U.S. DEPARTMENT OF ENERGY
Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

DOE Bioenergy Technologies Office (BETO)
2021 Project Peer Review

Analytical Development and Standardization for Biomass-derived Thermochemical Liquids

March 11th, 2021

Catalytic Upgrading Session

Jack Ferrell (NREL), Mariefel Olarte (PNNL), Jiheon Jun (ORNL)

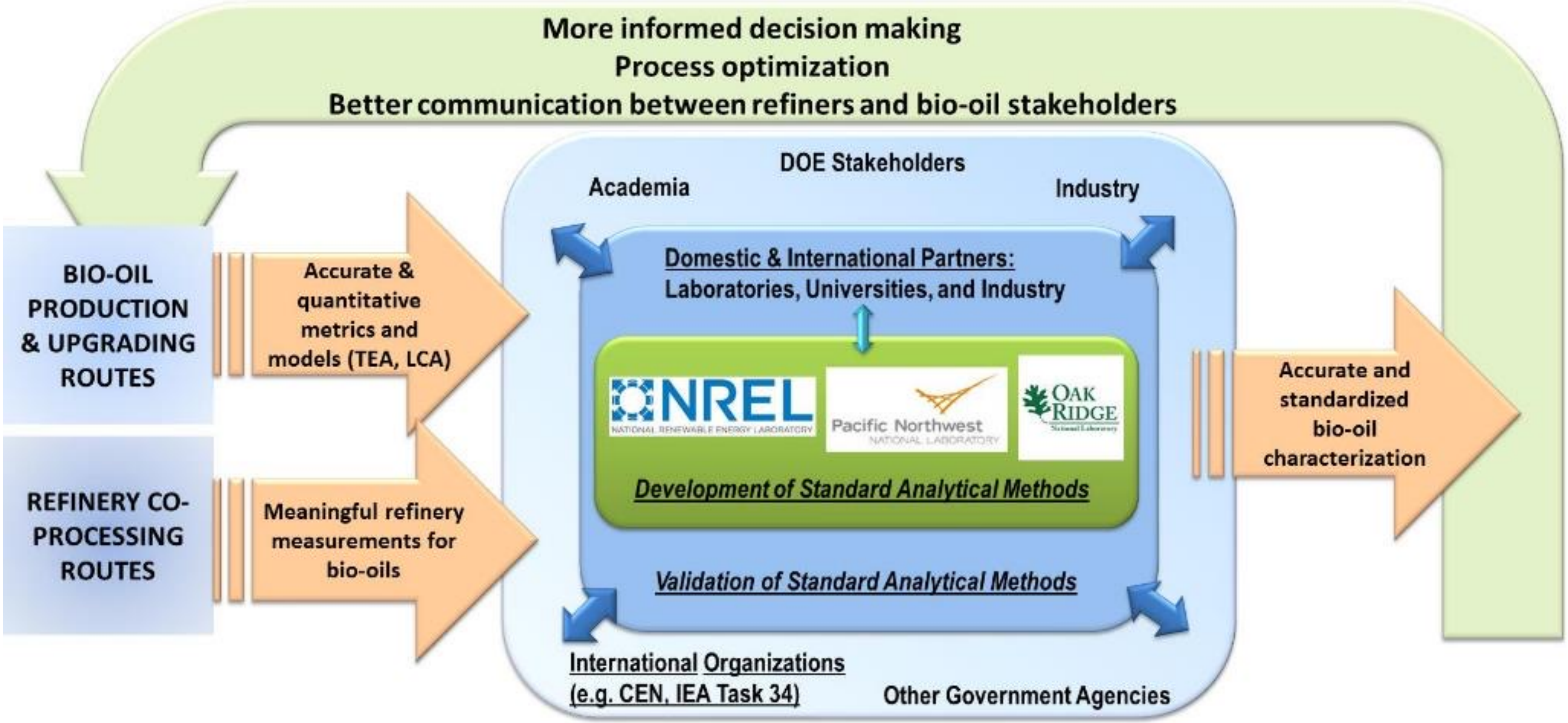
This presentation does not contain any proprietary, confidential, or otherwise restricted information

Why Bio-oil?

- **Fast pyrolysis (FP) and catalytic fast pyrolysis (CFP) promising deconstruction methods**
  - Raw FP bio-oil can be used in industrial burners, potentially as marine fuel
  - Downstream upgrading (hydrotreating or refinery co-processing) of FP and CFP to fuels and chemicals
- **Bio-oils are complex samples. FP bio-oils:**
  - Acidic liquid (pH ~2.5)
  - Contains over 300 compounds
  - 20-30 wt% water
  - Unstable with time (aging)
  - Very high oxygen content (~40 wt%)
  - Oxygen present across variety of functionalities
    - Acids, aldehydes, alcohols, esters, ethers, ketones, phenolics, sugars, furans
    - Oxygenated hydrocarbons of a wide variety of sizes: 40 – 2000 Da
    - Compounds monofunctional (acetic acid) and multifunctional (guaiacol)

- **<u>Goal:</u> Enable meaningful, consistent, and transferrable data on bio-oil via standardized analytical methods**
- **<u>Outcome:</u> Enable effective processing and commoditization of bio-oils**

1 - Management



Project Highlights

- Project started in 2014
- Become leaders in standardized bio-oil analysis – created suite of standard methods
- Created first of its kind ASTM method

1 - Management

- **Bilateral Communication**
  - **Project:** Constant communication between NREL/PNNL/ORNL. Project team has history of working together
  - **External stakeholders:** We have developed reputation in bio-oil analysis. Actively reach out to bio-oil stakeholders to solicit input. Stakeholders often reach out to us seeking input on bio-oil analysis
  - **BETO Projects:** We are engaged in bio-oil analysis activities across the national labs, and in frequent communication with projects working with bio-oils. BETO portfolio is aware of our standard methods, projects often reach out for input on bio-oil analysis
  - **BETO:** Quarterly meetings with technology manager. More frequent communication on project-relevant items
  - **ASTM:** Maintain active involvement in standards development
- **Method Development & Samples**
  - Individual lab takes lead on developing a specific analytical method, based on individual expertise at each lab
    - Other labs provide feedback, perform preliminary testing
  - Common bio-oil samples shared between labs for method development & standardization

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Pacific Northwest NATIONAL LABORATORY

OAK RIDGE National Laboratory

2 – Approach: Identify Analytical Needs

Standard analytical methods needed across multiple pathways

- Multiple pathways and technologies supported
- **Broad engagement across bioenergy community to determine needs**
  - Academia/National Labs/Industry

