Standardization of Analytical Techniques for Pyrolysis Bio-oil

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Grand Challenge: Complex Functionality of Biomass

Biomass

Cellulose

Hemicellulose

Lignin

Pathways

Pyrolysis
Gasification

Reactions

Decarbonylation
Decarboxylation
Cracking
Hydrogenation
Hydrogenolysis
Ring Opening
Alkylation
Oligomerization

Fuels

Gasoline

Diesel

Jet Fuel

Multi-functional catalysts are required to convert biomass into fuels
Pyrolysis & Upgrading Pathway

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

Standard analytical methods needed

- Fast Pyrolysis
- Catalytic Fast Pyrolysis
- Hydrotreating

Biomass → Hydrocarbon Biofuels
Project Overview

• Reliable analytics needed throughout process
  o Standard methods will enable research and the bioenergy industry

• Standardize quantitative analytical methods for bio-oils
  o Standard methods don’t exist that give chemical info
  o **Goal**: adoption of methods by community
    – Methods published\(^1\) as Laboratory Analytical Procedures (LAPs)

• Inter-laboratory validation via Round Robin

• Joint-project with PNNL and ORNL

\(^1\) [http://www.nrel.gov/bioenergy/bio-oil-analysis.html](http://www.nrel.gov/bioenergy/bio-oil-analysis.html)
Bio-oil Analysis Challenges

- Acidic liquid (pH ~2.5)
- Contains over 300 compounds
- 20-30 wt% water
- Unstable with time (aging)
- Very high oxygen content (~40 wt%)
  - Oxygen present across variety of functionalities
    - Acids, aldehydes, alcohols, esters, ethers, ketones, phenolics, sugars, furans
    - Oxygenated hydrocarbons of a wide variety of sizes: 40 – 2000 Da
    - Compounds monofunctional (acetic acid) and multifunctional (guaiacol)
History of Standardization

• Five major bio-oil Round Robins
  o 1988 (IEA), 1997 (EU PyNE, IEA),
    2000 (EU PyNE & IEA), 2012 (IEA)

• What worked
  o C,H,N,S (O by difference), Karl-Fischer,
    density, pH, kinematic viscosity,
    insoluble solids content

• What didn’t work
  o Xylene-distillation (water content),
    GC, HPLC, GPC, pyrolytic lignin,
    TAN, stability test based on viscosity

-For use as burner fuel

Chemical characterization techniques: methods that give info on chemical species or functional groups
Overview of Standardization Work

• Round Robin
  o Successful validation of chemical characterization techniques for bio-oil

• Techniques validated:
  o Gas Chromatography / Mass Spectrometry (GC/MS)
  o Carboxylic acid titration (CAN/TAN)
  o Carbonyl titration
  o $^{31}$P Nuclear magnetic resonance (NMR)
Bio-oil Sample

- Produced in 2010 at NREL in Pilot Plant\(^1\)
  - Oak, 500 °C
  - Not hot gas filtered
  - Have large quantity
  - Used for method development and validation

- Aging Test
  - 80 °C, 24 hours
  - 2.1% viscosity change
    - Very small change
    - *Oil stabilized during storage*

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<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>C (wt%)</td>
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</tr>
<tr>
<td>H (wt%)</td>
<td>6.8</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>0.07</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>48.6</td>
</tr>
<tr>
<td>S (wt%)</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Water (wt%)</td>
<td>23.1</td>
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<tr>
<td>Insoluble solids (wt%)</td>
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</tr>
<tr>
<td>K (ppm)</td>
<td>79</td>
</tr>
<tr>
<td>Na (ppm)</td>
<td>127</td>
</tr>
</tbody>
</table>

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

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\(^1\)Baldwin, RM, Feik, CJ, Energy & Fuels 27 (2013) 3224-3238
GC/MS – Quantification of Volatiles

- Literature survey: variety of columns, dimensions, and instrument parameters
- Mid-polar column gave best results
  - 14% (cyanopropoyl-phenyl)-PDMS
  - 60 m x 250 µm internal diameter, 0.25 µm film thickness
- Over 100 compounds identified
  - 31 calibrated & quantified
    - 22 wt% of sample
- 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

