NREL
Transforming ENERGY

Bio-oil Analytical Method Standardization with ASTM International

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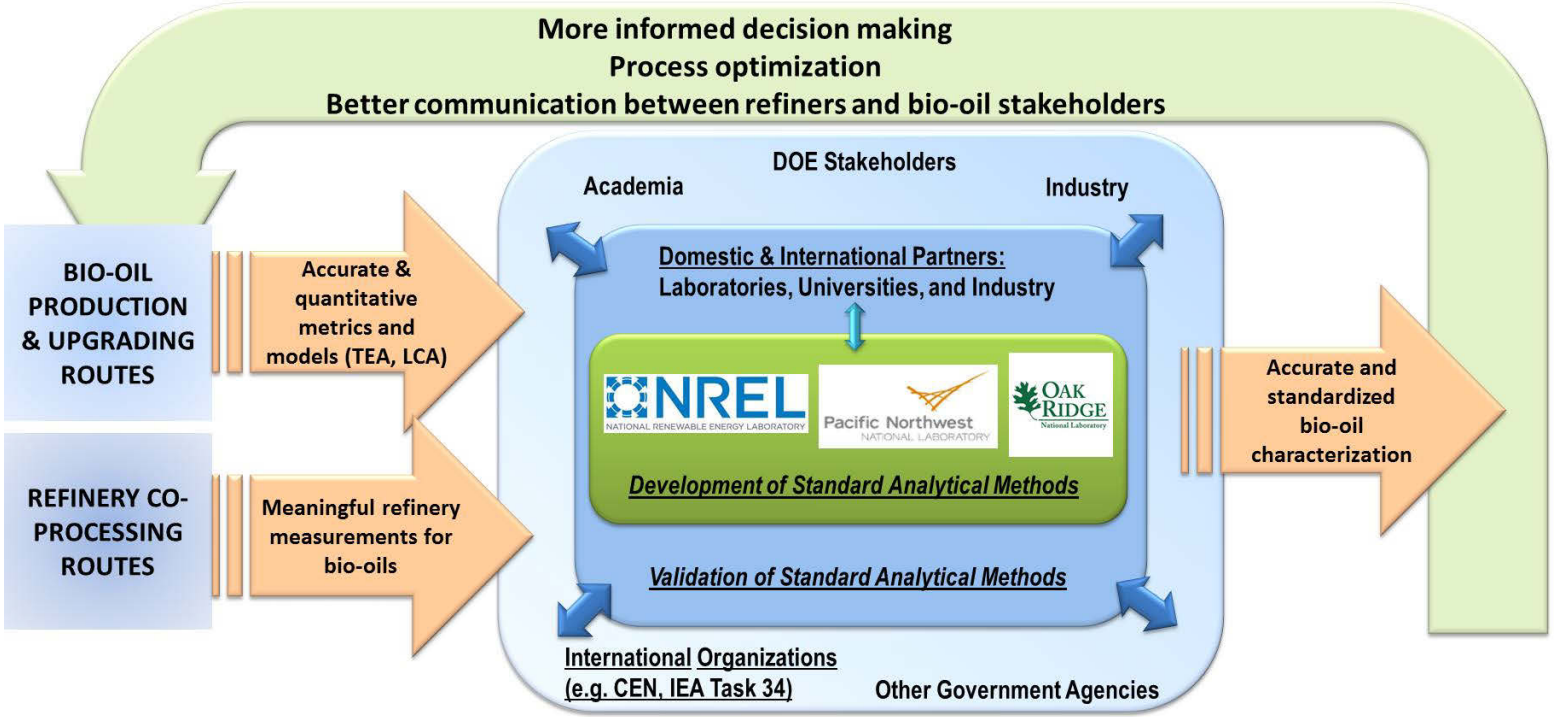
Development and Standardization of Techniques for Bio-oil Characterization



Standards in Fuel Production

- Feedstock: crude oil assays inform refineries/producers
  - Sweet/sour, density, distillation, carbon residue, acid number, sulfur, metals…
- Products: fuel specifications inform engine OEMs/users
  - Distillation, octane/cetane, viscosity, cloud point, stability…

