Accelerated Aging of Fast Pyrolysis Bio-oils

Stuart Black and Jack R. Ferrell III

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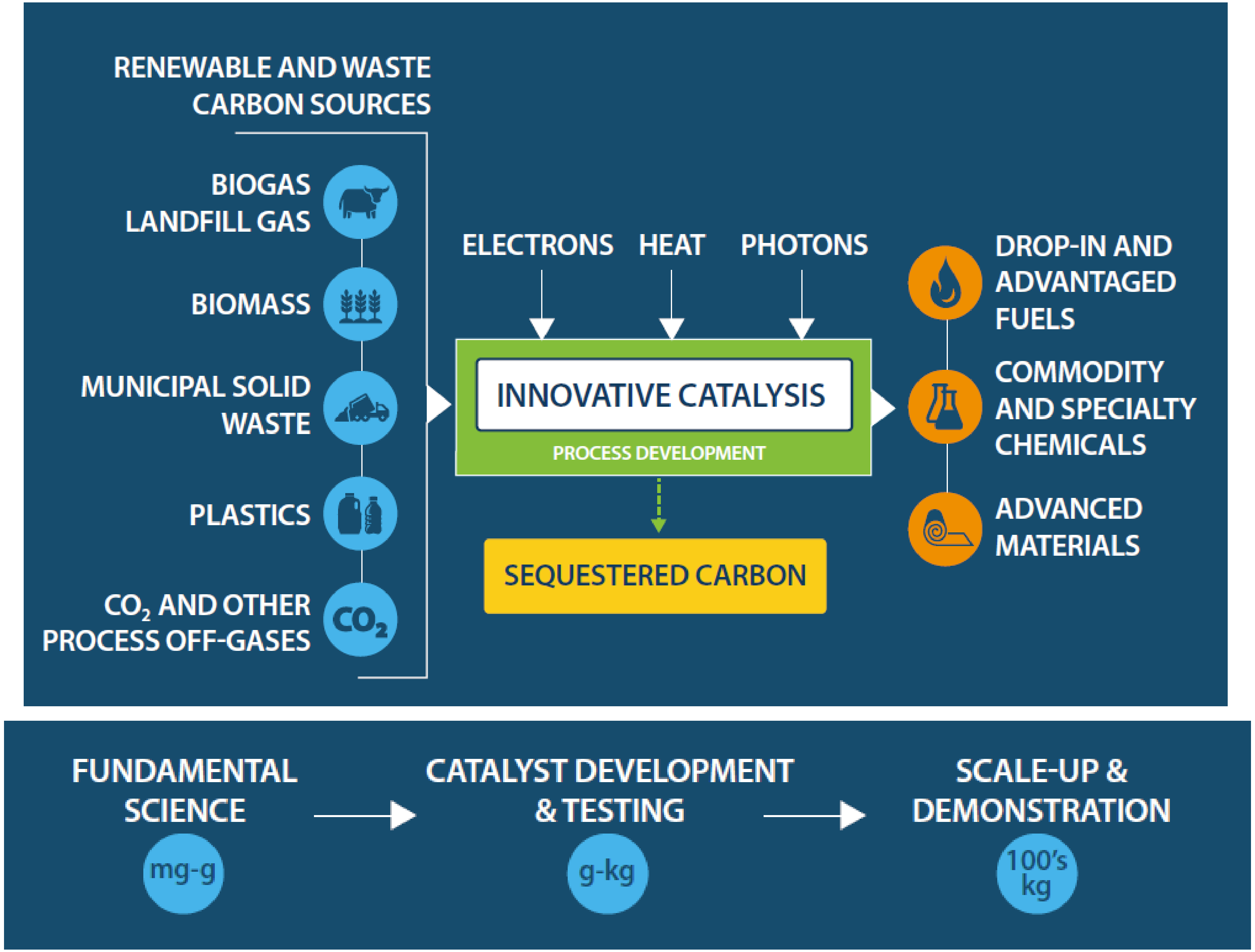
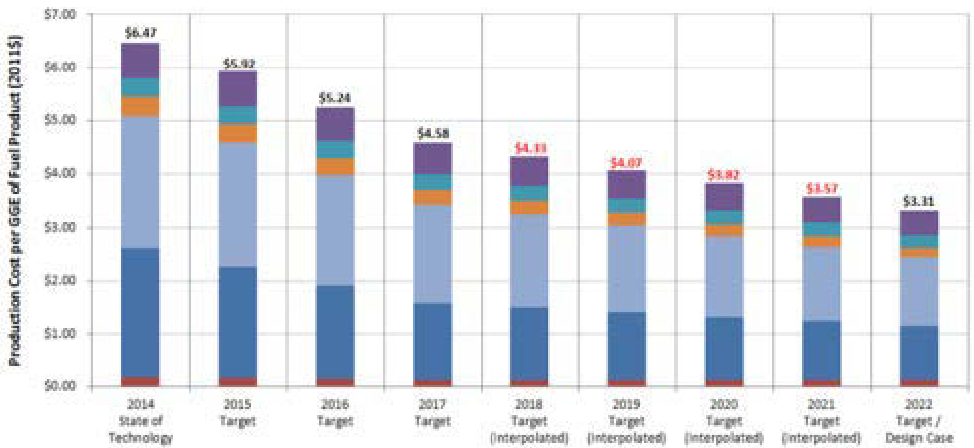
Catalytic Carbon Transformation @NREL

