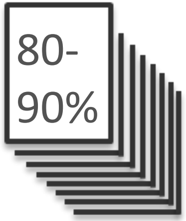
Incorporation of additional reaction pathways into model

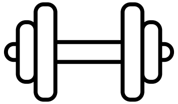


Pine pyrolysis vapors and VGO upgraded over FCC catalyst with MS and GC analysis

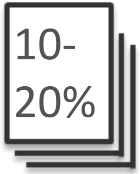
Online slip-stream MS during DCR co-processing runs and subsequent oil characterization

Model training with experimental data





Reserved experimental data sets for validation



2. Approach: Risk Mitigation

Top Potential Challenges

- Unacceptably large uncertainty
- Data collected across scales

Mitigations

- Add more data / variables to model
- Incorporate knowledge of reaction pathways
- Optimize sampling techniques to mass spectrometer
- Use of standards
- Submit condensed product for additional analysis if necessary

Go/ No Go

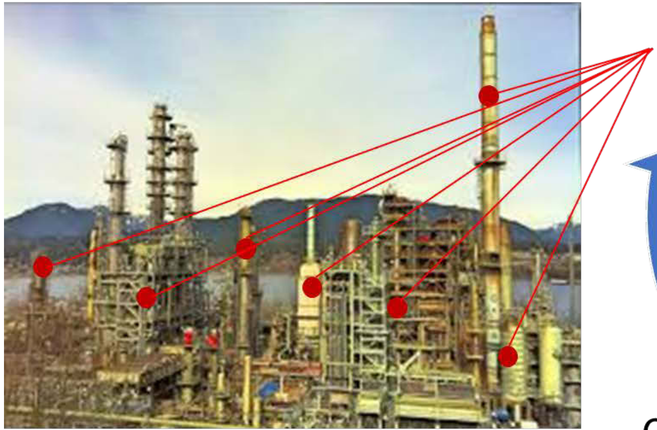
- Comparison of predicted condensed product component concentrations from on-line mass spectra with component concentrations measured from analysis of condensed product from co-processing experiments run on NREL's DCR reactor for the Bio-oil Co-processing Project

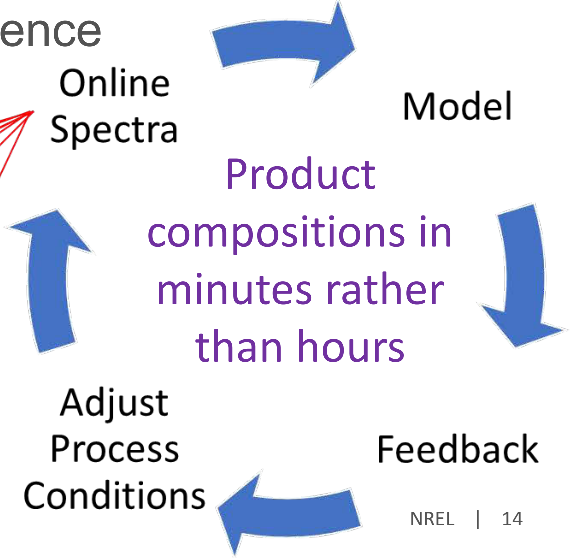
3. Impact

Enabling quick process optimization responses and **reducing costs** associated with process downtime, off-specification product distributions, and misdirected resources when **converting renewable feedstocks at refinery-scale**.

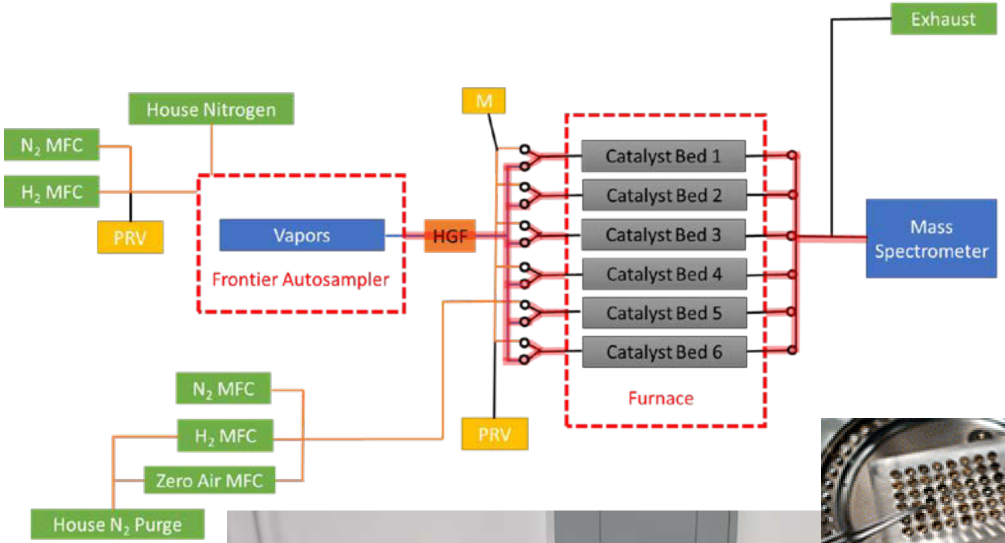
- Once expanded to all unit operations, these online process monitoring and prediction tools contribute to **digitization of refineries** and enable use of **artificial intelligence (AI)** to control process conditions
- Program will be shared **open source on Github** and process shared in **Biofuels Digest 8 Slide Guide**, in addition to publication and conference presentations, to assist refinery development of soft sensors tailored to their specific processes

