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DOE BETO 2019 Project Peer Review: ADO Integration & Scale-Up

Analytical Development and Standardization for Biomass-derived Thermochemical Liquids

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

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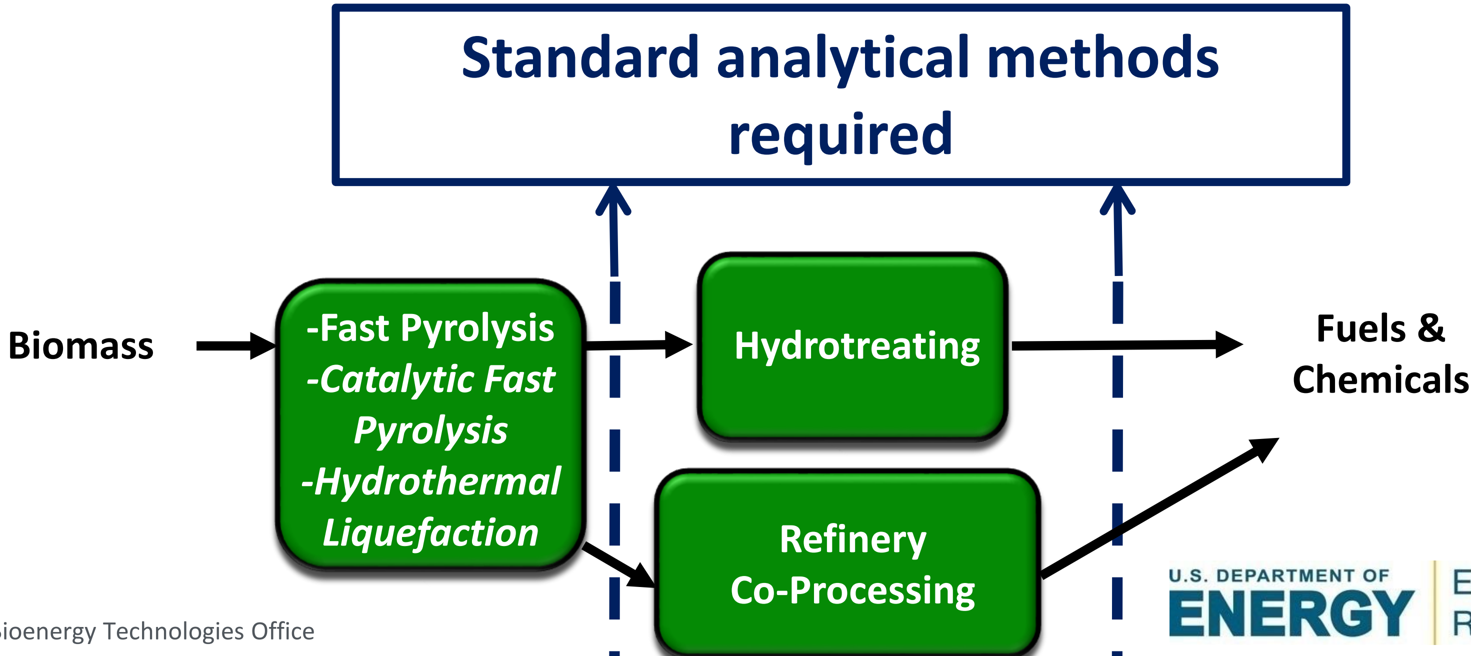
Problem Statement

<u>Research & Development</u>

- Bio-oils can be considerably different
  - Variability function of: feedstock, process conditions, production facility
- Accurate & reliable comparisons need to be made to inform R&D

<u>Industry</u>

- Integration with refinery infrastructure requires dependable data
  - Chemical composition
  - Materials compatibility
- ASTM standards will enable commerce with bio-oil



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Goal Statement

Goal: *Provide the public with a set of best practices and enable meaningful, consistent, and transferrable data between research laboratories and other stakeholders (including refiners) dealing with bio-oil*

Objectives:

- Standardize *quantitative* chemical analytical methods for bio-oil characterization
  - Standard methods **largely nonexistent** for bio-oil that provide chemical information
- Adoption of our standard methods by bioenergy community
  - Validated methods published as Laboratory Analytical Procedures (LAPs), which are **free and publicly available**
  - Generate **ASTM** standardized methods from LAPs

Outcome: Enable effective processing and commoditization of bio-oils

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Quad Chart Overview

Timeline

- Start: 10/1/2018
- End: 9/30/2021
- 14% Complete

Budget

	Total Costs Pre-FY17	FY17 Costs	FY18 Costs	Total Planned Funding (FY19 – FY21)
DOE Funded	$2,368k	$952k	$691k	2,400k
Partners: FY18: NREL (53%), PNNL (36%), ORNL (11%) FY19: NREL (38%), PNNL (34%), ORNL (28%)				

Current Method Validation Partners:

- Universities: Washington State University, UCT Prague
- Labs: VTT Technical Research Centre of Finland, Metrohm, Thunen Institute

