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DOE BETO 2017 Project Peer Review: Conversion R&D

Development and Standardization of Techniques for Bio-oil Characterization

March 8th 2017

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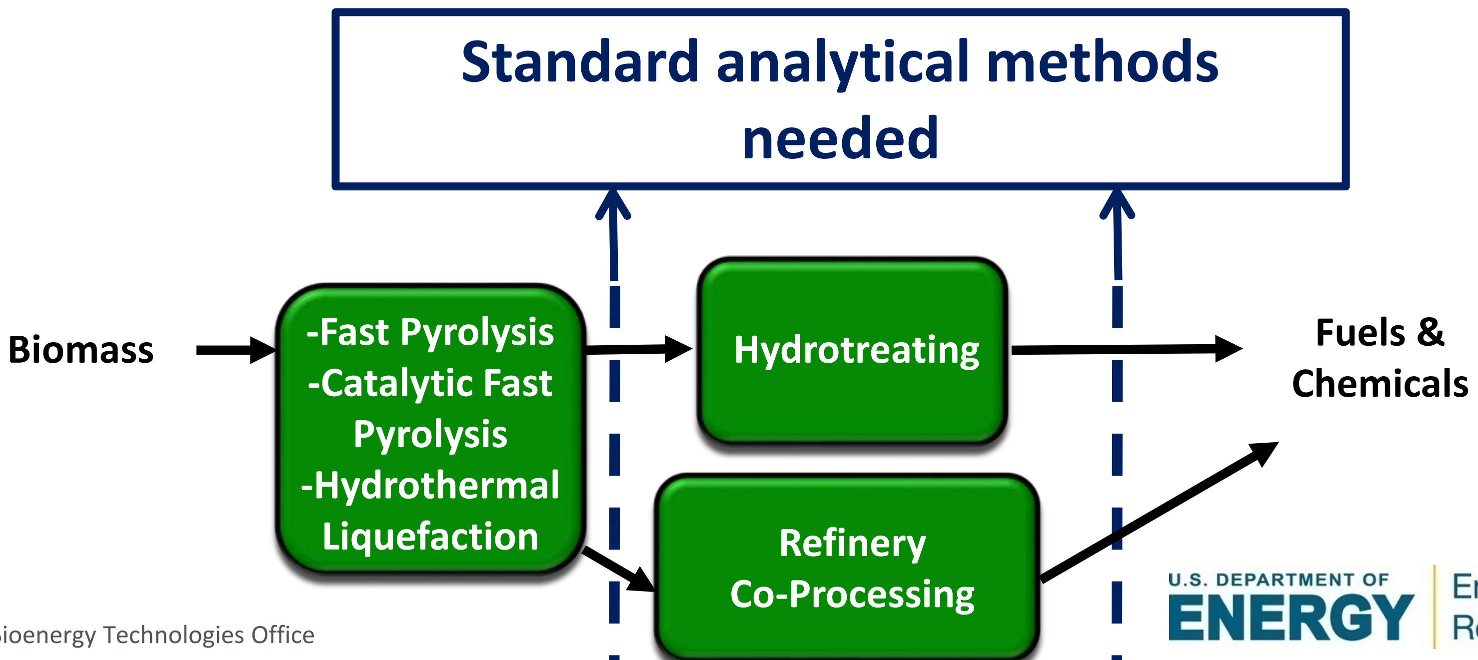
Problem Statement and Relevance

Research & Development

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

Industry

- Integration with refinery infrastructure requires trustworthy data
  - Chemical composition
  - Materials compatibility
- ASTM standards will enable sale & transfer of bio-oil



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 **do not exist** for bio-oil that provide chemical information
- Have bioenergy community adopt our standard methods
  - Validated methods will be published as Laboratory Analytical Procedures (LAPs), which are **free and publicly available**
  - Generate **ASTM** standardized methods from LAPs

Outcome: Enable commoditization of bio-oils

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Quad Chart Overview

Timeline

- Start: 10/1/2015
- End: 9/30/2018
- 50% Complete

BETO Barriers Addressed

- Ct-F: Efficient High-Temperature Deconstruction to Intermediates
- Ct-H: Efficient Catalytic Upgrading to Fuels and Chemicals
- Ct-K: Petroleum Refinery Integration of Intermediates
  - *Addressing barriers by reliable characterization of feed and products*