Standardized techniques and specifications provide a common language

Biofuel Standards

- D4806 – Ethanol blendstock
- D5798 – Ethanol blends between 51 % and 83%, flex fuel
  - Up to 15% ethanol (and other oxygenates) covered under gasoline spec, D4814
- D7862 – Biobutanol blendstock
- D6751 – Biodiesel blendstock, mono-alkyl esters from fats an oils (FAME)
- D7467 – Biodiesel blends between 6% and 20%
  - Up to 5% biodiesel covered under diesel spec, D975
- D7566 – Jet fuel containing synthetic hydrocarbons; HT fats and oils, Fischer-Tropsch, alcohol to jet…
- D7544 – Pyrolysis oil in industrial burners (limited scope)

- ***Bio-oil standards not well established through ASTM***

Detailed Product Requirements

Quality metrics

How to measure

Limits

TABLE 1 Detailed Requirements for Biodiesel (B100) Blend Stocks

Property	Test Method[A]	Grade No. 1-B S15	Grade No. 1-B S500	Grade No. 2-B S15	Grade No. 2-B S500
Sulfur,[B] % mass (ppm), max	D5453	0.0015 (15)	0.05 (500)	0.0015 (15)	0.05 (500)
Cold soak filterability, seconds, max	D7501	200	200	360[C]	360[C]
Monoglyceride content, % mass, max	D6584	0.40	0.40	...	...
			Requirements for All Grades		
Calcium and Magnesium, combined, ppm (µg/g), max	EN 14538	5	5	5	5
Flash point (closed cup), °C, min	D93	93	93	93	93
Alcohol control					
One of the following shall be met:					
1. Methanol content, mass %, max	EN 14110	0.2	0.2	0.2	0.2
2. Flash point, °C, min	D93	130	130	130	130
Water and sediment, % volume, max	D2709	0.050	0.050	0.050	0.050
Kinematic viscosity,[D] mm²/s, 40 °C	D445	1.9-6.0	1.9-6.0	1.9-6.0	1.9-6.0
Sulfated ash, % mass, max	D874	0.020	0.020	0.020	0.020
Copper strip corrosion, max	D130	No. 3	No. 3	No. 3	No. 3
Cetane number, min	D613	47	47	47	47
Cloud point,[E] °C	D2500	Report	Report	Report	Report
Carbon residue,[F] % mass, max	D4530	0.050	0.050	0.050	0.050
Acid number, mg KOH/g, max	D664	0.50	0.50	0.50	0.50
Free glycerin, % mass, max	D6584	0.020	0.020	0.020	0.020
Total glycerin, % mass, max	D6584	0.240	0.240	0.240	0.240
Phosphorus content, % mass, max	D4951	0.001	0.001	0.001	0.001
Distillation temperature, Atmospheric equivalent temperature, 90 % recovered, °C, max	D1160	360	360	360	360
Sodium and Potassium, combined, ppm (µg/g), max	EN 14538	5	5	5	5
Oxidation stability, hours, min	EN 15751	3	3	3	3

Product specific methods

[A] The test methods indicated are the approved referee methods. Other acceptable methods are indicated in 5.1.

Approved methods are required to meet spec

[B] Other sulfur limits may apply in selected areas in the United States and in other countries.

[C] For additional cold weather considerations, see Appendix X3.

[D] See X1.3.1. The 6.0 mm²/s upper viscosity limit is higher than petroleum based diesel fuel and should be taken into consideration when blending.

[E] The cloud point of biodiesel is generally higher than petroleum based diesel fuel and should be taken into consideration when blending.

[F] Carbon residue shall be run on the 100 % sample (see 5.1.12).

Who is ASTM International?

- Established in 1898 – Pennsylvania Railroad
- Formerly American Society for Testing and Materials, now ASTM International
- > 12,000 standards, > 30,000 members, ~150 committees

