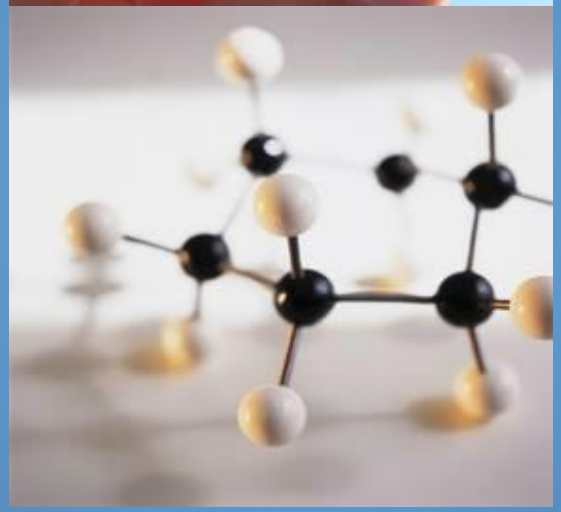


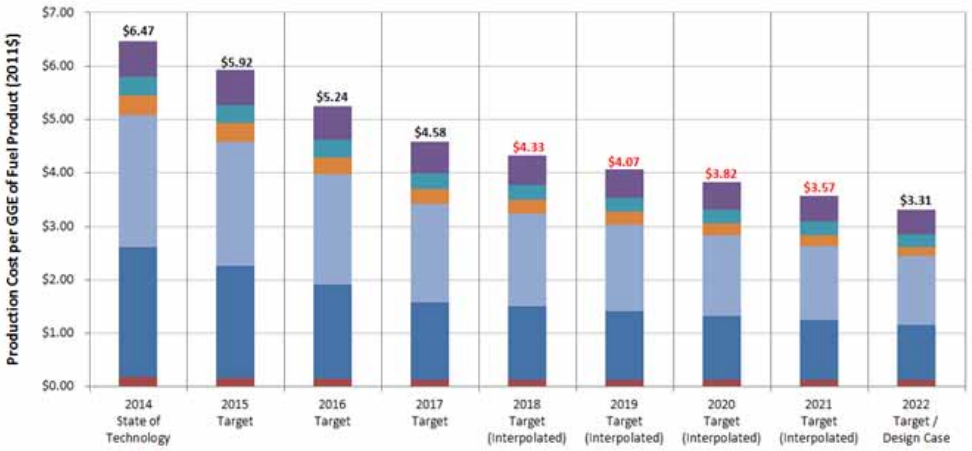
DOE BETO 2015 Project Peer Review: Conversion R&D

Development and Standardization of Techniques for Bio-oil Characterization

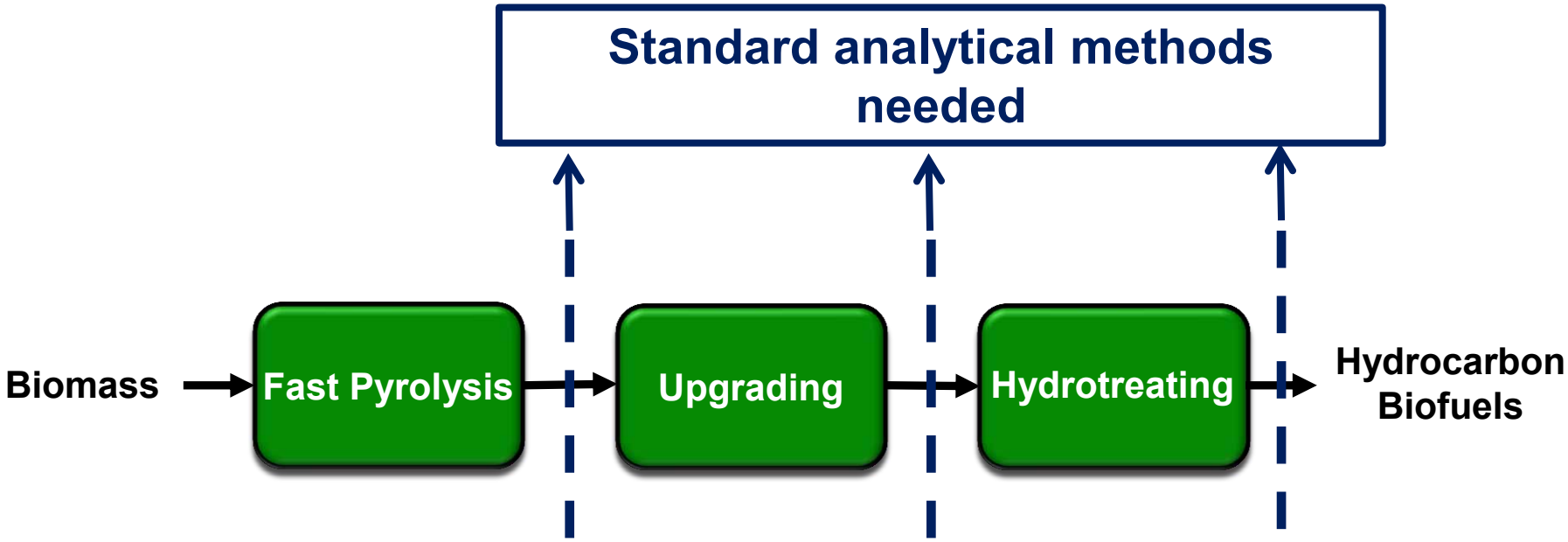
23 March 2015

Jack Ferrell, NREL; Mariefel V. Olarte, Asanga Padmaperuma, PNNL

Problem Statement



- Path to cost competitive biofuels requires innovation in each process step
- Integration with refinery infrastructure requires quality metrics
  - Reliable analytics needed



Goal Statement

- Standardize *quantitative* analytical methods for bio-oil characterization
  - Standard methods **do not exist** for bio-oil
- Adoption of methods by the community
  - Verified standard methods (< *10% inter-laboratory variability*) will be published as Laboratory Analytical Procedures (LAPs), which are **free and publicly available**
- Move towards more complete bio-oil analysis
  - Methods for crude oil may not be appropriate for bio-oil
- Enable commoditization of bio-oils

Quad Chart Overview

Timeline

- Start: 10/1/2013
- End: 9/30/2017
- 35% Complete

Budget

	Total Costs FY10 – FY12	FY13 Costs	FY14 Costs	Total Planned Funding (FY15 – FY17)
DOE Funded	$0k	$0k	$371k	$3,327k

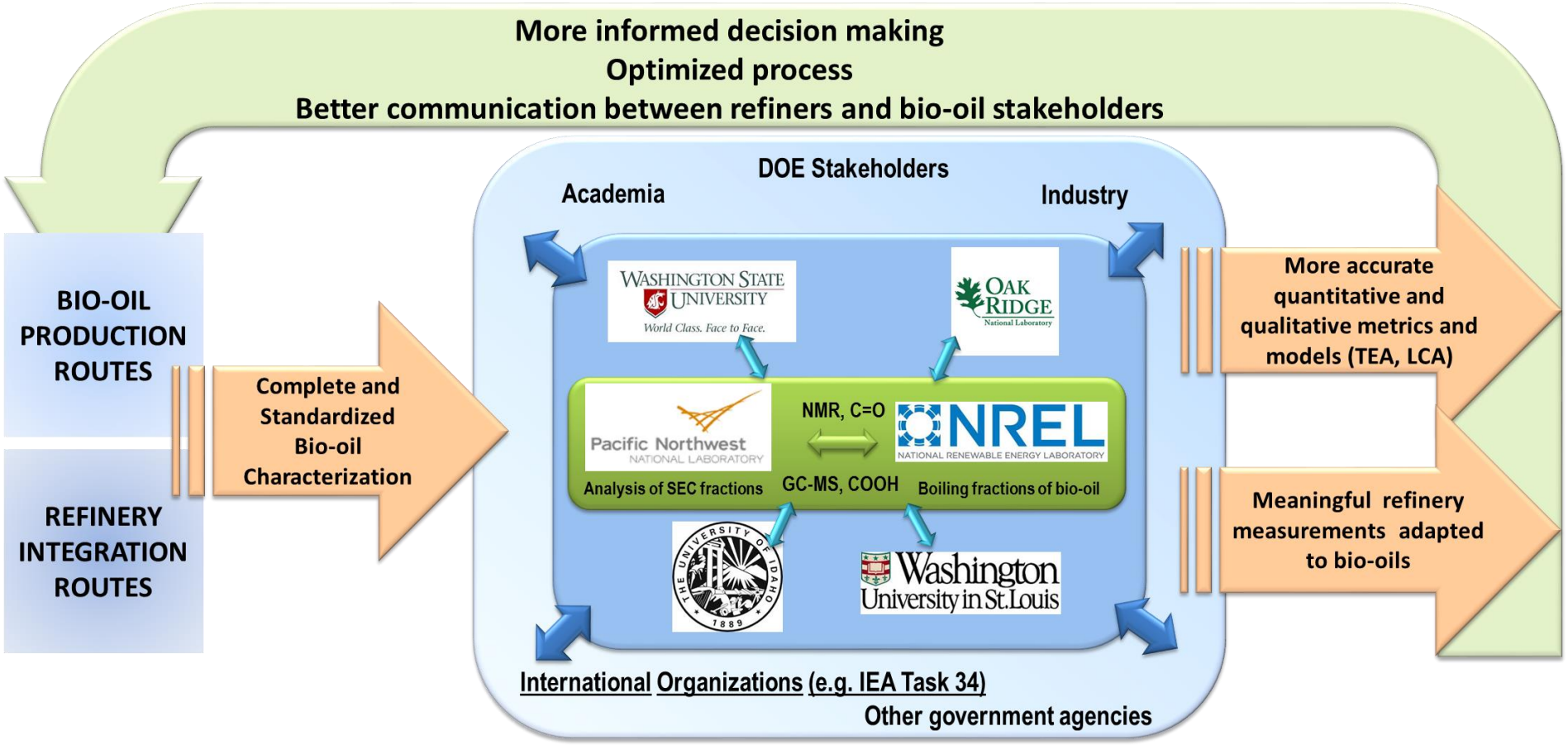
Barriers

- BETO Barriers Addressed
  - Tt-F: Deconstruction of Biomass to Form Bio-Oil Intermediates
  - Tt-H: Bio-Oil Intermediate Stabilization and Vapor Cleanup
  - Tt-J: Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
  - Tt-S: Petroleum Refinery Integration of Bio-Oil Intermediates