Budget

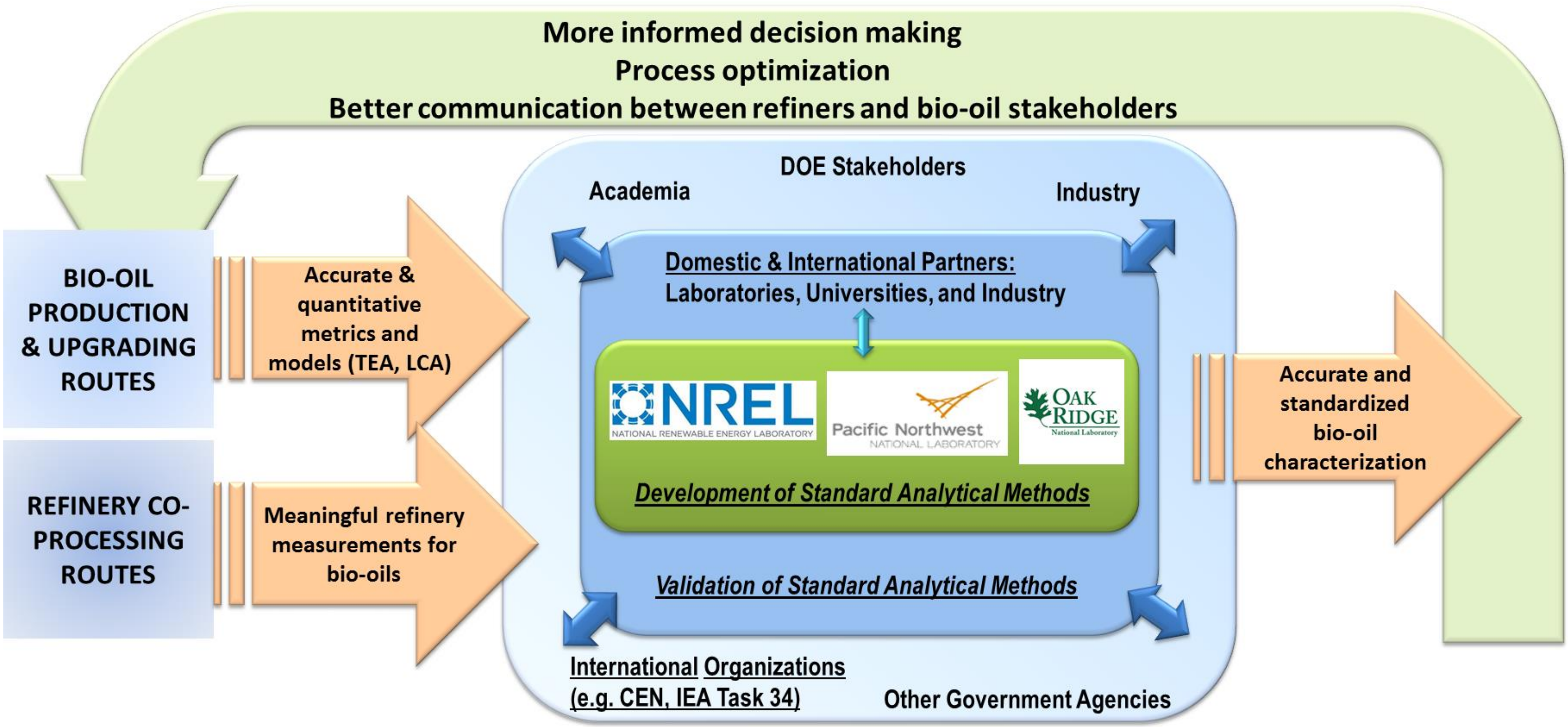
	Total Costs FY12 – FY14	FY15 Costs	FY16 Costs	Total Planned Funding (FY17* – FY18)
DOE Funded	$371k	$1017k	$980k	$2,200k

*FY17 funding has been reduced

Partners

- Partners
  - NREL (45%), PNNL (45%), ORNL (10%)
- Method Validation Partners:
  - Universities: Washington State University, Michigan State
  - Labs: VTT Technical Research Centre of Finland, Thunen Institute of Wood Research, CanmetENERGY

Project Overview



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

Outcome: Enable commoditization of bio-oils

Management Approach

- NREL, PNNL, and ORNL
  - Determine analytical needs from bioenergy community
    - **Engage both researchers & industry to determine needs**
      - *Quantitative & reliable methods top priority*
      - Oxygen-containing species and functional groups
      - Materials compatibility
      - Molecular weight distribution
  - Develop standard methods in **parallel**
    - Each lab individually develops a method based on expertise
  - **Engage bioenergy community** for method validation (Round Robin)
  - 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)

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Technical Approach

Challenge

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

Create ASTM Standard

Share: LAP, Publication

Approach

Develop Standard Method

Validate Method: Round Robin

< 10% Variability?

Yes → Share: LAP, Publication

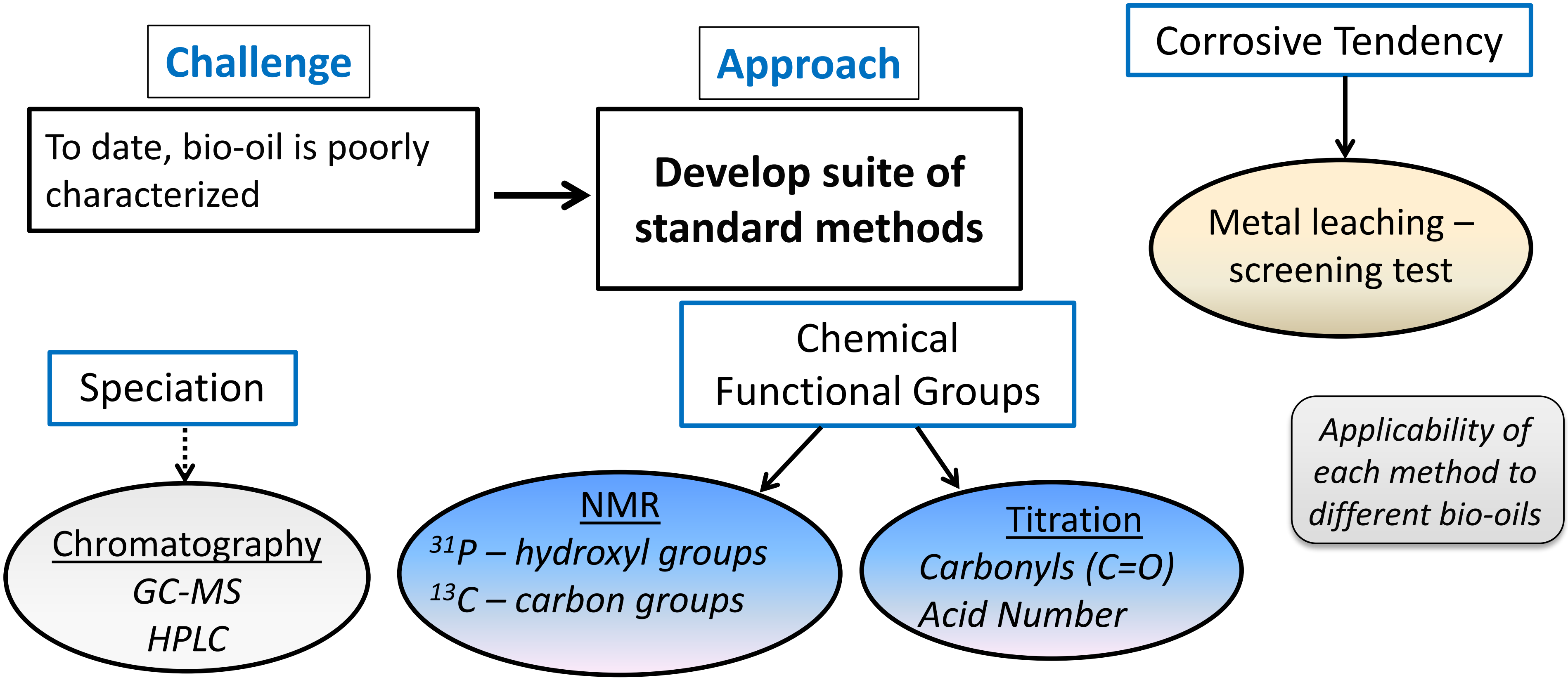
No → Reevaluate: Refine Method

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

Technical Approach



Success Factors

- Enable accurate & reliable comparisons of different bio-oils
  - Successful development/validation of methods addressing analytical needs
- Suite of standardized methods will create a **framework** for bio-oil analysis
  - Define appropriate methods for desired measurements on raw and upgraded oils