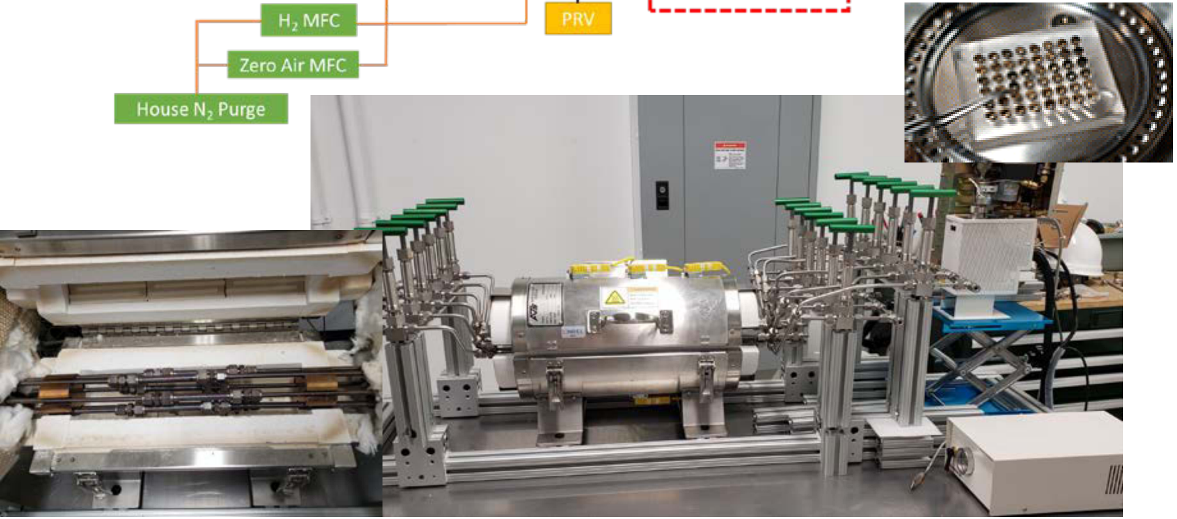
GitHub





4. Progress and Outcomes: Increased Experimental Throughput and Reproducibility





Completed design, assembly, readiness verification (RV), and reproducibility assessment of **only multibed, high throughput microscale reactor at NREL coupled with autosampler**