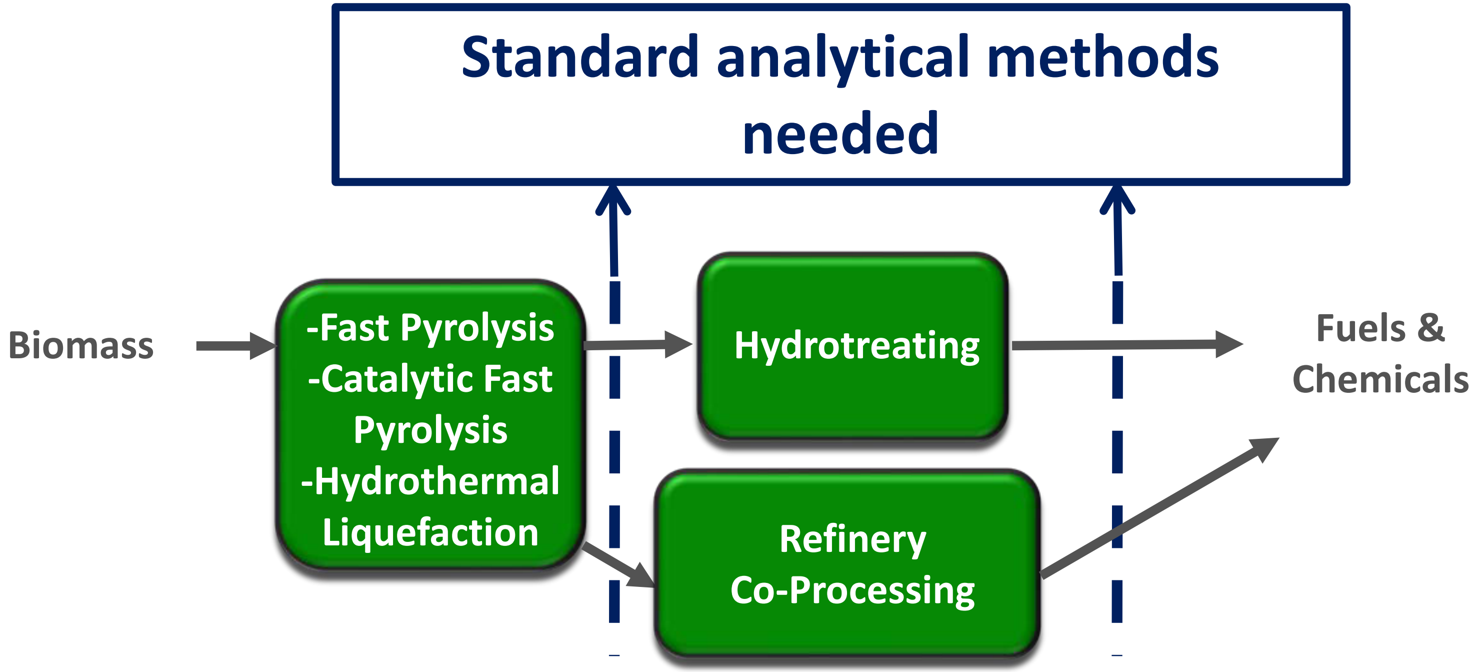


https://www.nrel.gov/bioenergy/thermochemical-processes.html

Thermochemical Conversion Pathways



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



Standard Analytical Methods

- **Laboratory Analytical Procedures (LAPs)**
  - Hosted on NREL website[1]
  - Free and publicly available
- LAPs define:
  - Scope (types of bio-oil samples)
  - Analytical protocol & variability
  - Data analysis procedures

- ASTM Standardization
  - Carbonyl titration: ASTM E3146


NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Quantification of Semi-Volatile Oxygenated Components of Pyrolysis Bio-Oil by Gas Chromatography/Mass Spectrometry (GC/MS)

Laboratory Analytical Procedure (LAP)

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Earl Christensen and Jack Ferrell
National Renewable Energy Laboratory

Mariefel V. Olarte and Asanga B. Padmaperuma
Pacific Northwest National Laboratory

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This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

ASTM INTERNATIONAL **Designation: E3146 – 18**

Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration[1]

This standard is issued under the fixed designation E3146; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