Partners

- Partners
  - NREL (50%), PNNL (50%)
  - ORNL (Round Robin)
- Leading Round Robin in FY15
  - Universities: Washington University St. Louis, University of Idaho, Washington State University
  - Labs: NREL, PNNL, ORNL, VTT Technical Research Centre of Finland, Thunen Institute of Wood Research, CanmetENERGY

Project Overview



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

Technical Approach

Challenge

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

Approach

Develop standard methods

Validate Methods: Round Robin

NREL NATIONAL RENEWABLE ENERGY LABORATORY

OAK RIDGE National Laboratory

Pacific Northwest NATIONAL LABORATORY

Washington University in St. Louis

THÜNEN

WASHINGTON STATE UNIVERSITY

VTT

CanmetENERGY *Leadership in ecoInnovation*

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Share: LAPs, publications

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

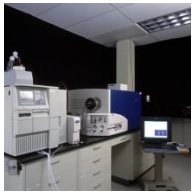
Challenge

Need to move towards complete bio-oil characterization

Approach

Develop suite of methods

- Compounds
  - Chromatography



- Hydroxyl Groups
  - NMR

- C=O (carbonyls)
  - Acid Content
    - Titration

- Boiling Range
  - TGA

Success Factors

- Accelerate the approach to cost competitive biofuels
  - Research in each processing step needs **complete** characterization of feed/products
- Create a **framework** for analysis that will be used by entire community
  - Spell out appropriate methods for desired measurements on raw and upgraded oils

Management Approach

- NREL and PNNL
  - Determine analytical needs from bioenergy community
  - Develop standard methods in **parallel**
  - **Cross-validate** standard methods (prior to Round Robin)
  - Open and constant **communication** between NREL and PNNL
- Annual Operating Plan (AOP), Project Management Plan (PMP)
  - Milestones defined prior to fiscal year
  - Risk management / abatement of uncertainties
  - Go / No-Go decision (3/31/2016): Round Robin Reproducibility: <10% variability in carbonyl quantification by titration
    - Significance: carbonyls are important **markers** in bio-oil

Standard Bio-oil for Method Development

- Produced in 2010 at NREL in Pilot Plant[1]
  - Oak, 500 ^{0}C
  - Not hot gas filtered
  - Have large quantity
- Aging Test
  - 80 ^{o}C, 24 hours
  - 2.1% viscosity change
    - Very small change
    - **Oil stabilized during storage**

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

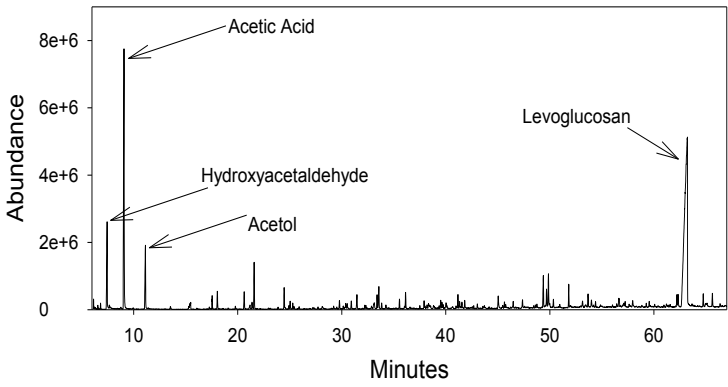
Current analysis methods do not fully describe the oil quality, nor fully inform downstream processing

[1]Baldwin, RM, Feik, CJ, 2013 Energy & Fuels 27: 3224-3238

Gas Chromatography – Mass Spectrometry (GC-MS): Quantification of Volatile Components

- Knowledge of specific compounds important for upgrading and refinery integration
- Literature survey[1]: **variety of columns, dimensions, and instrument parameters**
- Results highlight **importance of using a quantitative method** for GC-MS
  - Trends in results based on % peak area not always valid
    - Response factors unique to specific compound on MS detector
- Intra-laboratory variability: < 5% for each compound

Tentative ID	% Area	%
Levoglucosan	34.0	8.8
Acetic acid	12.2	4.3
Acetol	3.4	1.1
Hydroxyacetaldehyde	3.1	5.0
Furfural	1.5	0.34
Catechol	1.4	0.38
Syringol	1.3	0.14
3-Methyl-1,2-cyclopentanedione	1.2	0.22
5-Hydroxymethylfurfural	1.2	0.32
2(5H)-Furanone	0.8	0.26
Propanoic acid	0.7	0.39
4-Ethylguaiacol	0.7	0.04
Guaiacol	0.7	0.08
Creosol	0.6	0.07
2-Cyclopenten-1-one	0.5	0.08



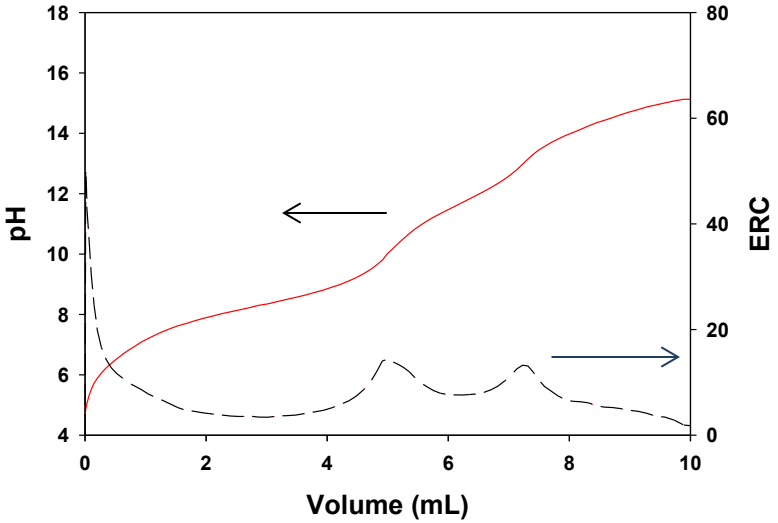
- **Method gives identity and concentrations of components in bio-oil**

[1]Sipila, K., et al. 1998 Biomass and Bioenergy 14: 103-113

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**
- Acid content of petroleum commonly measured by titration (ASTM D664) and expressed as total acid number (TAN)
- Modified D664, allowing for **increased precision** of the carboxylic acid number (CAN), and **detection of phenolics** at the second endpoint[1]
  - Changed the titrant from KOH to tetrabutyl ammonium hydroxide (TBAOH)
  - Changed pH electrode electrolyte from LiCl to tetraethyl ammonium bromide (TEABr)

- Results with bio-oil:
  - 1st endpoint: CAN = 81 ± 1 mg KOH/g
  - 2nd endpoint: TAN = 187 ± 2 mg KOH/g
  - Phenolic content PhAN= TAN – CAN = 99 ± 1 mg KOH/g

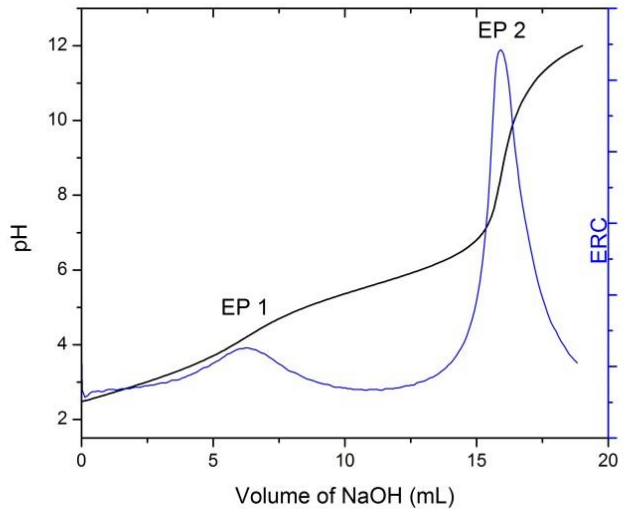


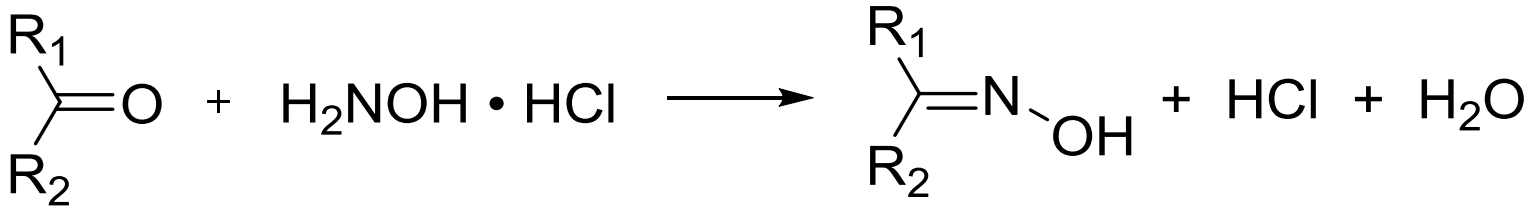
- **Simple, reliable titration method**
- **Gives concentrations of organic acids and phenolics**

[1] Christensen, ED, et al. 2011 Energy and Fuels 25:5462-5471.