Standard Bio-oil for Method Development & Standardization

- Produced in 2010 at NREL in Pilot Plant[1]
  - Oak, 500 ^{0}C
  - Not hot gas filtered
  - Large quantity on hand

- Typical Raw Fast Pyrolysis Bio-oil
  - High O content
  - 23% water
  - *Low insoluble solids*

Property	
C (wt%)	44.5
H (wt%)	6.8
N (wt%)	0.07
O (wt%)	48.6
S (wt%)	<0.005
Water (wt%)	23.1
Insoluble solids (wt%)	0.84
K (ppm)	79
Na (ppm)	127

Current analysis methods do not fully describe the oil quality, nor fully inform downstream processing

[1]Baldwin, RM and Feik, CJ, *Energy & Fuels* 27 (2013) 3224-3238

Gas Chromatography – Mass Spectrometry (GC-MS)

Quantification of Volatile Components

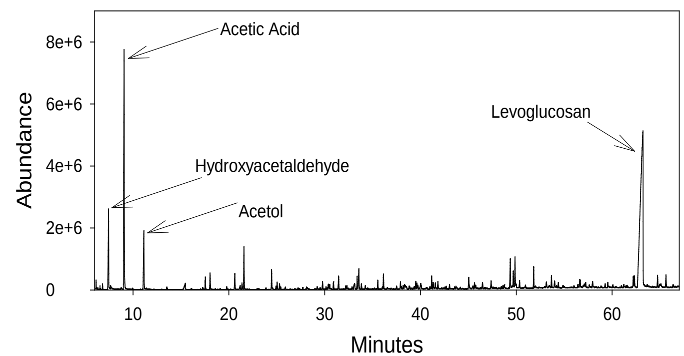
- Knowledge of specific compounds important for **upgrading** and **refinery integration**
- GC-MS very commonly used
- Standard GC-MS method developed
  - Over 100 compounds identified
  - 31 compounds quantified (22 wt% of bio-oil)
    - ~50 wt% maximum can be quantified with GC methods based on volatility

Catalyst Development: *Which oxygenated compounds must be removed during upgrading?*

Refinery Integration: *Which oxygenated compounds enter the refinery? In what amounts?*

Round Robin Results[1]

- 5 labs, duplicate samples, triplicate analysis
- 21 of 31 compounds < 20% variability
- 10 of 31 compounds > 20% variability
  - Variability defined as relative standard deviation (RSD)



[1] Ferrell et al. *Biofuels, Bioproducts & Biorefining* 10 (2016) 496-507

Carboxylic Acid Titration: CAN/TAN Analysis

- Organic acids and phenolics are abundant in bio-oil
  - Knowledge of acid content vital for upgrading and refinery integration
- Modified ASTM D664, allowing for **increased precision** of the carboxylic acid number (CAN), and **detection of phenolics** via the total acid number (TAN)

Materials Degradation: *What is acid content of stream entering refinery? How does this correlate with corrosivity?*

Upgrading: *What is acid content before and after different upgrading processes?*

Round Robin Results[1]

- CAN variability: < 5% RSD
  - **First time** acid titration has been successfully validated for bio-oil
  - **Acid content can be reliably quantified!**
  - Major step forward for bio-oil analysis
- TAN variability: < 3% RSD
  - Problems with TAN identification
    - Only 3 of 5 labs reported TAN

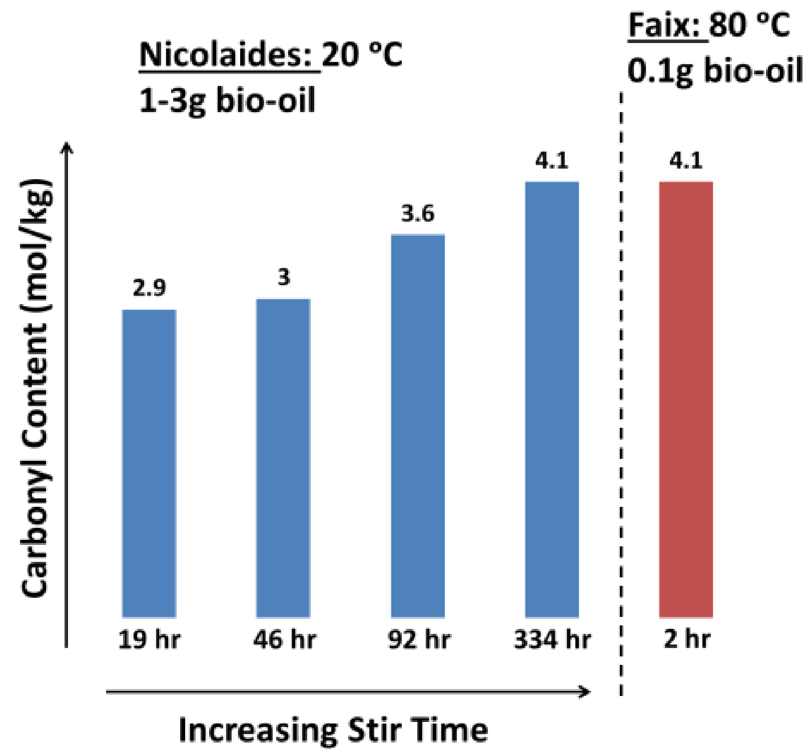
- Standard method: **Simple titration method** providing concentrations of organic acids and phenolics

[1] Ferrell et al. *Biofuels, Bioproducts & Biorefining* 10 (2016) 496-507

Carbonyl Quantification by Titration

- Carbonyls in bio-oil cause:
  - Aging during storage
  - Coke formation during upgrading
- Carbonyls quantified:
  - **Aldehydes and ketones**

