



National Laboratory
of the Rockies

Impact of Feedstock on CFP Biocrude Stability for Upgrading

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TCBiomass

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**National
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NLR team

- Martha Arellano-Trevino
- Anne Starace
- Steven Rowland
- Cheyenne Paeper
- Kellene Orton
- Rebecca Jackson
- Ella Slagle
- Bennet Addison
- Caleb Coatney
- Anne “Liz” Ware
- Darren Peterson

RTI team

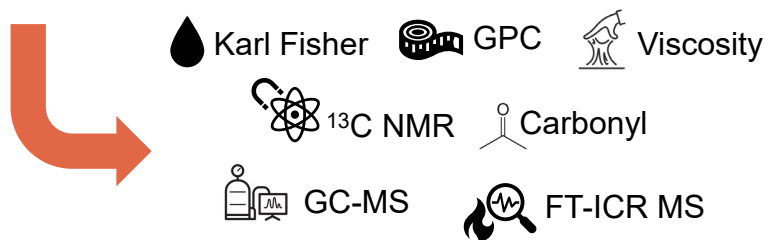
- David Dayton
- Melinda Barron
- Andrew Jones

This talk complements:

- “Impact of Feedstock Preprocessing on Biocrude Yield” by Melinda Barron on 8/25 at 3 pm
- “Advanced Analytical Methods to Support Biofuels Technology Development” by David Dayton on 8/27 at 1:20 pm

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) Bioenergy Technologies Office (BETO) under the Feedstock Conversion Interface Consortium Industrial Partnership Call, Award Number NL0054313

Project goals

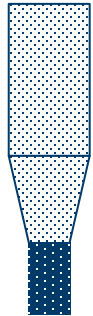


The objective of this collaborative project is to apply the NLR's comprehensive analytical capabilities to probe the molecular-level chemical composition of CFP biocrudes provided by RTI before and after accelerated aging to correlate thermal reactivity with upgrading performance via hydrotreating.

Oil aging

CFP biocrudes provided by RTI

2.5" FBR



ESP
Condensates



Alumina

*Zeolite



Corn Stover



1X Washed Corn Stover



2X Washed Corn Stover



4X Washed Corn Stover



6X Washed Corn Stover



8X Washed Corn Stover



Loblolly Pine



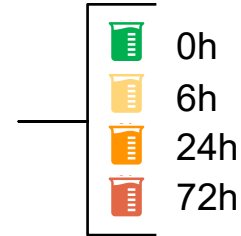
Loblolly Pine*



Switchgrass



White Oak



Accelerated aging method
(heating to 100 °C for Xh)

Characterization overview



GPC

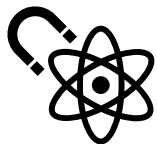


Viscosity

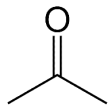


Karl Fisher

- Focus on 0h and 72h aged samples
- Focus on 1X and 8X Washed Corn Stover samples



^{13}C NMR



Carbonyl



GC-MS



FT-ICR MS

Feedstock identity and aging effects

Water content and viscosity

- Comparable water content in parent and 72h aged samples.
- Higher viscosity in 72h aged samples compared to parent bio-oils (3.7 – 23X higher!).

Carbonyl content, GPC and NMR

- In general, comparable to slightly lower carbonyl content in 72h aged samples compared to parent oils.
- Comparable number-average molecular weight (M_n) and weight-average molecular weight (M_w) for samples across different feedstocks. Higher molecular weight distribution in 72h aged samples compared to parent samples.
- Comparable carbon type content in parent and 72h aged samples.

GC-MS

Oxygenates detail

Aromatics detail

- In general, lower Total Mass Accounted for aged samples compared to parent oils. 80%+ of GC-MS identified compounds are oxygenates.
- Comparable oxygenates content in parent and 72h aged samples except for Switchgrass oils with lower phenols and higher carbonyls and acids in aged sample.
- For the aromatics, higher toluene content in aged samples compared to parent oils, except in corn stover.

FT-ICR MS

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

- Aged samples had a higher carbon number distribution compared with parent bio-oils.
- Aged samples had lower HC and higher oxygenates compared to parent oils.
- In general, higher double bond equivalent (DBE) distribution in aged samples.

$$\text{DBE} = \text{C} + 1 + \text{N}/2 - \text{H}/2 - \text{X}/2$$

Feedstock Summary

- ✓ Raw Corn Stover bio-oils seem the most stable after accelerated aging conditions with minimal changes in water content, molecular weight distribution, carbon type content, carbonyl content and GC-MS Total Mass Accounted.
- ✓ Switchgrass bio-oils appear to be the least stable.