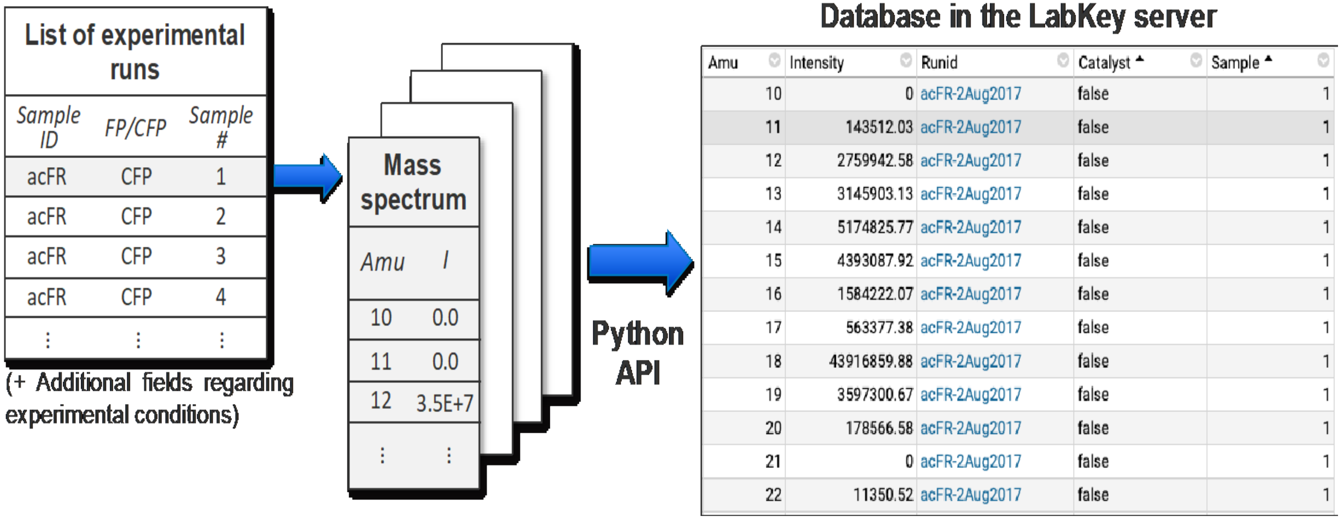
Increases throughput ~10x

Reproducibility assessment decreased day-to-day variability:

- ~3x with improved sampling of biomass vapors
- Additional ~30% with calibration standard correction

4. Progress and Outcomes: Data Management

Data management system developed for efficient development of predictive models and collaboration between other projects and laboratories



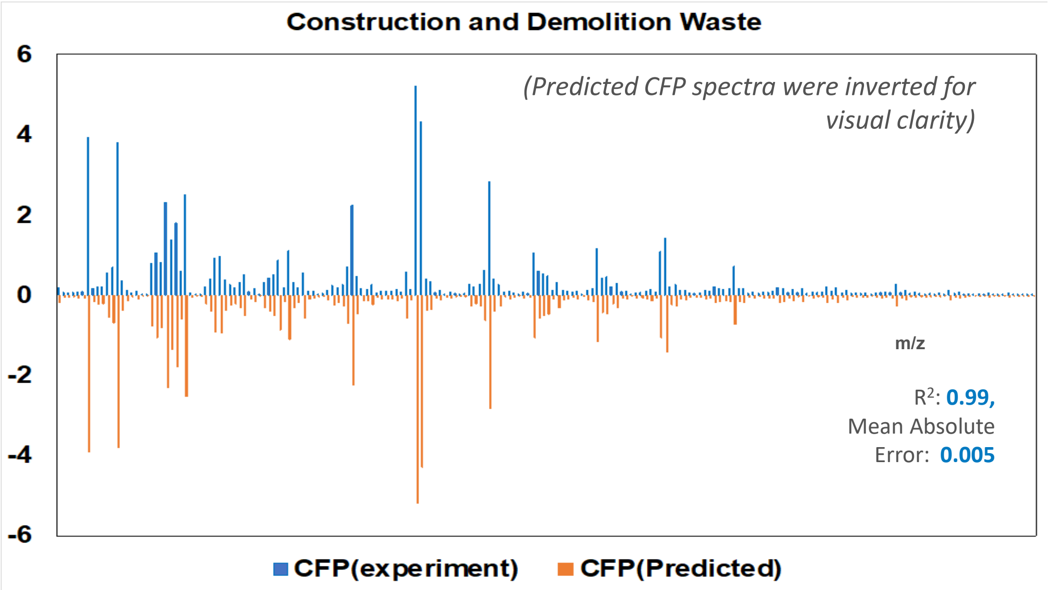
Amu	Intensity	Runid	Catalyst	Sample
10	0	acFR-2Aug2017	false	1
11	143512.03	acFR-2Aug2017	false	1
12	2759942.58	acFR-2Aug2017	false	1
13	3145903.13	acFR-2Aug2017	false	1
14	5174825.77	acFR-2Aug2017	false	1
15	4393087.92	acFR-2Aug2017	false	1
16	1584222.07	acFR-2Aug2017	false	1
17	563377.38	acFR-2Aug2017	false	1
18	43916859.88	acFR-2Aug2017	false	1
19	3597300.67	acFR-2Aug2017	false	1
20	178566.58	acFR-2Aug2017	false	1
21	0	acFR-2Aug2017	false	1
22	11350.52	acFR-2Aug2017	false	1

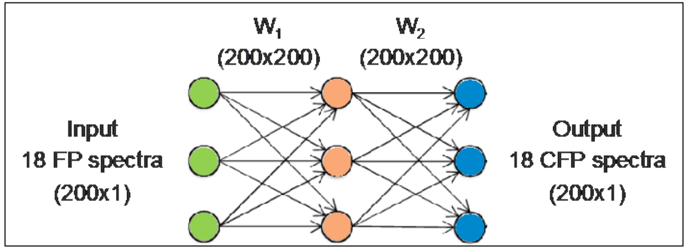
Using the Python application programming interface (API) for LabKey to upload data
Data analysis using structured query language (SQL)

Eliminates copy/paste error, increases throughput, enables collaboration

4. Progress and Outcomes : Preliminary Model Successfully Predicts Catalytic Upgrading

Developed a simple neural network model with one hidden layer using historic data