BETO Barriers Addressed

- Ct-F: Increasing the Yield from Catalytic Processes
- ADO-G: Co-Processing with Petroleum Refineries
- ADO-H: Materials Compatibility, and Equipment Design and Optimization
  - *Addressing barriers by reliable characterization of feed and products*

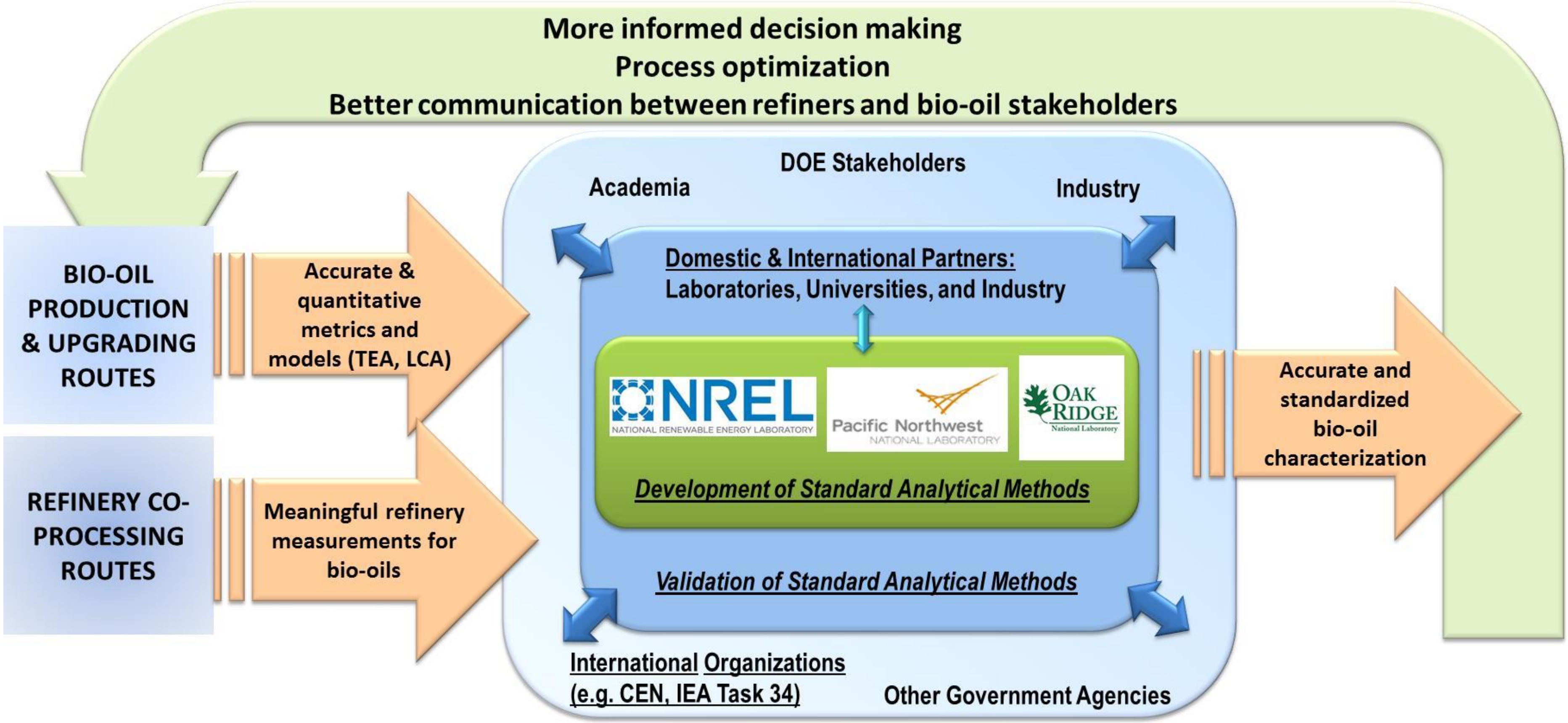
Objective:

- Standardize quantitative analysis methods for bio-oils that provide chemical information

End of Project Goal:

- Enable Correlation of Performance of Downstream Upgrading with Bio-oil Chemical Composition: Demonstrate that reliable chemical information on bio-oils, enabled by method development and standardization activities in this project, can be used to relate downstream upgrading performance, or materials compatibility issues, to bio-oil composition.

