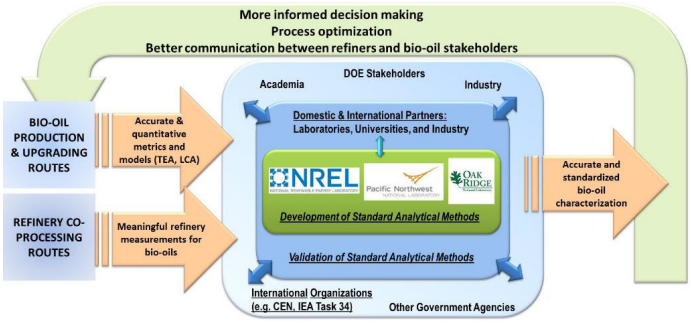
Standard Analytical Methods for Pyrolysis Bio-oils

Jack R. Ferrell III[1]*, Earl D. Christensen[1], Mariefel V. Olarte[2], Jiheon Jun[3], Dino Sulejmanovic[3], Joel Miscall[1], Jessica Olstad[1], Rebecca Jackson[1], Renee M. Happs[1], Anne E. Harman-Ware[1], Bennett Addison[1], Marie Swita[2], Teresa Lemmon[2], Ruoshui Ma[2], Joshua Taylor[2], Asanga B. Padmaperuma[2], Charles Doll[2], Andrew Plymale[2], Christopher Thompson[2], Matthew O'Hara[2], Raynella M. Connatser[3], James R. Keiser[3], and Samuel A. Lewis[3].

[1]National Renewable Energy Laboratory (NREL), Golden, CO [2]Pacific Northwest National Laboratory (PNNL), Richland, WA [3]Oak Ridge National Laboratory, Oak Ridge, TN



Overview

- Collaborative effort between NREL, PNNL, ORNL
- Methods developed/standardized for fast pyrolysis (FP), catalytic fast pyrolysis (CFP), and hydrothermal liquefaction (HTL) samples, and their upgraded products
- Standard analytical methods shared as Laboratory Analytical Procedures (LAPs)
  - **12 LAPs published: GC-MS, CAN/TAN, Carbonyl Titration, ^{31}P NMR, ^{13}C NMR, Accelerated Aging, ICP, CHN, Karl Fischer, Folin-Ciocalteu, Corrosivity Screening, Biogenic Carbon by LSC**
  - http://www.nrel.gov/bioenergy/bio-oil-analysis.html
- ASTM E3146-20: Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration

Aging

- Utilize carbonyl titration, more reliable measurement than viscosity
- Samples held at room temperature and in cold storage for > 3 years
- Existing aging protocol (80C/24h) too severe, ages samples more than 3 years of room temperature storage
- New aging protocol: 80C/2h, correlates to 1-3 months at room temperature

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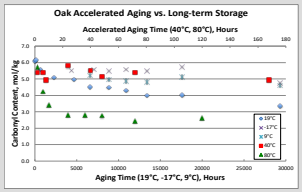
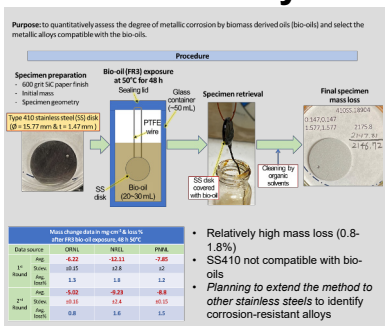


**fast pyrolysis bio-oils only*

Corrosivity



- Relatively high mass loss (0.8-1.8%)
- SS410 not compatible with bio-oils
- *Planning to extend the method to other stainless steels* to identify corrosion-resistant alloys

Phenol Content

- In raw bio-oils, phenols react with aldehydes, leading to instability
- Phenols are recalcitrant species during bio-oil hydroprocessing
- Modified Folin-Ciocalteu (FC) methods
  - Colorimetric method
  - Replaced gallic acid (wine-relevant) with guaiacol (bio-oil relevant) as reference compound
- Developed two methods for equipment adaptability: cuvette and well plate readers (high throughput) for *fast pyrolysis bio-oils*
  - Cuvette method showed good inter-laboratory repeatability (≤6% RSD):

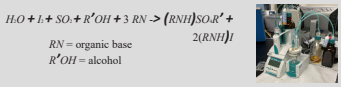
	Well Plate FC Ave	Well Plate RSD	Cuvette FC Ave	Cuvette FC RSD
Sample 1	18.1	5.1%	17.9	2.8%
Sample 2	18.3	5.8%	18.1	2.6%

- Well plate method was only tested in one laboratory and showed promising repeatability (≤ 5% RSD):

	Inter-lab FC Ave	Inter-lab FC RSD
Sample 1	17.0	4.2 %
Sample 2	17.1	5.0 %

Karl Fischer

- Volumetric Karl Fischer (KF) titration for water content
- Water typically the most abundant single component in FP bio-oils
- Procedure based on ASTM E203, but has been written specifically for bio-oil samples
- Both aqueous and organic phases can be measured, for both FP and CFP bio-oils
- Used alongside CHN to determine total carbon and oxygen content



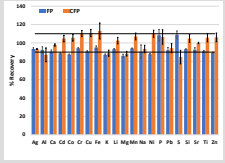
Replicate analyses of FP, CFP, and aqueous phase of CFP were conducted to provide interim intra-laboratory precision. Thirty independent analyses were conducted on each sample over the course of three days. The resultant **95% confidence interval** is as follows: r = (X * 0.022) + 0.67
r = repeatability, the difference between replicate analyses
X = the average mass % water of two replicate analyses