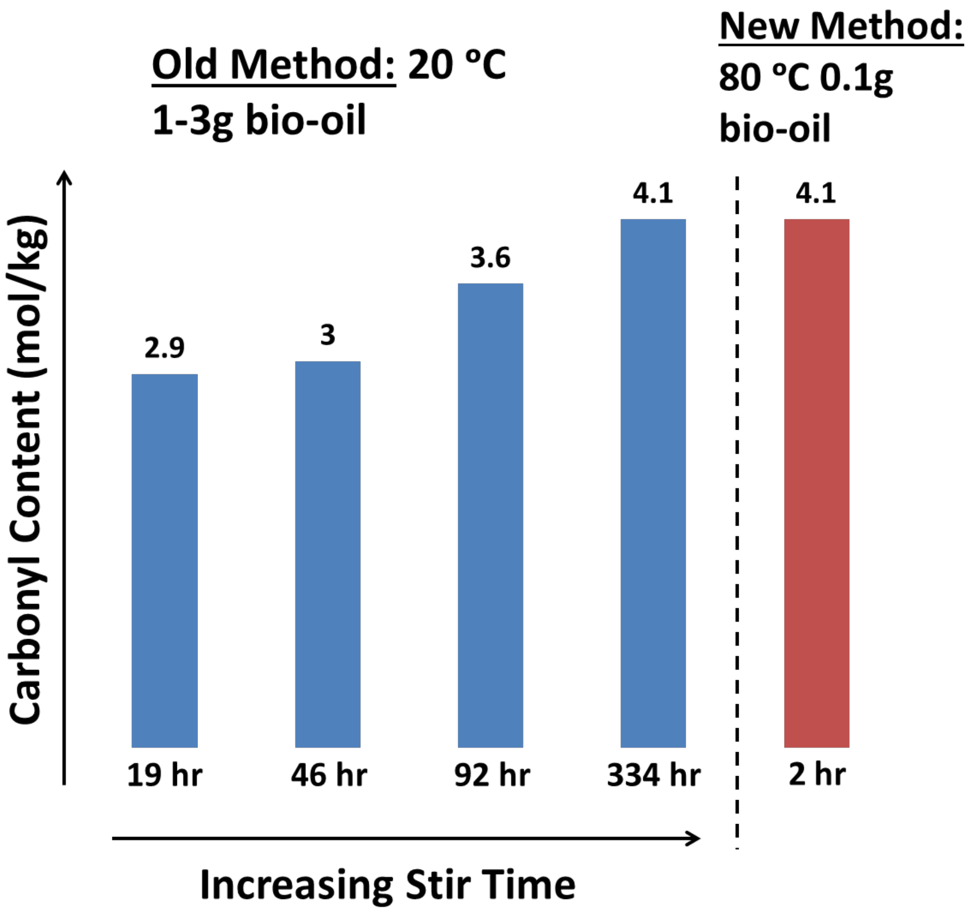
[1] http://www.nrel.gov/bioenergy/bio-oil-analysis.html

What is Fast Pyrolysis Bio-oil?

- 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)

Carbonyl Titration

- Method quantifies carbonyl content
  - Sum of aldehydes and ketones
- Carbonyls in fast pyrolysis bio-oil are problematic
  - **Aging** at room temperature
  - **Catalyst deactivation** during upgrading
- Developed[1-2] and validated[3] a new titration method, proven to be more useful than previously accepted method
  - Easier to perform (higher throughput)
  - More accurate, more reliable



[1]Black and Ferrell *Energy & Fuels* 30 (2016) 1071-1077
[2]Black and Ferrell *Journal of Visualized Experiments* (2017) e55165
[3]Ferrell et al. *Biofuels, Bioproducts & Biorefining* 10 (2016) 496-507

Bio-oil Samples

- 4 different fast pyrolysis bio-oil samples tested
  - *Pine, Oak, Blend1, Blend2*
- All samples exhibited properties typical of fast pyrolysis bio-oils
  - High water content, high oxygen content
  - Phase separation issues

	Water (wt%)	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Oxygen (wt%)	CAN (mg KOH/g)	TAN (mg KOH/g)	Insoluble Solids (wt%)
Pine	22.4	43.00	7.66	0.15	49.2	65.9	155.4	0.028
Oak	19.9	44.04	7.39	0.09	48.5	90.9	164.0	0.032
Blend1	31.0	38.88	8.04	0.32	52.7	67.2	149.8	0.005
Blend2	27.1	40.23	7.67	0.16	51.9	67.6	151.5	0.039