1 - Project Overview



<u>Goal</u>: Enable meaningful, consistent, and transferrable data between all stakeholders dealing with bio-oil

<u>Outcome</u>: Enable commoditization of bio-oils

2 - Management Approach

- NREL, PNNL, and ORNL
  - Determine analytical needs from bioenergy community
    - **Engage both researchers & industry to determine needs**
      - *Quantitative & reliable methods top priority*
      - Methods that provide chemical information
        - Oxygen-containing species and functional groups
      - Materials compatibility
  - Develop standard methods in **parallel**
    - Each lab individually develops a method based on expertise
  - **Engage bioenergy community** for method validation (Inter-laboratory studies)
  - Effective communication between NREL, PNNL, and ORNL
- Annual Operating Plan (AOP), Project Management Plan (PMP)
  - Risk management / abatement of uncertainties
  - **Methods stage-gated** along development & standardization process (Go/No-Go decisions)

2 - Technical Approach

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

Share: LAP, Publication

Create ASTM Standard

Feed Data Back to Relevant Consortia

Co-Optimization of Fuels & Engines

fcic FEEDSTOCK-CONVERSION INTERFACE CONSORTIUM

BIOPROCESSING SEPARATIONS CONSORTIUM

ChemCatBio Chemical Catalysis for Bioenergy

Agile BioFoundry

ASTM INTERNATIONAL Standards Worldwide

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 - Technical Approach

Challenge

To date, bio-oil is poorly characterized

Approach

Develop suite of standard methods

Processing

-Corrosivity: Metal leaching
-Bio-oil Aging
-Applicability of existing standards (petroleum or fuel industries)

Chemical Speciation

Chromatography
GC-MS
HPLC

Chemical Functional Groups

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

Data Science Techniques

-Bi
-C

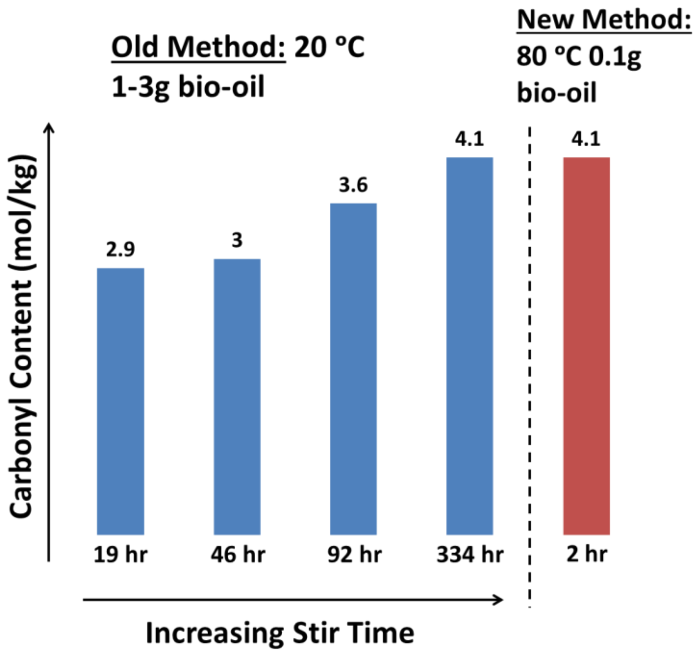
Real-time analyses

Success Factors

- Enable correlation of processing performance with bio-oil properties
- Suite of standardized methods will create a **framework** for bio-oil analysis
    - Define appropriate methods for desired measurements on different types of raw and upgraded oils

3 - Progress: Carbonyl Quantification by Titration

- Carbonyls in bio-oil cause **aging** and **catalyst deactivation**
- Developed[1] and validated[2] a new titration method, proven to be superior to previously accepted method
  - Easier to perform (higher throughput)
  - More accurate, more reliable
- Method has been used to **predict reactor plugging** during high temperature hydrotreatment
  - Fast pyrolysis bio-oils with > 1.5 mol carbonyl/kg will plug hydrotreater
- ***Developed simple, reliable method to predict performance for complex sample***



Similar Example

- **Cetane:** One metric, describing complex sample, that can predict performance in CI engine
  - ASTM D613

[1]Black and Ferrell *Energy & Fuels* 30 (2016) 1071-1077
[2]Ferrell et al. *Biofuels, Bioproducts & Biorefining* 10 (2016) 496-507

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3 – Progress: Carbonyl Titration - ASTM Standardization

- Approached ASTM to achieve next-level of standardization
- **Received approval** to create standard by *ASTM Subcommittee E48.05* on Biomass Conversion
- Formed task group for development of ASTM Standard Test Method
  - *Broad participation from bioenergy community* – over 20 different institutions including academia, research labs, industry, and regulatory agencies
- **Method approved** (1/2018)
  - *First ASTM method on chemical characterization of pyrolysis bio-oils*