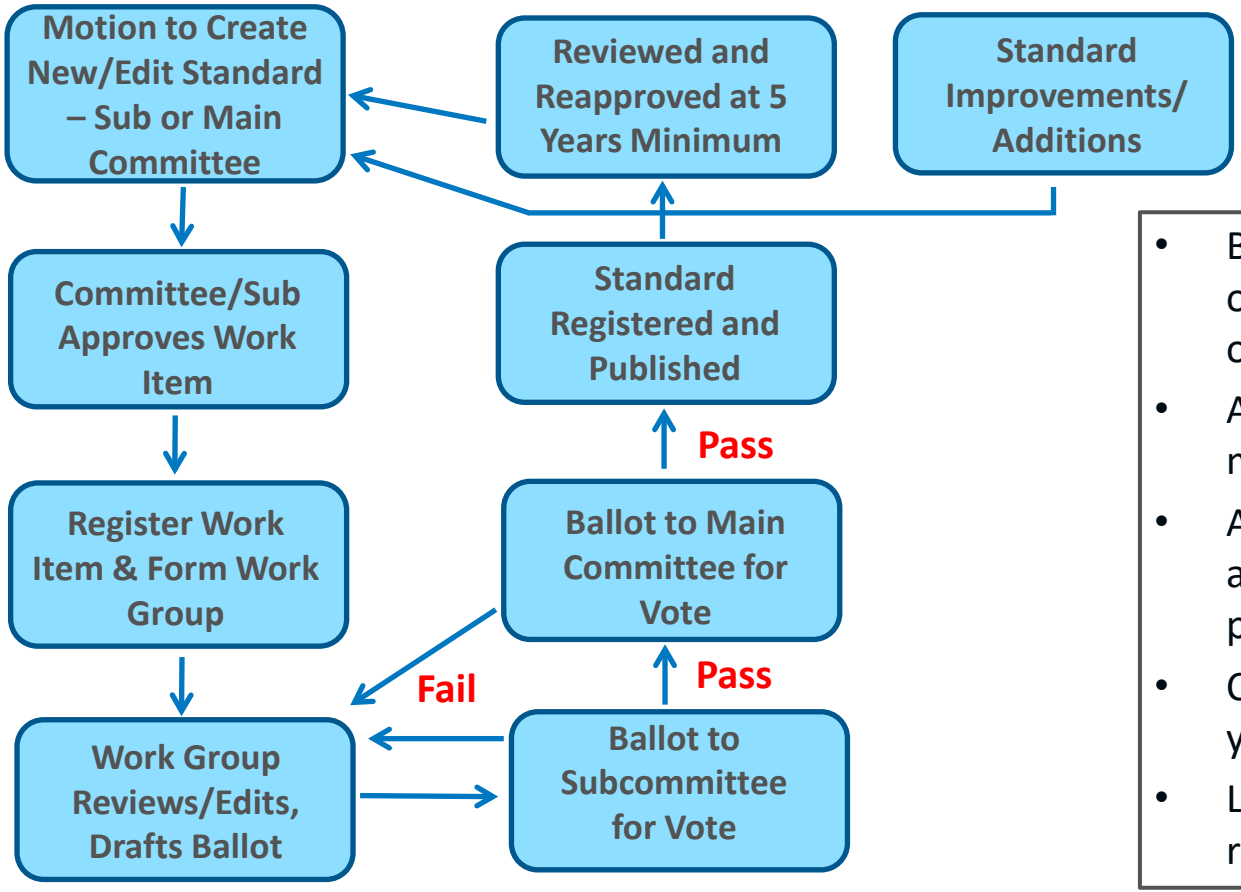
- D02 Committee on Petroleum Products, Liquid Fuels, and Lubricants
- E48 Committee on Bioenergy and Industrial Chemicals from Biomass

  - https://www.astm.org/ABOUT/history_book.html

ASTM Overview

- Voluntary collaboration across industry; producers, consumers, and regulators
  - Goal: reach data driven consensus on quality metrics and methods
  - Thoroughly vetted, reliable, defensible technical standards
- Performance based, not intended to specify formulations
  - ***Fit for purpose***
- Standards enable commerce
  - International product quality & safety specs (state and federal)
  - Trade agreements
- ASTM does not enforce regulations, but enables regulators
- ***ASTM standards facilitate emerging industries***
  - Technical guidelines for quality assurance and thus consumer confidence