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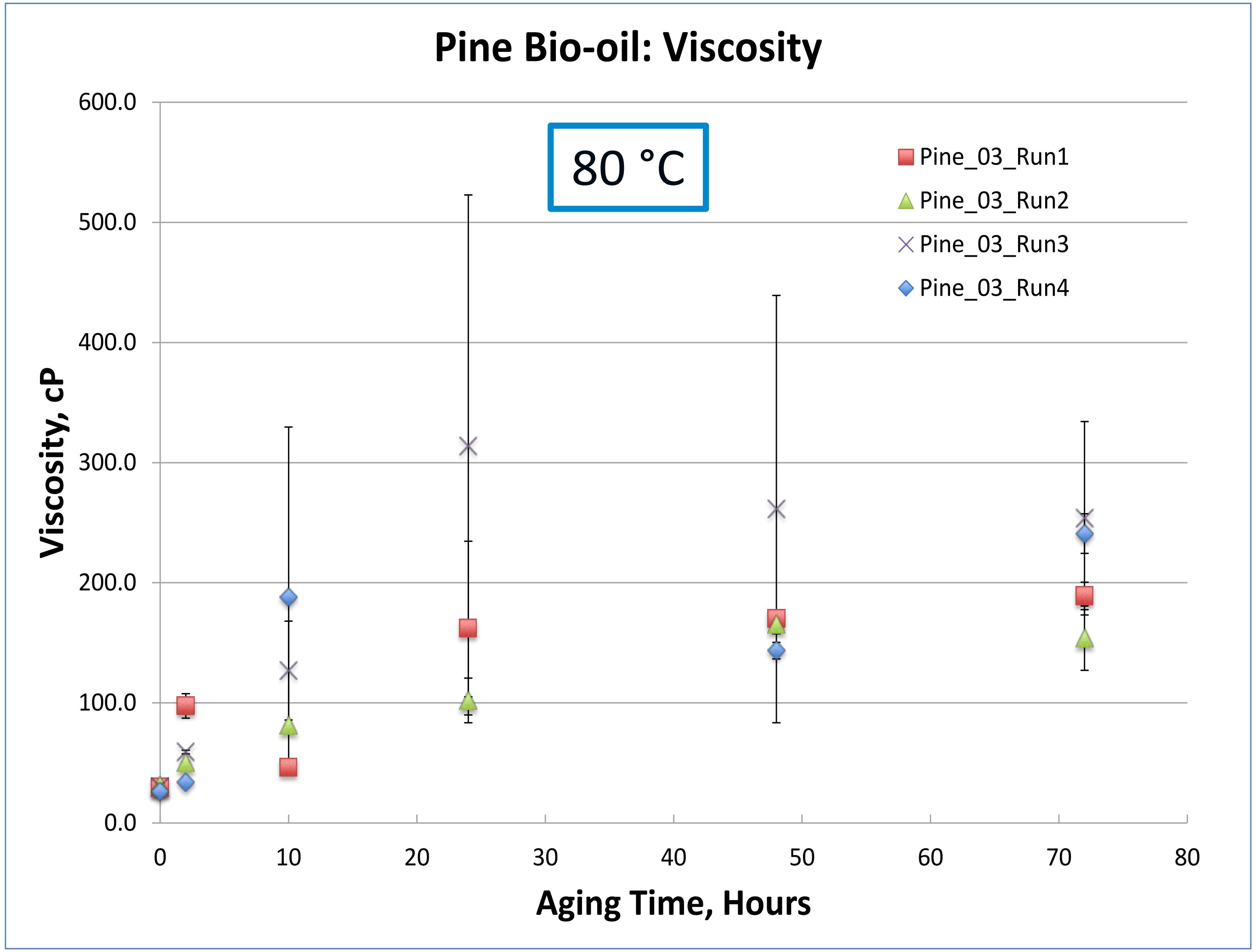
Existing Aging Test - Viscosity

- Viscosity cannot be measured when samples phase separate
  - Pine only sample where viscosity could be used
- Existing aging protocol: 24 hours @ 80 °C
  - Change in viscosity correlated to amount of aging