Carbonyl Quantification by Titration

- Carbonyls in bio oil:
  - **Stability** during storage
  - Coke formation during upgrading
  - **Aldehydes and ketones**
- Quantitative analysis via titration
- Conversion of C=O to oxime
- Titrate the liberated HCl using a base





- Modified Nicolaides method[1]
  - Intra-laboratory variability < 3%
  - Inter-laboratory variability < 3%

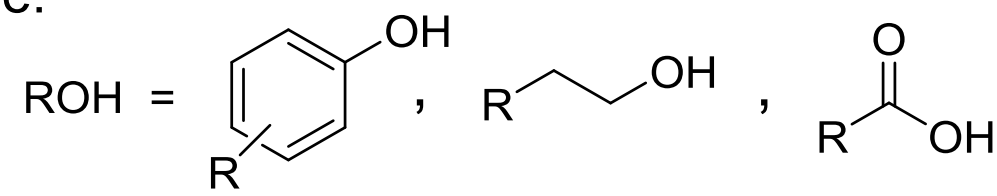
Results[1]
3.33 ± 0.11 mmol C=O/g

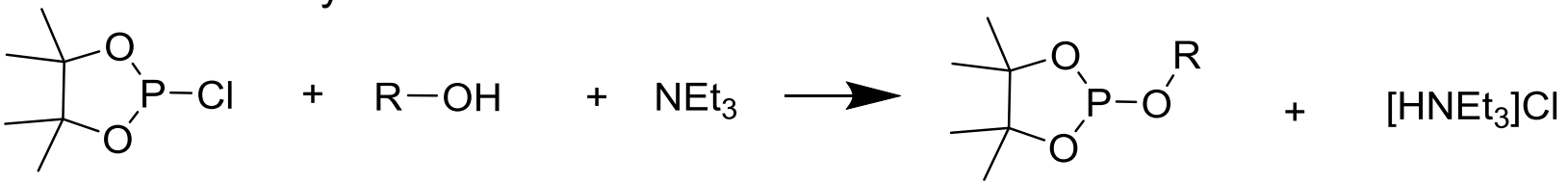
- **Simple, reliable titration method**
- **Gives concentration of carbonyls [aldehyde + ketone]**

[1]Nicolaides, GM. 1984. MASc Thesis, University of Waterloo

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

- Importance: hydroxyl groups present in functionalities relevant to **stabilization** and **upgrading** of bio-oils
- Use ^{31}P NMR method – ^{31}P 100% abundant
- Application to coals, carbohydrates and lignins[1,2]
- Can quantitatively determine:
  - Phenols
  - Aliphatic alcohol
  - Carboxylic acids





- **Method gives concentration of three hydroxyl groups: phenolic, aliphatic, carboxylic**

Functional group	Chemical shift, ppm	O - Wt., %
Aliphatic -OH	152 - 145	16.2 ± 0.4%
Phenolic -OH	138 – 145	8.1 ± 0.2%
Carboxylic -OH	134.6 - 136	7.6 ± 0.3%

[1]Wroblewski, AE, et al. 1988. Energy and Fuels 2: 765-774
[2]Argyropoulos, DS. 1995. Res. Chem. Intermed. 21: 373-395

Extension of Standard Methods to Other Bio-oils

- Fast pyrolysis oils
  - Stabilized Pine
    - 34.5% O
  - Medium O upgraded oil
    - 8.6% O (Oak)
  - Low O hydrotreated oil
    - 1.3% O (Pine)
- Hydrothermal liquefaction (HTL) oils
  - Wood (Pine, 14.1% O)
  - Algae (5.3% O, 4.8% N)

Standard Methods

- Functional Group methods
  - **Carbonyls**, **hydroxyl** groups, **carboxylic acids** (CAN) and **phenolics** (PhAN) **quantified**
- GC-MS
  - Standard method applicable to Stabilized pine sample
  - Upgraded, hydrotreated, and HTL oils **need new methods**

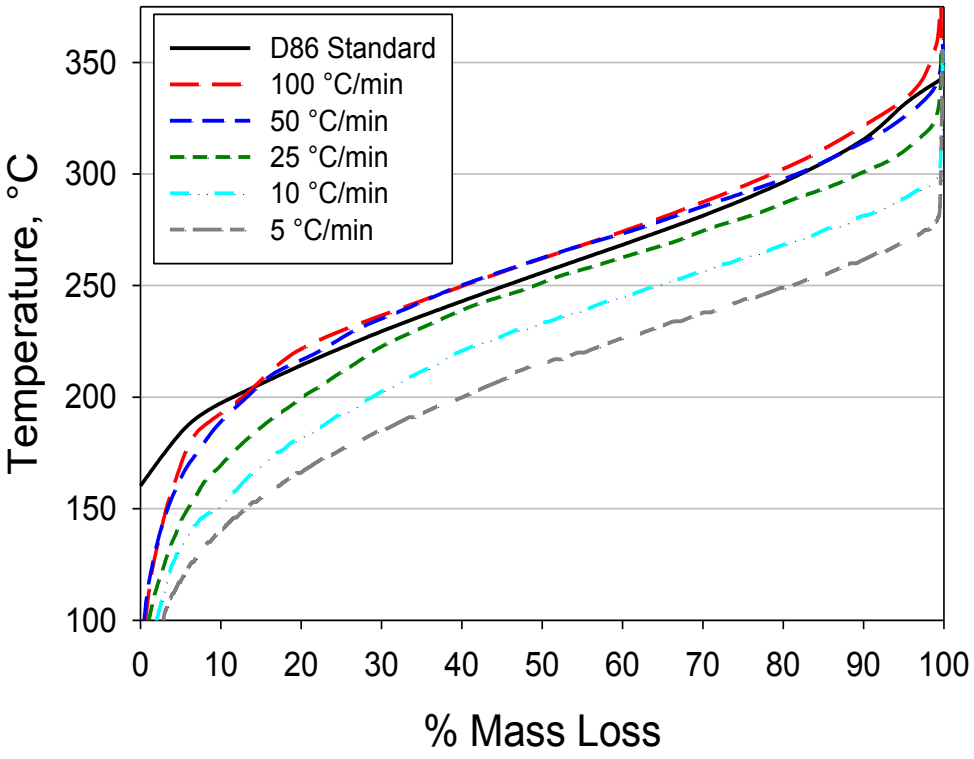
- **Functional group methods apply well to new bio-oils**
- **New methods needed for GC**

Simulated Distillation using Thermogravimetric Analysis (TGA)

- **Boiling range regulated** for gas, diesel, and jet fuels
- Batch distillation (ASTM D86) requires **100mL** sample
- GC-based simulated distillation works well for hydrocarbons
  - Oxygenated polar compounds in bio-oil

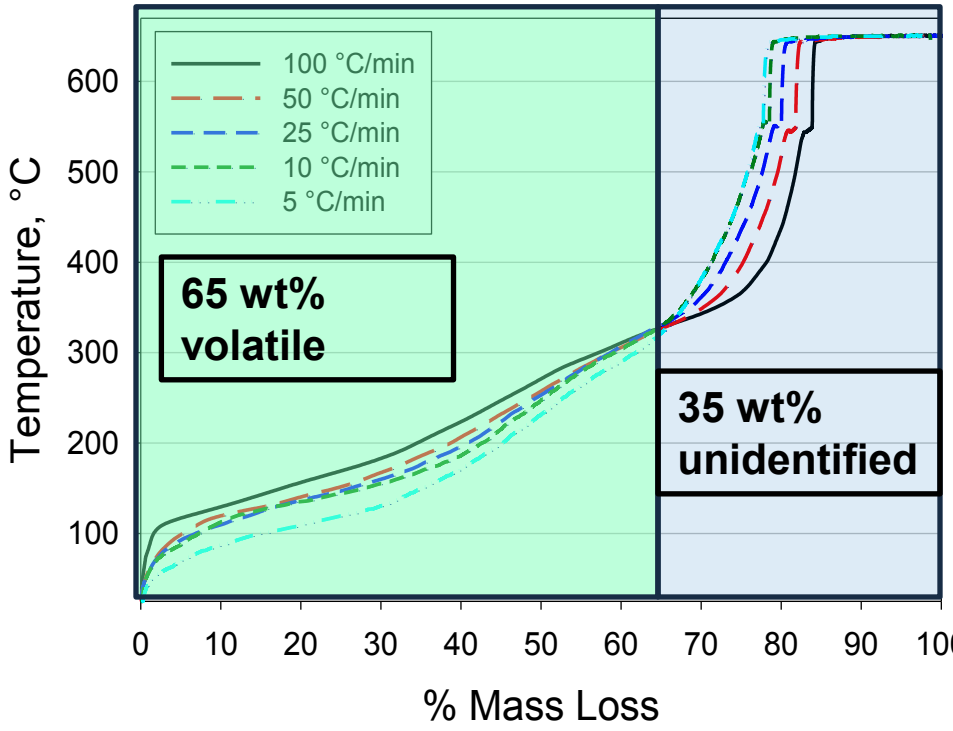
- With TGA, measure weight loss by evaporation as sample is heated – gives similar data to distillation curve
- D86 diesel standard used for method validation
- Different temperature ramps tested with D86 standard
  - 50 ^{0}C/min best fit to actual distillation

TGA can accurately simulate distillation



Simulated Distillation using Thermogravimetric Analysis (TGA)

- **Results with bio-oil**
- All ramp rates converge at ~65% mass loss[1]
- Results indicate mass loss above ~325°C is due to thermal degradation
  - ~35% bio-oil not volatile
- GC methods typically inject <300°C
- Batch distillation with bio-oil[2] generated 35-50% residue



- **Quick way to determine volatile fraction of bio-oil**
- **Needs to be expanded to other bio-oils and upgraded oils**

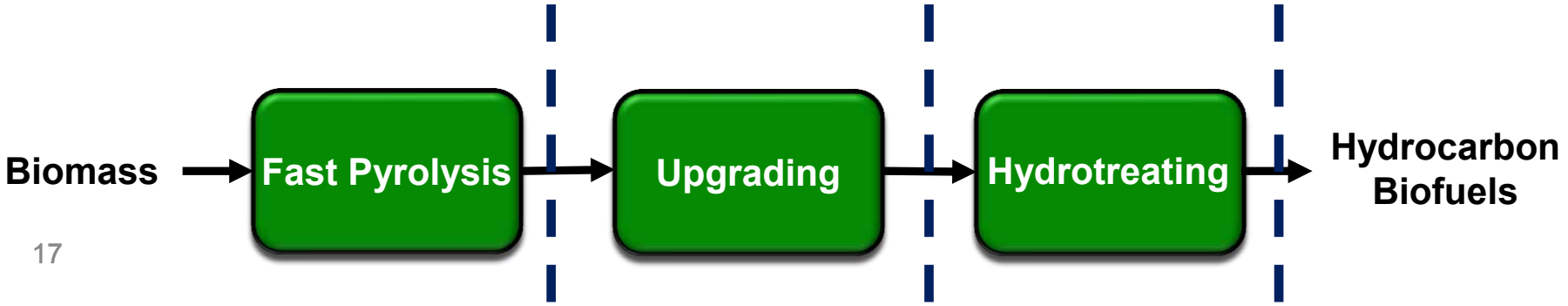
[1]Christensen, ED, et al., 2015. Energy and Fuels, *in preparation*