<table>
<thead>
<tr>
<th>Tentative ID</th>
<th>% Area</th>
<th>%</th>
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<td>Levoglucosan</td>
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<td>4.3</td>
</tr>
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<td>Acetol</td>
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<td>1.1</td>
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<td>Hydroxyacetaldehyde</td>
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<td>Furfural</td>
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</tr>
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<td>Catechol</td>
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<td>0.38</td>
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<tr>
<td>Syringol</td>
<td>1.3</td>
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<td>1.2</td>
<td>0.22</td>
</tr>
<tr>
<td>5-Hydroxymethylfurfural</td>
<td>1.2</td>
<td>0.32</td>
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<tr>
<td>2(5H)-Furanone</td>
<td>0.8</td>
<td>0.26</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>0.7</td>
<td>0.39</td>
</tr>
<tr>
<td>4-Ethylguaiacol</td>
<td>0.7</td>
<td>0.04</td>
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<td>Guaiacol</td>
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<td>0.08</td>
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<td>Creosol</td>
<td>0.6</td>
<td>0.07</td>
</tr>
<tr>
<td>2-Cyclopenten-1-one</td>
<td>0.5</td>
<td>0.08</td>
</tr>
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</table>
**GC/MS Validation**

- Sample A = Sample B
- Common (purchased) calibration standards
- 21/31 compounds less than 20% RSD\(^1\)
  - Variabilities seem high, but comparable to other standard methods (EPA 8270D)
- 10/31 > 20%
  - In most cases, high variation due to one lab reporting high/low
  - In most cases, compounds with high variability were present at lower concentrations

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample A average (µg/mL)</th>
<th>Variability A (%RSD)</th>
<th>Sample B average (µg/mL)</th>
<th>Variability B (%RSD)</th>
<th>Notes</th>
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<tbody>
<tr>
<td>Levoglucosan</td>
<td>83750</td>
<td>15%</td>
<td>81512</td>
<td>12%</td>
<td>Labs 3, 4 and 5 unable to produce linear calibration with R(^2) &lt; 0.99</td>
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<tr>
<td>Glycolaldehyde</td>
<td>47651</td>
<td>22%</td>
<td>51423</td>
<td>22%</td>
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<tr>
<td>Acetic Acid</td>
<td>44703</td>
<td>23%</td>
<td>47016</td>
<td>14%</td>
<td>Lab 4 Sample A reported value 50% of other labs reporting</td>
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<td>Acetol</td>
<td>12637</td>
<td>17%</td>
<td>12359</td>
<td>16%</td>
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<tr>
<td>Catechol</td>
<td>4057</td>
<td>38%</td>
<td>3313</td>
<td>51%</td>
<td>Lab 3 &lt; LOQ</td>
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<td>Propanoic acid</td>
<td>3805</td>
<td>14%</td>
<td>3925</td>
<td>12%</td>
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<tr>
<td>Furfural</td>
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<td>15%</td>
<td>3649</td>
<td>13%</td>
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<tr>
<td>5-Hydroxymethylfurfural</td>
<td>3239</td>
<td>24%</td>
<td>3217</td>
<td>23%</td>
<td></td>
</tr>
<tr>
<td>2(5)-Furanone</td>
<td>2519</td>
<td>12%</td>
<td>2498</td>
<td>12%</td>
<td></td>
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<tr>
<td>3-Methyl-1,2-cyclopentanediene</td>
<td>2036</td>
<td>19%</td>
<td>2098</td>
<td>18%</td>
<td></td>
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<tr>
<td>Syringol</td>
<td>1471</td>
<td>19%</td>
<td>1438</td>
<td>18%</td>
<td></td>
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<tr>
<td>Butanoic acid</td>
<td>1375</td>
<td>16%</td>
<td>1439</td>
<td>16%</td>
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<tr>
<td>Syringaldehyde</td>
<td>1149</td>
<td>13%</td>
<td>1163</td>
<td>6%</td>
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<td>777</td>
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<td>2-Cyclopenten-1-one</td>
<td>747</td>
<td>18%</td>
<td>750</td>
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<tr>
<td>Guaiacol</td>
<td>731</td>
<td>24%</td>
<td>738</td>
<td>25%</td>
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<td>Acetosyringone</td>
<td>721</td>
<td>9%</td>
<td>715</td>
<td>7%</td>
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<td>5-Methylfurfural</td>
<td>716</td>
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<td>719</td>
<td>17%</td>
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<tr>
<td>Creosol</td>
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<td>522</td>
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<td>Hydroquinone</td>
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<td>28%</td>
<td>514</td>
<td>26%</td>
<td></td>
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<tr>
<td>Phenol</td>
<td>498</td>
<td>32%</td>
<td>500</td>
<td>33%</td>
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<td>Apocynin</td>
<td>460</td>
<td>14%</td>
<td>460</td>
<td>13%</td>
<td></td>
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<tr>
<td>o-Cresol</td>
<td>323</td>
<td>15%</td>
<td>318</td>
<td>15%</td>
<td>Labs 5 &lt; LOQ</td>
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<td>4-Ethylguaiacol</td>
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<td>12%</td>
<td>315</td>
<td>15%</td>
<td>Labs 1 and 5 &lt; LOQ</td>
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<td>3-Hydroxy-2-butanol</td>
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<td>315</td>
<td>17%</td>
<td>Labs 1 and 5 &lt; LOQ</td>
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<td>19%</td>
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<td>2,4-Xylenol</td>
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<td>278</td>
<td>31%</td>
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<td>p-Cresol</td>
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<td>247</td>
<td>25%</td>
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<tr>
<td>m-Cresol</td>
<td>&lt;LOQ</td>
<td>NA</td>
<td>&lt;LOQ</td>
<td>NA</td>
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</tr>
</tbody>
</table>