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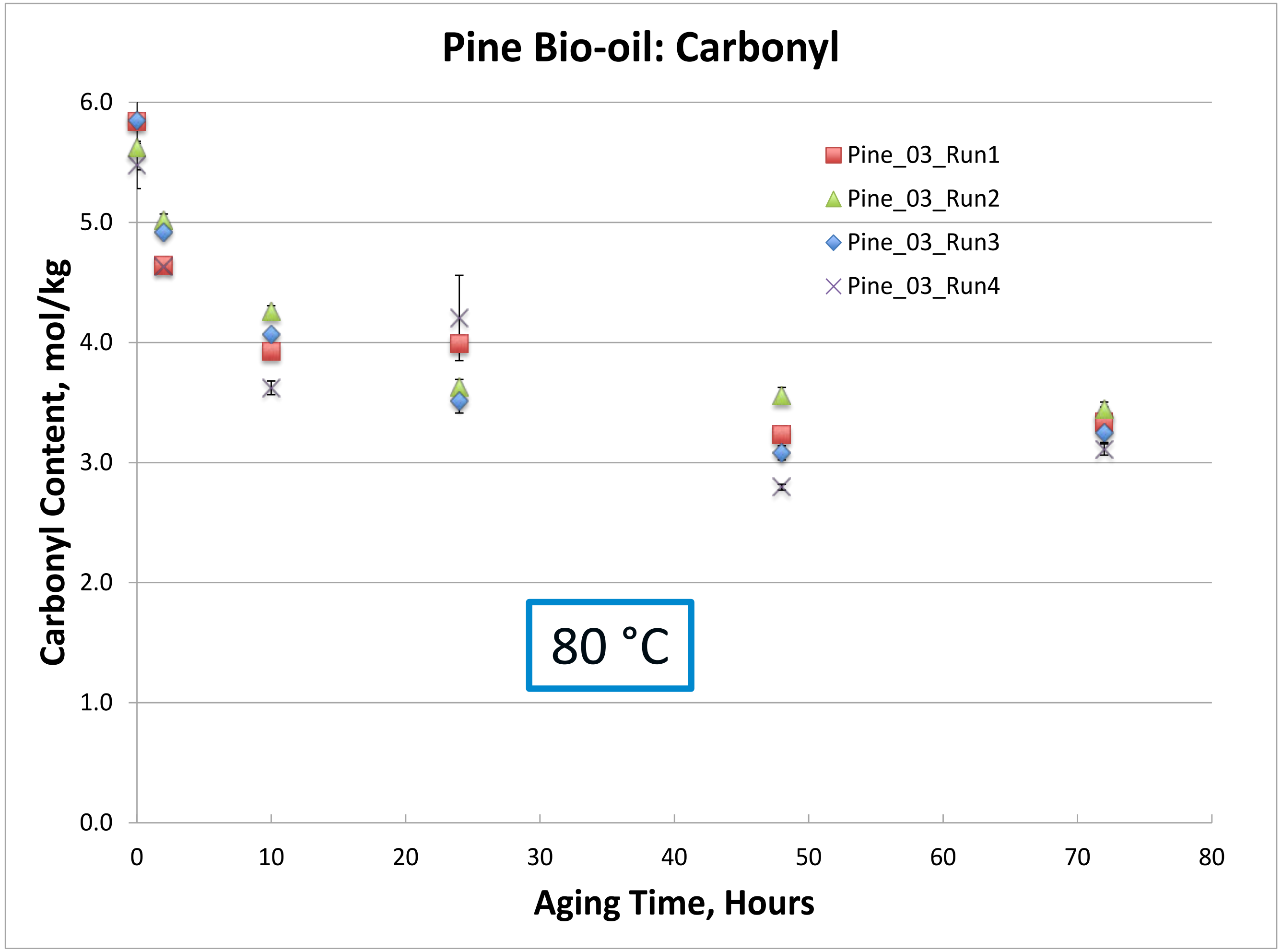
Carbonyl Content for Tracking Aging

- Significantly lower errors than viscosity measurement
- Can be applied to samples that have phase separated
- Employs standardized method for pyrolysis bio-oils

- *Carbonyl content is superior metric for tracking bio-oil aging*



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Accelerated Aging vs. Long-term Storage

- Accelerated aging tests
  - 40 °C and 80 °C for up to 160 hours
  - Carbonyl content used to track aging
- Long-term Storage
  - Room temperature and cold storage (at both -17 °C and 9 °C) for over 3 years
  - Carbonyl content used to track aging
- Long-term storage data used to calibrate accelerated aging protocol
  - For different types of fast pyrolysis bio-oil

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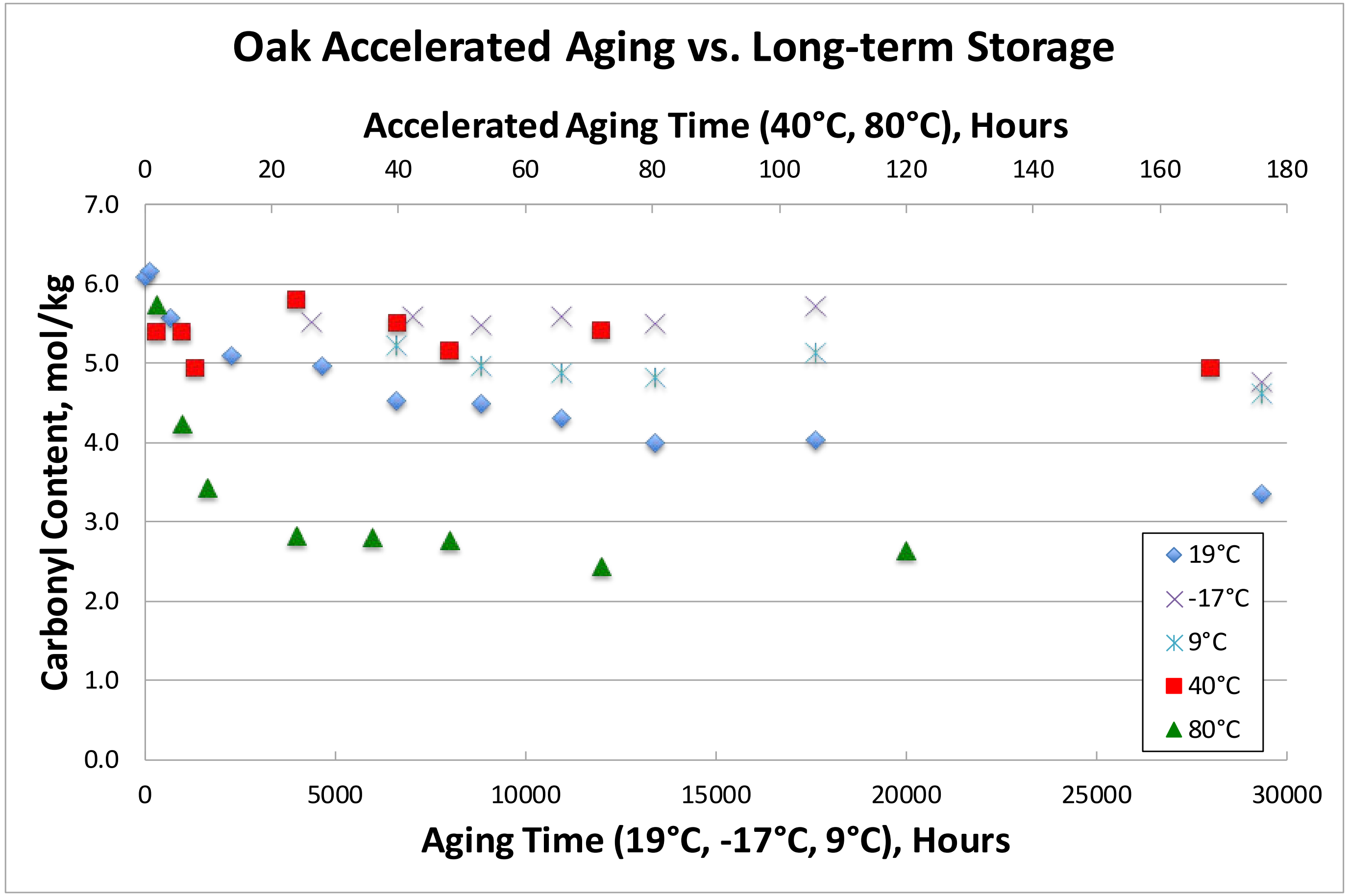
Accelerated Aging vs. Long-term Storage: Oak