[2]Czernik, S, et al., 2004 Energy and Fuels 18: 590-598

Relevance

- Addresses BETO Barriers
  - **Tt-F**: Deconstruction of Biomass to Form Bio-Oil Intermediates
  - **Tt-H**: Bio-Oil Intermediate Stabilization and Vapor Cleanup
  - **Tt-J**: Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
  - **Tt-S**: Petroleum Refinery Integration of Bio-Oil Intermediates

- Need to move away from methods used for crude oil
  - Methods developed for raw, upgraded, and hydrotreated bio-oils will be more accurate, precise, and appropriate
- **Accelerate research** for each processing step
  - Move towards more complete bio-oil analysis
  - Support development of *commercially viable* biofuel technologies



Relevance

- ***Enable accurate communication across the bioenergy industry***
  - Bio-oil producers and refiners have different priorities
  - Researchers, policy makers, and the bioenergy industry need to speak the same language
    - Started with methods for raw bio-oil
    - Transition to methods for upgraded and hydrotreated oils
- Key output:
  - **Laboratory Analytical Procedures** (LAPs)
    - Development and adoption of methods by community
    - Suite of LAPs will create a framework for analysis that will be used by entire community
      - Spell out appropriate methods for measurements on raw, upgraded, and hydrotreated oils

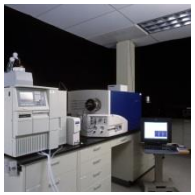
Future Work

Develop suite of methods

Carbonyl species

Acid species

.....→ HPLC



Unknown wt%

↓

SEC, distillation

↓

Suite of methods

Carbon Functional Groups → ^{13}C NMR

Esters → Colorimetry

Round Robin

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OAK RIDGE National Laboratory

Pacific Northwest NATIONAL LABORATORY

Washington University in St. Louis

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Out years: Transition to upgraded bio-oils

Summary

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

- Approach
  - Joint task between NREL and PNNL (started FY14)
  - Develop standard methods (LAPs) for bio-oils
    - Engage community to validate LAPs via Round Robin

- Technical accomplishments
  - Standardized existing methods for raw bio-oil
    - GC-MS, CAN/TAN, carbonyl titration, ^{31}P NMR
  - Development of new methods for bio-oil
    - TGA simulated distillation

Summary

- Relevance
  - **Enable** accurate communication across bioenergy industry
  - **Accelerate research** and development of *commercially viable* biofuel technologies
  - **Technology transfer** to stakeholders: LAP methods, peer-reviewed publications

- Future work
  - Standardize methods
    - ^{13}C NMR
    - HPLC for carboxylic acids and carbonyls
  - Development of new methods
    - Esters by colorimetry
    - SEC as separation technique
  - Unknown wt%: separation → suite of techniques
  - *Out Years: Method development and standardization for upgraded bio-oils*

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Heather Job
Evgueni Polikarpov
Deanna Auberry
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Leslie Rotness
Alan Zacher
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Corinne Drennan
Doug C. Elliott

Round Robin Partners

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(University of Idaho)
Manuel Garcia-Perez
(Washington State University)
Jim Keiser
(ORNL)
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(VTT Technical Research Centre of Finland)
Dietrich Meier
(Thunen Institute of Wood Research)
Jinwen Chen
(CanmetENERGY)

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.

- NMR = Nuclear Magnetic Resonance
- ERC = endpoint recognition criteria (1st derivative of titration curve)
- CAN = carboxylic acid number
- TAN = total acid number
- PhAN = phenolic acid number (TAN – CAN)
- 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
- SEC = size exclusion chromatography

Presentations

- "Oil Derived from Biomass: Qualitative and Quantitative Analysis of Oxygenates" (oral presentation), Padmaperuma AB, Olarte MV, Burton SD, Lee SJ, Lemmon TL, Drennan C, Ferrell JR, Christensen ED, Deutch S and Fouts L. *AIChE Annual Meeting* Atlanta GA, **Nov 16-21 2014**
- "Simulated Distillation of Pyrolysis Bio-Oil using Thermogravimetric Analysis" (poster presentation), Christensen ED, Deutch S, and Ferrell JR. *TCS2014: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products*, Denver, CO, **September 2-5, 2014**
- "Standardization and Development of Bio-oil Analytical Techniques" (poster presentation), Olarte MV, AB Padmaperuma, SD Burton, TL Lemmon, SJ Lee, C Drennan, J Ferrell, ED Christensen, S Deutch and L Fouts. *Biomass 2014*, Washington, DC, **July 29, 2014**
- "Crude oil derived from biomass: what is in it and implications on catalytic upgrading" (poster presentation) Padmaperuma AB, MV Olarte, SD Burton, SJ Lee, TL Lemmon, DL Auberry, DC Elliott, AH Zacher, C Drennan, GG Neuenschwander, and LJ Rotness, Jr. 2014. *248th ACS National Meeting and Exposition*, San Francisco, CA, **Aug 10, 2014**.
- "Development and Standardization of Techniques for Bio-oil Characterization" (oral presentation), Olarte MV, and AB Padmaperuma. *Invited seminar at NREL*, Golden, CO, **June 27, 2014**
- "Development and Standardization of Techniques for Bio-oil Characterization" (oral presentation), Christensen ED, and Ferrell JR. *Invited seminar at PNNL*, Golden, CO, **April 10, 2014**

Related Projects

Related NREL tasks (and associated WBS numbers):

- Thermochemical Feedstock Interface (WBS: 2.2.1.304)
- Computational Pyrolysis Consortium (WBS: 2.5.1.302)
- Integration and Scale Up (WBS: 2.4.1.301)
- Liquid Fuels via Upgrading of Syngas Intermediates (WBS: 2.3.1.305)
- Catalytic Pyrolysis Science (WBS: 2.3.1.313)
- 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)
- Hydrothermal Processing of Biomass (WBS: 2.2.2.301)
- Computational Pyrolysis Consortium (WBS: 2.5.1.303)

Technical Approach – Challenges and Abatements

Challenge	Abatement
Identifying critical sources of deviation/variation between current individual laboratory practices and equipment	❑ Detailed methods (LAP) and spreadsheets will be made available ❑ Addition of a validation mixture not originally proposed
Bio-oil changes during shipment and handling	❑ Consistent shipping and storage methods
Availability of reagents	❑ Synthesis method for TMDP identified and implemented

FY14 Milestones

NREL FY14 Milestones

Q1	12/31/2013	Regular	Determination of the bio-oil boiling fraction: Determine the amount of a pyrolysis oil sample that is analyzable by gas chromatography methods.
Q2	3/31/2014	Regular	Development of best practices for carboxylic acid titrations: Development of standard sample preparation and analytical methodology for carboxylic
Q3	6/30/2014	Regular	Development of best practices for GC/MS: Development of standard sample preparation and analytical methodology for GC/MS analysis of a pyrolysis oil sample.
Q4	9/30/2014	Regular	Inter-laboratory transfer of developed best practices and validation between NREL and PNNL: Transfer of best practice methods from PNNL for validating their developed methods. Successful application of methodologies using NREL equipment with comparable results to PNNL. (Joint with PNNL)

PNNL FY14 Milestones

Q1	12/31/2013	Regular	Analyses of pyrolysis oil from NREL using conventional methods
Q2	3/31/2014	Regular	Development of best practices for ^{31}P NMR
Q3	6/30/2014	Regular	Development of best practices for carbonyl titration
Q4	9/30/2014	Regular	Inter-laboratory transfer of developed best practices and validation between PNNL and NREL: Transfer of best practice methods from NREL for validating their developed methods. Successful application of methodologies using PNNL equipment with comparable results to NREL. (Joint with NREL)

FY15 Milestones

NREL FY15 Milestones

Q1	12/31/2014	Regular	Expand methods developed in FY14 (using a standard bio oil) to other bio oil types by implementing them on five new bio oil sample types, including low (e.g. upgraded) and high oxygen contents, and HTL oils from algae and wood.
Q2	3/31/2015	Regular	Development of a standard method for ^{13}C NMR: Development of standard sample preparation and analytical methodology of a bio-oil sample using ^{13}C nuclear magnetic resonance (NMR) for functional group analysis.
Q3	6/30/2015	Regular	Development of standard HPLC methods: Report on the development of standard sample preparation and analytical methodology using HPLC for the determination of both carboxylic acid and carbonyl content of a bio-oil sample.
Q4	9/30/2015	Regular	(1) Complete preparation of a manuscript summarizing the results of the round-robin for submission to a high impact peer-reviewed journal. Standard methods are needed to compare results from different laboratories, and the round robin will demonstrate the robustness of each standardized method. (2) Reproduce Christensen effort (landmark paper) to determine fate of heteroatoms in mid-to-fully upgraded bio oil fractions (e.g. gasoline, diesel, jet), with specific focus on heavy fractions. At least three (3) fractions will be tested, using conventional analytical techniques as well as at least three (3) standardized analytical techniques developed under this collaboration.