Multiple Samples

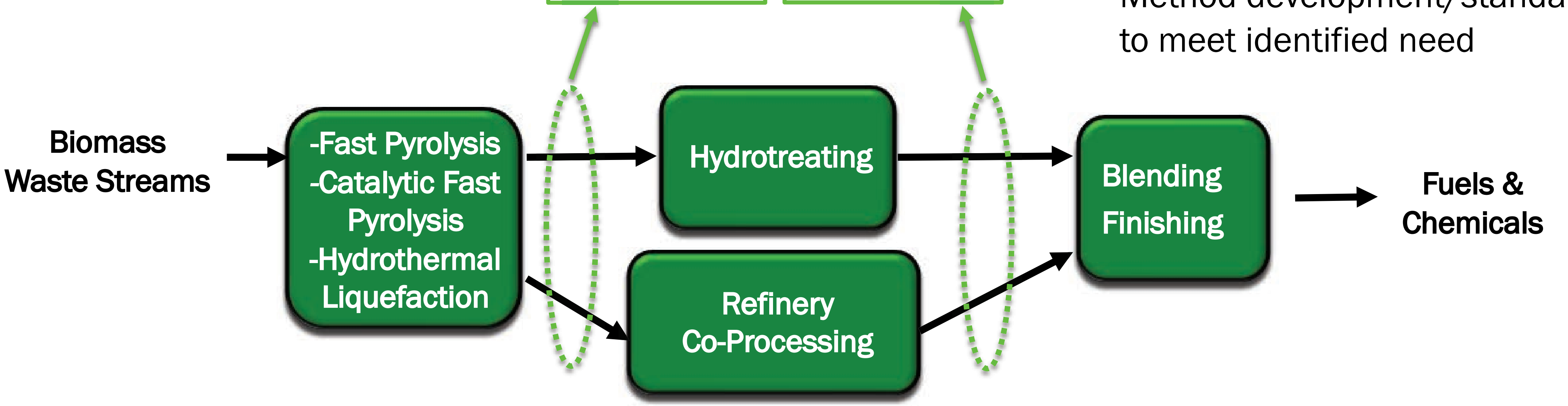
Broad range of oxygen content and chemical/physical properties

Raw bio-oils and biocrudes

Upgraded bio-oils and biocrudes

Determining Analytical Needs

- Obtain feedback from many different stakeholders
- Feedback points to common needs
  - ***Quantitative methods***
  - ***Chemical information (species, functional groups)***
- Method development/standardization to meet identified need



2 – Approach: Method Development & Standardization

Challenge

Data on bio-oil needs to be meaningful, consistent, and transferrable

Approach

Engage Bioenergy Industry to Determine Analysis Needs

Develop Tailored Method to Address Defined Need

Standardize Method: Inter-Laboratory Study (ILS)

< 10% Variability?

Yes

Publish: Laboratory Analytical Procedure (LAP)

Create ASTM Standard

Feed Data Back to Relevant Consortia

No

Reevaluate: Refine Method

Success Factors

- Develop and validate reliable standard methods (< *10% Inter-Laboratory variability*) to share with bio-oil community
- Adoption of methods by the bioenergy community

2 – Approach: Create Framework for Analysis

Challenge

To date, bio-oil is poorly characterized

→

Approach

Develop suite of standard methods

Chemical Speciation

↓

GC-MS; HPLC
Karl Fischer (H_2O)
CHN analysis
ICP (inorganics)

Chemical Functional Groups

↓

-^{31}P – hydroxyl groups
-^{13}C – carbon groups
-Carbonyls (C=O)
-Acid Number
-Phenolics
-Sugars
-Residual oxygenates

Processing

↓

-Corrosivity: Metal leaching
-Bio-oil Aging

Future Work →

-Laser Induced Breakdown Spectroscopy (LIBS): N, O, S, Cl

-Liquid Scintillation Counter: ^{14}C in co-processed samples

-Organic Phase ICP: simpler method, no acid digestion

Success Factors

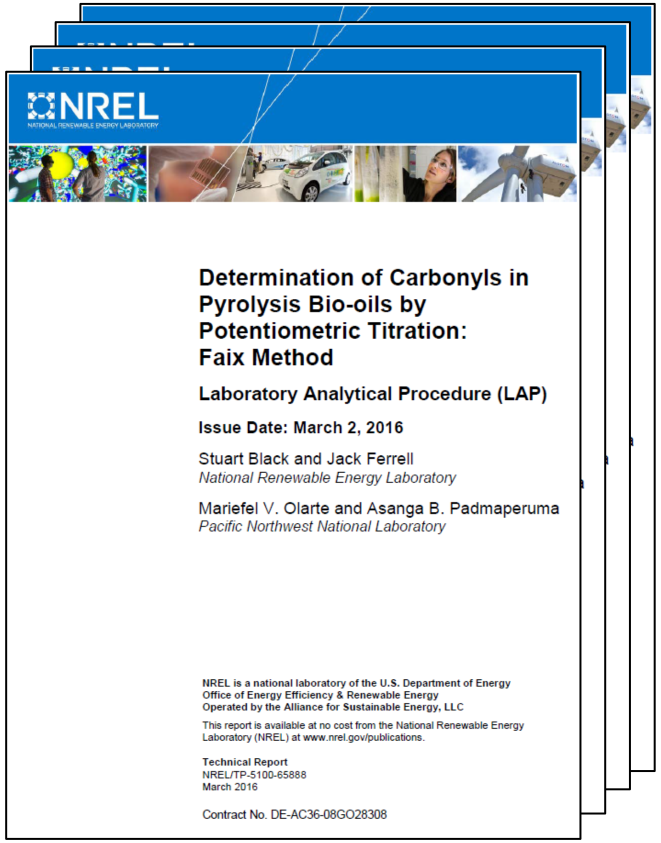
- Enable correlation of processing performance with bio-oil properties
- Suite of standardized methods will create a **framework** for bio-oil analysis - assays

Future work:

- Identify/develop methods to measure critical attributes required for downstream processing in collaboration with Conversion and SDI projects

3 – Impact: Laboratory Analytical Procedures

- **Laboratory Analytical Procedures (LAPs)**
  - Hosted on NREL website[1]
  - Free and publicly available
- **4 methods previously published**
  - GC-MS
  - CAN/TAN titration
  - Faix carbonyl titration
  - ^{31}P NMR
- **6 methods published in 2021:**
  - Aging (fast pyrolysis bio-oils)
  - ICP (Na, K, Mg, Ca, S, P, Fe)
  - CHN (elemental analysis)
  - Karl Fischer (H_2O content)
  - Folin-Ciocalteu (Phenol content)
  - ^{13}C NMR (carbon functional groups)


NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Determination of Carbonyls in Pyrolysis Bio-oils by Potentiometric Titration: Faix Method

Laboratory Analytical Procedure (LAP)

Issue Date: March 2, 2016

Stuart Black and Jack Ferrell
National Renewable Energy Laboratory

Mariefel V. Olarte and Asanga B. Padmaperuma
Pacific Northwest National Laboratory

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

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Technical Report
NREL/TP-5100-65888
March 2016

Contract No. DE-AC36-08GO28308

- **Easily-accessible route for method dissemination**
- **Bioenergy community is adopting these methods**

- LAPs define:
  - Scope (types of bio-oil samples)
  - Sample preparation
  - Analytical protocol
  - Data analysis procedures
  - Method variability
- Usage statistics:
  - **Page views: 500/quarter**
  - **Downloads: 100/quarter**
  - **Citations: 48**

[1] http://www.nrel.gov/bioenergy/bio-oil-analysis.html

3 – Impact: ASTM Standardization

- ASTM standards **widely-accepted** route for standard analytical methods
- ASTM E3146 *first ASTM method on the chemical characterization of bio-oils*
  - Applies to range of pyrolysis bio-oils 0.5 mol/kg < Carbonyl < 8 mol/kg
  - Applies to fast pyrolysis, catalytic fast pyrolysis, some hydrotreated and co-processed samples
- Timeline
  - Method approved 2018
  - Completed ASTM inter-laboratory study in 2019
  - Method updated with precision statement in 2020
- Plan to continue engagement with ASTM
  - FY21 Q4 – ballot another method at ASTM
  - *Bio-oil aging (referencing ASTM E3146)*

Creating ASTM standards to facilitate worldwide-adoption of our *chemical characterization* methods

ASTM INTERNATIONAL

Designation: E3146 – 20

Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration[1]

This standard is issued under the fixed designation E3146; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