- Holding at 24 hours @ 80 °C for is too harsh a protocol
  - Correlates to over 3 years of room temperature aging
- Accelerated aging at 80 °C rapidly promotes aging processes
  - Extensive condensation of aldehydes and phenols within hours



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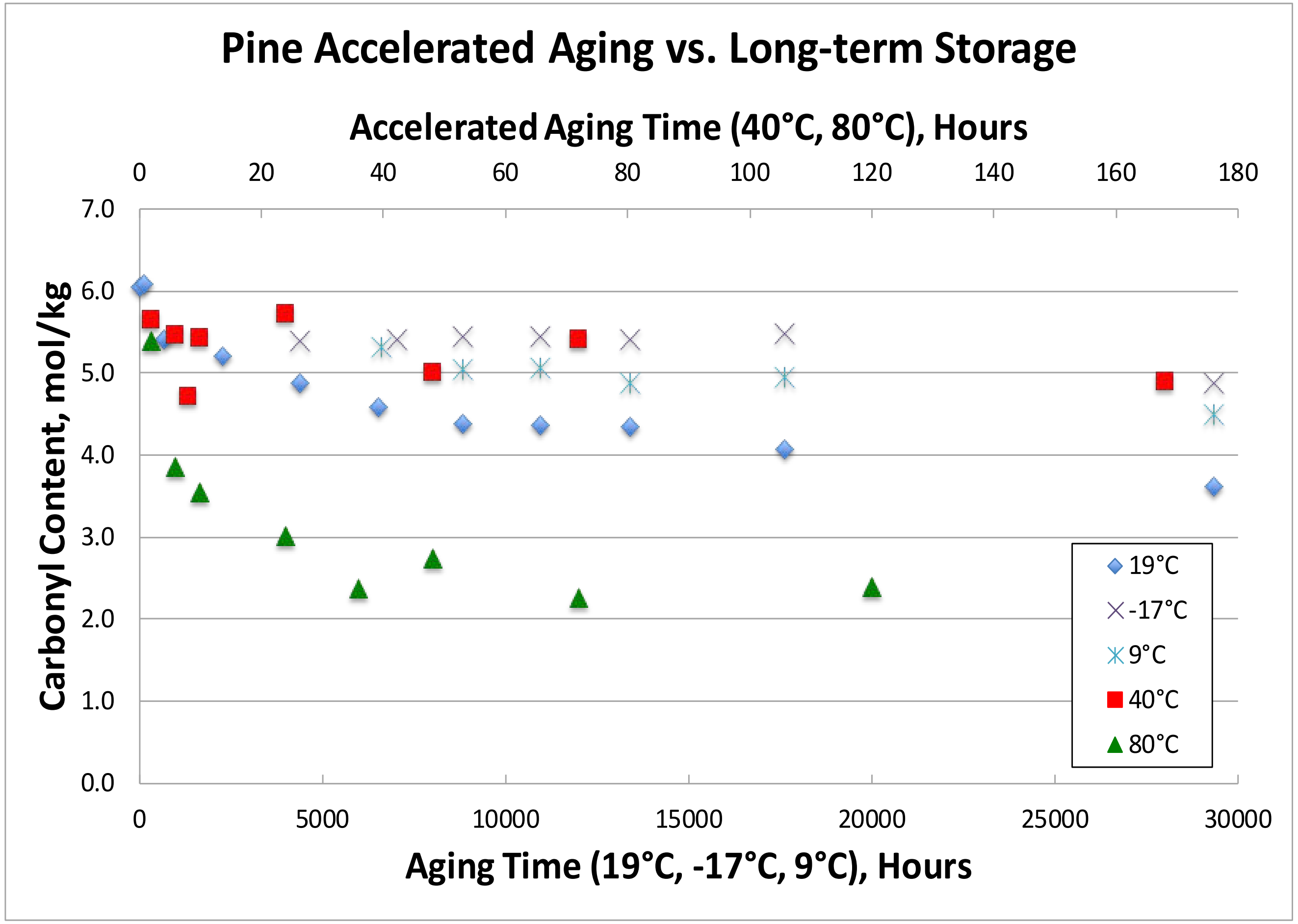
Accelerated Aging vs. Long-term Storage: Pine