PNNL FY14 Milestones

Q1	12/31/2014	Regular	Same as NREL (above)
Q2	3/31/2015	Regular	PNNL will develop colorimetric techniques to analyze for ester functionalities in bio-oils. In the current FY14, we have standardized methods to analyze acids, alcohols, phenols and carbonyls.
Q3	6/30/2015	Regular	Literature survey for determining analytical technique correlation. PNNL will conduct a survey of existing data on bio-oils to determine possible correlation between viscosity, density, O content and KF values. Findings will be summarized in a report.
Q4	9/30/2015	Regular	Same as NREL (above)

Data Comparisons: FY14 Standard Methods

- Carboxylic acids
  - PNNL
    - CAN: 1.52 mmol/g
    - Carboxylic-OH: 1.81 mmol/g
      - 19% difference
  - NREL
    - CAN: 1.44 mmol/g
    - Carboxylic-OH: 1.28 mmol/g
      - 11% difference
- Phenolics
  - PNNL
    - PhAN (TAN-CAN): 2.37 mmol/g
    - Phenolic-OH: 3.9 mmol/g
      - 39% difference
  - NREL
    - PhAN (TAN-CAN): 1.89 mmol/g
    - Phenolic-OH: 2.67 mmol/g
      - 29% difference

Cross Validation of Standard Methods

- GC-MS
  - 8 of 31 calibrated compounds had > 20% difference between NREL and PNNL
- CAN/TAN
  - CAN: PNNL (85.1 mg KOH/g); NREL (81 mg KOH/g)
    - 5% difference
  - TAN: PNNL (218.5 mg KOH/g); NREL (187 mg KOH/g)
    - 14% difference
- ^{31}P NMR
  - Aliphatic-OH: PNNL (7.79 mmol/g); NREL (5.45 mmol/g)
    - 30% difference
  - Phenolic-OH: PNNL (3.9 mmol/g); NREL (2.67 mmol/g)
    - 32% difference
  - Carboxylic-OH: PNNL (1.81 mmol/g); NREL (1.28 mmol/g)
    - 29% difference
- Carbonyl titration
  - PNNL (3.333 mmol/g); NREL (3.301 mmol/g)
    - 1% difference

GC-MS Cross Validation

- Attention to detail in instrument parameters/setup
  - MS transfer line temperature
  - Inlet liner type/orientation
  - Incorporated into LAPs for Round Robin
- Differences in sample aging during transport and storage
  - Addition of validation mixture for Round Robin

Target Compound	Reported NREL values, ppm	PNNL Average, ppm	% Difference between NREL and PNNL values
Glycolaldehyde	50420	35515	**-29.6**
Acetic Acid	43410	42551	-2.0
Acetol	11490	12974	12.9
3-Hydroxy-2-butanone	380	338	-11.0
Propanoic acid	3890	3567	-8.3
Butanoic acid	1470	1231	-16.3
2-Cyclopenten-1-one	750	748	-0.3
Furfural	3430	3563	3.9
5-methylfurfural	630	563	-10.7
2(5)-Furanone	2580	2431	-5.8
3-Methyl-1,2-cyclopentanedione	2170	2176	0.3
3-Methyl-2(5)-furanone	500	487	-2.6
Phenol	580	532	-8.3
Guaiacol	800	778	-2.8
o-Cresol	580	353	**-39.2**
Maltol	970	664	**-31.5**
Creosol	670	685	2.3
p-Cresol	520	240	**-53.8**
m-cresol	280	198	**-29.2**
2,4-Xylenol	430	385	-10.5
4-ethylguaiacol	420	340	-19.1
Eugenol	390	342	-12.3
5-Hydroxymethylfurfural	3180	3058	-3.8
Catechol	3800	4649	**22.3**
Syringol	1380	1572	13.9
Vanillin	560	604	7.9
Hydroquinone	590	464	**-21.3**
Apocynin	460	524	13.9
Levoglucosan	88000	78751	-10.5
Syringaldehyde	1200	1054	-12.1
Acetosyringone	910	675	**-25.9**

Gas Chromatography – Mass Spectrometry (GC-MS) Method

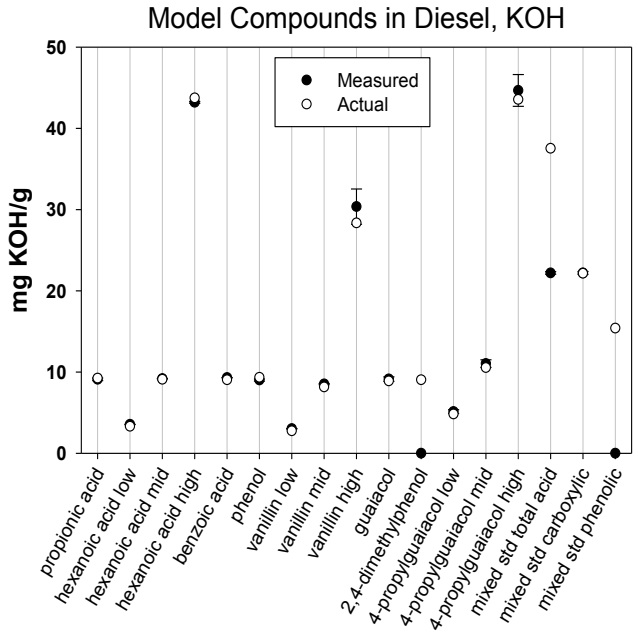
- Internal standards: isoamyl ether, 1-octanol, methyl laurate
- Acetonitrile used as solvent
- 8 calibration standards, each containing 31 compounds. $R^2 > 0.995$ required for calibration curve
- The GC/MS instrument parameters are as follows:
  - Carrier gas: Helium; Carrier gas flow rate: 1 mL/min (constant flow); Injection volume: 1 µL; Injection port temperature: 250 °C; Split injection ratio: 30:1; Initial oven temperature: 45 °C, 10 min hold time; Oven ramp rate: 3 °C/min; Final oven temperature: 250 °C, 5 min hold time; MSD transfer line temperature: 280 °C; Source temperature: 230 °C; Quad temperature: 150 °C; MSD scan range: m/z 29-600

Compound	Average Concentration (µg/mL)	Standard Deviation	Uncertainty
Levoglucosan	88,000	1,100	3,000
Glycolaldehyde	50,420	1,100	3,100
Acetic acid	43,410	445	1,240
Acetol	11,490	139	385
Propanoic acid	3,890	110	310
Furfural	3,430	20	60
5-Hydroxymethylfurfural	3,180	50	150
2(5H)-Furanone	2,580	25	70
3-Methyl-1,2-cyclopententanedione	2,170	50	50
Butanoic acid	1,470	40	110
Syringol	1,380	20	60
Syringylaldehyde	1,200	15	40
Maltol	970	15	40
Acetosyringone	910	10	30
Guaiacol	800	8	20
2-Cyclopenten-1-one	750	8	20
Creosol	670	5	15
5-Methylfurfural	630	3	9
Hydroquinone	590	5	15
o-Cresol	580	4	12
Phenol	580	6	18
Vanillin	560	7	20
p-Cresol	520	5	13
3-Methyl-2(5H)-furanone	500	8	20
Apocynin	460	5	15
2,4-Xylenol	430	2	6
4-Ethylguaiacol	420	2	5
Eugenol	390	3	10
3-Hydroxy-2-butanone	380	4	12
Catechol	290	3	7
m-Cresol	280	3	7

Carboxylic Acid Titration Method

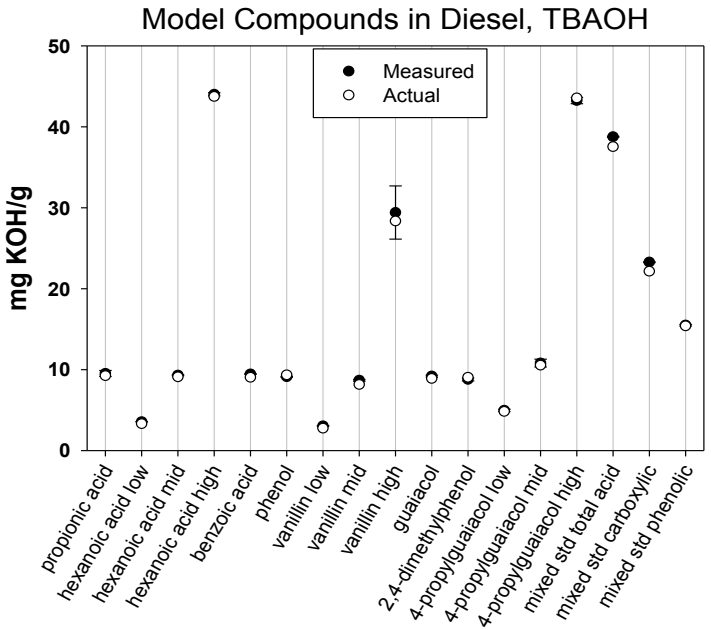
KOH Titrant

- Hindered phenol not detected
- When phenolics mixed with carboxylics, do not detect both
- Only CAN detected in bio-oil
- CAN = 83 ± 3 mg KOH/g



TBAOH titrant

- Hindered phenol accurately measured
- Can detect both carboxylics and phenols in mixture
- Better CAN and TAN precision with bio-oil
- CAN = 81 ± 1, TAN = 187 ± 2 mg KOH/g



^{31}P NMR Parameter Considerations

- Pulse angle
  - Improved sensitivity
  - Literature values: 45° and 90°
    - At different number of scans, std. deviation ranged from ±0.2 wt% to ±1.6 wt%
  - **90° is better**

- Relaxation delay
  - Allow sufficient time for nuclei spins to return to equilibrium after excitation
  - Important for quantification
  - Literature values: 12 and 25 s
    - At different number of scans, std. deviation ranged from ±0.2 wt% to ±0.4 wt%, with the 25s giving higher values
  - **25 s is better**

- Number of scans
  - Number of scans affect signal to noise ratio (resolution)