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

INTERNATIONAL

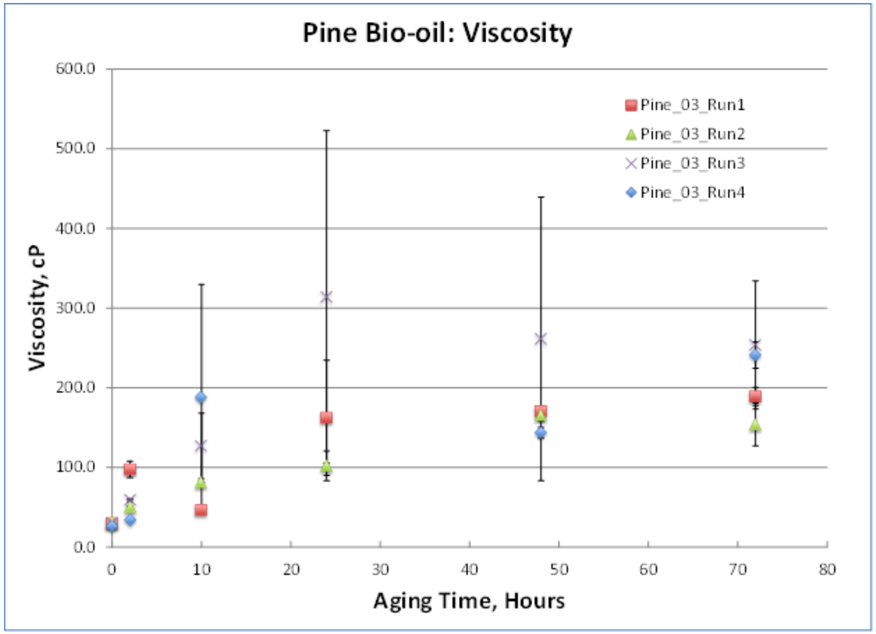
Designation: E3146 – 18

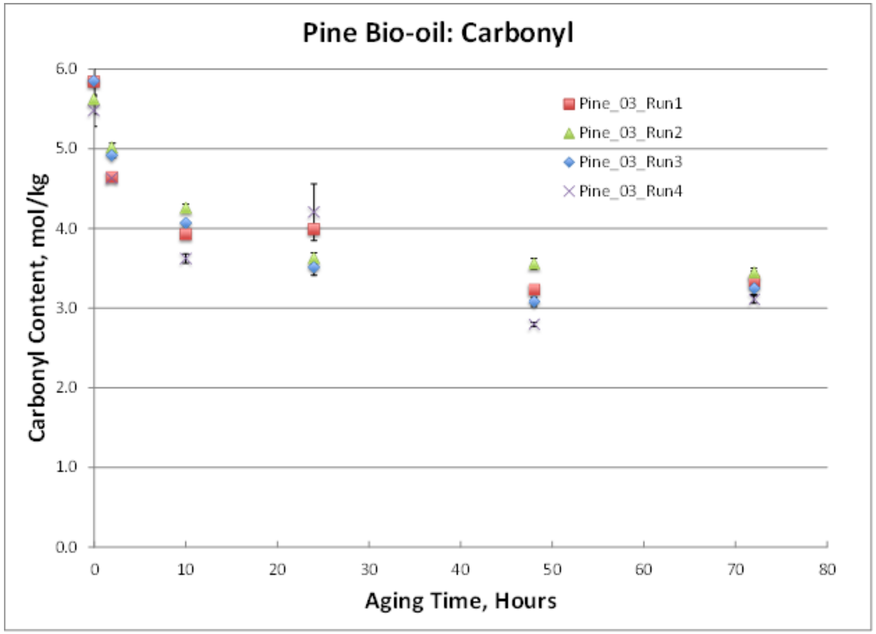
Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration[1]

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 – Progress: New 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
- Recent work has demonstrated **carbonyl content can be used to track bio-oil aging**
- Tested different accelerated aging protocols; compared to room-temp aging
- Commonly-used aging test, holding samples at 80 °C for 24 hours, is overkill
  – ~10 hours at 80 °C correlates to 2 years of room temperature aging
- **New accelerated aging test**: 80 °C for 2 hours[1]
  – Equivalent to 9 months at room temp