- **Two methods tested**
  - Nicolaides[1]: *commonly used for bio-oils for the past 30 years*
    - 12-24 hours of stirring, titration at room temperature
  - Faix[2]: **new method**, developed by this project[3] for bio-oils
    - 2 hours stirring time, titration at 80 ^{o}C



- **Commonly-used technique (Nicolaides) *significantly underestimates* carbonyl content in bio-oil**

[1] Nicolaides, MASc Thesis, University of Waterloo, 1984
[2] Faix et al. *Holzforschung* 52 (1998) 268-272
[3] Black and Ferrell *Energy & Fuels* 30 (2016) 1071-1077

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Carbonyl Titration Validation

Round Robin Results[1]

- Nicolaides variability: 10% RSD
- Faix variability: 5% RSD
  - **First successful validation** of carbonyl titration for bio-oils
  - **Carbonyls can be reliably quantified!**
  - Significant accomplishment for bio-oil analysis

Predicting Performance:
> 1.5 mmol carbonyl/g will lead to plugging during high temp hydrotreatment of raw fast pyrolysis oils

Storage & Handling:
New aging test being developed using Faix method, which is much more reliable than viscosity measurement

- Faix method advantages:
  - More accurate
  - Easier to perform (higher throughput)[2]
  - More reliable

- **New, simple titration method can reliably quantify carbonyls**

[1] Ferrell et al. *Biofuels, Bioproducts & Biorefining* 10 (2016) 496-507
[2] Black and Ferrell *Journal of Visualized Experiments* 120 (2017) e55165

^{31}P NMR: Quantification and Classification of Hydroxyl Groups

- Quantification of **oxygen-containing functional groups** critical
  - Will inform upgrading research and co-processing

- Can quantitatively determine[1]:
  - Phenols
  - Aliphatic alcohol
  - Carboxylic acids

Upgrading: *Which oxygen functionalities, in what amounts, are removed during catalytic upgrading?*

Refinery Integration: *What oxygen functionalities are being fed to refinery? In what amounts?*

<u>Round Robin Results</u>

- Aliphatic-OH: 9% RSD
- Phenolic-OH: 10% RSD
- Carboxylic-OH: 15% RSD
  - **First time** NMR has been successfully validated for bio-oil
  - **Hydroxyl groups can be reliably quantified**

[1] Ben and Ferrell *RSC Advances* 6 (2016) 17567-17573

Relevance

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

Enabling Commoditization of Bio-oils

Research Community Needs

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

Standard Methods

-GC-MS
-CAN/TAN
-Carbonyl titration
-^{31}P NMR

ASTM INTERNATIONAL
Standards Worldwide

Industry Needs

- Industrial commercialization routes require dependable data
  - Chemical composition
  - Materials compatibility
- ASTM standards will enable sale & transfer of bio-oil

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Relevance

- Laboratory Analytical Procedures
  - 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)
  - Inter-laboratory variability
  - Detailed analytical protocol
  - Data analysis
- Usage statistics (5/1/16 – 1/4/17)
  - **Page views: > 1600**
  - **Downloads: 285**

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

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Relevance

- ASTM standardization
- **Widely-accepted** route for standard analytical methods
- ASTM D7544: Standard Specification for Pyrolysis Liquid Biofuel (2012)
  - Bio-oil spec for use in industrial burners
- **Received approval** to create standards by ASTM Subcommittee E48.05 on Biomass Conversion
- Currently forming task group for Faix carbonyl titration
  - *Widespread participation from international bio-oil community*
- Coordinating our ASTM efforts with the European Committee for Standardization (CEN)

NREL National Renewable Energy Laboratory
Pacific Northwest National Laboratory
Oak Ridge National Laboratory
Michigan State University
VTT
Iowa State University
RTI International
HNEI Hawai'i Natural Energy Institute, University of Hawai'i at Mānoa
Thünen
USDA Agricultural Research Service
Honeywell UOP
Ensyn
Petrobras
Metrohm
SR Southern Research
coolplanet
Washington State University
University of Kentucky Center for Applied Energy Research
California Environmental Protection Agency Air Resources Board
Valmet
Fortum

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

Future Work

Sugars quantification

Molecular weight distribution

Identify & standardize best method

Materials degradation screening test

Validation of metal leaching test

Successful Round Robin?

Yes

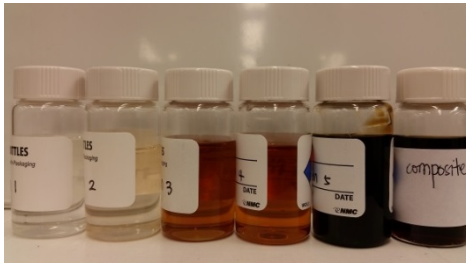
Publish LAP

ASTM INTERNATIONAL Standards Worldwide

Expand to upgraded oils

- Catalytic fast pyrolysis bio-oils
- Hydrotreated bio-oils

Fractionated upgraded oil



Olarte, et al. Submitted to *Fuel*. Revision under review.

-Approval by ASTM E48.05 for carbonyl titration

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Summary

- Overview
  - 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 Round Robin
  - Publish validated methods as LAPs
    - **Pursue ASTM standardization** with most reliable methods

- Technical accomplishments
  - Standardized methods for raw bio-oil
    - GC-MS, CAN/TAN, carbonyl titration, ^{31}P NMR
      - Developed new (better) carbonyl titration method
    - **First successful standardization** of these methods

Summary

- Relevance
  - Addressing analytical needs of bioenergy industry
  - Published standard methods as LAPs
    - *LAPs are being adopted* by bio-oil community
  - **Received approval by ASTM** to create carbonyl titration standard
  - Helping to **enable commoditization** of bio-oils

- Future work
  - Method development & standardization
    - Sugars, molecular weight, materials degradation
    - Emphasize catalytic fast pyrolysis and hydrotreated bio-oils
  - Approval by ASTM E48.05 for carbonyl titration

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Heather Job

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Juan Lopez Ruiz

Gary Neuenschwander

Leslie Rotness

Miki Santosa

Craig Lukins

Igor Kutnyakov

Andy Schmidt

Doug Elliot

Corinne Drennan

Round Robin Partners

Washington State University

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VTT Technical Research Centre of Finland

Anja Oasmaa; Ville Paasikallio

Thunen Institute of Wood Research

Dietrich Meier

DOE BETO for funding this work

Questions

Additional Slides

Definitions / Abbreviations

- Round Robin: an inter-laboratory test, where each method is tested multiple times by independent scientists. Each scientist follows the same set of instructions, which are the LAPs.