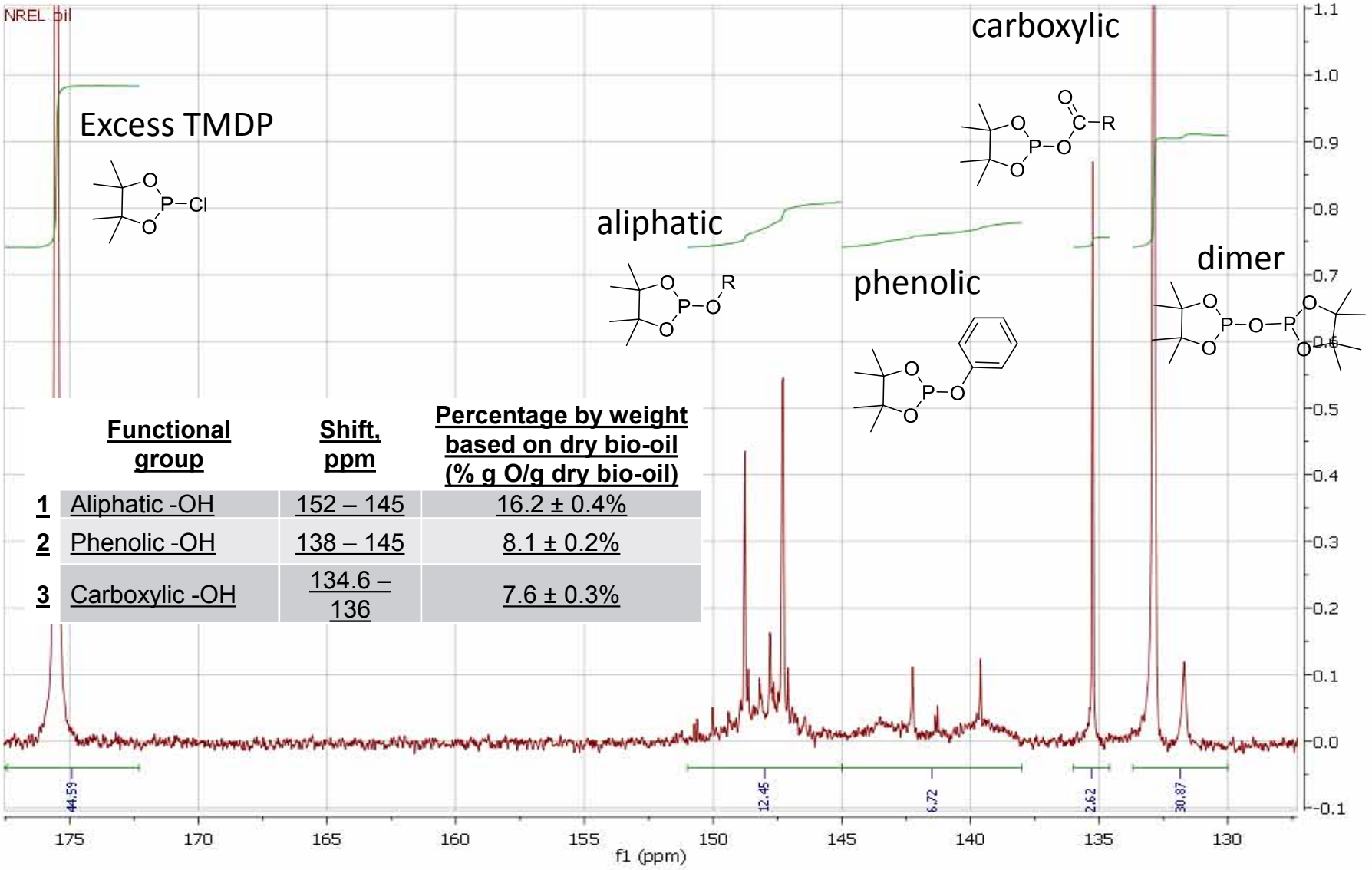
$$S/N \alpha (\text{number of scans})^{0.5}$$

  - Literature values: 128, 256 and 512 scans
    - A difference of between 1 to 5 h total analysis time
    - With same pulse angle, std. deviation ranged from ±0.2 wt% to ±0.4 wt%
  - Between 128 and 512 scans

^{31}P NMR Parameter Considerations

- Magnet strength
  - Required slight refitting of shift ranges
  - Comparing 300 MHz and 500 MHz, std deviation was from ±0.03 wt% to ±0.1 wt%
- Acquisition time
  - Increasing acquisition from 0.6 s to 1.2 s allowed for easier phasing and background subtraction
- MestreNova Analysis
  - Background subtraction: Polynomial fit (filter 400, polynomial order 6) or Bernstein polynomial fit (order = 6)

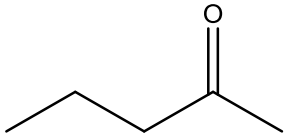
^{31}P NMR spectrum of bio-oil



	Functional group	Shift, ppm	Percentage by weight based on dry bio-oil (% g O/g dry bio-oil)
1	Aliphatic -OH	152 – 145	16.2 ± 0.4%
2	Phenolic -OH	138 – 145	8.1 ± 0.2%
3	Carboxylic -OH	134.6 – 136	7.6 ± 0.3%

Carbonyl Titration: Method validation - 2-pentanone

- Several 50 mL aliquots titrated
  - Ave: 3.23 mmol (STD Dev 0.0088)
  - Error 0.7% (measured vs added)
- Aged the sample for 2 weeks
  - 3.26 mmol (0.2% error)
- Added ethyl acetate and acetic acid prior to titration
  - No change
- Oximation reaction done in the presence of ethyl acetate
  - No change



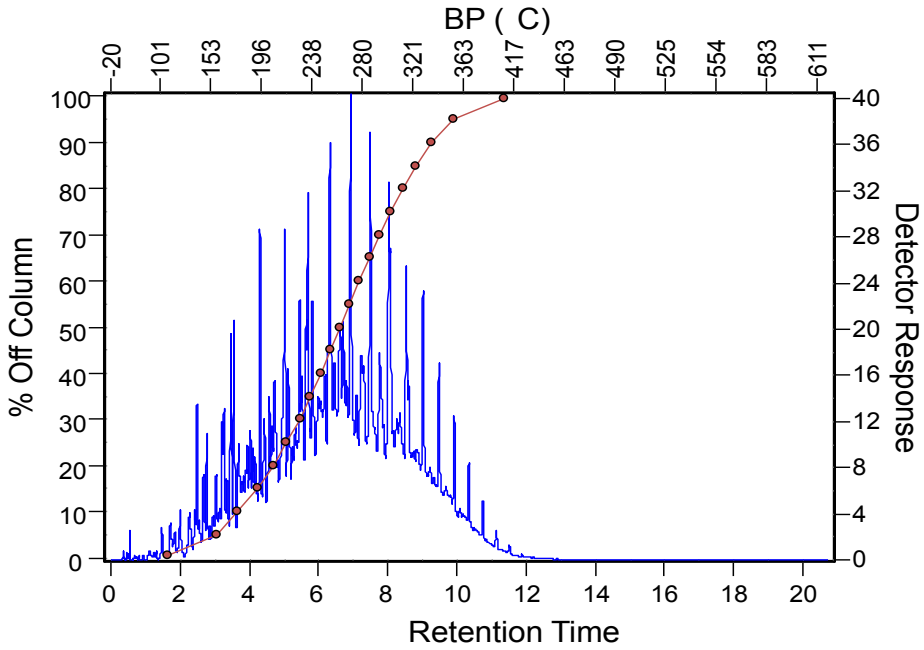
3.25 mmol in 50 mL

Instrument: Metrohm Titrando 836

GC-Based Simulated Distillation

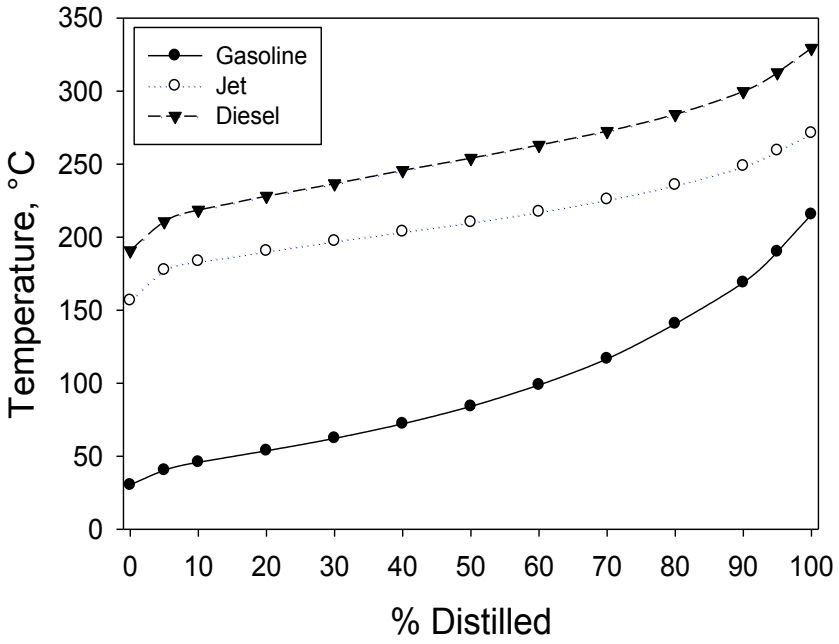
- Provides boiling range data with small sample size
- Gas chromatography used to calibrate boiling points of **hydrocarbons** with retention time
- Correlation with physical distillation applied to fit data to standard method

- **Polar compounds bias results** due to differing retention times related to boiling points and response factors
  - Ethanol (boiling point = 78 °C) co-elutes with isopentane (boiling point = 28 °C)

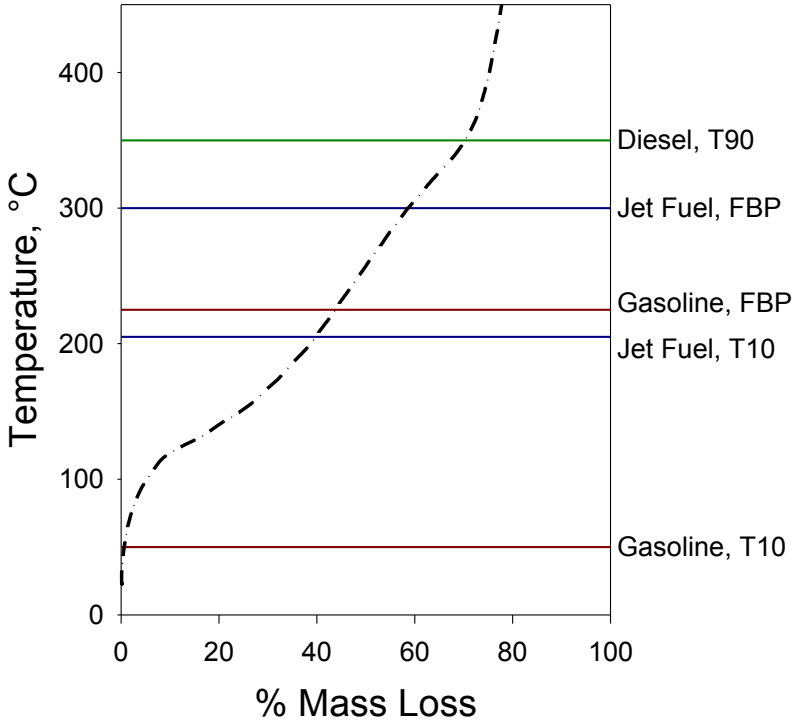


Simulated Distillation using Thermogravimetric Analysis (TGA)

- **Boiling range regulated** for gas, diesel, and jet fuels



- TGA simulated distillation can estimate amount of bio-oil that will distill into **specific fuel products**