3 – Impact: Meeting Needs of Bioenergy Community

- Addressing analytical needs of bioenergy community
  - Engaged both researchers & industry to determine analytical needs
  - Successfully developed & standardized methods

Research Community Needs

- Accurate comparisons needed to inform R&D across different pathways
- Bio-oil variability as function of
  - Feedstock
  - Process conditions
  - Production facility

Enabling Commoditization of Bio-oils

-Suite of standard methods

ASTM INTERNATIONAL
Standards Worldwide

Industry Needs

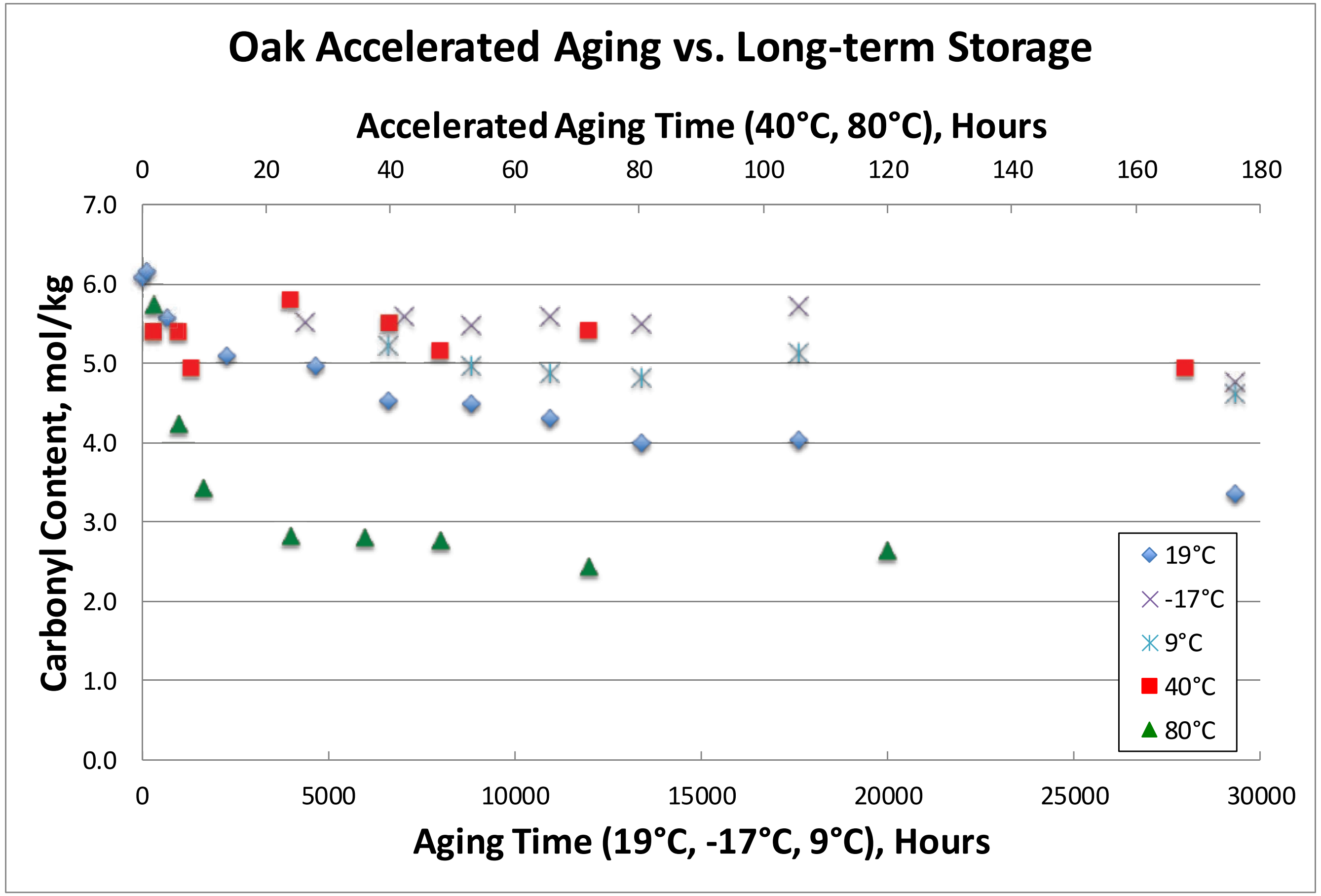
- Industrial commercialization routes require reliable data
  - Chemical composition
  - Materials compatibility
- ASTM standards will enable commerce with bio-oil

Impact to BETO

- Methods developed & standardized in this project will enable ongoing efforts across BETO portfolio
  - Pyrolysis
  - Hydrothermal Liquefaction
  - Hydrotreating
  - Co-processing

4 – Progress and Outcomes: Accelerated Aging Test

- Knowledge of aging behavior critical for **storage & transport** of *fast pyrolysis bio-oils*
- Carbonyls known to cause bio-oil aging, leading to an increase in viscosity and decrease in carbonyls over time
- Demonstrated that carbonyl content better-suited to tracking aging than viscosity
- Tested different accelerated aging protocols; compared to room-temp aging
- Commonly-used aging test, holding samples at 80 °C for 24 hours, is overkill
  - 24 hours at 80 ˚C correlates to >3 years of room temperature aging
- **New accelerated aging test**: 80 °C for 2 hours[1,2]
  - Equivalent to 1-3 months at room temp
- Low inter-laboratory variability (<3% RSD)
  - Met recent Go/No-Go decision



[1]Black and Ferrell *RSC Advances* 10 (2020) 10046-10054
[2]Laboratory Analytical Procedure (LAP): https://www.nrel.gov/bioenergy/bio-oil-analysis.html

4 – Progress and Outcomes: Residual Oxygenates

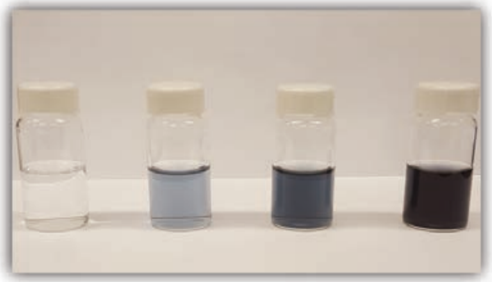
- Small mounts of oxygenated molecules will persist through upgrading
  - Need to quantify these species in hydrotreated and co-processed samples (total O content <0.5%)
- Residual oxygenates can affect downstream processing, material compatibility, stability, and engine performance
  - **Quantification of residual oxygenates will be needed for market acceptance** of these products, especially for jet fuel
- Solid phase extraction (SPE) is used to isolate oxygenates/polars from hydrocarbon matrix – with subsequent quantification by GC/MS-FID
- Majority of residual oxygenates are phenols
  - Great repeatability for these compounds, often < 1% relative standard deviation (RSD)