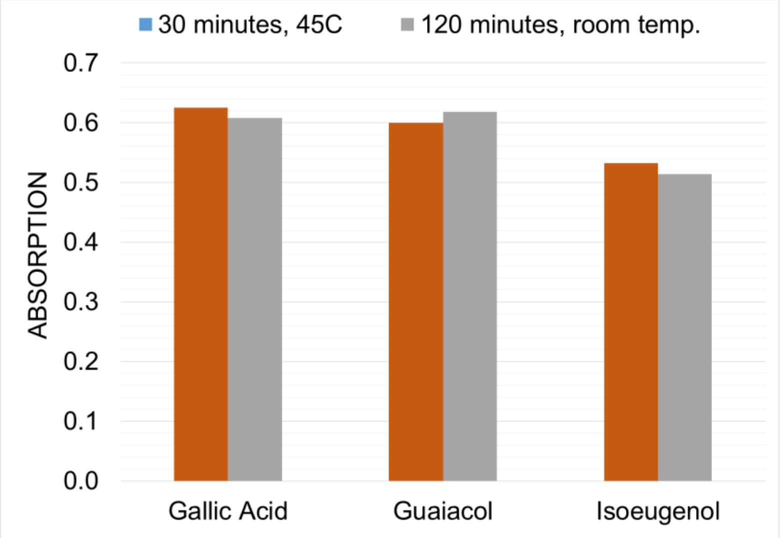


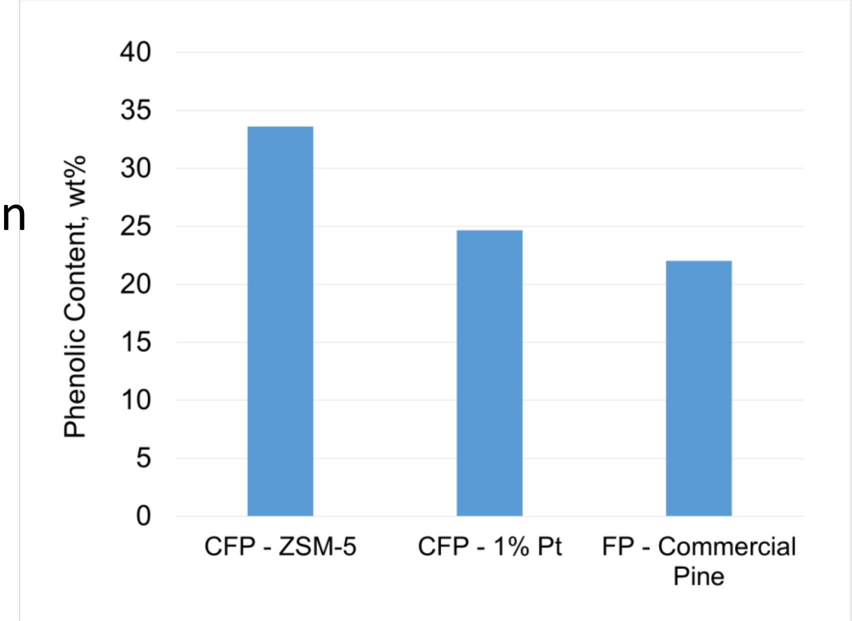


[1] To be submitted to *Sustainable Energy & Fuels*

3 – Progress: Phenols - Modified Folin-Ciocalteu

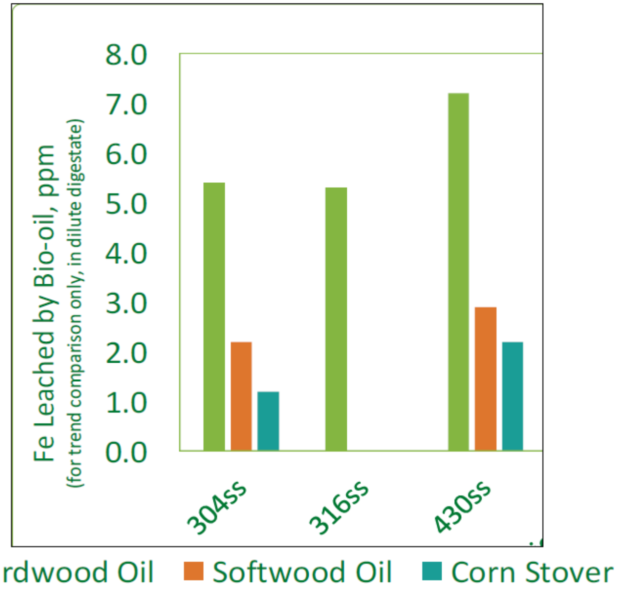
- Quantification of phenols is important
  - Phenols present in FP, CFP and HTL oils
  - In upgraded oils, phenols can be a source of acidity and impact corrosion.
  - In lignin-rich feeds, phenols can be targeted products.
- Phenol measurement methods using UV-Vis varied but affected by interfering bio-oil/biocrude components.
- Tested 4 methods: Only modified Folin-Ciocalteu showed no interference with sugar and sugar derived compounds at even 3x the typical bio-oil amount
- Decreased analysis time by a factor of 4 by using elevated temperature to hasten reaction.