Washing effects

Water content, viscosity and NMR

Samples are 0h aged unless otherwise indicated

- Washing treatment produced bio-oils with a higher water content (~1.76X higher) compared to raw sample. Little difference between 1X vs 8X Wash treatment.
- Washing treatment produced bio-oils with a lower viscosity (~50% lower) compared to raw sample. Viscosity stabilized from 2X wash onwards.
- Washing treatment produced bio-oils with a higher Aliphatic C-O carbon content (lower Aromatic C-H) compared to the raw sample. Minimal difference between 1X vs 8X washes.

Carbonyl content and GPC

Samples are 0h aged unless otherwise indicated

- Washing treatment produced bio-oils with a higher carbonyl content (~1.4X higher) compared to raw sample. No difference between 2X vs 8X Wash treatment.
- Washing treatment produced bio-oils with the same number-average molecular weight (Mn) and weight-average molecular weight (Mw) compared to raw sample.

GC-MS

Samples are 0h aged unless otherwise indicated

Oxygenates detail

Aromatics detail

- Washing treatment produced bio-oils with a higher oxygenates content (lower aromatics) and higher Total Mass Accounted compared to the raw sample.
- Bio-oils from a washed feedstock had a higher furan and acid content (lower phenols and carbonyls) compared to the raw sample.
- Washing treatment produced bio-oils with a higher toluene content (lower indene and naphthalene) compared to the raw sample.

FT-ICR MS

Samples are 0h aged unless otherwise indicated

- 1X washing treatment produced bio-oils with lower carbon number (CN) distribution and 8X washing resulted in a higher CN distribution compared to raw sample.
- In general, washing treatment produced compounds with higher O content compared to raw sample. 1X washing treatment produced bio-oils with similar HC distribution and 8X washing resulted in a lower HC distribution compared to parent feedstock.
- 1X washing treatment produced bio-oils with lower DBE distribution and 8X washing resulted in a higher DBE distribution compared to raw feedstock.

Corn Stover Washing Summary

- ✓ Washing treatment to the feedstock seem to provide benefits to the stability of the resulting bio-oils mostly by lowering the viscosity of the samples.
- ✓ Benefits can be reaped as early as the 2nd washing.

Catalyst effects

Water content and viscosity

Samples are 0h aged unless otherwise indicated

- Bio-oils from Loblolly Pine produced with a zeolite catalyst had 1.48X times more water than oils produced with an alumina catalyst.
- Oils produced with a zeolite catalyst were 7.6X times more viscous than oils produced with an alumina catalyst.

Carbonyl content, GPC and NMR

Samples are 0h aged unless otherwise indicated

- Comparable carbonyl content on both Loblolly Pine samples regardless of catalyst used.
- Higher molecular weight distribution for bio-oils produced with a zeolite catalyst.
- Bio-oils from Loblolly Pine produced with a zeolite catalyst had higher Aliphatic C-O carbon and lower Aromatic C-H carbon content than oils produced with an alumina catalyst.

GC-MS

Samples are 0h aged unless otherwise indicated

Oxygenates detail

Aromatics detail

- Lower Total Mass Accounted and higher Aromatic content on oils produced with a zeolite catalyst.
- Higher sugar and lower phenol content on oils produced with a zeolite catalyst.
- Bio-oils produced with a zeolite catalyst had higher naphthalene and xylene but lower 3+ ringed content than oils produced with an alumina catalyst.

FT-ICR MS

Samples are 0h aged unless otherwise indicated

- Bio-oils produced with a zeolite catalyst had a higher carbon number distribution than oils produced with an alumina catalyst.
- Lower HC content and more compounds with higher O content for oils produced with a zeolite catalyst.
- Samples produced with a zeolite catalyst had higher DBE distribution.

Catalyst Summary

- The alumina catalyst samples are less viscous, have a lower mass distribution, lower oxygenates content and lower aliphatic C-O content compared to samples produced with a zeolite catalyst.

Conclusions



RTI provided bio-oils produced with a variety of feedstocks and catalysts. The samples were subjected to accelerated aging. Stability was compared across feedstock identity, aging time, washing treatment and catalyst type conditions

Raw corn stover bio-oils seem the most stable after accelerated aging conditions. Switchgrass bio-oils appear to be the least stable.

Washing the corn stover seems to provide benefits to the stability of the resulting bio-oils. Benefits can be reaped as early as the 2nd washing.

Bio-oils produced with an alumina catalyst seem to be more stable compared to samples produced with a zeolite catalyst.

 Karl Fisher  GPC  Viscosity

 ¹³C NMR  Carbonyl

 GC-MS  FT-ICR MS

We characterized the parent and aged samples with a full suite of techniques

Thank you!

Any questions?

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