Bio-based Carbon Content Test Method Evaluation

October 19, 2018
Recent Publication

**Biobased carbon content quantification through AMS radiocarbon analysis of liquid fuels** (Haverly, Fenwick, Patterson, Slade)

- The data included in this presentation has been peer-reviewed and accepted for publication in Fuel
- Published online with the following unique link: [https://doi.org/10.1016/j.fuel.2018.10.081](https://doi.org/10.1016/j.fuel.2018.10.081)
- Will appear in the February 1, 2019 issue of Fuel
- Published with open access rights – free to any who wish to review it
ASTM D6866 evaluation study summary

- Single-blind, randomized sample set
- 15 different sample types
  - 2 different petroleum diesels
  - 3 different biomass-based diesels produced in 2017
  - 13 different renewable content levels
- 120 total samples tested
  - Each lab received duplicates of each of the 15 different sample types
  - Four labs were included in the study

<table>
<thead>
<tr>
<th>Actual weight% Biobased Carbon</th>
<th>Average measured weight% Biobased Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.47%</td>
<td>0.43%</td>
</tr>
<tr>
<td>0.99%</td>
<td>1.01%</td>
</tr>
<tr>
<td>1.50%</td>
<td>1.46%</td>
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<tr>
<td>1.98%</td>
<td>1.95%</td>
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<tr>
<td>2.46%</td>
<td>2.43%</td>
</tr>
<tr>
<td>2.95%</td>
<td>2.90%</td>
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<tr>
<td>3.35%</td>
<td>3.39%</td>
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<td>3.95%</td>
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<td>4.33%</td>
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<td>4.93%</td>
<td>4.93%</td>
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<tr>
<td>5.53%</td>
<td>5.51%</td>
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<tr>
<td>7.41%</td>
<td>7.51%</td>
</tr>
<tr>
<td>9.99%</td>
<td>9.97%</td>
</tr>
</tbody>
</table>
Graphical comparison with actual values

- Eight test results per point
  - Average values with error bars (standard error)
- Excellent correlation
  - Slope = 1.00
  - Correlation coefficient = 0.999
  - Results for individual labs are similar
Residuals confirm accuracy

- Plot depicts the residual of each individual test result compared to its actual bio-based carbon content.
- Equal distribution of results indicates no bias.
Duplicate testing improved results

- Plot depicts the residual of the average of each duplicate test compared to its actual bio-based carbon content.
- Averaging duplicate test results improved accuracy.
- Duplicate residuals are more tightly grouped around zero.
Statistical performance measures

- Evaluating each data point from each lab as a single test resulted in favorable statistical measures – significant improvement over measures published in ASTM D6866
- Averaging the duplicates from each lab resulted in even more accurate and precise measurements

<table>
<thead>
<tr>
<th></th>
<th>Single Tests</th>
<th>Average of Duplicate Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy (absolute)</td>
<td>0.26%</td>
<td>0.18%</td>
</tr>
<tr>
<td>Precision (relative)</td>
<td>0.26%</td>
<td>0.18%</td>
</tr>
<tr>
<td>Limit of Detection</td>
<td>0.40%</td>
<td>0.40%</td>
</tr>
</tbody>
</table>
Statistical measures were determined using common methods

• Accuracy:
  – Determined as 2 times the standard deviation of all of the sample residuals (not inclusive of blanks due to blank correction)
  – 95% confidence that a test result will fall within this difference from the actual biogenic carbon content

• Precision:
  – Determined as 2 times the pooled standard deviation of all 14 biogenic carbon levels tested
  – 95% confidence that any two given test results for the same sample will fall within this difference from one another

• Limit of Detection:
  – Determined as 3 times the standard deviation of all of the blanks
  – 99.7% confidence that a value is not zero
Data processing

• Percent modern carbon (pMC) results for all 120 samples were sent to REG

• Two corrections were applied to raw test results
  1. Bio-based carbon year assignment
     • Necessary, because atmospheric $^{14}$C content is decreasing over time
     • The $^{14}$C content in a sample is determined by the year atmospheric carbon was fixed in plant biomass
  2. Blank correction
     • Blank = sample with no bio-based carbon (e.g. petroleum diesel)
     • Blank result is subtracted from each test result (lab-specific)
     • Accounts for cumulative systematic error
     • A common practice in scientific studies

• Carbon year 2015 was used for these 2017 renewable fuels
Carbon year probability distributions

- Monte Carlo analysis was used to determine renewable carbon life cycle probability distribution
- Time it takes for carbon to come out of the atmosphere and make it into a renewable fuel
- Most feedstocks showed a mean life cycle of ~ 2 years
Carbon year assignment

- Roughly linear decay of atmospheric $^{14}\text{C}$ levels necessitates a simple correction to more accurately determine renewable carbon content determination
- Annual adjustment factors are published in the ASTM method D6866-16
- Measured values showed the best agreement with actual values for 2015

![Regression Slope vs Reference Year Graph](chart.png)

Notes:

Source:
## Relevant Publications

<table>
<thead>
<tr>
<th>Ref #</th>
<th>Citation</th>
<th>Radiocarbon Method</th>
<th>Blank Correction?</th>
</tr>
</thead>
</table>