Impact of Feedstock Preprocessing on Biomass Quality Attributes

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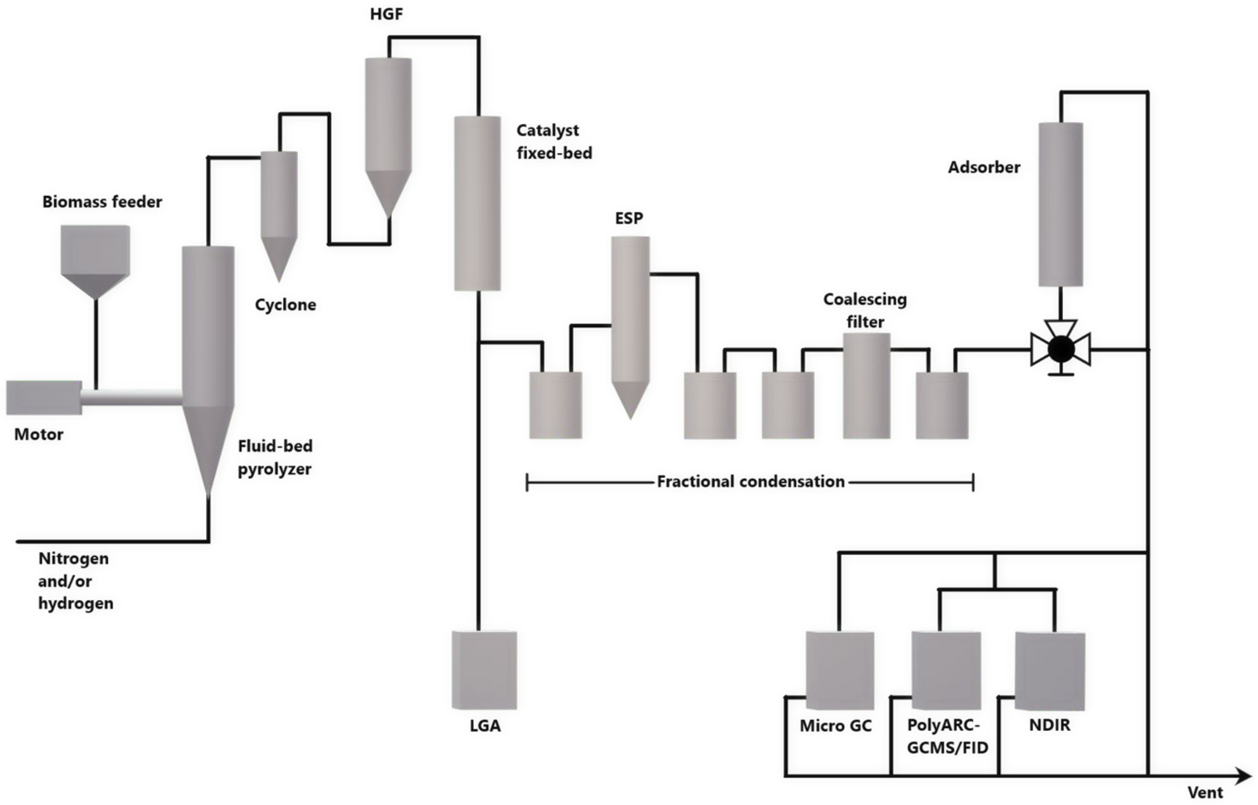
Battelle Energy Alliance manages INL for the
U.S. Department of Energy's Office of Nuclear Energy
Idaho National Laboratory

Introduction

ExxonMobil is assessing viability of converting biomass to fuels and/or chemicals with INL and NREL performing feedstock selection and conversion screening

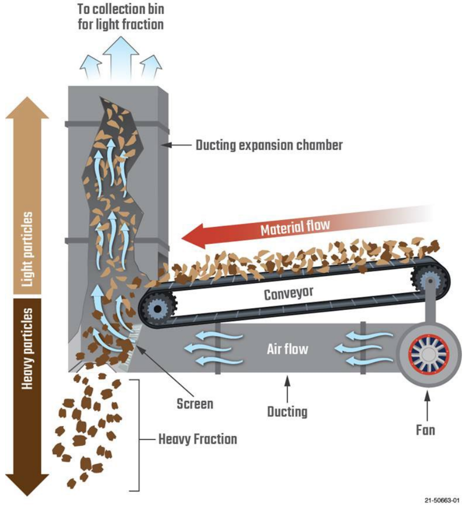
- Feedstock preprocessing (INL):
  - Pine, Poplar, Corn Stover
  - Exploratory analysis of:
    - Particle size
    - Anatomical fractions
    - Torrefaction
    - Acid pretreatment
- Fast pyrolysis in 2-inch Fluidized Bed Reactor (NREL):
  - Temperature series with 0.5 mm clean pine
    - 450°C, 500°C, 550°C, 600°C
  - Particle size series with clean pine at 500°C
    - 0.5 mm, 1 mm, 2 mm particles
  - Experiments with different feeds (0.5 mm 500°C)
    - Clean pine, forest residues, bark, corn stover, poplar, acid pretreated feed
  - Torrefied pine (230°C, 250°C, 275°C)



Preprocessing

Mechanical Classification

Anatomical tissue fractions isolated from whole residues




Forest Residue


White Wood


Bark


Needles

Size reduction

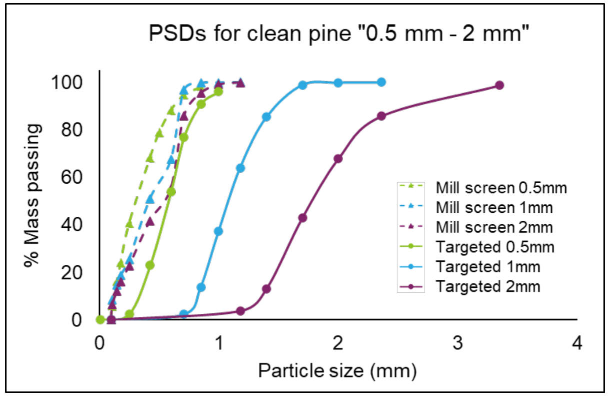
Fractional milling and screening to get desired particle size distribution