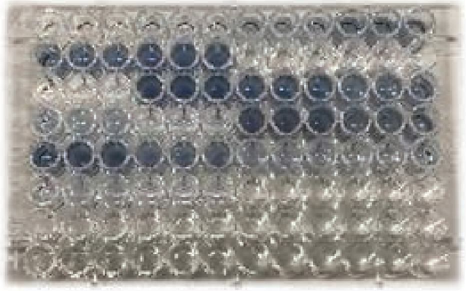
Compound	Class	Carbon #	Average wt%	% RSD
Phenol, 2-methyl-	Phenol	7	0.08	2.03
Phenol, 2,6-dimethyl-	Phenol	8	0.83	0.62
Phenol, 2-ethyl-	Phenol	8	0.13	2.69
Phenol, 2,4-dimethyl-	Phenol	8	0.25	0.70
Phenol, 3,5-dimethyl-	Phenol	8	0.02	6.87
Phenol, 2-ethyl-6-methyl-	Phenol	9	0.44	0.70
Phenol, 2,4,6-trimethyl-	Phenol	9	0.31	0.85
Phenol, 2-propyl-	Phenol	9	0.07	0.83
C9 Phenol	Phenol	9	0.02	3.62
C9 Phenol	Phenol	9	0.04	1.30
Phenol, 2,3,6-trimethyl-	Phenol	9	0.13	1.41
C9 Phenol	Phenol	9	0.05	0.64
C9 Phenol	Phenol	9	0.09	0.56
2,5-Diethylphenol	Phenol	10	0.07	0.47
2-Methyl-6-propylphenol	Phenol	10	0.28	0.12
C10 Phenol	Phenol	10	0.11	0.48
Phenol, 2-ethyl-4,5-dimethyl-	Phenol	10	0.14	0.67
C10 Phenol	Phenol	10	0.03	0.47
C10 Phenol	Phenol	10	0.03	1.26
C10 Phenol	Phenol	10	0.03	1.28
C10 Phenol	Phenol	10	0.05	1.00
Phenol, 2-butyl-	Phenol	10	0.02	2.79
C10 Phenol	Phenol	10	0.03	8.72
C10 Phenol	Phenol	10	0.04	0.66
Phenol, 4-(1-methylpropyl)-	Phenol	10	0.08	0.60
Benzene, 1-methoxy-4-(1-methylpropyl)-	Methoxybenzene	11	0.05	8.24
C11 Methoxybenzene	Methoxybenzene	11	0.06	8.08
C11 Methoxybenzene	Methoxybenzene	11	0.08	7.76
C11 Phenol	Phenol	11	0.08	7.14
C11 Methoxybenzene	Methoxybenzene	11	0.11	7.74
C11 Methoxybenzene	Methoxybenzene	11	0.04	8.13
2-Ethyl-5-n-propylphenol	Phenol	11	0.05	0.69
C11 Methoxybenzene	Methoxybenzene	11	0.05	0.57

4 – Progress and Outcomes: Phenolic Content

- **Importance of quantifying phenols**
  - In bio-oils, phenols can react with aldehydes to form resin-type compounds to cause catalyst deactivation and reactor plugging.
  - In upgraded oils, phenols can be a source of acidity (increase refinery CAN numbers) and indicator of decreased hydrotreating capability
  - In lignin-rich feeds, phenols can be targeted products.
- **Modified Folin-Ciocalteu (FC)**
  - Colorimetric method
  - Replaced gallic acid (wine-relevant) with guaiacol (bio-oil relevant) as reference compound
  - ***Developed two methods for equipment adaptability:*** cuvette and well plate readers (high throughput) for fast pyrolysis bio-oils
    - **Cuvette method** showed good inter-laboratory repeatability (≤5% RSD)
    - **Well plate method** was only tested in one laboratory and showed promising repeatability (≤ 6% RSD)
  - Upgraded oils have solubility issues with the FC matrix

– **Folin-Ciocalteu (FC) intra- and inter-laboratory test results**





	Well Plate FC Ave	Well Plate RSD	Cuvette FC Ave	Cuvette FC RSD
Sample 1	18.1	**5.1%**	17.9	**2.8%**
Sample 2	18.3	**5.8%**	18.1	**2.6%**

- INTRA-lab cuvette RSD less than 5% (one lab)

	Inter-lab FC Ave	Inter-lab FC RSD
Sample 1	17.0	**4.2 %**
Sample 2	17.1	**5.0 %**

- INTER-lab cuvette RSD about 5% (3 labs)
- Candidate for ASTM method

4 – Progress and Outcomes: ASTM Inter-Laboratory Study

- ASTM Inter-Laboratory Study (ILS) on carbonyl titration (ASTM E3146)
- ILS conducted in FY19
  - 9x9 ILS design: 9 labs, 9 samples in blind duplicate (18 samples per lab)
  - Three types of bio-oil
    - Fast pyrolysis, catalytic fast pyrolysis, and hydrotreated fast pyrolysis
  - Low, medium, and high carbonyl concentration for each bio-oil type – prepared by spiking methyl isobutyl ketone (MIBK)
- Method updated with precision statement from ILS data
  - **repeatability (r)** = $0.1878(X + 0.15)^{0.35}$ mol/kg (intra-lab precision)
  - **Reproducibility (R)** = $0.6865(X + 0.15)^{0.35}$ mol/kg (inter-lab precision)
    - X = average of two results, each obtained from a complete execution of ASTM E3146
  - FP bio-oil with 5 mol/kg carbonyl content: r = 0.33 mol/kg; R = 1.22 mol/kg

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THE UNIVERSITY OF TENNESSEE KNOXVILLE
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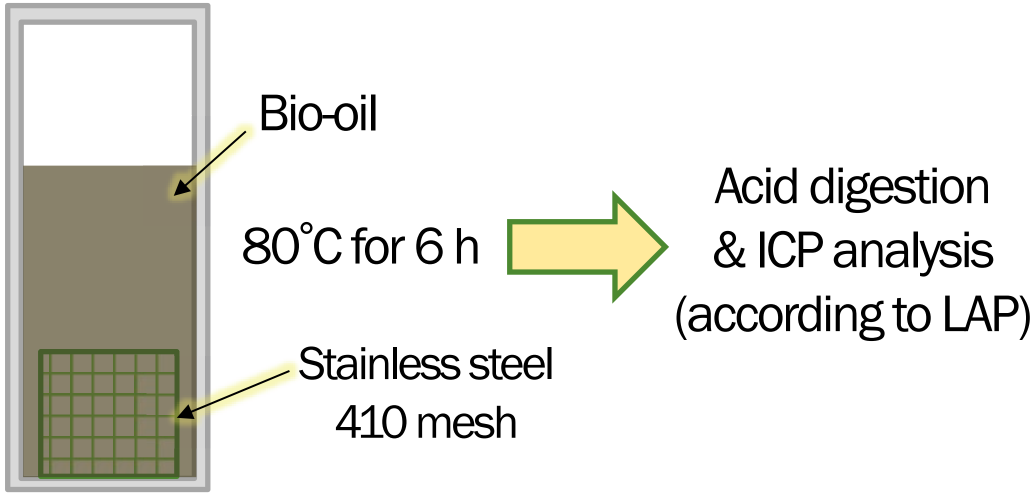
ASTM INTERNATIONAL Standards Worldwide

4 – Progress and Outcomes: Corrosivity Screening Test

- Metal leaching test is being developed as a ***direct measure of corrosivity*** toward the metallic materials (more focus on '*corrosion system*' than '*characterization of corrosive species*')
- Fe and Cr metal ion concentration after leaching was determined by ICP-MS.
- All participant labs used the same LAP. In the initial runs, the inter-laboratory variability (%RSD) values were high. We are currently tuning the analytical procedure to minimize the RSD value.