- HTL = hydrothermal liquefaction
- NMR = nuclear magnetic resonance
- CAN = carboxylic acid number
- TAN = total acid number
- GC-MS = gas chromatography – mass spectrometry
- TGA = thermogravimetric analysis
- HPLC = high performance liquid chromatography
- TEA = techno-economic analysis
- LCA = life cycle assessment
- ASTM = American Society of Testing and Materials
- LAP = laboratory analytical procedure

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*, 2016, Submitted (Revision in Review)
- "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.

Presentations

- “Oil derived from biomass: qualitative and quantitative analysis of oxygenates.” Asanga B Padmaperuma, Mariefel V Olarte, Sarah D Burton, Suh-Jane Lee, Teresa Lemmon, Corinne Drennan, Jack Ferrell, Earl Christensen, Steve Deutch, Lisa Fouts. Oral Presentation, *AIChE Annual Meeting*, Atlanta, GA, November 16-21, 2014
- "Development and Standardization of Techniques for Bio-oil Characterization." J. Ferrell, M.V. Olarte, A.B. Padmaperuma. Oral Presentation. *2015 BETO Peer Review*, Washington DC, March 2015.
- “Thermogravimetric Analysis of Bio-oils and Upgraded Products.” Earl Christensen, Steve Deutch, Jack Ferrell, Mariefel V. Olarte, Asanga B. Padmaperuma. Oral presentation, *Spring Meeting of the American Institute of Chemical Engineers*, Austin, Texas, April 27, 2015.
- “Qualitative and quantitative analysis of oxygenates in oils derived from biomass.” Asanga B. Padmaperuma, Mariefel V. Olarte, Sarah D. Burton, Suh-Jane Lee, Teresa Lemmon, Corinne Drennan, Jack Ferrell, Earl Christensen, Steve Deutch, Lisa Fouts, Stuart Black. Oral presentation, *Spring Meeting of the American Institute of Chemical Engineers*, Austin, Texas, April 27, 2015.
- “Analysis of distillate fractions from hydroprocessing of oak pyrolysis oil.” Mariefel V. Olarte, Asanga B. Padmaperuma, Jack Ferrell, Earl D. Christensen. Oral presentation, *TCBiomass*, Chicago, IL, November 2-5, 2015.
- “Analysis of different fractions of hydrotreated oil.” Mariefel V. Olarte, Jack Ferrell, Asanga B. Padmaperuma, Earl D. Christensen, Teresa L. Lemmon, Stuart Black, Marie S. Swita, Haoxi Ben, Sarah D. Burton, Heather M. Job, Beth Hofstad, Gary, G. Neuenschwander, Leslie J. Rotness, Daniel M. Santosa, Craig D. Lukins, Igor Kutnyakov, Rich Lucke, Richard T. Hallen, Alan H. Zacher, Douglas C. Elliott, Corinne Drennan. Poster Presentation, *TCBiomass*, Chicago, IL, November 2-5, 2015
- “The need to standardize analytical methods for bio-oil analysis.” M.V. Olarte, J. Ferrell, A. B. Padmaperuma, E. Christensen, Poster presentation. *Bioenergy 2015: Opportunities in a Changing Energy Landscape*, Washington DC, June 23-24, 2015.
- “Analysis of distillate fractions from hydroprocessing of oak pyrolysis oils.” A.B. Padmaperuma, M.V. Olarte, C. Drennan, J. Ferrell, E.D. Christensen, Oral Presentation. *251st American Chemical Society National Meeting & Exposition*, San Diego, California, March 13-17, 2016.
- “Distillate Fractions from Hydrotreated Bio-Oils: Comprehensive Analyses”. M.V. Olarte, J.R. Ferrell, A.B. Padmaperuma, E.D. Christensen, C. Drennan. Oral Presentation. *2016 AIChE Spring Meeting & 12th Global Congress on Process Safety*, Houston, Texas, April 10-14, 2016.

Presentations

- "Standardization of Chemical Characterization Techniques for Pyrolysis Bio-oil." J.R. Ferrell III, M.V. Olarte, E.D. Christensen, A.B. Padmaperuma, R.M. Connatser, F. Stankovikj, D. Meier, V. Paasikallio, oral presentation – speaker & panelist, Track 4: Advanced Biofuels & Biobased Chemicals, *International Biomass Conference & Expo*, Charlotte, NC, April 13th, 2016.
- "Standardization of Analytical Techniques for Pyrolysis Bio-oil." J.R. Ferrell III, E.D. Christensen, M.V. Olarte, A.B. Padmaperuma, R.M. Connatser, oral presentation, Session 2.2: Pyrolysis (Analytical), TCS 2016: *Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products*, Chapel Hill, NC, November 2nd, 2016.
- "The effect of nitrogen and sulfur-containing molecules on standard methods for accurate determination of oxygenates." A.B. Padmaperuma, et al. Poster presentation. TCS2016, *Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products*, Chapel Hill, NC, November 2016.