Impact


High aspect ratio

Shear


Uniform aspect ratio

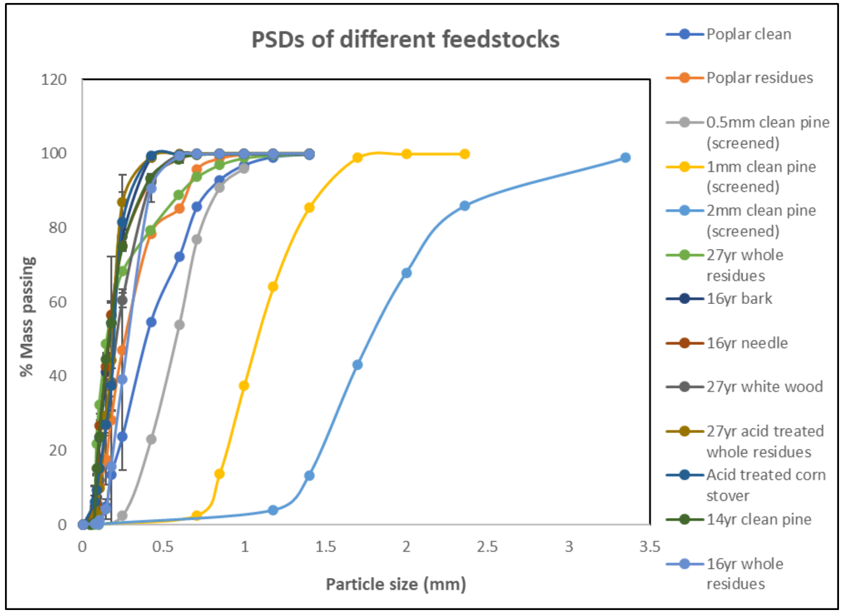


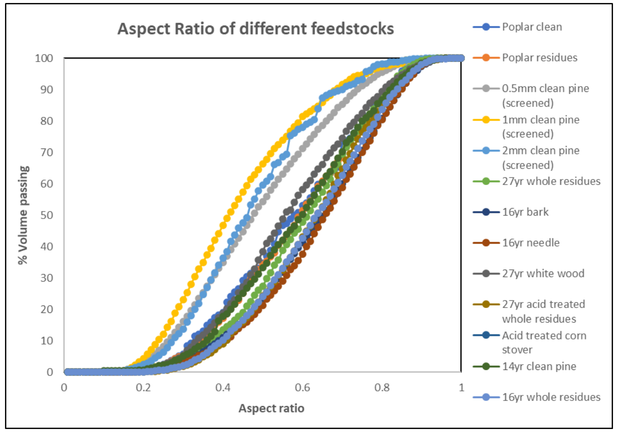
Pretreatment

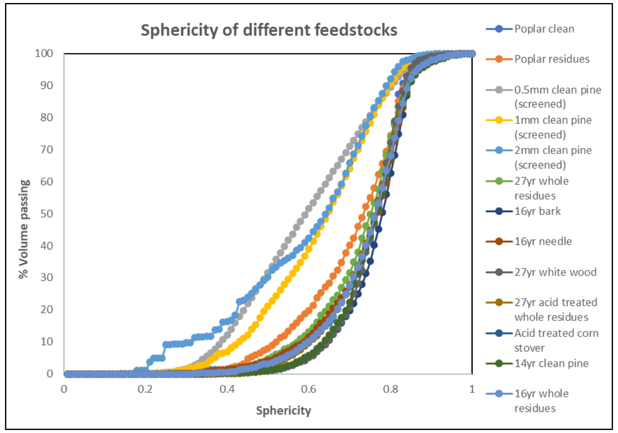
Torrefaction to increase carbon concentration and reduce acidity

Acid leaching to reduce inorganics

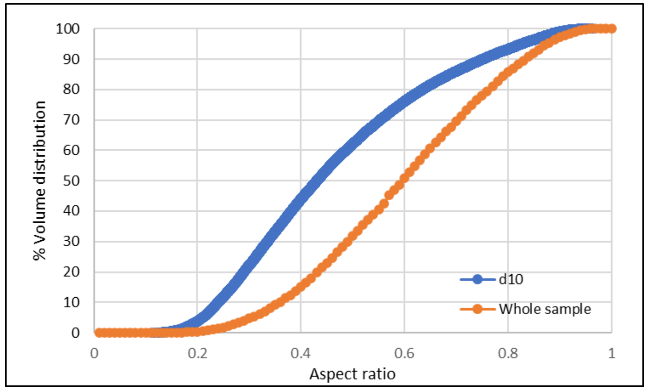
Physical Characterization

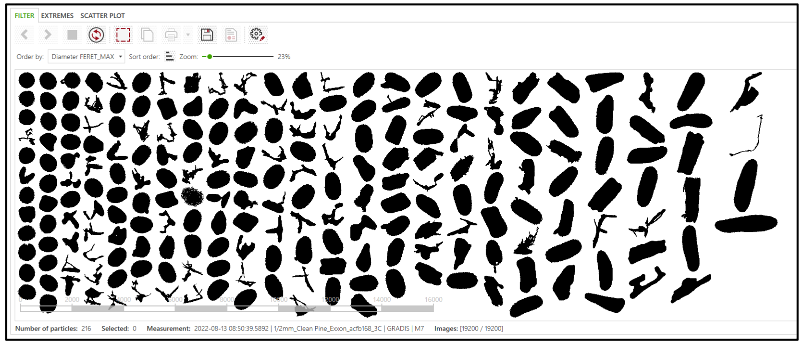


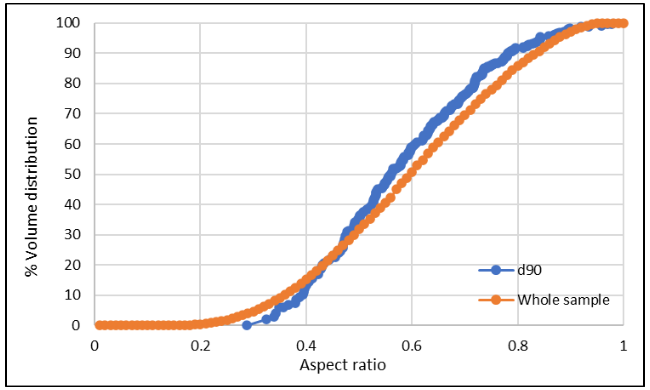




Whole sample size and shape distributions

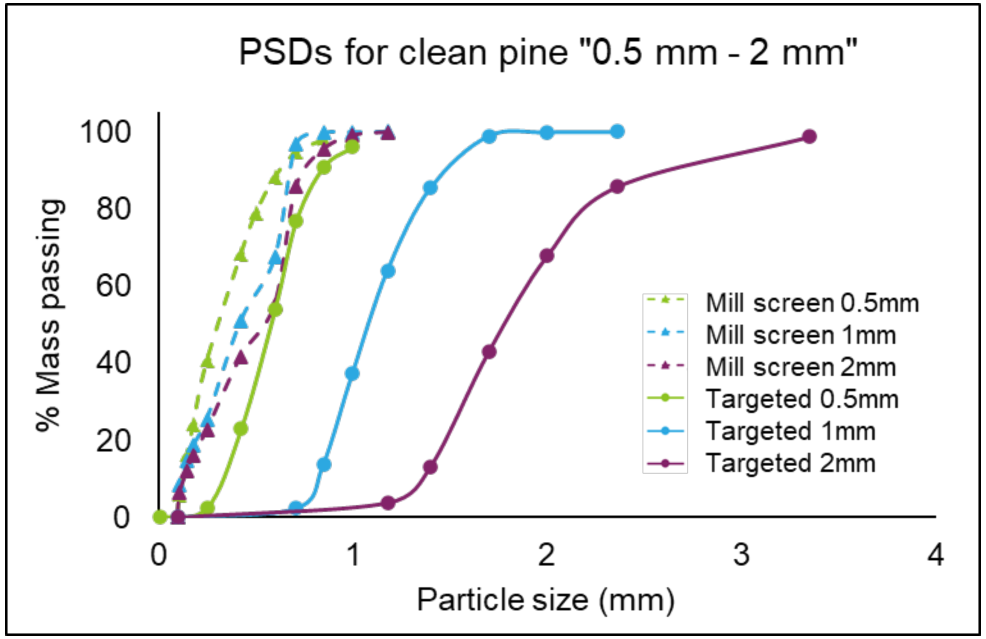


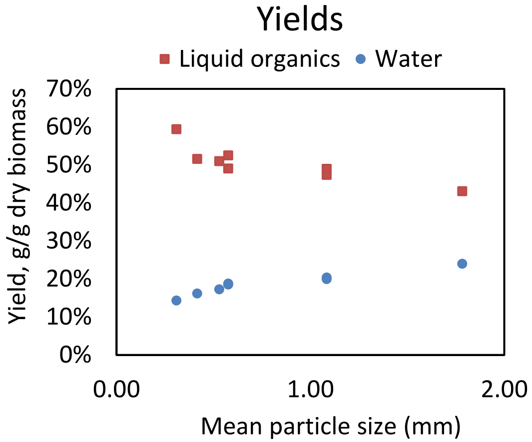


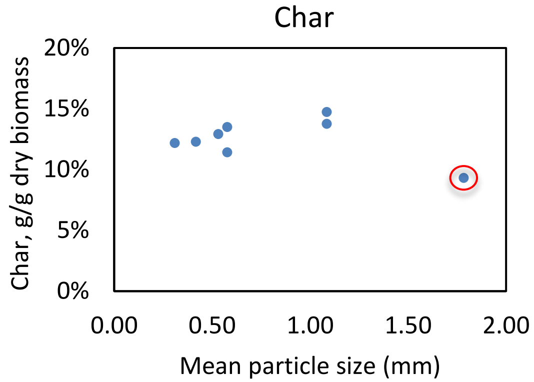


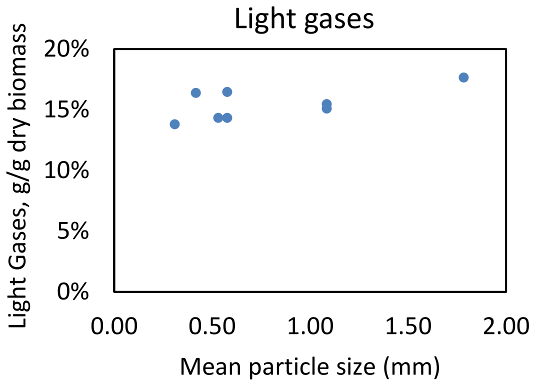
Size and shape variations within sample

Impact of Particle size









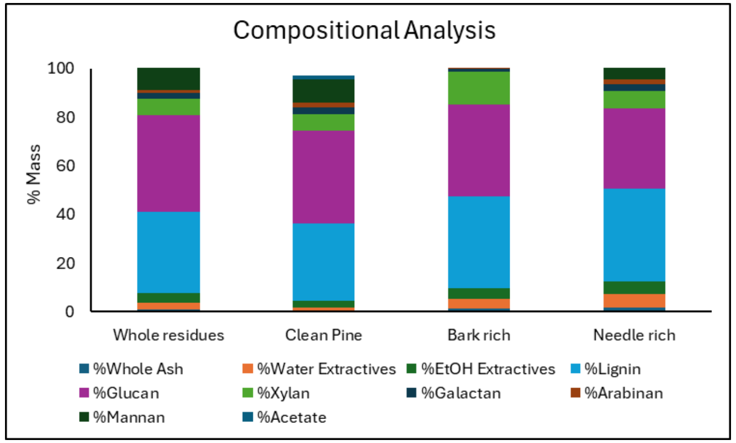
PSDs developed based on mill screen size and targeted particle mean size