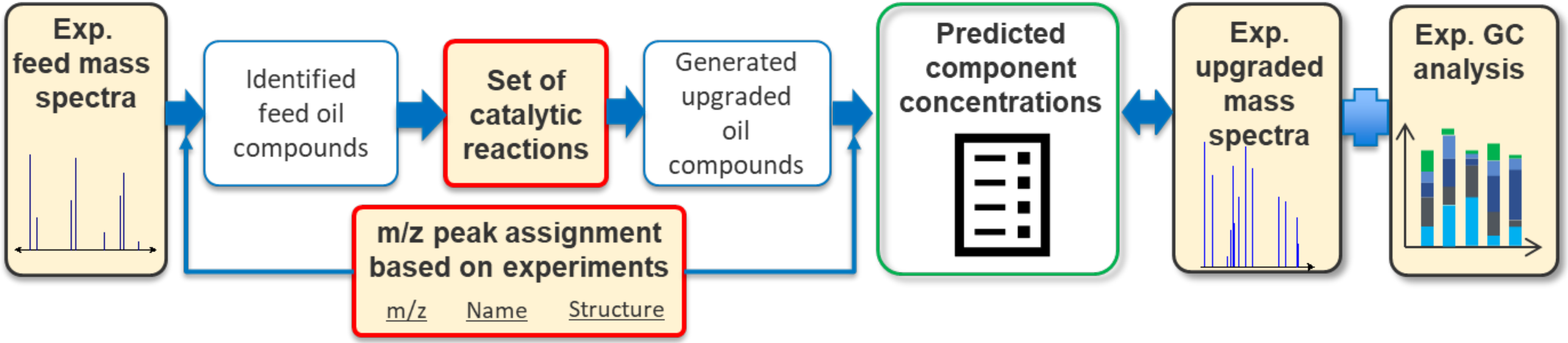


Accurate preliminary result, but limited in complexity (18 experiments)

Model can only predict amount of complexity it was trained on

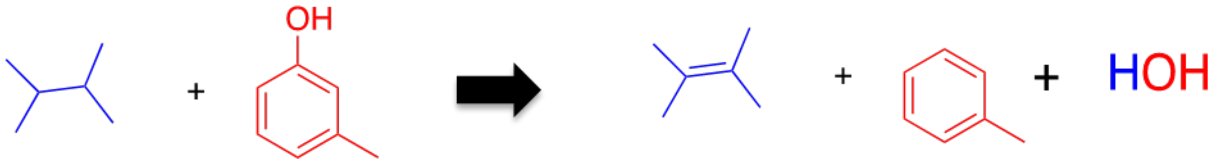
4. Progress and Outcomes: Reaction Pathways Incorporated into Co-Processing Model

Identified co-processing reactions from literature and historic data and incorporated into new neural network model for co-processing



Example SMARTS pattern of hydrodeoxygenation (HDO) via hydrogen transfer from alkane (VGO) to phenolics (bio-oil) during co-processing:

[C:1]-[C:2]. [c:3]1:[c:4]:[c:5]:[c:6]:[c:7](-[O:9]):[c:8]:1 >> [C:1]=[C:2]. [c:3]1:[c:4]:[c:5]:[c:6]:[c:7]:[c:8]:1. [O:9]



Summary

Management: Iteratively evaluate needs with feedback from experimental task, modeling tasks, Bio-oil Co-processing project, and industrial advisors

Technical Approach: Collect experimental data sets across scales to develop a predictive model to predict condensed product component concentrations from online mass spectra

Impact: Enabling quick process optimization responses and reducing costs associated with process downtime, off-specification product distributions, and misdirected resources

Progress:

- Increased throughput of microscale catalytic experiments to enable sufficient data generation for development of statistical models
- Preliminary neural network model and data management system developed

Quad Chart Overview

Timeline

- Start: 1 October 2019
- Finish: 30 September 2022

	FY20(10/01/2019 – 9/30/2020)	Active Project
DOE Funding	$500,000.00	FY20 $500,000.00 FY21 $400,000.00 FY22 TBD

Project Partners (NA)

Barriers addressed

Ft-J Operational Reliability

ADO-G Co-Processing with Petroleum Refineries

Project Goal

Through the development of a predictive tool specific to co-processing of VGO and pyrolysis oil over FCC catalyst, provide a template for the development of predictive models based on on-line, slip stream mass spectrometry that can be applied to a variety of unit operations, feeds, and catalysts.

End of Project Milestone

Improve statistical computational tool specific to co-processing pyrolysis oil and VGO in an FCC unit, post program open source on GitHub, and publicize (Biofuels Digest, conference presentations, publications) to provide refinery operators with an accelerated pathway to develop predictive tools specific to their unit operations and processes.

Funding Mechanism NA

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Q&A

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