	μg Fe g^{-1} mesh g^{-1} oil	St.dev.	%RSD
ORNL	15889	917	5.8
NREL	6408	617	9.6
PNNL	10839	205	1.9
Inter-lab	11045	4744	42.9

- Updated leaching procedure modified steps that introduced error (heating method, methanol wash)
- Preliminary results using updated LAP have **much lower variability (~5% RSD)**

Quad Chart Overview

Timeline
- 10/1/2018
- 9/30/2021

	FY20	Active Project
DOE Funding	$800k	$2.4M

Project Partners
- NREL ($300k/year)
- PNNL ($275k/year)
- ORNL ($225k/year)
- Multiple external partners participate in inter-laboratory studies

Barriers addressed
- Ct-F: Efficient High-Temperature Deconstruction to Intermediates
- ADO-G: Co-Processing with Petroleum Refineries
- ADO-H: Materials Compatibility, and Equipment Design and Optimization

Project Goal
Support the commoditization of bio-derived and co-processing liquids through development and standardization of chemical characterization methods that will be relevant to researchers, bio-oil producers, and refiners.

End of Project Milestone
Submit ASTM Ballot (9/30/2021): Based on method development to-date, submit a ballot to ASTM based on an analytical method developed in this project for bio-oil analysis. Inter-laboratory studies between NREL/PNNL/ORNL must produce <10% RSD inter-laboratory variability for a method to be considered for ASTM submission. (NREL/PNNL/ORNL)

Funding Mechanism
AOP Project (Continuing)

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ORNL

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Jim Keiser

Method Validation Partners:

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Pacific Northwest National Laboratory
Oak Ridge National Laboratory
Natural Resources Canada / Ressources naturelles Canada – CanmetENERGY
Washington State University
VTT
University of Chemistry and Technology Prague
RTI International
USDA Agricultural Research Service
Aarhus University
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Summary

- **Overview:** Bio-oils provide promising routes to fuels & chemicals
- **Management:** Collaborative project between NREL/PNNL/ORNL. External stakeholders provide feedback and participate in method validation
- **Approach:** Determine analytical needs. Targeted method development & standardization. Create framework for analysis
- **Impact:** Meet analytical needs of bioenergy community and share methods (LAPs & ASTM)
- **Progress and Outcomes:** Accelerated aging test, residual oxygenates, phenolic content, ASTM Inter-laboratory study, Corrosivity screening

4 – Progress and Outcomes: Preliminary Testing of Methods

- **Biogenic carbon: Liquid Scintillation Counter (LSC)**
  - Quantification of ^{14}C in biogenic and fossil samples
  - Preliminary testing in collaboration with SCR project (Strategies for Co-processing in Refineries, 2.4.2.305), resulting in a publication
  - Main challenge: Quenching effect due to color
    - **FY21 focus** – Follow-on method development; focus on quenching effect of colored matrices

Fuel
Volume 291, 1 May 2021, 120084

Full Length Article

Determination of low-level biogenic gasoline, jet fuel, and diesel in blends using the direct liquid scintillation counting method for ^{14}C content

Charles G. Doll, Andrew E. Plymale, Alan Cooper, Igor Kutnyakov, Marie Swita, Teresa Lemmon, Marlefel V. Olarte, Huamin Wang

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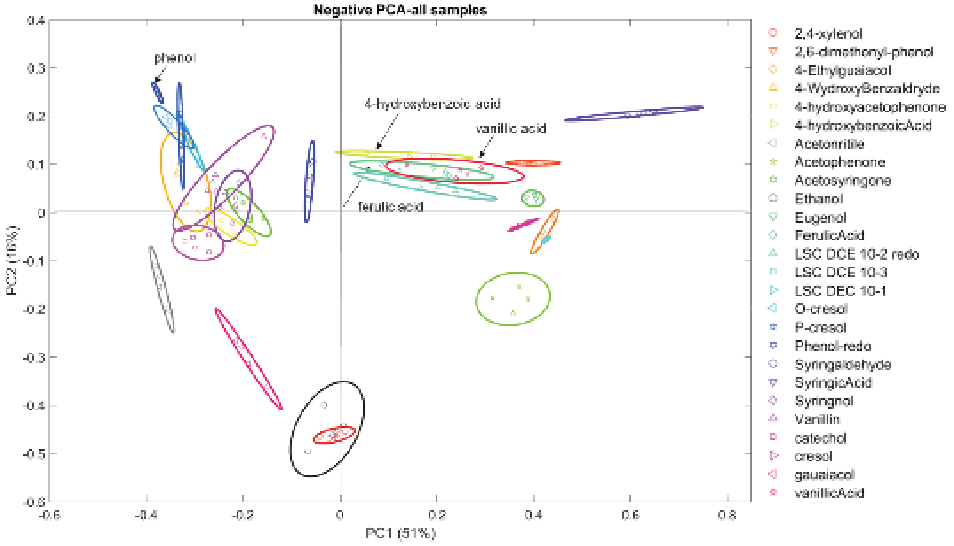
Highlights

- Tri-Carb and Quantulus instruments performed comparably.
- The direct 1 wt% biogenic fuel blends were accurately and precisely determined using the direct LSC method.
- Quench correction to increase data accuracy was required for darker colored diesel samples.

- **Phenolics: Time-of-Flight/Secondary Ion Mass Spectroscopy (TOF-SIMS)**
  - Chemical mapping of signature peaks of various phenolic compounds
  - Determination whether signature peaks of model compounds can be easily identified in upgraded bio-oils
  - Technique still under evaluation



4 – Progress and Outcomes: Corrosion and Metal Chelation

Goal: To confirm if formic acid (a common & corrosive species in bio-oils) be more corrosive with a strong chelating species (native in bio-oils).

Formic acid solution: previously caused higher leaching for ss410 meshes (FY19 results)

EDTA: a surrogate chelator (to mimic 'potential' strong chelator(s) native to bio-oils)

ORNL chelation study Test matrix	10 wt% formic acid (A)	10 wt% formic acid + 0.01 M EDTA (B)	10 wt% formic acid + 0.1 M EDTA (C)	0.1 M EDTA
Fe powder	1st round	1st round	1st round	1st round
Fe-5Cr-1Mo steel powder	2nd round	2nd round	2nd round	2nd round
ss410 (Fe-11.5Cr) powder	1st round	1st round	1st round	1st round
ss430 (Fe-17Cr) powder	2nd round	2nd round	2nd round	2nd round

After exposure in respective solutions (~50˚C and 6 h), ICP-MS analysis for Fe (& Cr) ions will be conducted.

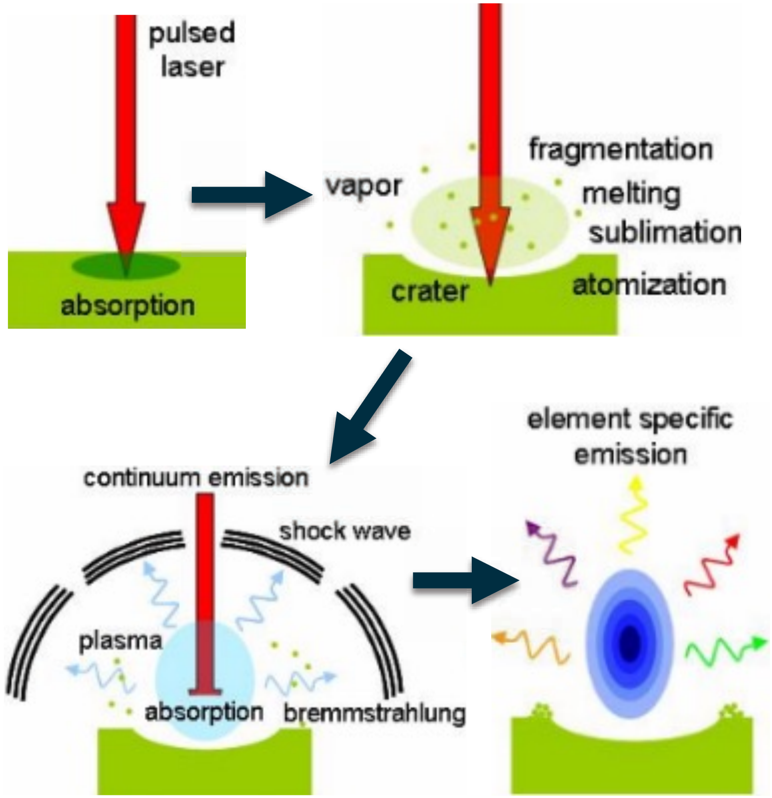
If **(A) > (B) & (C)** : chelator(s) likely suppress(es) corrosion of steels