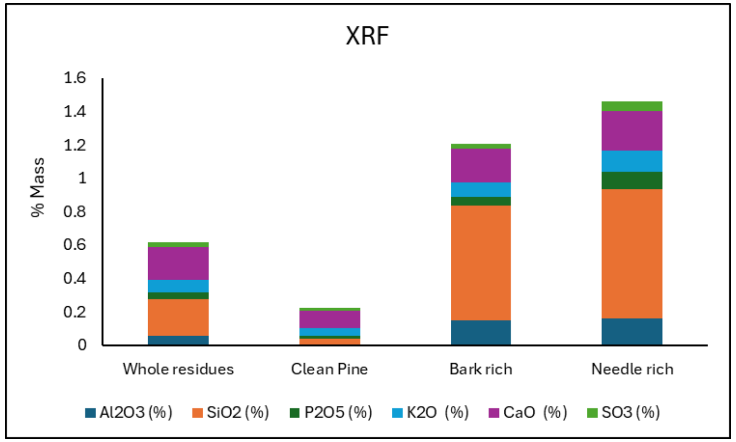
With increase in particle size

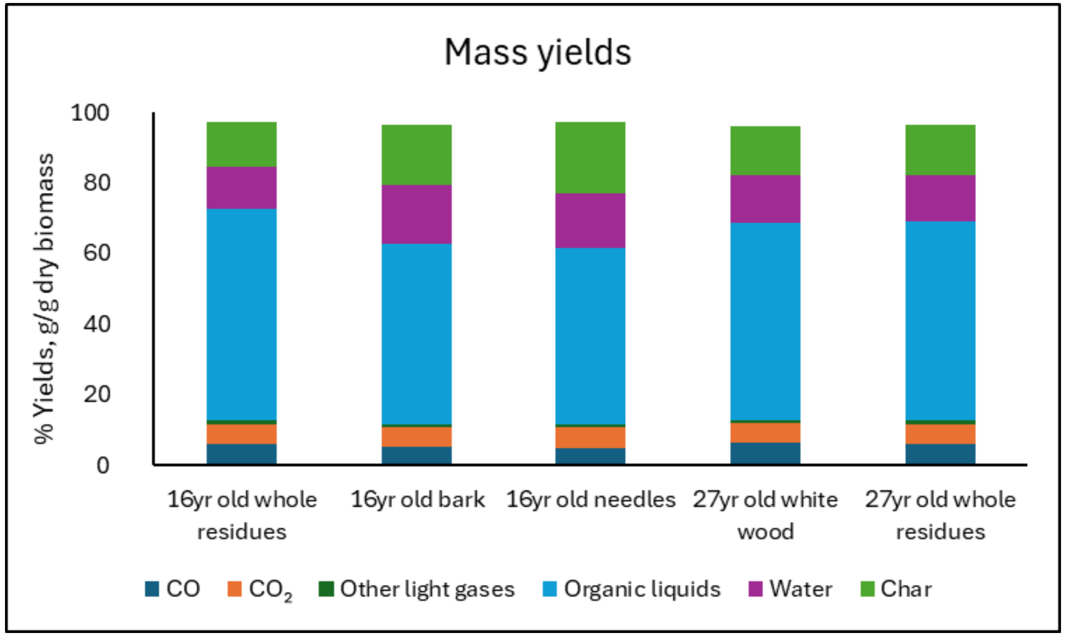
- Liquid-range organics decrease
- Water yield increases
- Char yield increases
- Light gas yields increase

Advanced milling and sieving circuits help control particle size and enable higher yield