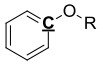
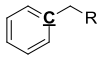
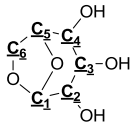
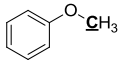
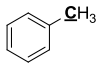
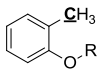


Fractionation by Size Exclusion

- Liquid chromatography technique: no need to increase temperature
- Use size exclusion to fractionate bio-oil
  - Complete mass balance
  - Analyze each fraction
- Challenge
  - Minimize bio-oil entrainment in column
    - Able to recover about 98% using a short column with series of solvents
    - Scale-up in process

^{13}C NMR Standard Method

- Sample prep
  - 250 µl bio-oil dissolved in DMSO (250 µl)
  - 5 mg/ml chromium (III) acetylacetonate ($Cr(acac)_3$)
- Instrument: Bruker 400 MHz NMR spectrometer
  - Inverse gated decoupling pulse sequence (zgig), and 90° pulse angle
  - T1 was measured using Inversion-Recovery method and calculated with Bruker's TopSpin software
    - Pulse delay should be set to five times T1
      - Need to add relaxant for decrease NMR time
    - 5 mg/ml $Cr(acac)_3$, T1 = 0.46s
  - 3s pulse delay, 1k scans, run time = 1.5 hours

Type of carbons	Range (ppm)	Structure
Carbonyl	215.0 – 166.5	
Aromatic C-O	166.5 – 142.0	
Aromatic C-C	142.0 – 125.0	
Aromatic C-H	125.0 – 95.8	
Levoglucosan	C1 102.3, C2 72.0 C3 73.7, C4 71.7 C5 76.5, C6 64.9	
Aliphatic C-O	95.8 – 60.8	
Methoxyl	60.8 – 55.2	
Aliphatic C-C	55.2 – 0.0	
Methyl – Aromatic	21.6 – 19.1	
Methyl – Aromatic’	16.1 – 15.4	

^{13}C NMR Standard Method

- Chemical shift assignment ranges

^{13}C NMR Quantitative Standard Method – Results with Standards #1 and #2

	Functional groups (carbon mol%)		
	Aliphatic carbons	Aromatic carbons	Double bonds
Based on the concentrations in Standard #1	72.42	27.08	0.51
Based on NMR data	70.74	28.70	0.55

	Different types of carbons (carbon mol%)			
	C	CH	CH2	CH3
Based on the concentrations in Standard #1	10.77	22.88	40.87	25.48
Based on NMR data	10.22	21.58	41.34	26.84

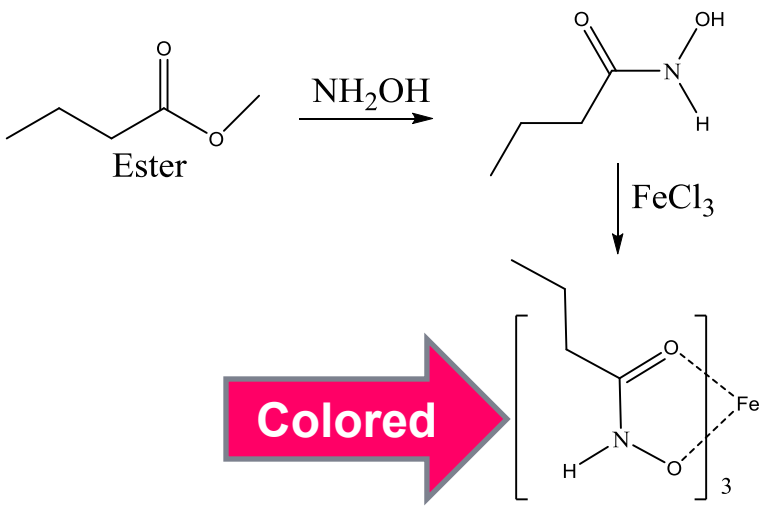
Calculation methods	Different types of carbons (carbon mol%)			
	C	CH	CH2	CH3
Based on the concentrations in Standard #2	0	0	19.49	80.51
Based on NMR data	0	0	19.05	80.95

This ^{13}C NMR method gives quantitative results

Ester Determination using Colorimetry

- ^{13}C NMR method does not separate acids and esters
- Esters form a colored complex
  - Absorbance measured at 540nm
  - Quantified using standard ester solutions
- Will report [ester] in bio-oils as mmol/g
- Selectivity to ester groups in bio-oils needs to be established

Reaction scheme



Ester Standard

Bio-oil

Extension of Standard Methods: Five new bio-oils

- 2.12.4.7-2 – High oxygen content catalytically upgraded bio-oil (**Stabilized Pine**)

This bio-oil was the product of the stabilization process using reduced Ru/C. Pine-wood derived pyrolysis oil was processed at 140 °C under 1200 psig H2. This oil was produced under the Core Pyrolysis and Catalytic Upgrading project at PNNL.

- 2.12.4.7-3 – Medium oxygen content catalytically upgraded bio-oil (**Med Ox HDO oil (oak)**)

This bio-oil was derived from the catalytic upgrading of oak pyrolysis oil using noble metal catalysts (Pd/C and Ru/C) at a dual temperature setting of 140°C/350-380°C under 1500 psig H2. This oil was produced under the Home Heating Oil project at PNNL.

- 2.12.4.7-4 – Low oxygen content catalytically upgraded bio-oil (**Low Ox HDO oil (pine)**)

This bio-oil was the product of the dual temperature processing of pine-derived bio-oil with sulfided catalysts (RuS/C followed by commercially-supplied sulfided catalyst) at 170-200°C/350-400°C under 2000 psig H2. This oil was produced under the Core Pyrolysis and Catalytic Upgrading project at PNNL.

- 2.12.4.7-5 – Hydrothermal liquefaction (HTL) biocrude derived from wood (**HTL wood**)

Pine was hydrothermally liquefied under 3000 psig of inert atmosphere (N2) at 350°C. The oil analyzed was a composite product and was further treated to remove impurities such as inorganic elements. This oil was produced under the Hydrothermal Liquefaction project at PNNL.

- 2.12.4.7-6 – Hydrothermal liquefaction (HTL) biocrude derived from algae (**HTL algae**)

Tetraselmis spp. alga was hydrothermally liquefied under 3000 psig of inert atmosphere (N2) at 350°C. Further treatment to remove impurities such as inorganic elements was done to the oil. This oil was produced under the National Alliance for Advanced Biofuels and Bioproducts (NAABB) consortium project.

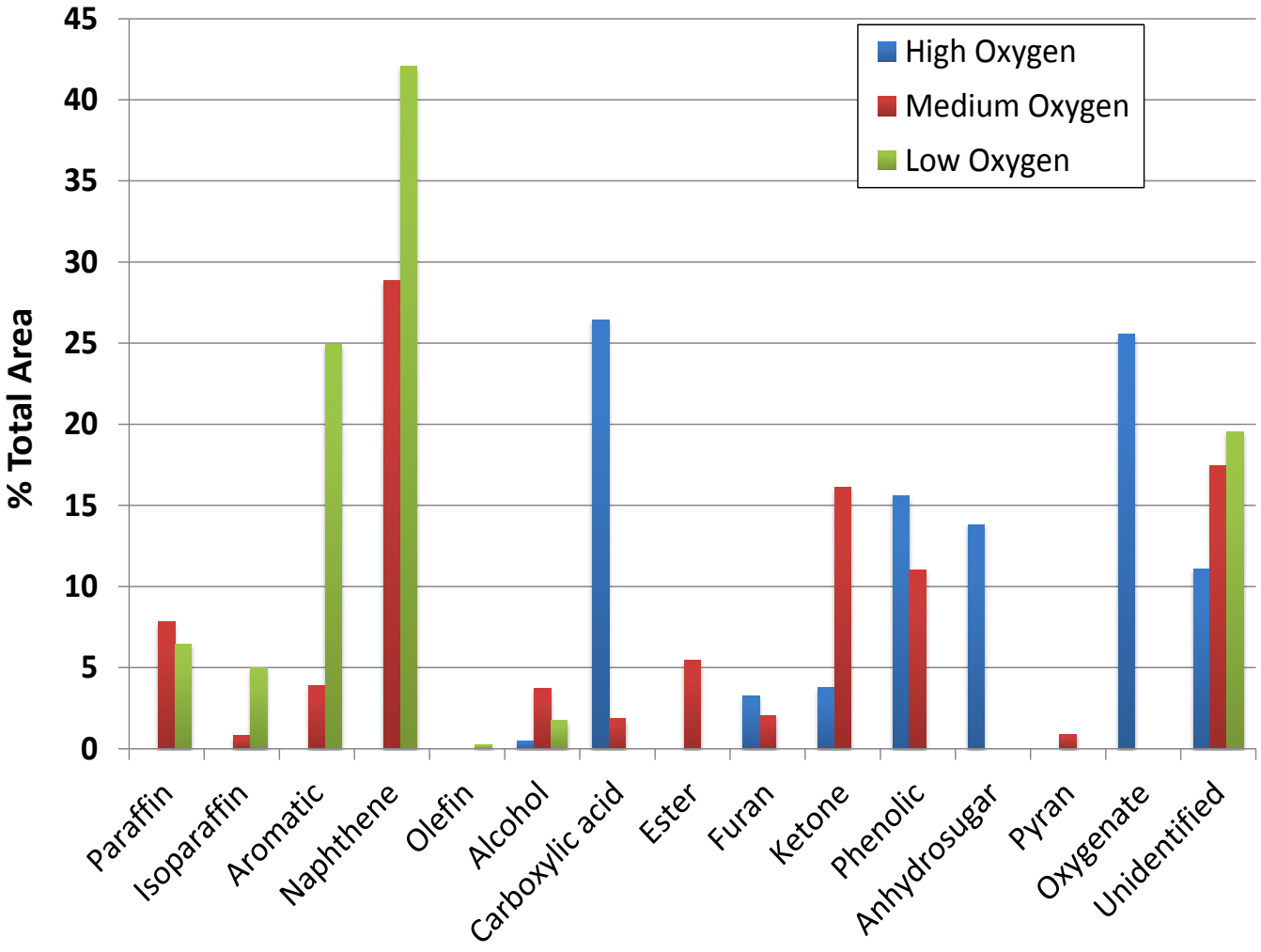
Five new bio-oils: Elemental analysis, water content, TAN