If **(A) < (B) & (C)** : chelator(s) likely enhance corrosion of steels

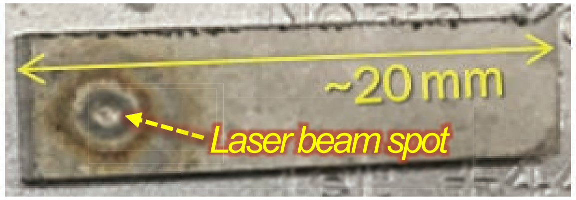
4 – Progress and Outcomes: LIBS

Laser-Induced Breakdown Spectroscopy

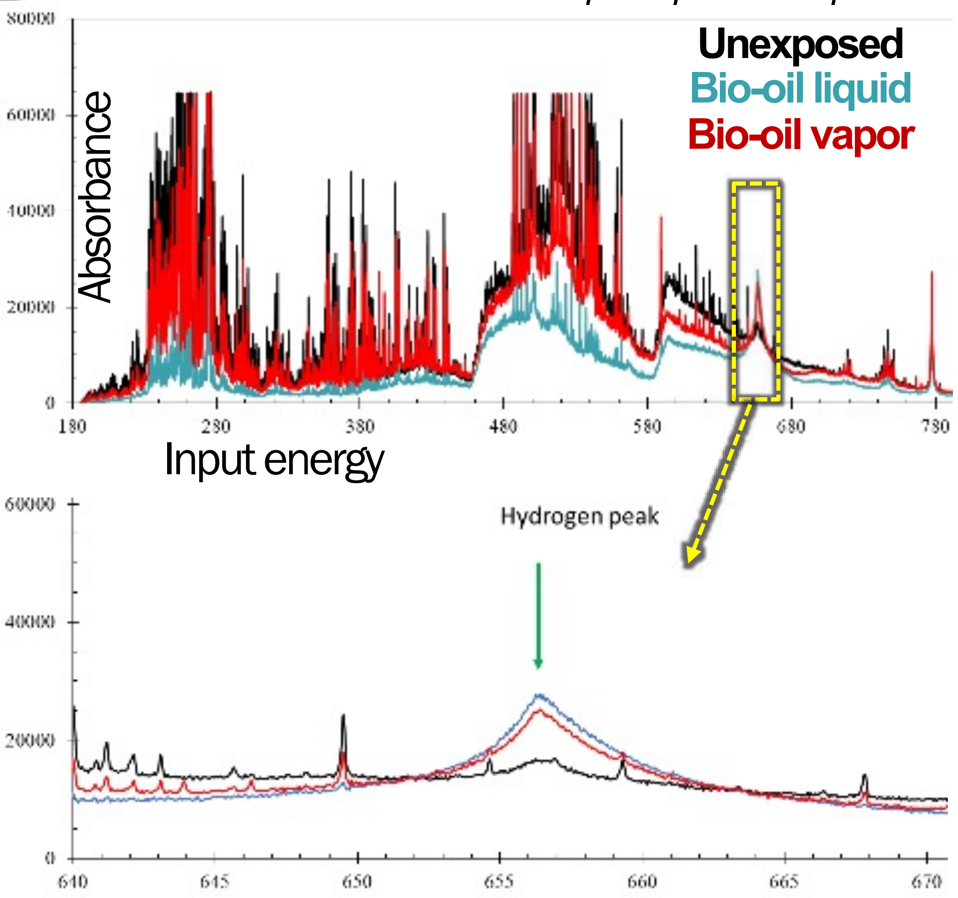
New method for measurement of low atomic number elements (N, O, S, Cl) in bio-oils

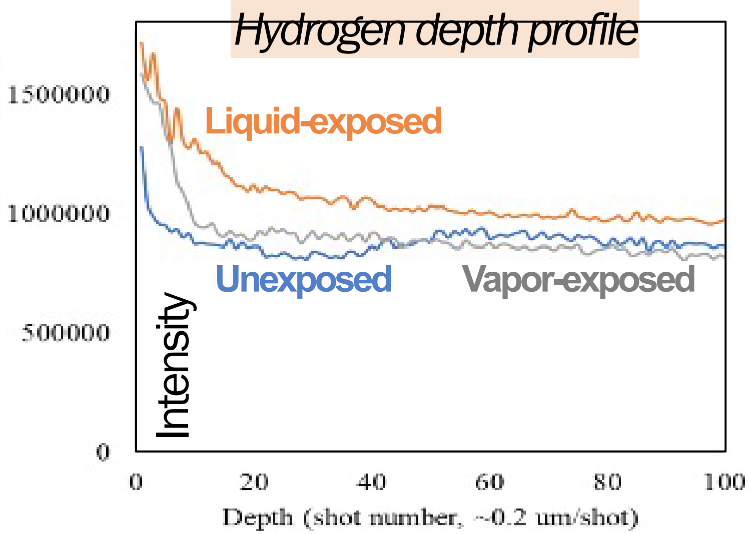


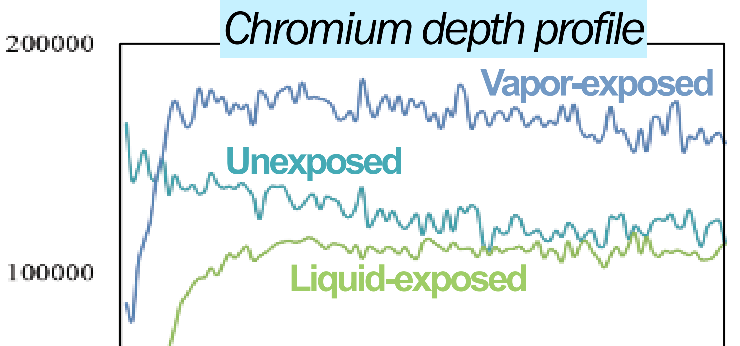
Example:
2.25Cr-1Mo steel, bio-oil exposed



Bio-oil vapor exposed sample







'Detected Cr depletion at the alloy surface by bio-oil exposure

2019 Peer Review Comments

- **Reviewer Comment**: This project clearly meets an industry need and the described approach offers a high likelihood of success; dissemination of the knowledge should help drive acceptance and utilization of the standards and methodologies developed.
  - Response: We thank the reviewer for the comment.
- **Reviewer Comment**: This project is targeted towards development of analytical methods to characterize the bio-oils produced in pyrolysis processes (FP, CFP, HTL). Chemical compositions of these bio-oils vary widely and there are no standard methods to measure the chemical composition. A number of very useful analytical methods were developed and disseminated to various participants to validate them.
  - Response: We thank the reviewer for the comment.
- **Reviewer Comment**: This project is a perfect example of work that should be done by national labs to promote biofuel understanding and specifications.
  - Response: We thank the reviewer for the comment.
- **Reviewer Comment**: Valuable R&D work supportive of industry needs. It's aspirational to think that national labs would ever be considered to be a repository of standards - the collaboration with ASTM is key to this work for global dissemination.
  - Response: We thank the reviewer for the comment, and agree that engagement with ASTM is essential for global dissemination (and use) of our methods. In addition, we believe the publication of Laboratory Analytical Procedures (LAPs) is very useful for the research community, and is also a good first step before approaching ASTM with a specific analytical method.
- **Reviewer Comment**: Standardization of analytical procedures is a key an valuable goal. Project generated positive results including publication of an ASTM procedure. More information on milestones and project management criteria would have been valuable.
  - Response: We thank the reviewer for the comment. In the future we will aim to clearly provide more information on milestones and specifics on project management.