- Aging at 40 °C more closely mimics long-term aging for all samples
  - An accelerated aging test would take longer at 40 °C – up to 120 hours
- New aging test proposed: **80 °C for 2 hours**
  - Correlates to 1-3 months of storage at room temperature



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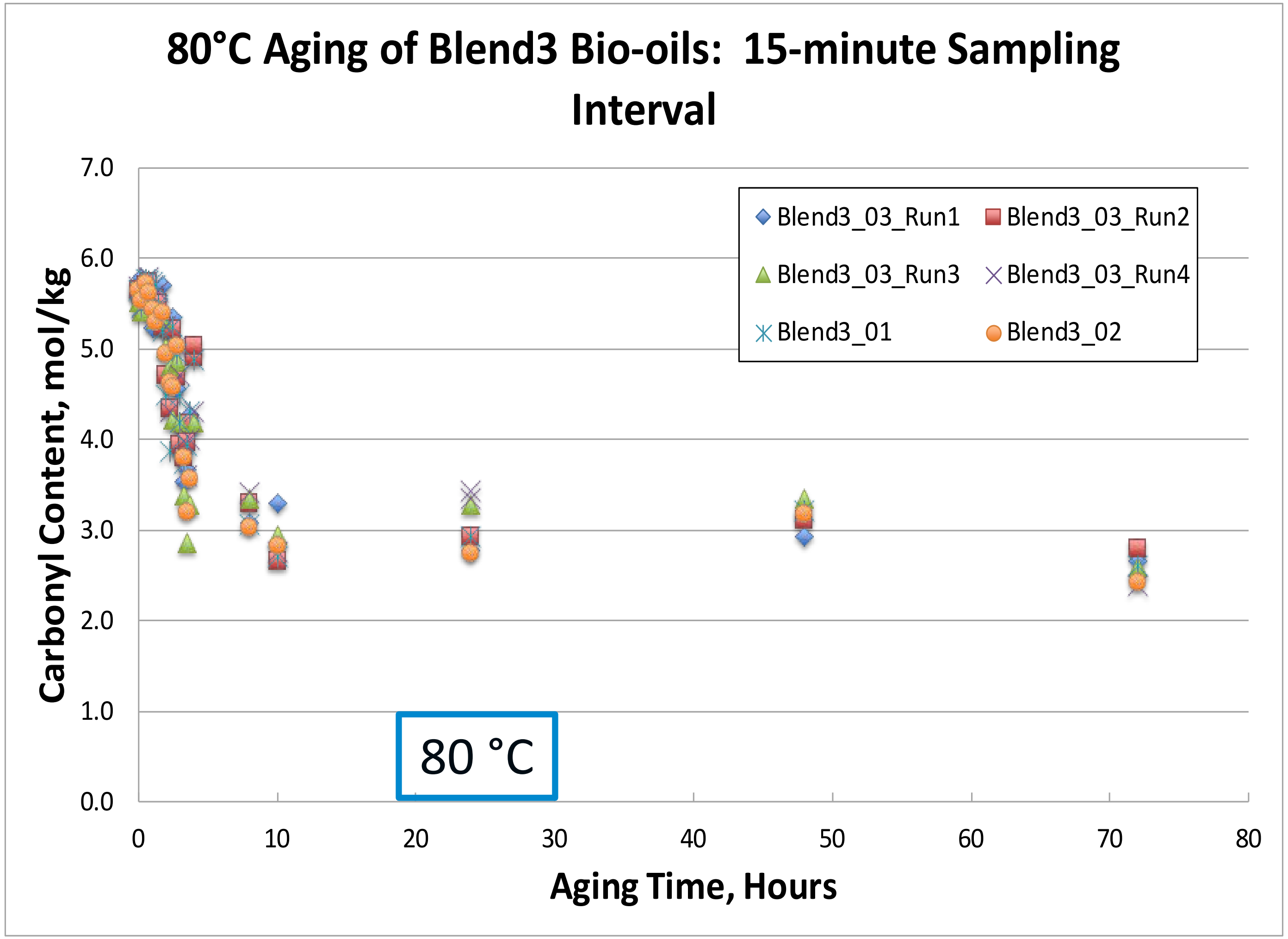
15-minute Aging Sampling Interval