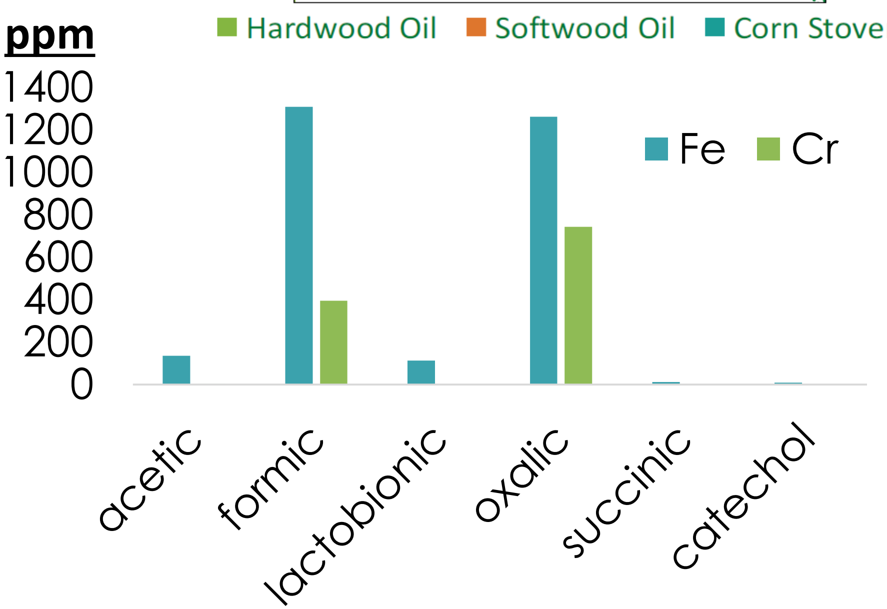


3 – Progress: Corrosivity - Metal Leaching Test

- Material degradation upon exposure to bio-oils remains a concern
- True corrosion testing *requires liters of bio-oil*
- Metal leaching test being developed as a screening tool for corrosivity[1]
  - Immerse metal screen in **5mL bio-oil;** 80 °C for 4 hours
  - Quantify amount of Fe leached using ICP
  - Reproducibility good: 5% RSD (n=5, single lab)
- Leaching trend with bio-oil type matches corrosion studies



- Metal leaching also tested on *known corrosive species* in bio-oils
  - Leaching in 2% solutions of each species
- Lays groundwork for **correlation of corrosivity with chemical composition**



[1] In collaboration with the Materials Compatibility Project (WBS# 2.4.2.301; PI Jim Keiser – ORNL)

4 - Relevance

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

Research Community Needs

Industry Needs

Enabling Commoditization of Bio-oils

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

Relevance to BETO

- **Methods developed & standardized in this project will enable ongoing efforts across BETO portfolio**
  - **FY22 Verification on Catalytic Fast Pyrolysis**
    - Enable correlation of upgrading performance with chemical composition
  - **Feedstock Conversion Interface Consortium**
    - Relating bio-oil chemical properties to feedstock

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4 - Relevance

- **Laboratory Analytical Procedures (LAPs)**
  - Hosted on NREL website[1]
  - Free and publicly available
- **4 methods published**
  - GC-MS
  - CAN/TAN titration
  - Faix carbonyl titration
  - ^{31}P NMR
- LAPs define:
  - Scope (types of bio-oil samples)
  - Analytical protocol & variability
  - Data analysis procedures
- Usage statistics
  - **Page views: 500/quarter**
  - **Downloads: 100/quarter**
  - **Citations: 35**


NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Quantification of Semi-Volatile Oxygenated Components of Pyrolysis Bio-Oil by Gas Chromatography/Mass Spectrometry (GC/MS)

Laboratory Analytical Procedure (LAP)

Issue Date: March 2, 2016

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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-5100-65889
March 2016

Contract No. DE-AC36-08GO28308

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

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

4 - Relevance

- ASTM standards **widely-accepted** route for standard analytical methods
- ASTM E3146 *first ASTM method on the chemical characterization of bio-oils*
  - First focused on bio-oil as an intermediate to be upgraded
  - Applies to range of pyrolysis bio-oils
    0.5 mol/kg < Carbonyl < 8 mol/kg
- Convened diverse group to participate in ASTM task group
  - Strong response *demonstrates need for ASTM standards*
  - Leading task group **avenue to determine real needs** of bioenergy industry
- Plan to continue engagement with ASTM

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

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5 - Future Work

Method Development & Standardization

Chemical Characterization

- *-Phenolics (UV or HPLC)*
- *-Hydroxy aldehydes & organic acids (LC-ESI-MS)*
- *-N, -S heteroatoms*
- *-Residual oxygenates for co-processing (SPE-GC)*

Processing

- *-Corrosivity: Metal leaching*
- *-Bio-oil Aging*
- *-Applicability of existing standards (petroleum or fuel industries)*

Successful Method Validation?

Yes

Publish LAP

ASTM

- -Complete **ASTM-approved ILS** for ASTM E3146 (Carbonyl Titration)
- -Update E3146 with precision statement
- -Updated method approved

INTERNATIONAL

Standards Worldwide

Summary

Standardized *quantitative* chemical analytical methods needed for bio-oils

Approach

- Joint task between NREL, PNNL, and ORNL
- Develop standard methods for bio-oils
  - Engage community to validate methods via ILS
- Publish validated methods as LAPs
    - **Pursue ASTM standardization** with most reliable methods

Progress

- Successfully developed & standardized methods for bio-oil
  - GC-MS, Acid Number, ^{31}P NMR, *Carbonyl Titration*, ^{13}*C NMR, Aging, Sugars Analysis, Corrosivity*
  - 4 methods published as LAPs; being adopted by bioenergy community
  - **ASTM E3146 approved**

Relevance

- Addressing analytical needs of bioenergy community
- Helping **enable commoditization** of bio-oils

Future work

- Method development & standardization to address needs of bioenergy community
- ASTM ILS for E3146, re-approval of method by ASTM

Acknowledgements

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VTT
Thünen
RTI International
USDA Agricultural Research Service
Aarhus University
Honeywell UOP
Ensyn
Iowa State University
Petrobras
Southern Research
Michigan State University
Metrohm
Tesoro
HNEI Hawai'i Natural Energy Institute, University of Hawai'i at Mānoa
University of Kentucky Center for Applied Energy Research
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Fortum