Publications

- "Determination of Carbonyl Groups in Pyrolysis Bio-oils Using Potentiometric Titration: Review and Comparison of Methods." S. Black* and J.R. Ferrell III, ***Energy & Fuels***, 2016, 30, 1071.
- "In-Depth Investigation on Quantitative Characterization of Pyrolysis Oil by ^{31}P NMR." H. Ben* and J.R. Ferrell III*, ***RSC Advances***, 2016, 6, 17567.
- "Standardization of Chemical Analytical Techniques for Pyrolysis Bio-oil: History, Challenges, and Current Status of Methods." J.R. Ferrell III*, M.V. Olarte, E.D. Christensen, A.B. Padmaperuma, R.M. Connatser, F. Stankovikj, D. Meier, and V. Paasikallio, ***Biofuels, Bioproducts & Biorefining***, 2016, 10, 496.
- "Quantitative ^{13}C NMR Characterization of Fast Pyrolysis Oils." R.M. Happs, K. Iisa, and J.R. Ferrell III*, *RSC Advances*, 2016, 6, 102665.
- "Determination of Carbonyl Functional Groups in Bio-oils by Potentiometric Titration: the Faix Method." S. Black and J.R. Ferrell III*, ***Journal of Visualized Experiments***, 2017, 120, e55165.
- "Characterization of Upgraded Fast Pyrolysis Oak Oil Distillate Fractions from Sulfided and Non-Sulfided Catalytic Hydrotreating." M.V. Olarte*, A.B. Padmaperuma, J.R. Ferrell III, E.D. Christensen, R.T. Hallen, R.B. Lucke, S.D. Burton, T.L. Lemmon, M.S. Swita, G. Fioroni, D.C. Elliott, C. Drennan, ***Fuel***, 2017, 202, 620.
- "Determination of Hydroxyl Groups in Pyrolysis Bio-oils using 31P NMR." M.V. Olarte, A.B. Padmaperuma, J. Ferrell*, H. Ben, ***Laboratory Analytical Procedure***, 2016, NREL/TP 5100-65887.
- "Determination of Carbonyls in Pyrolysis Bio-oils by Potentiometric Titration: Faix Method." S. Black, J. Ferrell*, M.V. Olarte, A.B. Padmaperuma, ***Laboratory Analytical Procedure***, 2016, NREL/TP 5100-65888.
- "Quantification of Semi-Volatile Oxygenated Components of Pyrolysis Bio-Oil by Gas Chromatography/Mass Spectrometry (GC/MS)." E. Christensen, J. Ferrell*, M.V. Olarte, A.B. Padmaperuma, ***Laboratory Analytical Procedure***, 2016, NREL/TP 5100-65889.
- "Acid Number Determination of Pyrolysis Bio-oils using Potentiometric Titration." E. Christensen, J. Ferrell*, M.V. Olarte, A.B. Padmaperuma, ***Laboratory Analytical Procedure***, 2016, NREL/TP 5100-65890.
- "Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration." **ASTM E3146**, developed by subcommittee E48.05, 2018. https://www.astm.org/Standards/E3146.htm

Publications

- “Methods and Challenges in the Determination of Molecular Weight Metrics of Bio-oils.” A.E. Harman-Ware, J.R. Ferrell III*, Review Paper in ***Energy & Fuels***, 2018, 32, 8905.
- “Characterization of Catalytic Fast Pyrolysis Oils: The Importance of Solvent Selection for Analytical Method Development.” A.E. Harman-Ware, J.R. Ferrell III*, ***Journal of Analytical and Applied Pyrolysis***, 2018, 132, 190.
- “Determining aromatic and aliphatic carboxylic acids in biomass-derived oil samples using 2,4-dinitrophenylhydrazine and liquid chromatography-electrospray injection-mass spectrometry/mass spectrometry.” S.A. Lewis Sr.*, R.M. Connatser*, M.V. Olarte, J.R. Keiser, ***Biomass and Bioenergy***, 2018, 108, 198.
- “Aging of Fast Pyrolysis Liquids: A New Method Based on Carbonyl Titration.” S. Black, J.R. Ferrell III*, **RSC Advances**, 2020, 10, 10046-10054.
- “Development of Quantitative 13C NMR Characterization and simulation of C, H, O contents for pyrolysis oils based on the 13C NMR analysis.” R. Wang, Y. Luo, H. Jia, J.R. Ferrell III; H. Ben*, **RSC Advances**, 2020, 10, 25918-25928.
- “Molecular Weight Distribution of Raw and Catalytic Fast Pyrolysis Oils: Comparison of Methodologies.” A.E. Harman-Ware, K. Orton, C. Deng, S. Kenrick, S. Rowland, D. Carpenter, J.R. Ferrell III*, **RSC Advances**, 10, 3789-3795.
- “Accelerated Aging of Fast Pyrolysis Bio-oil using Carbonyl Titration.” S. Black, J.R. Ferrell III*, ***Laboratory Analytical Procedure***, 2021
- “Determination of Carbon, Hydrogen, and Nitrogen in Bio-oils.” J. Miscall, E.D. Christensen, J. Olstad, S. Deutch, J.R. Ferrell III*, ***Laboratory Analytical Procedure***, 2021
- “Determination of Water content in Bio-oils by Volumetric Karl Fischer Titration.” J. Miscall, E.D. Christensen, S. Deutch, R. Jackson, J.R. Ferrell III*, ***Laboratory Analytical Procedure***, 2021
- “Elemental Analysis of Bio-oils and Deoxygenated Products by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).” E.D. Christensen, S. Deutch, J.R. Ferrell III*, ***Laboratory Analytical Procedure***, 2021
- “Determination of Carbon Functional Groups in Pyrolysis Bio-oils using 13C NMR.” R.M. Happs, A.E. Harman-Ware, H. Ben, J.R. Ferrell III*, ***Laboratory Analytical Procedure***, 2021
- “Determination of Phenolic Groups in Bio-oils using Revised Folin-Ciocalteu Methods: Single Cuvette and Plate Reader.” M. Swita, T. Lemmon. R. Ma, J. Taylor, A.B. Padmaperuma, M.V. Olarte*, E.D. Christensen, J.R. Ferrell III, ***Laboratory Analytical Procedure***, 2021