ICP

- Concentrations of inorganic elements is a key quality metric
  - Certain inorganics impact upgrading and product quality
- Inductively coupled plasma optical emission spectroscopy (ICP-OES) is employed to measure elements of interest in FP and CFP bio-oils
- Developed a direct organic ICP method using diglyme solvent
- *Microwave-assisted digestion ICP method also developed*
- Organic ICP can detect: Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, P, Pb, Pt, S, Si, Sr, Ti, Zn, Y

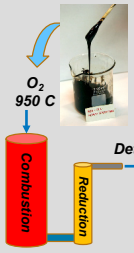
Insoluble in hydrocarbon solvent

Miscible with diglyme



CHN

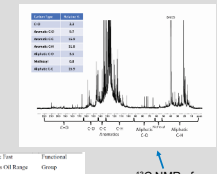
- Elemental analysis via combustion – CHN, O by difference (KF)
- Used to track carbon balance of production processes
- Oxygen content used to track upgrading effectiveness



- FP and CFP bio-oils and their aqueous phases, and distillate range hydrotreated products in scope
- Procedure similar to ASTM D5291, but sample preparation, instrument parameters, and quality control have been optimized for bio-oils

^{13}C NMR

- Method optimized for quantification of different carbons in different functional groups in FP and CFP bio-oils



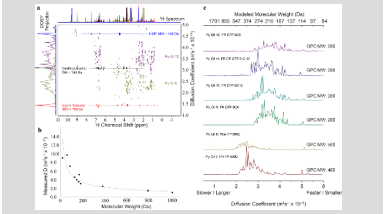
^{13}C NMR of a CFP bio-oil

Type of Carbon (Functional Groups)	Test Pyrolysis Oil Range (ppm)	Catalytic Test Pyrolysis Oil Range (ppm)	Functional Group Structure
Carboxyl*	230.0 – 166.5	230.0 – 166.5	
Aromatic C-O	166.5 – 142.0	166.5 – 142.0	
Aromatic C-C	142.0 – 125.0	142.0 – 132.0	
Aromatic C-H	125.0 – 95.8	132.0 – 95.8	
Aliphatic C-O	95.8 – 60.8	95.8 – 60.8	
Methoxyl	60.8 – 55.2	60.8 – 55.2	
Aliphatic C-C**	55.2 – 0.0	55.2 – 0.0	

*Peaks may be overlapped with one of the Oxoacyl peaks at ~174.5 ppm. **Peaks may be overlapped with one of the Oxoacyl peaks at ~21.74 ppm

Chemical shift assignment ranges for FP & CFP bio-oils

DOSY NMR



^{1}H Diffusion Ordered Spectroscopy (DOSY) NMR data used to estimate molecular weight distributions of various pyrolysis oils from a set of 12 model compounds. **a.** Overlay of five different two-dimensional (2D) DOSY spectra showing the ^{1}H spectrum on the horizontal axis and the NMR-measured diffusion coefficient for each resolved ^{1}H signal on the vertical axis. Shown are three model compounds: 5-hydroxymethylfurfural (blue, MW = 126 Da); coniferyl alcohol (black, MW = 180 Da); and a synthetic lignin tetramer (red, MW 784 Da). Also shown are 2D DOSY plots for pyrolysis oils 8 (gold, Pine FP 500C) and 12 (FR CFP BCB). Diffusion information is illustrated as 1D DOSY projections on the left with color-coded traces. **b.** Measured diffusion coefficient versus known molecular weight for 12 model compounds, and the corresponding best fit model (dotted line), which can then be used to translate measured diffusion coefficient with estimated molecular weight. **c.** DOSY projections for 6 unique pyrolysis oils. For comparison, molecular weight estimates previously estimated using Gel Permeation Chromotography (GPC) are indicated for each oil. Results suggest a molecular weight distribution of roughly 300 – 600 Da for fast pyrolysis oils 7 and 8 (500C) while all CFP oils reveal similar MW distributions of roughly 100-300 Da.

Biogenic C by LSC

- **Goal** - develop a method to quantitatively measure the amount of biogenic carbon in a blended product liquid
- Liquid scintillation counting (LSC) was chosen due to affordability, portability, simple sample preparation, and acceptable accuracy
- Accelerator Mass Spectrometry (AMS) commonly used for ^{14}C detection
  - AMS is more sensitive than LSC, but costly and time consuming
- Developed and identified two LSC methods using a colored matrix (fossil fuel) that show less than 10% difference compared to AMS analysis.
- Quench curve method:

Sample	AMS (wt%)	2 hr LSC (wt%)	% difference	5 hr LSC (wt%)	% difference
1 wt% gasoline	0.93	1.05	12.9%	0.92	-1.5%
1 wt% jet	1.12	1.77	57.9%	1.21	8.1%
1 wt % diesel	1.35	1.60	18.3%	1.33	-1.7%

- Direct ^{14}C spiking method:

Sample	AMS (wt%)	2 hr LSC (wt%)	% difference	5 hr LSC (wt%)	% difference
1 wt% gasoline	0.93	1.08	16.1%	0.95	2.2%
1 wt% jet	1.12	1.72	53.6%	1.12	0.0%
1 wt % diesel	1.35	1.63	20.7%	1.29	-4.4%

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