- Aging samples taken in 15-minute intervals for first 4 hours of aging
- Aging process occurs in two stages
  - 1. Sharp drop in carbonyl content during first 4 hours
    - Depletion of reactive carbonyls
  - 2. Nearly constant carbonyl content from 4 hours to 72 hours
    - Unreactive carbonyls (2-3 mol/kg)

- 80 °C for 24 hours could be used to quantify unreactive carbonyl content



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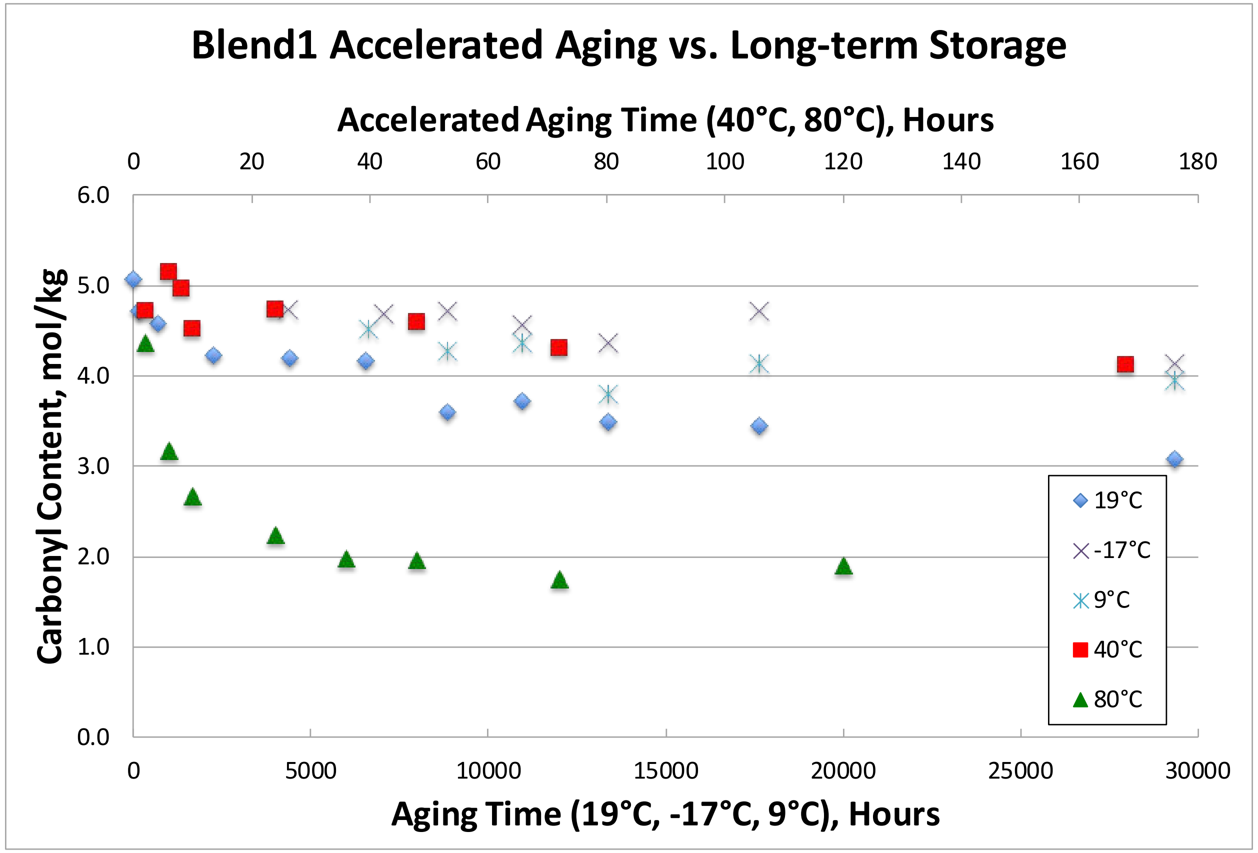
Cold Storage

- ***Aging still proceeds in cold storage***
  - Even at -17 °C
- ~10% reduction in carbonyl content after 6 months
- Carbonyl contents reduced by ~20% after 3.4 years

- Data shows that bio-oil aging is suppressed, but not stopped, with cold storage
- Colder temperatures (-17 °C) suppress aging processes further than milder temperatures (9 °C)

- *Implications for archiving of samples*
  - The properties of a fresh bio-oil cannot be preserved



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Conclusions

- Carbonyl content is a better metric for tracking aging than viscosity
- Existing aging test (24 hours @ 80 °C) is too severe, and correlates to more room temperature aging than would realistically occur
- New aging test proposed: 2 hours @ 80 °C
  - Correlates to 1-3 months of room temperature storage
- Aging is slowed in cold storage, but still occurs

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Dino Sulejmanovic

Jiheon Jun

Bioenergy Technologies Office,
DOE EERE

Questions?

Please contact Jack Ferrell
Jack.Ferrell@nrel.gov

Standard Analytical Methods:
http://www.nrel.gov/bioenergy/bio-oil-analysis.html

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