Elemental analysis, water and acid content of five new bio-oils								
		ASTM Method	FP oil (oak)	Stabilized (pine)	Med Ox HDO oil (oak)	Low Ox HDO oil (pine)	HTL wood	HTL algae
Sample#			2.12.4.7-1	2.12.4.7-2	2.12.4.7-3	2.12.4.7-4	2.12.4.7-5	2.12.4.7-6
Carbon	wt %	D 5291	57.7	43.45	79.72	85.34	78.02	78.57
Hydrogen	wt %		5.76	8.02	11.57	13.3	7.66	9.99
Nitrogen	wt %		0.24	0.04	0.05	0.05	0.15	4.78
Oxygen	wt %	D 5373	36.28	34.49	8.62	1.27	14.13	5.27
Sulfur	wt %	D 1552	0.02	0.04	0.04	0.04	0.02	1.4
O-as is (by dif)	wt %		48.64	49.55	9.72	1.31	18.93	10.81
Water content by KF	wt %	D 6869	29.01	27.72	1.37	0.00	6.43	6.63
TAN	mmol-KOH/g	D 3339	136.46	124.34	55.78	0.00	42.1	54.14

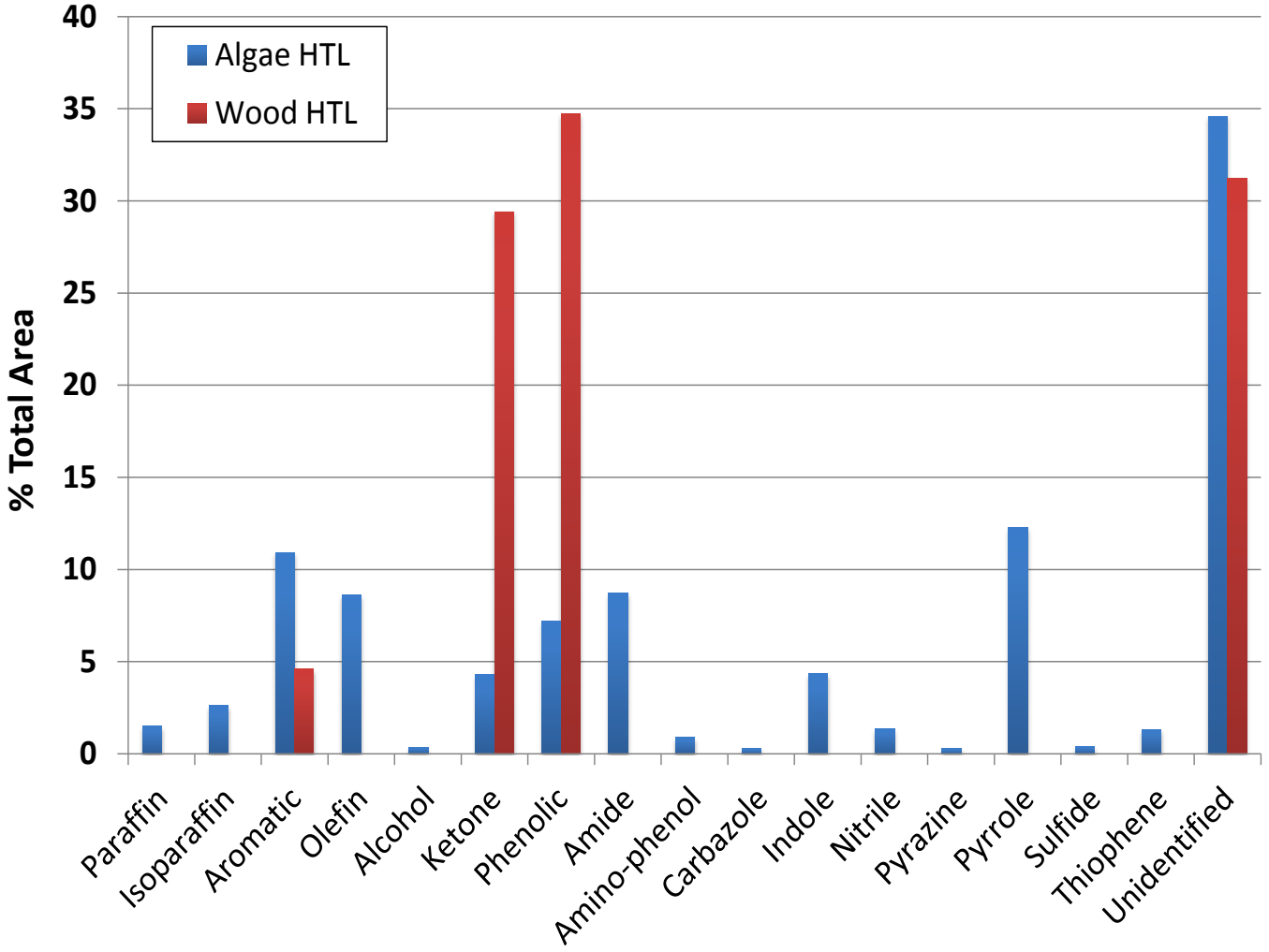
Five new bio-oils: Carbonyl titration, ^{13}C NMR, ^{31}P NMR

Results of carbonyl and hydroxyl group determination							
		FP oil (oak)	Stabilized (pine)	Med Ox HDO oil (oak)	Low Ox HDO oil (pine)	HTL wood	HTL algae
Sample#		2.12.4.7-1	2.12.4.7-2	2.12.4.7-3	2.12.4.7-4	2.12.4.7-5	2.12.4.7-6
Carbonyl titration	mmol/g	3.3	2.53	1.05	0.00	1.06	1.68
from ^{13}C NMR	mmol/g	1.34	1.97	0.08	0.00	2.07	0.58
^{31}P - Acids	mmol/g	1.82	1.69	0.97	0.00	0.41	0.67
^{31}P - Phenols	mmol/g	3.90	1.72	0.92	0.00	4.44	0.29
^{31}P - Alcohols	mmol/g	7.79	4.05	0.51	0.00	0.12	0.01

Qualitative GC-MS – Upgraded Pyrolysis Oils



Qualitative GC-MS – Hydrothermal Liquefaction Oils



Five new bio-oils – Quantitative GC-MS

- All concentrations listed in µg/mL
- Limits in quantitation determined from the lowest calibration point
  - New calibration standards needed for all oils beyond the high oxygen stabilized pine
- New methods would need to be developed for **best analytics**
  - Low oxygen HDO oil
  - Algae HTL oil
  - Wood HTL oil

	High Oxygen	Medium Oxygen	Low Oxygen	Algae HTL	Wood HTL
Glycolaldehyde	14191	<3000	<3000	<3000	<3000
Acetic acid	38505	<5000	<5000	<5000	<5000
Acetol	20013	<500	<500	<500	<500
3-Hydroxy-2-butanone	1473	<350	<350	<350	<350
Propanoic acid	1266	<500	<500	<500	<500
Butanoic acid	<400	5412	<400	<400	<400
2-Cyclopenten-1-one	<650	<650	<650	<650	<650
Furfural	1273	<650	<650	<650	<650
5-Methylfurfural	<650	<650	<650	<650	<650
2(5H)-Furanone	1381	<600	<600	<600	<600
3-Methyl-1,2-cyclopentanedione	996	<700	<700	<700	<700
3-Methyl-2(5H)-furanone	<500	<500	<500	<500	<500
Phenol	<650	<650	<650	1081	971
Guaiacol	841	<600	<600	<600	2174
o-Cresol	<850	<850	<850	<850	<850
Maltol	<650	<650	<650	<650	<650
p-Cresol	<950	<950	<950	971	<950
m-Cresol	<400	422	<400	<400	<400
Creosol	697	<400	<400	<400	1192
2,4-Xylenol	<500	1153	<500	<500	<500
4-Ethylguaiacol	<500	<500	<500	<500	2301
Eugenol	<500	<500	<500	<500	<500
5-Hydroxymethylfurfural	458	<400	<400	<400	<400
Catechol	<700	<700	<700	<700	<700
Syringol	1670	<400	<400	<400	<400
Vanillin	357	<300	<300	<300	<300
Hydroquinone	<500	<500	<500	<500	<500
Apocynin	<350	<350	<350	<350	<350
Levoglucosan	15926	<5000	<5000	<5000	<5000
Syringylaldehyde	625	<400	<400	<400	<400
Acetosyringone	<500	<500	<500	<500	<500

Five new bio-oils – Carboxylic acid titration (CAN/TAN)

	High Oxygen	Medium Oxygen	Low Oxygen	Algae HTL	Wood HTL
CAN, mg KOH/g	103.02	46.87	ND	47.70	27.61
TAN mg KOH/g	151.40	65.62	ND	65.98	156.89

- Method applied well to new bio-oils
- Low O HDO oil did not contain sufficient acidic components to be detected by titration
  - All other oils showed the presence of acidic components that can be associated with both carboxylic acids and phenolic compounds

HPLC: Carboxylic Acids

- Method to be developed for extraction, speciation and quantification of carboxylic acids in bio-oils
- High-performance liquid chromatography (HPLC) used to identify and quantify carboxylic acids ranging from formic (C1) to heptanoic (C7)
- Acids speciated with HPLC column formulated for rapid analysis of organic acids and detected with UV/Vis detector
  - Phenomenex fast acids column, sulfonated styrene divinyl benzene.
- Extraction methods using either liquid-liquid partitioning or solid phase extraction (SPE) will be optimized for isolating carboxylic acids from bio-oil
  - Potential for SPE using ion exchange resins to preferentially isolate organic acids
- Detailed composition of acidic compounds measured

HPLC: Carbonyls (Aldehydes and Ketones)

- Carbonyls measured using HPLC after derivatization with 2,4-dinitrophenylhydrazine (DNPH)
- Methodology commonly employed for analysis of carbonyls in air, automotive exhaust, and water
  - Standard methods published by EPA, OSHA, ASTM
- Methodology to be adapted and optimized for analysis of bio-oils
- Compounds speciated with HPLC column formulated for separation of derivatized carbonyls and detected with UV/Vis
  - Restek Allure AK, proprietary stationary phase
- Detailed characterization of carbonyls measured