Whole residues vs anatomical fractions



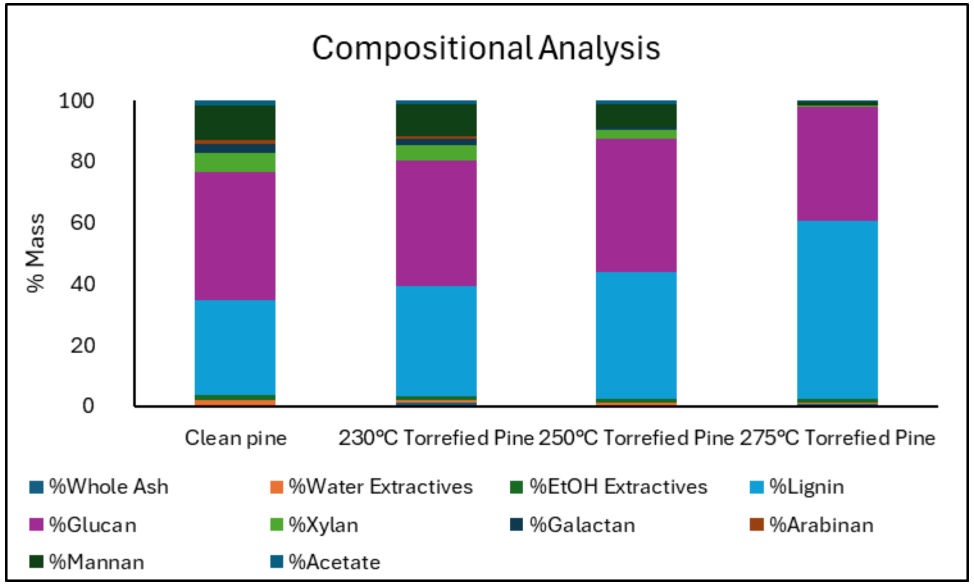


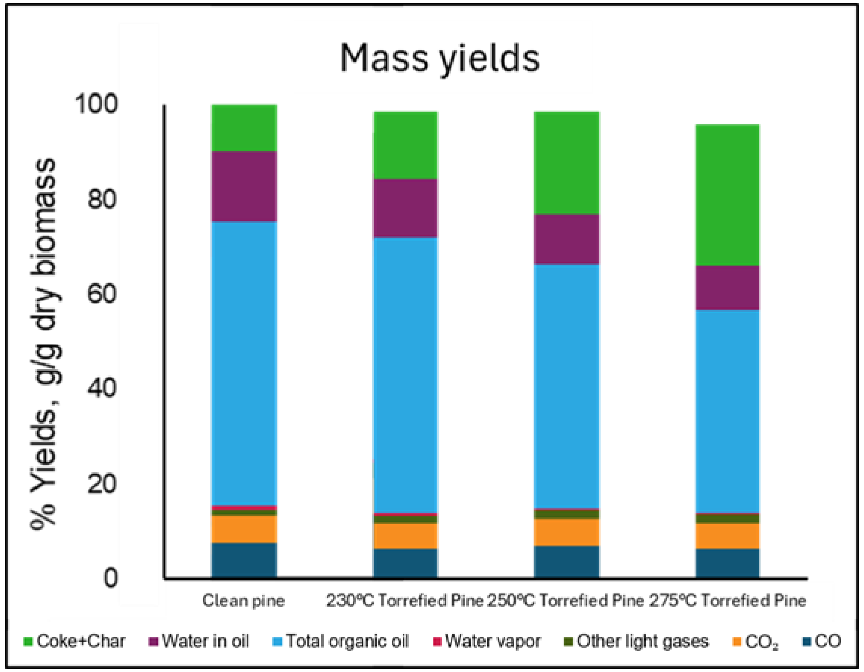


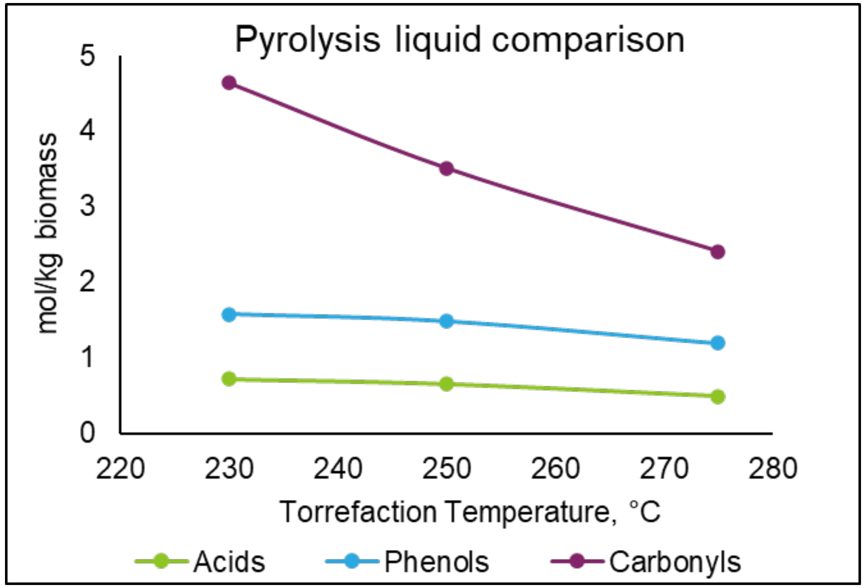
- Residues have more ash, higher extractives, higher lignin (needles and bark highest), less glucose and xylan
- Needles and bark have higher concentrations of P and S in addition to K and Ca
- Bark and needles produced less oil and gases, and more water and char (compared to white wood and residues).
- 16-yr-old whole residues produced highest oil yield, and lowest water and char yields

Different anatomical tissues have different conversion performance

Impact of Torrefaction



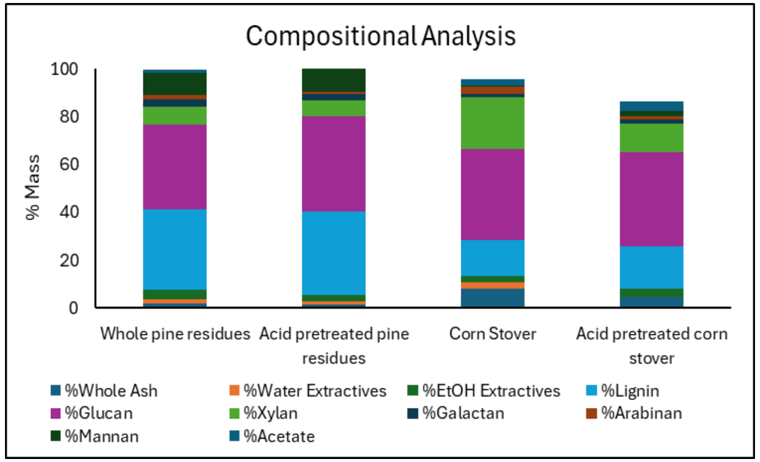


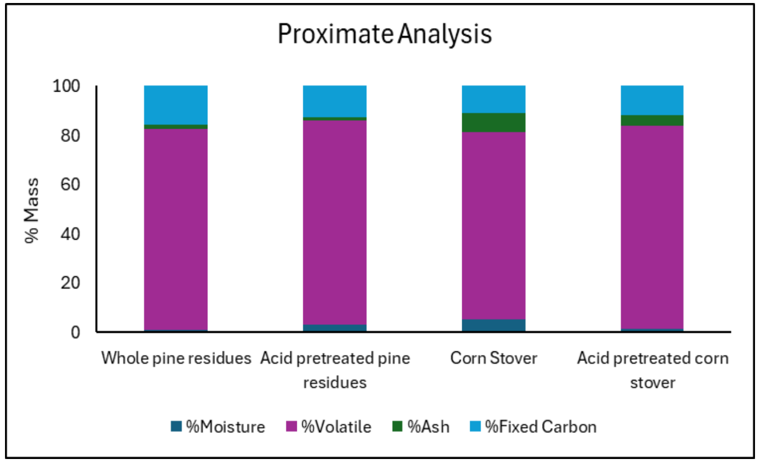


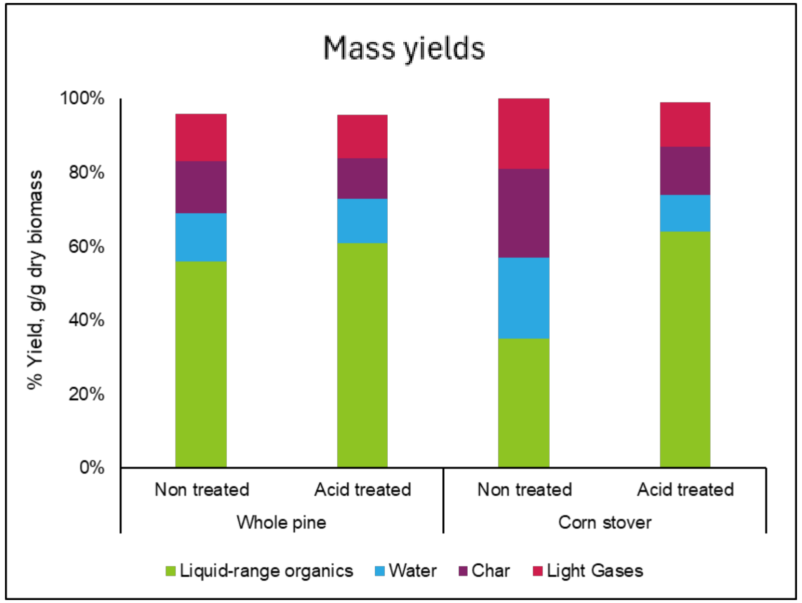
- Hemicellulose degrades, thereby increasing the relative concentration of lignin
- Carbon content increases
- Torrefaction decreases organic yield
  - Decreases carbonyls, acids and phenols – improving oil quality
  - Decreases water
- Char content increases

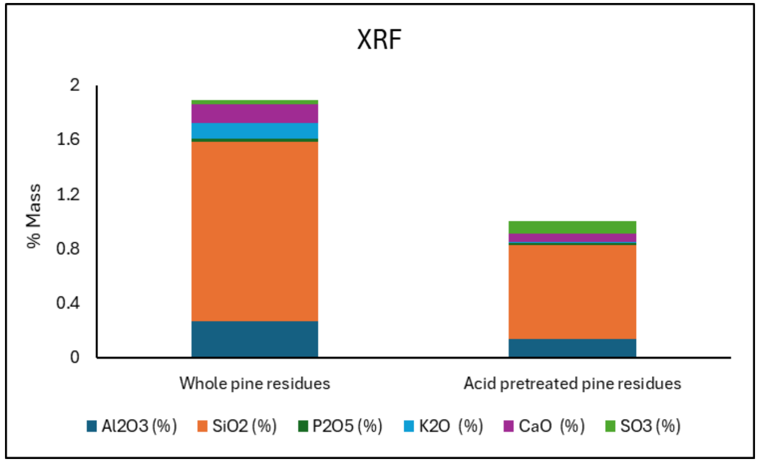
Quality of pyrolysis oil improves with torrefaction due to decreasing water, carbonyls and acids