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\(^1\)Ferrell et al. *Biofuels, Bioproducts & Biorefining* 10 (2016) 496-507
Carboxylic Acid Titration (CAN/TAN)

- 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)

- Intra-laboratory results with bio-oil:
  - 1\(^{st}\) endpoint: CAN = 81 ± 1 mg KOH/g
  - 2\(^{nd}\) endpoint: TAN = 187 ± 2 mg KOH/g
  - Phenolic content PhAN = TAN – CAN = 99 ± 1 mg KOH/g

### CAN/TAN Validation

#### CAN numbers reliable

#### Problems with TAN identification

- Method robust with phenolic model compounds
- Large # of phenolics in bio-oil leads to multiple endpoints for TAN
- Method needs further refinement before TAN numbers can be trusted

<table>
<thead>
<tr>
<th>Endpoint</th>
<th>Sample</th>
<th>Lab1</th>
<th>Lab2</th>
<th>Lab3</th>
<th>Lab4</th>
<th>Lab5</th>
<th>Average</th>
<th>%RSD</th>
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<tr>
<td>CAN</td>
<td>A</td>
<td>78.8</td>
<td>83.1</td>
<td>81.8</td>
<td>84.4</td>
<td>89.0</td>
<td>83.5</td>
<td>4.5</td>
</tr>
<tr>
<td>TAN</td>
<td>A</td>
<td>184.3</td>
<td>181.0</td>
<td>N/A</td>
<td>181.7</td>
<td>N/A</td>
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<tr>
<td>CAN</td>
<td>B</td>
<td>81.1</td>
<td>82.3</td>
<td>80.3</td>
<td>82.9</td>
<td>90.0</td>
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<td>4.7</td>
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<td>B</td>
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<td>188.8</td>
<td>N/A</td>
<td>180.9</td>
<td>N/A</td>
<td>184.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Units = mg KOH/g
Carbonyl Titration (Nicolaides method)

- Carbonyls in bio oil:
  - Instability 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

\[
\begin{align*}
\text{R}_1 \text{C}=\text{O} \text{R}_2 + \text{H}_2\text{NOH} \cdot \text{HCl} & \rightarrow \text{R}_1\text{N}=\text{OH} \cdot \text{R}_2 + \text{HCl} + \text{H}_2\text{O} \\
\end{align*}
\]

**Results**

3.33 ± 0.11 mmol C=O/g
Carbonyl Titration (Faix method)

- Two methods tested, modified from existing methods in literature
  - Nicolaides: this is the method typically used for bio-oils\(^1\)
    - 12-18 hours of stirring, titration at room temperature
  - Faix: lesser known method\(^2\), developed at NREL for bio-oils
    - 2 hours stirring time, titration at 80 °C

- Results show that the Nicolaides method as-used significantly underestimates carbonyls in bio-oil\(^3\)
  - Results consistent with consistent stirring time

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\(^1\) Nicolaides, GM. MAsc Thesis, University of Waterloo, 1984
\(^3\) Black S. and Ferrell J. Energy & Fuels 30 (2016) 1071-1077
Carbonyl Titration Validation

- First time carbonyl titration tested in Round Robin
- In addition to being more accurate and easier to perform, the Faix method is more reliable
  - Carbonyl quantification important (upgrading, stability)
  - Could lead the way to a stability test based on carbonyl titration
    - Commonly-used stability test based on viscosity is not very reliable