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Questions

2017 Peer Review Comments

Reviewer Comments:

- Developing standardized analytical methods is a requirement for commercializing biofuels. It also provides a basis for accurate and independent evaluation of the results between platforms. The time and costs of analytical methods can be a significant part of the experimental program. Developing routine methods that can be used to follow continuous operation is critical. It is particularly useful to have this work conducted by a national lab with independent funding. The results from the study of very wide application and are costly. It is difficult for developers to afford funding the required effort to developing these methods internally. One weakness is the failure to include commercial analytical labs on the team to speak towards practicality in the real world. Another is the lack of focus on methods that can be run outside of a sophisticated analytical lab. Robust methods are needed for analysis by a small analytical lab at the plant location. The speed of the analysis is critical. Feedback is needed as rapidly as possible to guide operations. The potential for same day turnaround should be a goal.
- Excellent progress by analysis team in very challenging mixtures coming from bio-oils. Key will be ageing understanding for future to define if stabilization is truly sufficient. Carbonyl titration ASTM standard is good first step but rest of work needs to be accelerated as could have substantial impact on conversion teams and their approaches. Simple should be the guide for future methods as actual plants will not be able to routinely run complex methods due to cost of equipment and personnel trained to run such equipment.
- Well managed project that provides important standardization for bio-oil analysis. The methods will be validated by Round Robin test to confirm target accuracy. Extensive contact with bio-oil developers, process designers, users etc. is important to ensure that the standardized analysis methods include all the parameters that will be needed for sizing and construction materials selection of equipment handling bio-oil in future IBR.
- Overall a very logical and timely project. Approach is pragmatic and this work should be prioritized given its value to the biofuels/bioenergy industry. It is critically important that this effort does not call pyrolysis liquid an oil or try to build the new ASTM specs on older ASTM specs associated with oil. Naming conventions are very important in chemistry and to the extent that a produced standard is meaningful, consistent, and transferrable, as a community of practice we need to stop addressing pyrolysis liquids as bio-oils. This project is strategically positioned to effect that change. Adoption and use of new standards will be more impactful if efforts are made to ensure that commercial labs have all available equipment and also comfort level with what is being proposed. Workshops should be held and commercial labs should be approached to solicit their feedback/review.
- Getting detailed, reliable characterization of pyrolysis oil will be a major factor in widespread pyrolysis oil acceptance. I'm not convinced the right methods were selected for investigation.

2017 Peer Review Comments: Response to Comments

Response to Reviewer Comments:

- Thank you very much for the comments. We will get feedback from commercial analytical labs moving forward, and have already begun this process. We have also emphasized simple analytical methods in our work, and our two most reliable methods are titrations with quick turnaround times. Furthermore, our development of a new carbonyl titration method not only resulted in a more accurate method, but cut down analysis time from 24 hours to 2 hours. This method has been used to successfully predict plugging during high temperature hydrotreatment of raw pyrolysis liquids. We are currently using this method to develop a new aging test, as previous aging tests based on the viscosity measurement were unreliable. While we have emphasized simple and quick analytical techniques, we have also pursued more advanced techniques such as chromatography and NMR. These methods are widely-used by the research community, and researchers also benefit from analytical standardization. Standardization of these advanced techniques will allow for detailed comparisons between different pyrolysis samples, and these comparisons are critical to inform research and development across the pyrolysis platform. As this project serves the needs of both the research community as well as the emerging pyrolysis industry, we have chosen to pursue analytical standardization of both simple and more advanced techniques.

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.

Publications

- "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
- "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.

Applicability of Methods to Different Bio-oils

- Some methods *apply to many different bio-oils* (e.g., FP, CFP, hydrotreated)
  - Carbonyl titration, Acid number
- Other techniques *need a specific method for each different type of bio-oil*
  - GC, HPLC
- Certain techniques only require small changes to apply to different types of bio-oils[1]
  - ^{13}C NMR – different solvent, different integration region for FP than for CFP, hydrogreated[2]
  - **Solvent selection critical for different bio-oils**
- High amounts of –N, -S heteroatoms (algae HTL oil) often cause interference