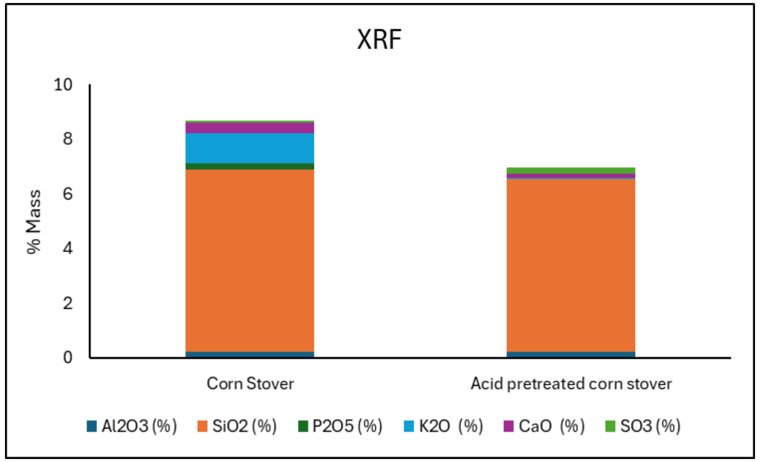
Impact of acid treatment

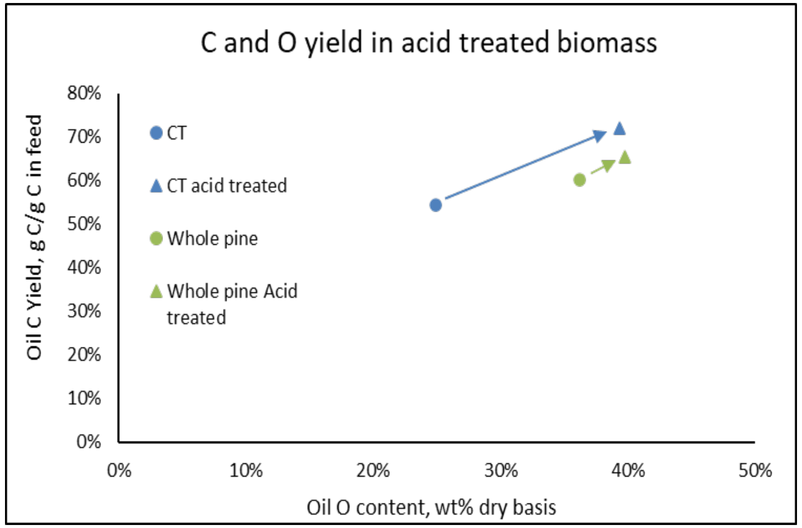












- Acid treatment reduces ash, water extractives, and C5 sugars

Acid treated materials reduces inorganics and increases liquid product yield

Conclusions

- Advanced milling and sieving circuits help control particle size and enable higher yield
  - Controlling physical attributes to have a narrow distribution and smaller mean size enables better conversion
- Different anatomical tissues have different conversion performance
  - Bark and needles have higher contamination and poorer conversion performance and should be removed
- Quality of pyrolysis oil improves with torrefaction due to decreasing water, carbonyls and acids
- Acid treated materials reduces inorganics and increases liquid product yield

Biomass Feedstock National User Facility (BFNUF)

Capabilities

- Feedstock Preprocessing
- Mechanical Deconstruction
- Materials Conditioning
- Interfacial Properties
- Feedstock Characterization

Solutions

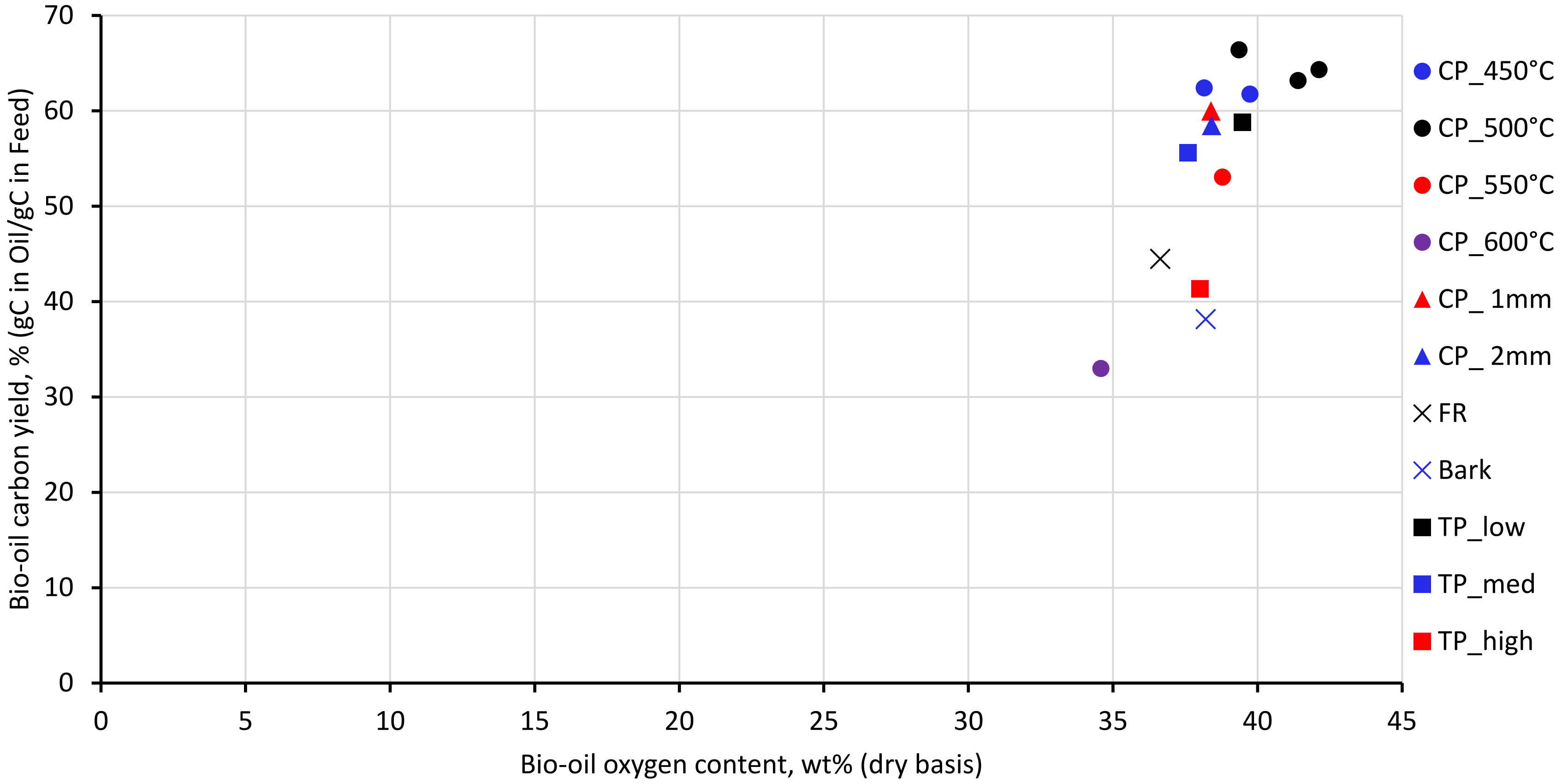
- Enrich Feedstock
- Maximize Conversion
- Characterize and Manage Variability
- Improve Flowability
- Storage And Stability

Idaho National Laboratory

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy. INL is the nation's center for nuclear energy research and development, and also performs research in each of DOE's strategic goal areas: energy, national security, science and the environment.