Related Projects

Related NREL tasks (and associated WBS numbers):

- Thermochemical Feedstock Interface (WBS: 2.2.1.304)
- Consortium for Computational Physics and Chemistry (CCPC) (WBS: 2.5.1.302)
- Thermochemical Platform Analysis (WBS: 2.1.0.302)
- Integration and Scale Up (WBS: 2.4.1.301)
- Catalytic Upgrading of Pyrolysis Products (WBS: 2.3.1.314)
- Catalyst Development and Testing (WBS: 2.3.1.315)

Related PNNL tasks (and associated WBS numbers):

- Bio-oil Quality Improvement and Catalytic Hydrotreating of Bio-oils (WBS: 2.3.1.302)
- Electrochemical Methods for Upgrading Pyrolysis Oils (WBS: 2.12.1.5)
- Thermochemical Conversion Interface (WBS: 1.3.4.101)
- Catalytic Fast Pyrolysis & Product Bio-oil Upgrading (WBS: 2.3.1.312)
- Hydrothermal Processing of Biomass (WBS: 2.2.2.301)
- Consortium for Computational Physics and Chemistry (CCPC)(WBS: 2.5.1.303)

Risks and Mitigation

Risks

Name	Status	Target Completion Date	Severity	Response	Description
Method not applicable		9/30/2018	L	Accept	A specific analytical method does not result in the quantification result that was expected
Methods rejected by ASTM subcommittee		9/30/2018	M	Accept	ASTM subcommittee not interested in chemical characterization methods for pyrolysis bio-oils, and work group not formed.
ASTM decision process prolonged		9/30/2018	M	Accept	ASTM subcommittee and main committee do not approve methods in a timely manner. Every negative votes need to be addressed and adjudicated.

Mitigation

Method not applicable: Mitigate by further analytical method development, and by pursuing other analysis techniques. As bio-oil is an extremely complex mixture, method development will not always proceed as planned. In this circumstance, additional method development is often needed for the analysis technique in question. For example, a different sample preparation, or different instrument parameters, may lead to the expected quantification result for bio-oil. Beyond additional method development, this risk will also be mitigated by pursuing other analysis techniques that are capable of providing complementary information. For example, to mitigate the risk of HPLC quantification of individual carbonyl compounds in bio-oil, carbonyl titration will be pursued as it can provide the total carbonyl content of a bio-oil. Risk Classification: Scope. Risk Probability: Medium.

Methods rejected by ASTM subcommittee: Mitigate by actively engaging ASTM subcommittee to obtain permission to form work group. Once work group is formed, proactively engage work group to arrive at a robust method description, which then has a better chance of approval by subcommittee. Leveraging team members who have experience with the ASTM approval process will also mitigate this risk. Risk classification: Schedule, Scope. Risk Probability: Medium/High

ASTM decision process prolonged: Once work group is approved, mitigate by frequent work group meetings to draft a complete ballot by target deadline. Meetings can be as frequent as weekly for an hour. Developed LAP procedures will be leveraged as a good starting point. Leveraging active participation of team members in the process will also mitigate the risk. Risk classification: Schedule. Risk Probability: Medium

FY16 Milestones (Q1 – Q2)

NREL, PNNL, and ORNL FY16 Milestones

Q1 (12/31/2015) Quarterly Milestone (Regular)
Development of TGA simulated distillation method for a CFP bio-oil: Determine the amount (wt%) of a CFP bio-oil sample that is analyzable by gas chromatography methods (**NREL**).

Q1 (12/31/2015) Quarterly Milestone (Regular)
Development of ^{31}P NMR, carbonyl titration and CAN/TAN methods for nitrogen- and sulfur-rich HTL oils: Determine if nitrogen- and sulfur- groups quantitatively affect methods optimized for oxygen functional groups (**PNNL**).

Q2 (3/31/2016) Go/No-Go - see below (**NREL, PNNL, ORNL**).

Name	Description	Criteria	Date
Round Robin Reproducibility (NREL and PNNL)	Carbonyl quantification via titration is repeatable (e.g. utilizable as a standard method)	< 10% variability using a standard bio-oil sample during the Round Robin	3/31/2016

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FY16 Milestones (Q3 – Q4)

NREL, PNNL, and ORNL FY16 Milestones

Q3 (6/30/2016) Quarterly Milestone (Regular)
Development of GC-MS method for a catalytic fast pyrolysis bio-oil: Development of standard sample preparation and analytical methodology for GC-MS analysis of a CFP bio-oil sample. For development of a quantitative method, calibration standards will be made in-house containing known amounts of the most prevalent compounds in CFP bio-oil (**NREL**).

Q3 (6/30/2016) Quarterly Milestone (Regular)
Report on inter-laboratory validation of FY15 standard methods: Inter-laboratory variability (target $\leq$ 10%) will be determined using FP oil for methods standardized in FY15: HPLC for the determination of carboxylic acid and carbonyl content, 13C NMR for analysis of carbon functional groups, and colorimetric determination of esters (**NREL, PNNL, ORNL**).

Q3 (6/30/2016) Quarterly Milestone (Regular)
Development of a method for predicting bio-oil thermal stability (FP, HTL, and hydrotreated oil) by using methods developed in this project (carbonyl titration, hydroxyl determination, CAN/TAN acidity) and refinery-relevant methods such as the Conradson carbon residue (**PNNL**).

Q4 (9/30/2016) Annual Milestone (Regular)
Development of miscibility protocols for upgraded bio-oils: Standardize solvent selection for at least two (2) upgraded bio-oils using at least three (3) solvents (e.g. acetone, ethanol, hexane). Solvent selection needs to be standardized to ensure that upgraded bio-oils are fractionated with solvents that allow for maximum characterization of the oil. Solvent selection for each bio-oil will be guided by phase separation, emulsion formation, and extraction efficiency. Target is no phase separation, no emulsion formation, and maximum extraction efficiency (> 50% mass basis) (**NREL**).

Q4 (9/30/2016) Quarterly Milestone (Regular)
Production, fractionation and analysis of hydrotreated oil: Bio-oil will be processed to produce upgraded oils with oxygen content of not more than 3.5 wt%. Applicability of typical thermal properties test of petroleum crude oil [9] will be applied and evaluated (**PNNL**).