Fast Pyrolysis Bio-oil

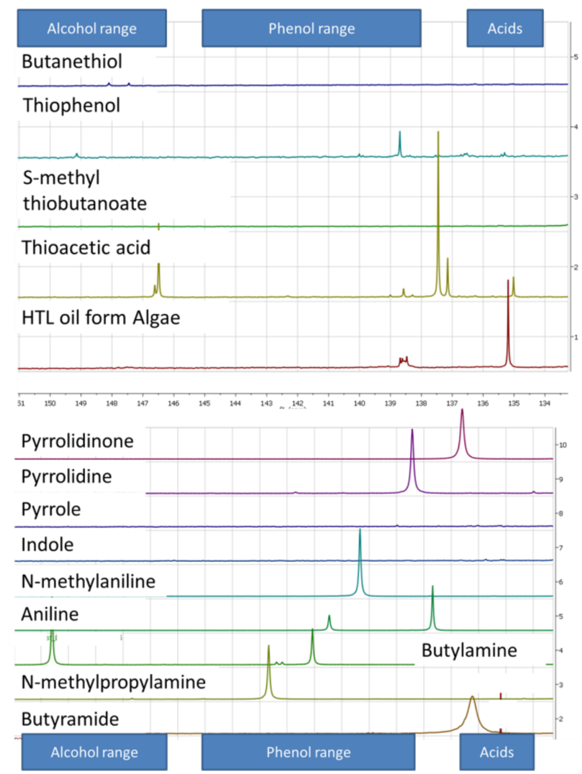
Catalytic Fast Pyrolysis (CFP) Bio-oil

	^{13}C Chemical Shift Region (ppm)	
Carbon Type	**Raw Oil**	**CFP, Hydrotreated CFP Oil**
C=O, Carbonyl	215.0 - 166.5	215.0 - 166.5
Aromatic C-O	166.5 - 142.0	166.5 - 142.0
Aromatic C-C	142.0 - 125.0	142.0 - 132.0
Aromatic C-H	125.0 - 95.8	132.0 - 95.8
Aliphatic C-O	95.8 - 60.8	95.8 - 60.8
Methoxyl	60.8 - 55.2	60.8 - 55.2
Aliphatic C-C	55.2 - 0	55.2 - 0
Solvent	Dimethyl Sulfoxide-d_6 (DMSO)	Dichloromethane-d_2 (DCM)

[1]Ware and Ferrell *J. Analytical Appl. Pyrolysis 132 (2018) 190-199*
[2]Happs and Ferrell *RSC Advances* 6 (2016) 120665 – 102670

The Effect of N and S Containing Molecules

- Objective: Evaluate how N – and S – containing compounds affect the methods developed for oxygenates
- Some feedstocks will have different heteroatom compositions
  - Algae-HTL oil will have a high nitrogen and a sulfur content
- GC-MS study of an algae-HTL oil was used to identify N – and S – containing compounds



Key Findings

- Hydroxyl determination by ^{31}P NMR
  - Most N – and S – containing model compounds would interfere
- Carbonyl determination by Faix method
  - All S – containing molecules interfered
  - Some N – containing molecules had no effect
- Modified acid titration
  - None of the N – containing molecules had an effect
  - S – containing molecules interfered

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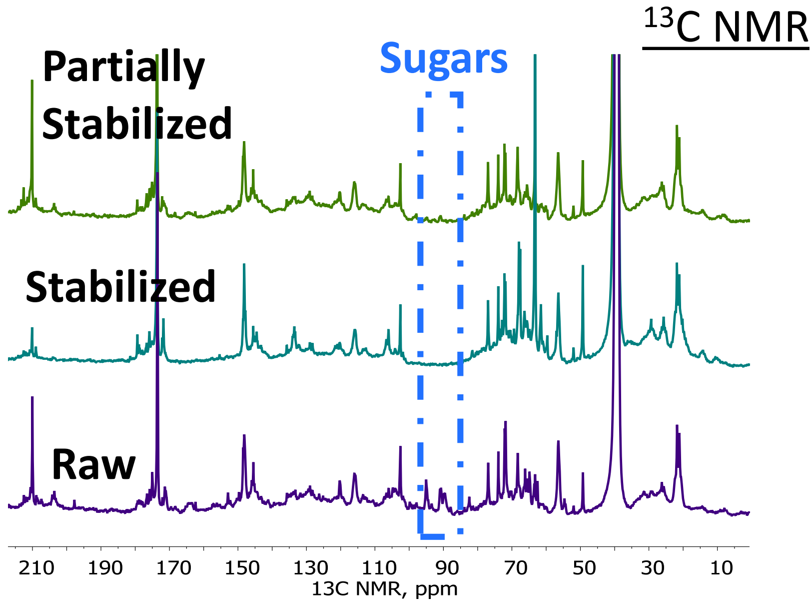
Sugars & Carbohydrate-Derived Components

- Sugars and other carbohydrate-derived compounds are problematic
  - Present in raw and partially-stabilized bio-oils
  - *May cause operational issues* such as reactor plugging
- GC-MS difficult for sugars
  - *Potential thermal reactions* prior to quantification
  - May underestimate sugar content
- **HPLC better suited for sugars analysis** than GC
  - Identifies more compounds
  - More accurate – 2x more levoglucosan & glycoaldehyde
- Trade-off between ease (GC) and accuracy (HPLC)



Compound	HPLC	Quantitative GC-MS
	Wt. %	
cellobiose	0.0	-
glucose	0.8	-
fructose	1.1	-
arabinose	2.3	-
fucose	1.4	-
levoglucosan	6.1	2.6
glycoaldehyde	11.7	5.8