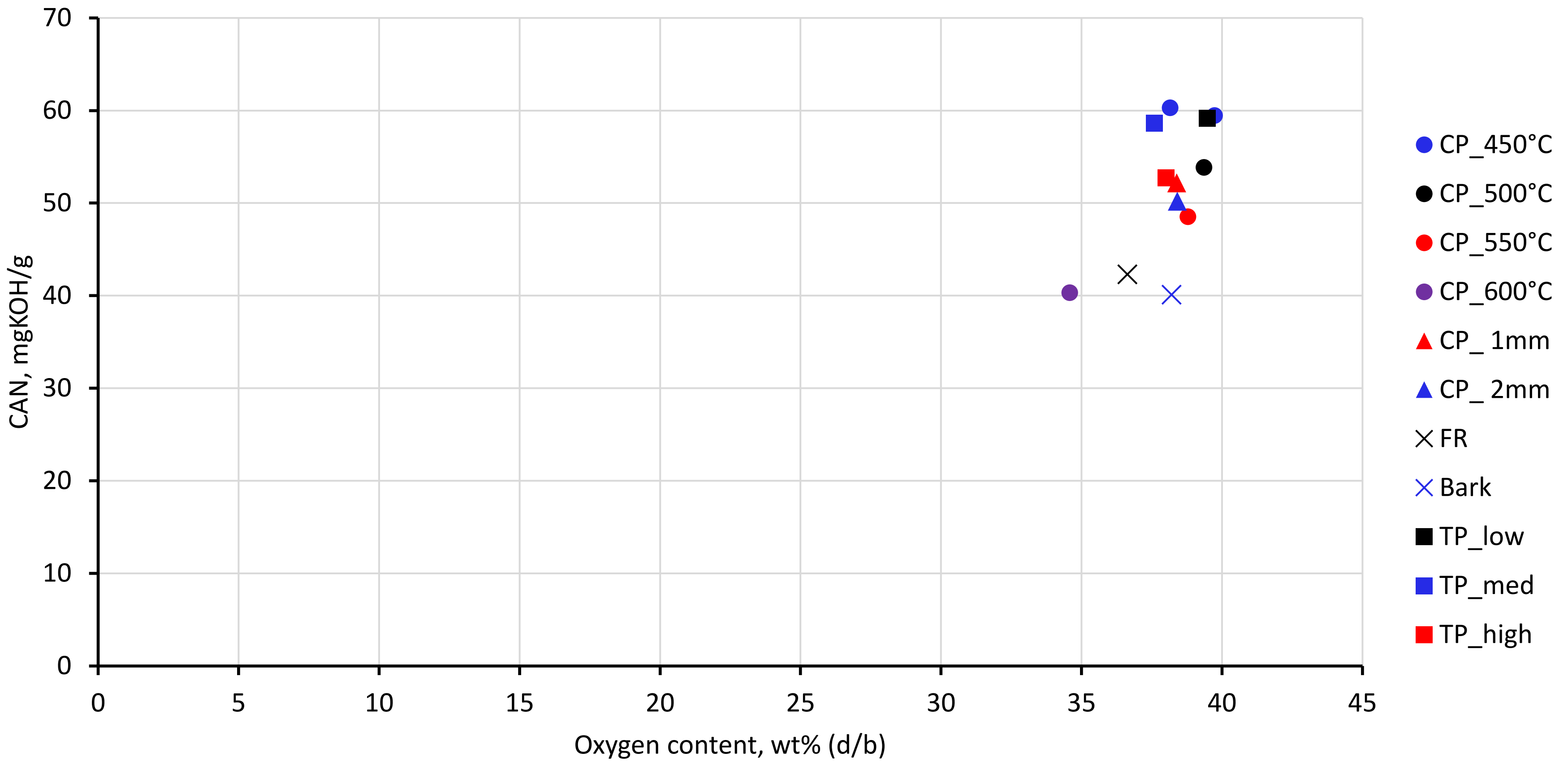
Supplemental Slides

Oil C Yield vs. O Content



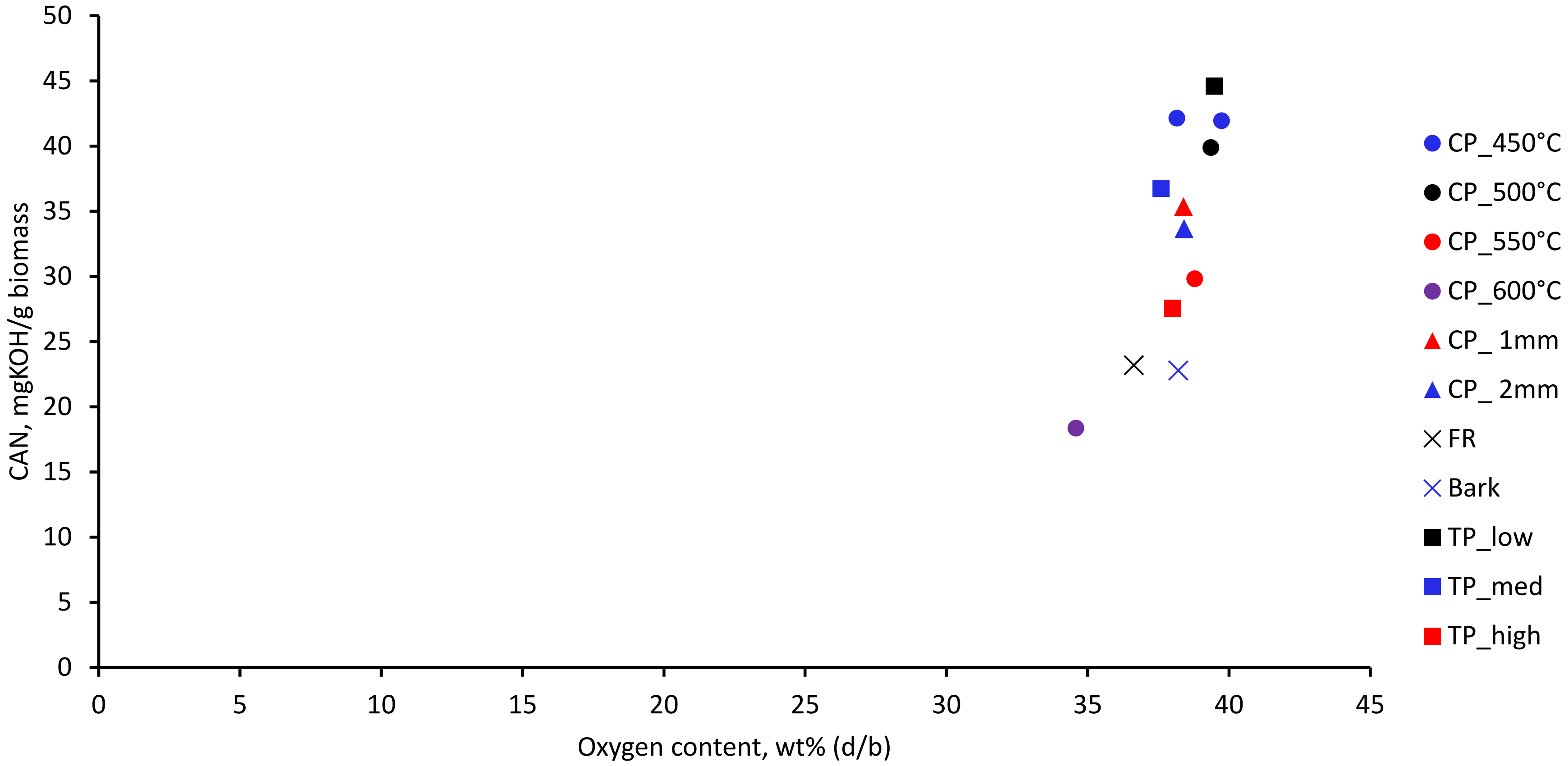
- Liquid carbon yield increases as oxygen content increases
- For pine, C yields in order: 500C > 450°C > 550°C > 600°C

Carboxylic Acid Number vs. O Content



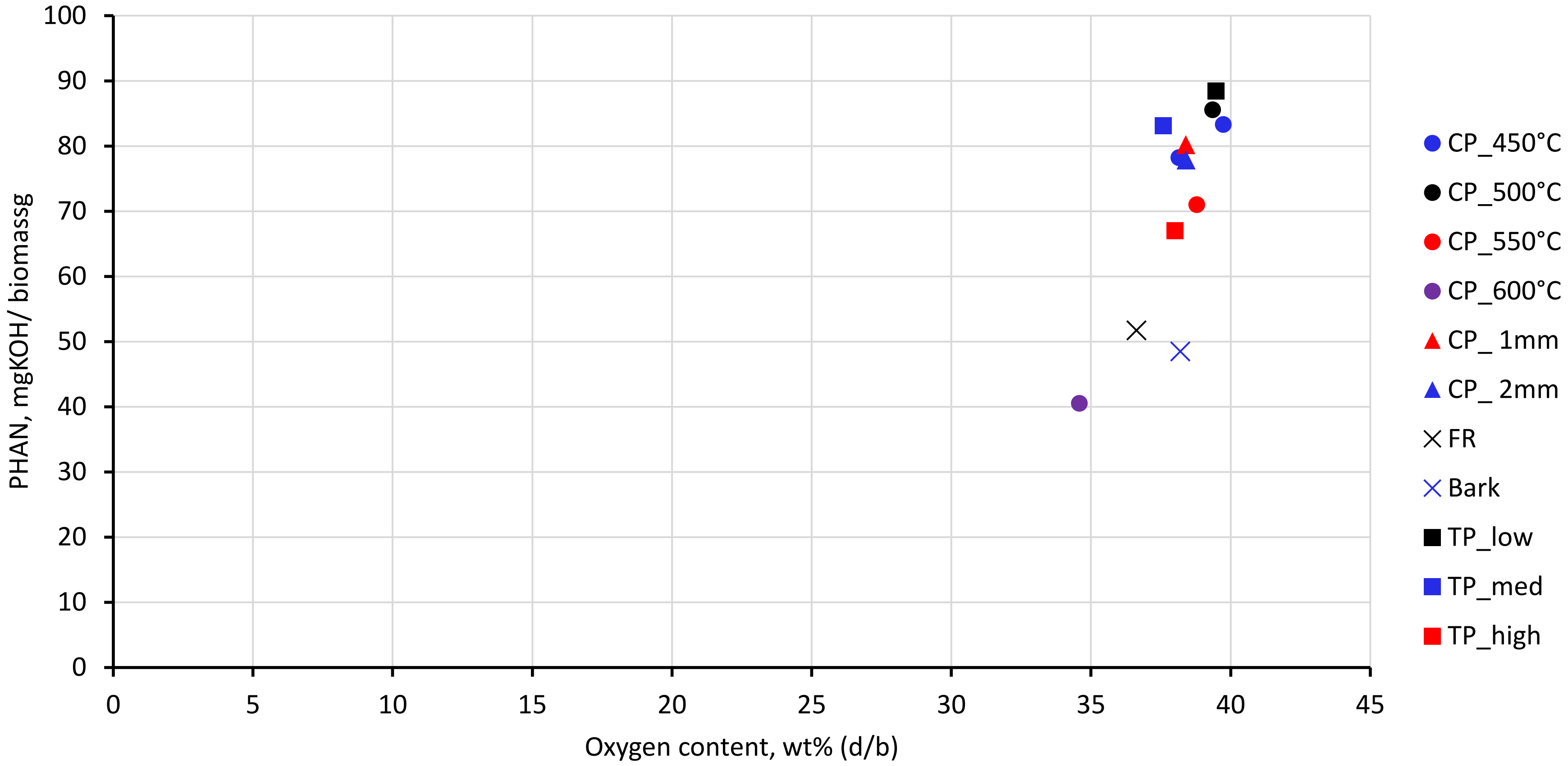
- Carboxylic acid number lowest in forest residue and bark oil and clean pine @ 600°C