FY19 Milestones

Development of an Accelerated Aging Test for Bio-oil: Develop a new method to predict bio-oil aging behavior based on carbonyl content.	Test at least 2 accelerated aging temperatures for at least 3 bio-oil samples, and compare carbonyl contents to long-term aging studies performed at room temperature. Existing aging tests based on viscosity have exhibited unacceptably high inter-laboratory variabilities, and industrial entities have a need to predict how a bio-oil will change with time. The method developed in this milestone will allow industry to determine whether they can still chemically process bio-oil after it has been shipped or stored for a period of time. (NREL)	12/31/2018	Annual SMART
Method Development for HTL, Co-Processing, or Hydrotreated Samples.	Complete evaluation of the applicability of an existing ASTM standard for phenol quantification (e.g., ASTM D1783 Standard Test Methods for Phenolic Compounds in Water) for biomass-derived oils and develop an alternative method if the existing standardized method is not applicable due to matrix considerations. This can be determined by model compound recoveries after following the procedure. A simple method for phenol quantification does not exist, and phenol quantification is important for downstream upgrading. (PNNL)	3/31/2019	Quarterly
Method Development for Hydroxyl Aldehydes and Organic Acids in HTL and CFP Samples.	Complete development of a LC-ESI-MS/MS method using targeted extraction and 2,4-DNPH derivatization for quantification of hydroxyl aldehydes and large organic acids in HTL and CFP samples. Knowledge of hydroxyl aldehydes, which contain a carbonyl functional group, will inform both bio-oil aging processes and downstream upgrading. Organic acids are also an important class of molecules to quantify, as they have implications for materials degradation in processing facilities. (ORNL)	6/30/2019	Quarterly
Data received on ASTM-approved Interlaboratory Study (ILS).	Complete the experimental portion of the ASTM-approved ILS for ASTM E3146, and send data from all partners to ASTM for analysis. The ASTM ILS will test 3 samples: FP, CFP, and a hydrotreated FP sample. To achieve ASTM-approval, the ILS must involve at least 6 participating laboratories testing each sample in duplicate (guidelines in ASTM E691). This ILS is required to provide a precision statement for ASTM Standard Test Method E3146. (NREL/PNNL)	9/30/2019	Quarterly

FY20 Milestones

ILS Preparation	Complete writing of the detailed analytical protocols in Laboratory Analytical Procedure (LAP) format for at least 1 method developed in this project. Additionally, select and prepare bio-oil samples to be analyzed by partner laboratories in a preliminary ILS (ruggedness study). This milestone will complete all preparation needed for a successful ILS, the results of which will be reported with the FY20 Q4 Annual Milestone. (NREL, PNNL, ORNL)	12/31/2019	Quarterly
Corrosive Tendency (ORNL) and Phenol Quantification (PNNL)	Optimize a method to indicate corrosive tendency by measuring and correlating both (1) indicator metals leached from alloy screens; and (2) degree of chelation of alloy metals by bidentate oxygenates in real oils. These tests will be aligned with capabilities of industrial contract labs and may include electrochemical impedance spectroscopy. (ORNL) Verify and develop method for phenol quantification for co-processed and hydrotreated oil products. Previous method development optimized for FP and eventually applied to CFP and HTL using Folin-Ciocalteu method showed that this method is not applicable for mostly hydrocarbon matrix. ASTM methods will be queried for applicability and quantification. Applicability of the previously developed CAN/TAN/PhAN will also be evaluated. GC-MS will confirm the presence or absence of phenols in samples (PNNL).	3/31/2020	Quarterly
Method Development for Residual Oxygenates in Co-Processing Samples.	Develop a method to quantify total oxygenated compounds in hydrotreated bio-oil distillate fractions. Method designed to identify and quantify individual components and groupings of oxygenated compounds in gasoline, jet, and diesel range distillates derived from hydrotreated bio-oils. Methodology will be based on solid phase extraction (SPE) to isolate oxygenates from the hydrocarbon matrix followed by analysis with GC-MS to identify and quantify compounds. (NREL)	6/30/2020	Quarterly
Bio-oil Method Development and Standardization.	Based on method development in FY19, complete a small-scale ILS (testing at least 1 method). Determine the inter-laboratory variability (defined as the % RSD from participating laboratories) and revise method(s) if variability is too high (> 10% RSD) or publish LAP for method(s) with low variabilities (< 10% RSD) in this ILS. The ILS completed in this milestone is a critical step to arriving at a method which is suitable for a standardization agency, and method(s) with the lowest variabilities will subsequently be taken to ASTM for consideration. (NREL/PNNL/ORNL)	9/30/2020	Annual SMART

Go/No Go

Name	Description	Criteria	Date
Successful development of at least 1 analytical method that holds promise for enabling improved downstream processing or determining materials compatibility issues.	Based on method development to-date, as well as method verification efforts between NREL, PNNL, and ORNL, demonstrate at least 1 analytical method that is both reliable (having low inter-laboratory variability) and holds promise for enabling improved downstream processing or delineating materials compatibility issues when bio-oils are introduced into processing facilities.	$\leq$ 10% inter-laboratory variability (defined as relative standard deviation) is required for a method to be deemed reliable, and move into the next phase of standardization, which is a small-scale ILS (Q4 FY20) ahead of ASTM standardization efforts.	3/31/2020

-Delayed due to Covid.

-Successfully met milestone 12/31/2020

FY21 Milestones

Method Development for Residual Oxygenates in Co-Processing Samples.	Develop a method to quantify total oxygenated compounds in hydrotreated bio-oil distillate fractions. Method designed to identify and quantify individual components and groupings of oxygenated compounds/polars in fuel range distillates derived from hydrotreated bio-oils. Methodology will be based on solid phase extraction (SPE) to isolate oxygenates from the hydrocarbon matrix followed by analysis with GC-MS or GCxGC-MS to identify and quantify compounds. Knowledge of the identity and amount of residual oxygenates will be very important for helping transition these upgraded biomass-derived products into the marketplace. (NREL) *This milestone delayed from FY20 due to Covid-19.*	12/31/2020	Quarterly
Corrosive Tendency	Optimize a method to indicate corrosive tendency by measuring and correlating both (1) indicator metals leached from alloy screens; and (2) degree of chelation of alloy metals by bidentate oxygenates in real oils. These tests will be aligned with capabilities of industrial contract labs and may include electrochemical impedance spectroscopy. (ORNL) *This milestone delayed from FY20 due to Covid-19.*	12/31/2020	Quarterly
Development of Laser Induced Breakdown Spectroscopy with bio-oils	Method development of Laser Induced Breakdown Spectroscopy (LIBS) for bio-oil samples, with a focus on quantification of main group elements: N, O, S, Cl,. To our knowledge, LIBS has not been applied to bio-oil analysis, and has many benefits including minimal sample preparation and very fast turnaround time. Additionally, reliable analysis of these low-Z elements, such as Cl and S, remains a need for the bio-oil community. (ORNL)	3/31/2021	Quarterly
Liquid Scintillation Counter (LSC) for ^{14}C detection	Two methods of sample preparation will be investigated. The first method, direct LSC analysis of fuel samples, is the most straight forward but requires relatively long count times and quenching can be an issue. We will build upon preliminary work done at PNNL with biodiesel and under the SCR project. The second method involves combustion of samples, capture of CO_2, and concentration of the carbon for LSC analysis. While this method is more complicated it would allow lower detection limits and shorter LSC analysis times due to the higher C-14 content and eliminate quenching concerns. (PNNL)	6/30/2021	Quarterly
Development of Organic ICP Method	Method development for direct organic ICP analysis of bio-oils. Standard organic phase ICP methods for fuels and oils utilize non-polar solvents, in which bio-oils are not entirely soluble. This task will focus on selecting solvents with adequate solvency, volatility, and viscosity for direct ICP analysis with validation of method accuracy and precision. (NREL)	6/30/2021	Quarterly
Submit ASTM Ballot	Based on method development to-date, submit a ballot to ASTM based on an analytical method developed in this project for bio-oil analysis. Inter-laboratory studies between NREL/PNNL/ORNL must produce <10% RSD inter-laboratory variability for a method to be considered for ASTM submission. (NREL/PNNL/ORNL)	9/30/2021	Annual Milestone