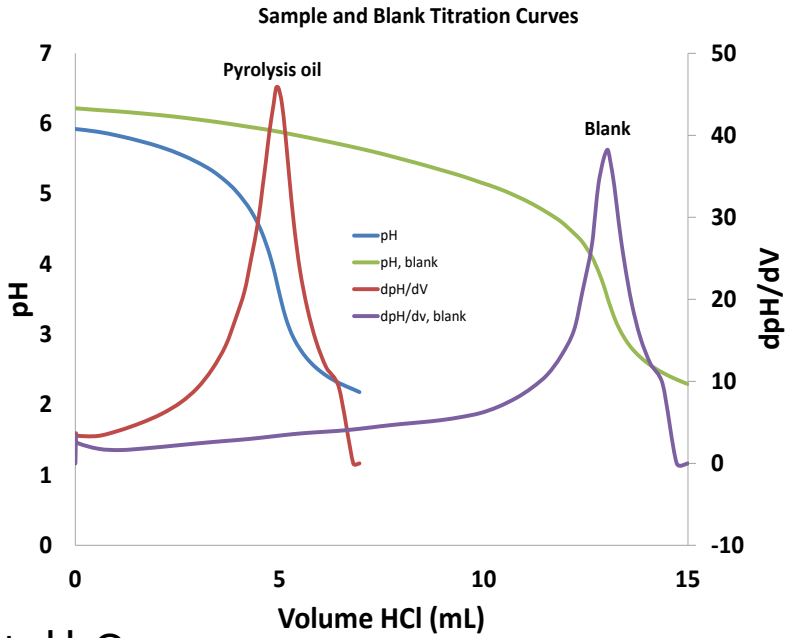
Consensus Process

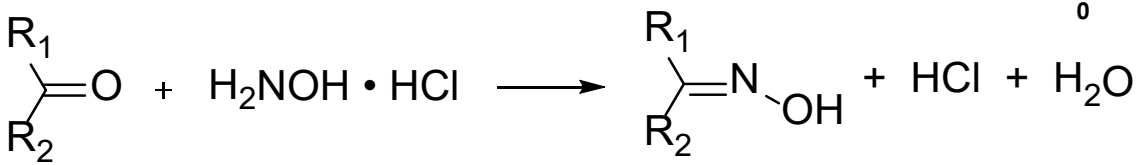


- Balanced voting – one vote per organization per committee, mix of producers and users
- Any member can vote negative; must provide written justification
- All negative votes must be addressed; withdrawn, persuasive, or non-persuasive
- Contentious ballots may take years!
- Living documents – constant review and update

New Standard: Bio-oil Carbonyl Titration

- Carbonyls implicated in instability of pyrolysis oils during storage and hydrotreating
- Titration based on method by Faix et al.





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

ASTM E3146

- Subcommittee E48.05 on Biomass Conversion – ballot passed
- Subcommittee E48 on Bioenergy and Industrial Chemicals from Biomass – one negative vote about definition of fast pyrolysis, withdrawn with agreement definition would be fixed

- Initial method published as E3146-18; ILS required within first 5 years or method withdrawn
- Balloted with improved FP definition per agreement with negative voter, passed and published as E3146-18a
- *First ASTM method for chemical characterization of bio-oils*

ASTM Interlaboratory Study

- Precision and bias determined by ILS
  - E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
  - D6300 Standard Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
- **Reproducibility (R)** – interlaboratory precision; same material different locations; 95% confidence interval between two labs
- **repeatability (r)** – intra-laboratory precision; same material, same operator, same equipment, same day; 95% confidence interval for one person
- Minimum criteria: 6 labs, 3 materials, blind duplicate, must span the range of the test method's scope
  - Absolute bare minima, 8 or more labs recommended in case of outliers

E3146 ILS

- D6300 guidelines
- Scope: fast pyrolysis oils, catalytic pyrolysis oils, and hydrotreated products
- Range: 0.5 to 8 mol/kg carbonyls
- Three materials at three concentrations in blind duplicate – 18 samples per lab
- Base oils spiked with MTBE to create ranges of concentrations
- Sent to 10 labs, 9 reported data

Oil types:	Low (base)	mid	high
Hydrotreated pyrolysis oil (low range)	0.5	1	2
Catalytic pyrolysis oil (mid range)	2.3	5	7
Fast pyrolysis oil (high range)	3.5	6	8

ILS Results

- Method balloted and re-issued as E3146-20, with complete precision statement

$$r = 0.1878(X + 0.15)^{0.35} \text{ mol/kg}$$

$$R = 0.6865(X + 0.15)^{0.35} \text{ mol/kg}$$

X = average of two results

Sample	Average	min	max
HT-Low	0.1	0.0	0.6
HT-Mid	0.5	0.2	0.9
HT-High	1.6	1.2	2.3
CFP-Low	2.9	2.4	3.4
CFP-Mid	5.1	4.5	6.1
CFP-High	6.8	5.8	7.3
FP-Low	3.7	3.4	4.1
FP-Mid	5.6	4.2	7.7
FP-High	7.5	5.6	8.9

ASTM Research Report RR:E48-1000

Next Steps

- Bio-oil assays: CHONS, KF water, ICP metals, TAN, Carbonyls…
- HT products: Fuel properties/applicability of current ASTM specifications for hydrocarbon fuels
- Contaminants: Biomass elements and oxygenates carried through upgrading processes – HT, HC, FCC, etc.
- Fuel quality impacts: Blended fuel properties and combustion quality

Thank you!

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