Carboxylic Acid Yield vs. O Content



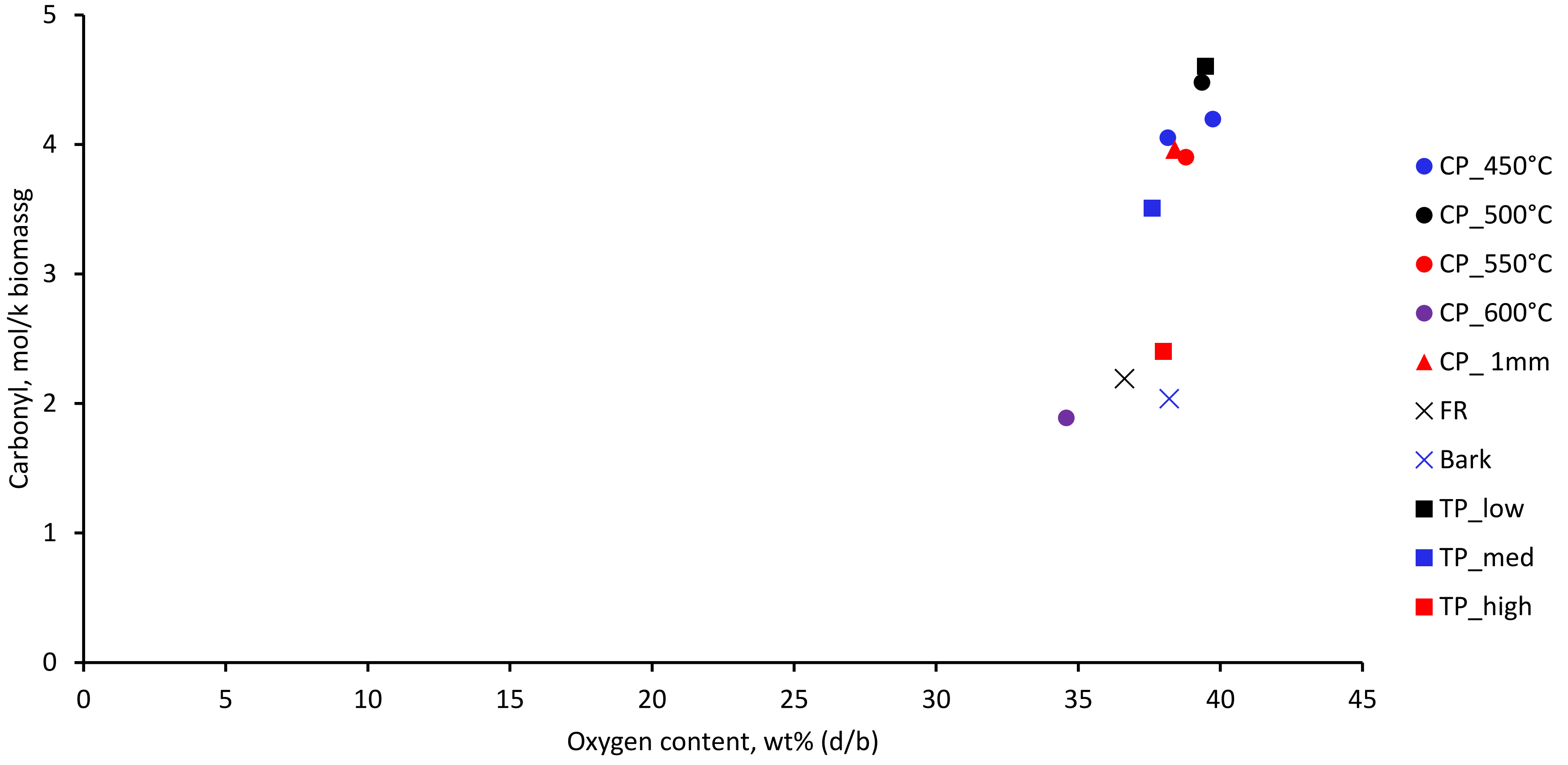
- Carboxylic acid number lowest in forest residue and bark oil and clean pine @ 600°C

Phenolics vs. O Content

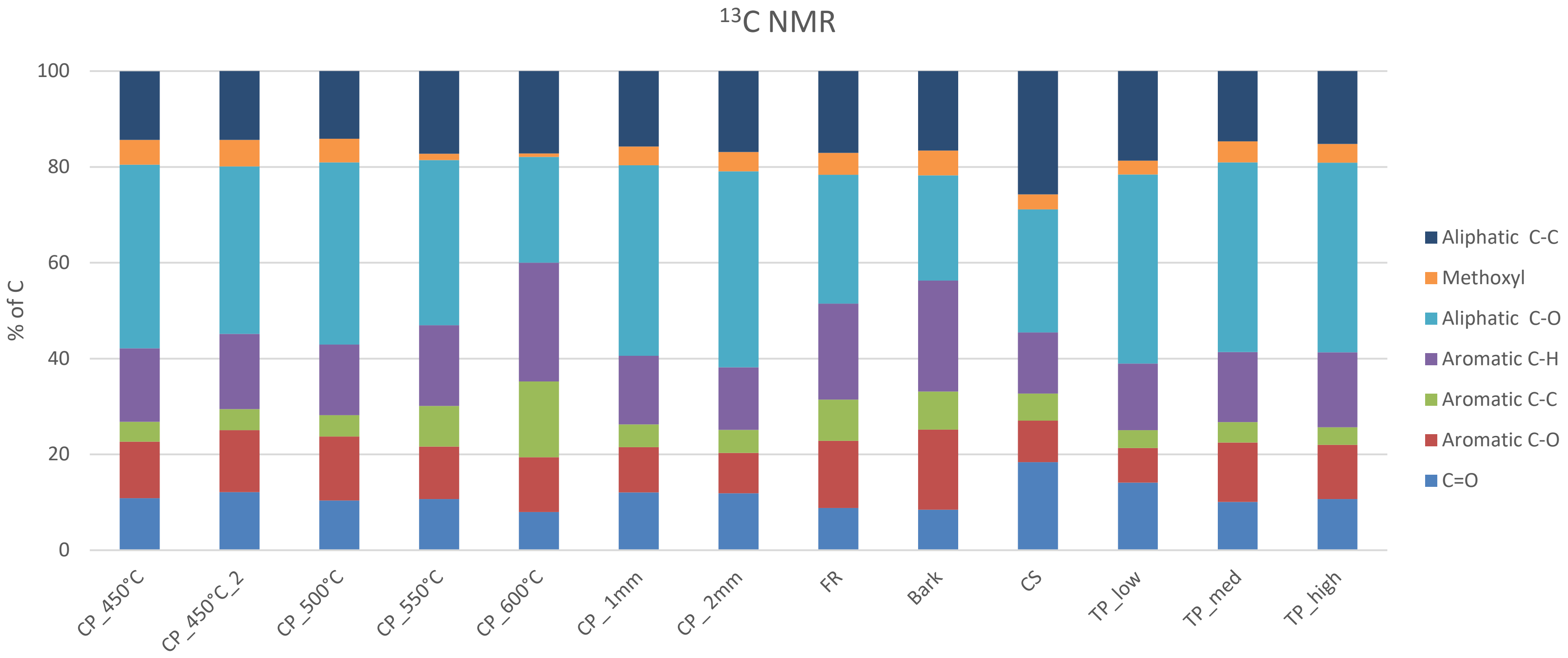


- Forest residue, bark, and pine @ 600°C have lower phenolics than the rest
- For clean and torrefied pine, inverse relationship with oil oxygen content?