FY17 Milestones

NREL, PNNL, and ORNL FY17 Milestones
Q1 (12/31/2016) Quarterly Milestone (Regular) Complete initial development of a robust screening method to indicate corrosive potential of bio-oils by measuring metal leaching. This protocol will include time, temperature, and rinsing steps, as well as provision of a reproducible source of metal shavings, gratings, or screens. (**ORNL**)
Q2 (3/31/2017) Annual Milestone (Regular) Initiate ASTM standardization process. In FY17, we plan to approach ASTM with our two most reliable methods developed to-date: carbonyl titration and carboxylic acid titration. Report on engagement with ASTM to-date, including formation of work group within ASTM subcommittee E48.05 on biomass conversion or D02.06 on analysis of liquid fuels and lubricants. Provide timeline for drafting methods and for the remaining process leading up to having methods voted on for approval by ASTM subcommittee. (**NREL, PNNL, ORNL**)
Q3 (6/30/2017) Quarterly Milestone (Regular) Provide a preliminary method for sugars quantification based on a review of existing methods in literature and proof of concept testing of the most promising two methods. Sugars content of bio-oil affects the processability of bio-oil and the characteristics of the product upgraded oil; thus, it is an important metric in assessing bio-oil quality, especially in the comparison of different methods and feedstocks in bio-oil production. (**PNNL**)
Q4 (9/30/2017) Quarterly Milestone (Regular) Review of reliable characterization methods of molecular weight distributions for bio-oils. Summarize available techniques (at least 2) & their limitations for reliable analysis of bio-oils molecular weight (at least two types – e.g., raw and upgraded). Accurate, reliable and standardized characterization of molecular weight is a critical missing piece for bio-oil analysis, and will help provide information on the distribution of gasoline and middle distillate fuels in upgraded bio-oils. (**NREL**)

FY17 Go/No-Go

Go/No-Go Decision (80 character limit)	Description	Criteria	Date	Actions
Submit at least one standard analytical method developed in this project to ASTM subcommittee E48.05 or D02.06 for approval	Prior to approval by subcommittee, a work group must be formed for each analytical method. Methods are then drafted, with feedback from work group, prior to putting a method on ballot to subcommittee for approval.	While the ASTM standardization process can be both lengthy and political, the goal is to have at least one method submitted to subcommittee E48.05 or D02.06 for approval by the end of FY17 (NREL, PNNL, ORNL)	9/30/2017	

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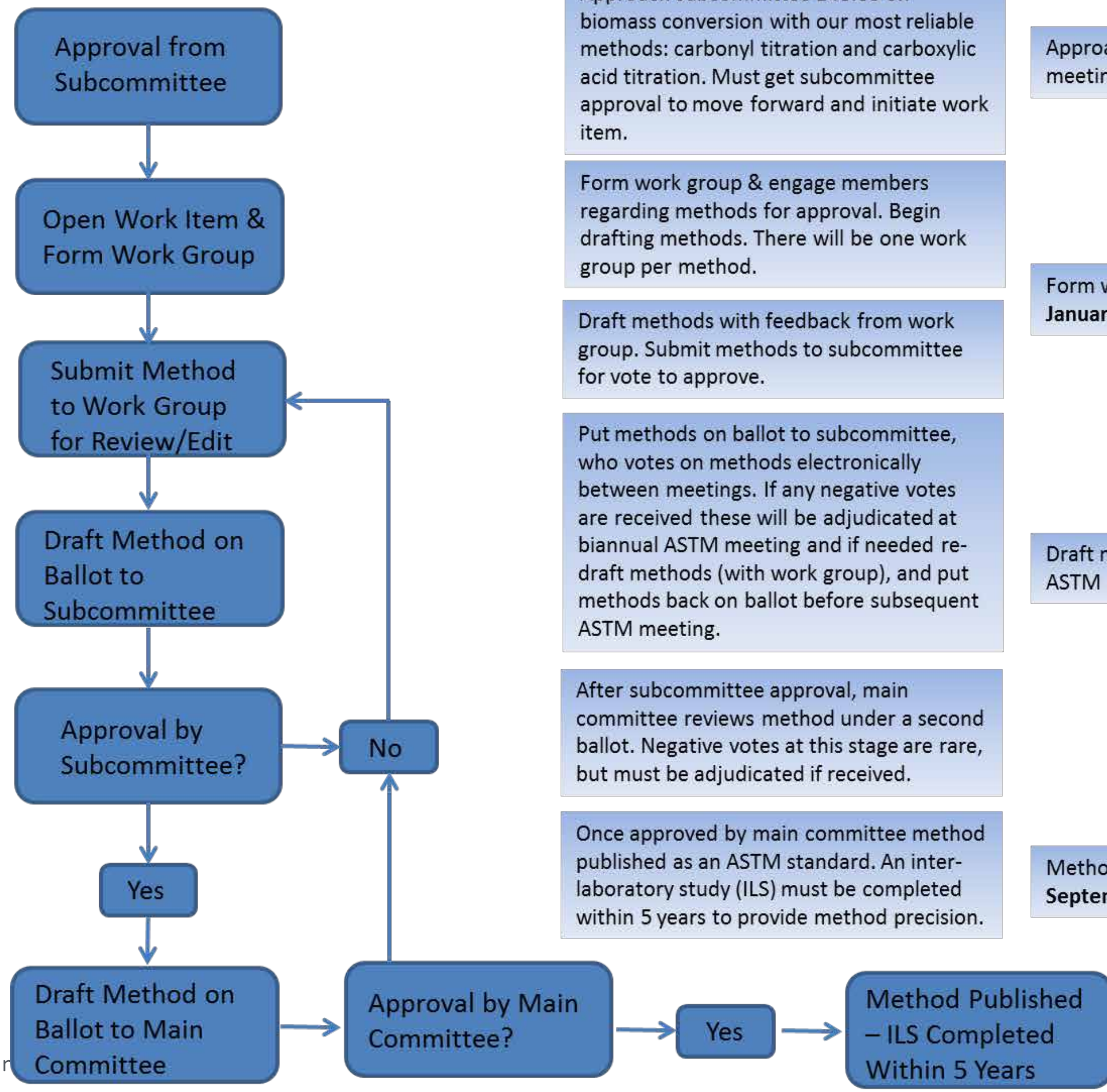
ASTM Standardization Process & Timeline



Approach subcommittee E48.05 on biomass conversion with our most reliable methods: carbonyl titration and carboxylic acid titration. Must get subcommittee approval to move forward and initiate work item.

Approach subcommittee E48.05: ASTM meeting, **December 2016**

Form work group & engage members regarding methods for approval. Begin drafting methods. There will be one work group per method.

Form work group, draft methods: **January – May 2017**

Draft methods with feedback from work group. Submit methods to subcommittee for vote to approve.