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
<th>Lab1</th>
<th>Lab2</th>
<th>Lab3</th>
<th>Lab4</th>
<th>Lab5</th>
<th>Average</th>
<th>% RSD</th>
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<td>3.33</td>
<td>2.70</td>
<td>2.87</td>
<td>2.83</td>
<td>3.41</td>
<td>3.03</td>
<td>10.6</td>
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<td>Faix</td>
<td>A</td>
<td>3.59</td>
<td>3.98</td>
<td>3.84</td>
<td>3.96</td>
<td>N/A</td>
<td>3.84</td>
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<td>3.35</td>
<td>3.26</td>
<td>2.88</td>
<td>2.79</td>
<td>3.42</td>
<td>3.14</td>
<td>9.1</td>
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<td>B</td>
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<td>4.06</td>
<td>3.90</td>
<td>4.04</td>
<td>N/A</td>
<td>3.89</td>
<td>6.1</td>
</tr>
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</table>

Units = mol C=O/kg
• Importance: hydroxyl groups present in functionalities relevant to stabilization and upgrading of bio-oils
• Can quantitatively determine¹:
  – Phenols
  – Aliphatic alcohol
  – Carboxylic acids

\[
\text{ROH} = \begin{array}{c}
\text{Phenol} \\
\text{Aliphatic alcohol} \\
\text{Carboxylic acid}
\end{array}
\]

\[
\begin{align*}
\text{POCl}_3 + R-\text{OH} + \text{NEt}_3 & \rightarrow \text{PO}^\ominus \text{OR} + [\text{HNEt}_3]\text{Cl} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Chemical shift, ppm</th>
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<tbody>
<tr>
<td>Aliphatic -OH</td>
<td>152 - 145</td>
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<tr>
<td>Phenolic -OH</td>
<td>138 – 145</td>
</tr>
<tr>
<td>Carboxylic -OH</td>
<td>134.6 - 136</td>
</tr>
</tbody>
</table>

¹ Ben H. and Ferrell J. RSC Advances 6 (2016) 17567-17573
### Validation of $^{31}$P NMR

<table>
<thead>
<tr>
<th>-OH Group</th>
<th>Sample</th>
<th>Lab1</th>
<th>Lab2</th>
<th>Lab3</th>
<th>Lab4</th>
<th>Lab5</th>
<th>Average</th>
<th>%RSD</th>
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<tbody>
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<td>A</td>
<td>4.99</td>
<td>5.40</td>
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<td>5.21</td>
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<td>A</td>
<td>2.39</td>
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<td>2.20</td>
<td>1.91</td>
<td>2.39</td>
<td>2.27</td>
<td>9.9</td>
</tr>
<tr>
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<td>A</td>
<td>1.19</td>
<td>1.22</td>
<td>1.11</td>
<td>1.42</td>
<td>0.99</td>
<td>1.19</td>
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<td>5.30</td>
<td>4.97</td>
<td>5.35</td>
<td>5.12</td>
<td>5.19</td>
<td>2.9</td>
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<tr>
<td>Phenolic</td>
<td>B</td>
<td>2.46</td>
<td>2.49</td>
<td>2.60</td>
<td>2.02</td>
<td>2.46</td>
<td>2.41</td>
<td>9.3</td>
</tr>
<tr>
<td>Carboxylic</td>
<td>B</td>
<td>1.25</td>
<td>1.17</td>
<td>1.30</td>
<td>1.59</td>
<td>0.99</td>
<td>1.26</td>
<td>17.4</td>
</tr>
</tbody>
</table>

Units = mmol OH/g

- First time NMR tested in bio-oil Round Robin
- Aliphatic and phenolic OH groups can be quantified reliably
- Carboxylic OH groups
  - Higher variability: ~15%
  - Present at ~ half the concentration of phenolics
Conclusions

• **Techniques validated:**
  - Gas Chromatography / Mass Spectrometry (GC/MS)
    - 21/31 compounds < 20% variability
  - Carboxylic acid titration (CAN/TAN)
    - CAN very reliable, 5% variability
  - Carbonyl titration
    - Faix method very reliable, 5% variability
  - $^{31}$P NMR
    - Aliphatic & Phenolic groups < 10% variability
    - Carboxylic groups ~15% variability

Successful validation of *chemical characterization* techniques for bio-oil
Acknowledgments

NREL
Earl Christensen
Stuart Black
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Sarah Burton
Teresa Lemmon
Marie Swita
Heather Job
Doug Elliot

Round Robin Partners
Washington State University
- Manuel Garcia-Perez
- Filip Stankovikj

ORNL
- Jim Keiser
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Analytical Methods:
http://www.nrel.gov/bioenergy/bio-oil-analysis.html

Method validation publication:
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Carbonyl titration publication:
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$^{31}$P NMR publication:
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