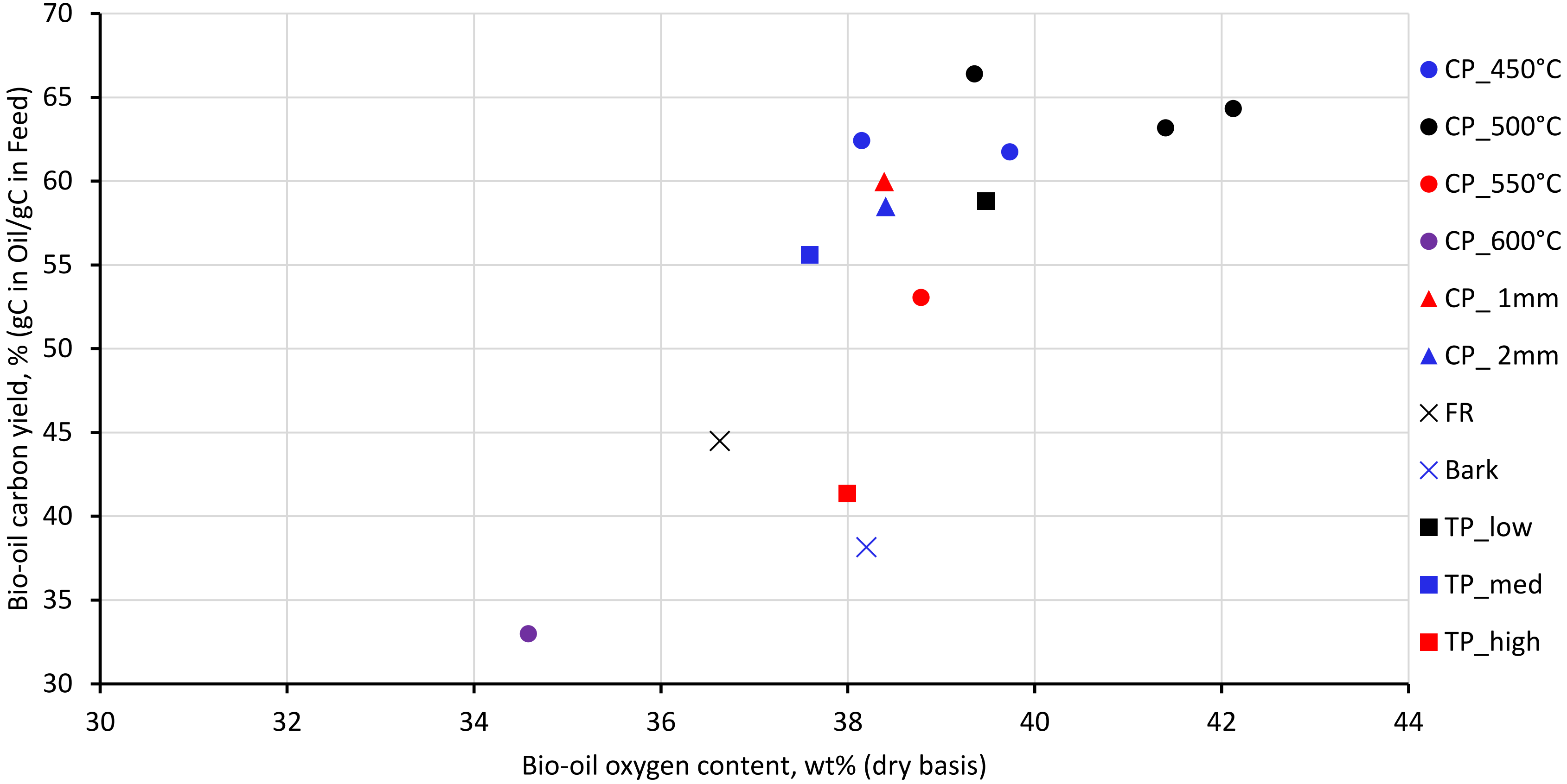
Carbonyls vs. O Content



Composition by ^{13}C NMR



Oil C Yield vs. O Content



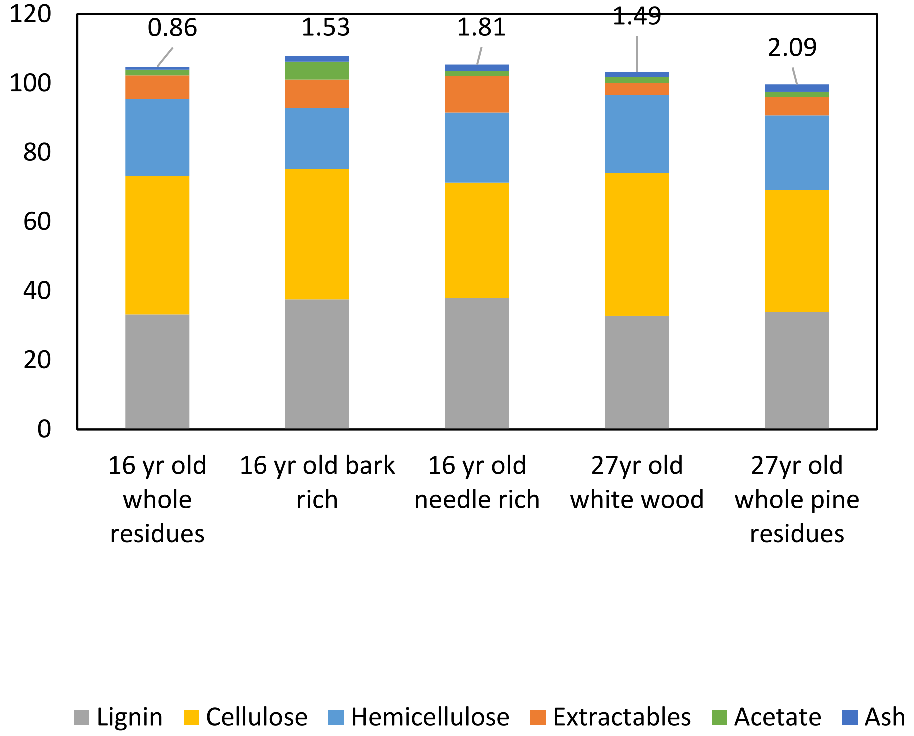
wt% dry	Carbon	Oxygen
Clean pine	51%	42%
Clean pine 1mm	51%	42%
Clean pine 2 mm	51%	42%
230°C Torrefied Pine	52%	41%
250°C Torrefied Pine	54%	40%
275°C Torrefied Pine	58%	35%
Forest Residue	47%	36%
Bark	53%	38%
Corn Stover	45%	40%

- Liquid carbon yield increases as oxygen content increases
- For pine, C yields in order: 500C > 450°C > 550°C > 600°C

Metal distribution in feedstocks

ICP, ppm	16 yr old whole residues	16yr old Bark	16yr old Needles	Whitewood_27yr old residues	27yr old whole pine residues
Ag	<10	<10	<10	<10	<10
Al	**329**	**534**	**645**	**438**	**750**
Ba	<10	<10	<10	<10	12
Ca	**1682**	**1635**	**1841**	**889**	**1091**
Cd	<10	<10	<10	<10	<10
Co	<10	<10	<10	<10	<10
Cr	<10	<10	<10	<10	22
Cu	<10	<10	<10	40	<10
Fe	**179**	**262**	**265**	**294**	**688**
Ga	<10	<10	<10	<10	<10
K	**833**	**905**	**1437**	**888**	**999**
Li	11	<10	<10	<10	<10
Mg	**398**	**418**	**577**	**256**	**369**
Mn	**73**	**82**	**119**	**91**	**113**
Na	**467**	**463**	**584**	**163**	**383**
Ni	<10	<10	<10	<10	<10
P	**182**	**229**	**490**	**80**	**129**
Pb	<10	<10	<10	<10	<10
S	**141**	**198**	**370**	**114**	**95**
Sr	<10	<10	<10	<10	<10
Zn	19	<10	25	28	16

Wood Composition



- Needles have the highest contents of Ca, K, Mg, Mn, Na, P, and S.
- 27 yr old whole pine residues had highest Al and Fe (highest ash).