Put methods on ballot to subcommittee, who votes on methods electronically between meetings. If any negative votes are received these will be adjudicated at biannual ASTM meeting and if needed re-draft methods (with work group), and put methods back on ballot before subsequent ASTM meeting.

Draft methods on ballot at subcommittee: ASTM meeting, **June 2017**

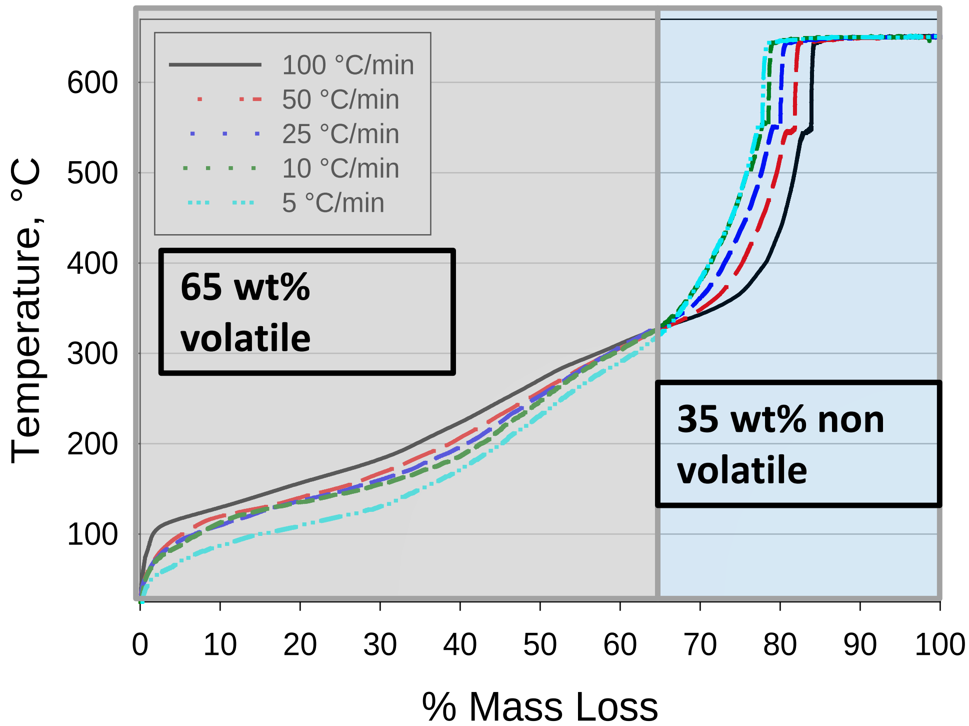
After subcommittee approval, main committee reviews method under a second ballot. Negative votes at this stage are rare, but must be adjudicated if received.

Once approved by main committee method published as an ASTM standard. An inter-laboratory study (ILS) must be completed within 5 years to provide method precision.

Method approved by main committee: **September 2018**

What is the Volatile Fraction of Fast Pyrolysis Bio-oil?

- Developed simulated distillation method
  - Thermogravimetric Analysis (TGA)
- Results indicate mass loss above ~325°C is due to thermal degradation
  - ~35% bio-oil not volatile
- Gas Chromatography (GC) methods typically inject <300 °C
  - Maximum ~50 wt% can be analyzed by GC



- **Quick way to determine volatile fraction of bio-oil**

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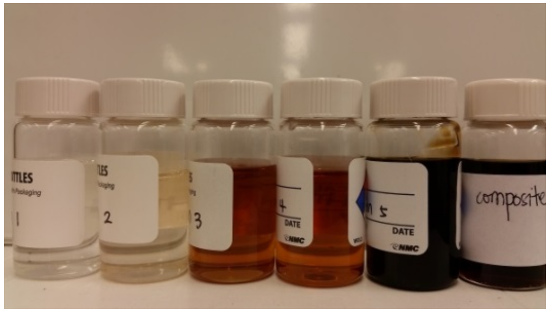
Analysis of Upgraded Bio-oil Fractions

- Hydrotreated the same pyrolysis oils using two different catalysts
- Produced two different levels of deoxygenation
- Fractions become more aromatic as BP increases
- LOC showed predominantly hydrocarbons present
- MOC fractions contain acids, aldehydes and phenolics (MOC 2 highest)



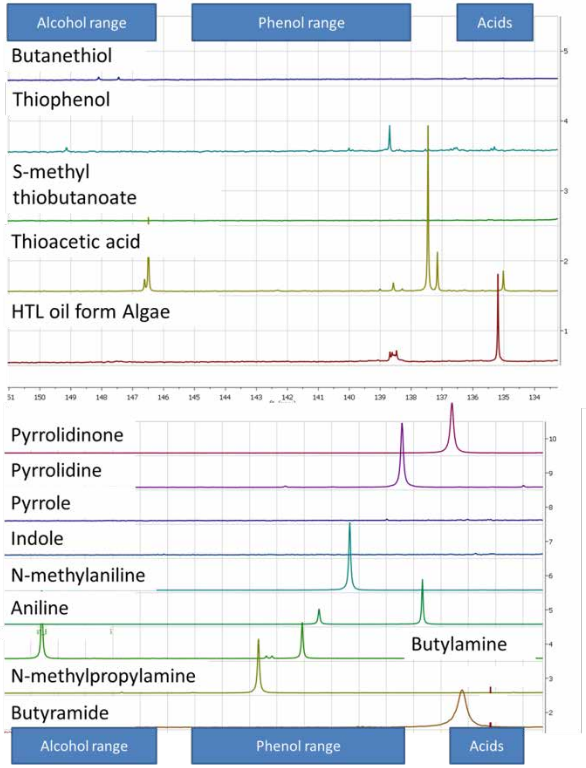
Distillation cut-off points for low oxygen content (LOC) and medium oxygen content (MOC) oils

Fraction 1	20°C-150°C, atmospheric
Fraction 2	150°C-184°C, atmospheric
Fraction 3	184°C-250°C, atmospheric
Fraction 4	250°C-338°C (atm.), vacuum applied (107°C-198°C @ 6 mmHg)
Fraction 5	>340°C (atm.), vacuum applied (>198°C @ 6 mmHg)

"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*, 2016, Submitted (Revision in Review)

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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