Impact of Tree Age and Anatomical Fraction on Forest Residue Pyrolysis and Hydrotreating

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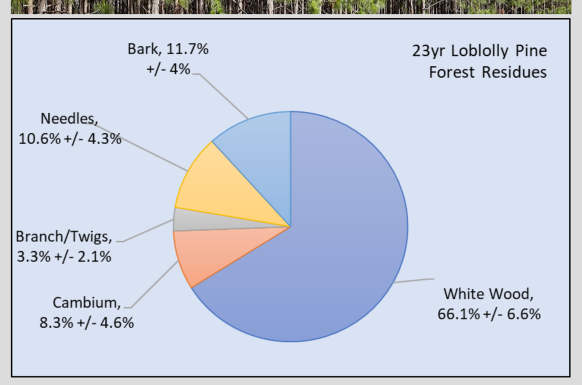
Introduction

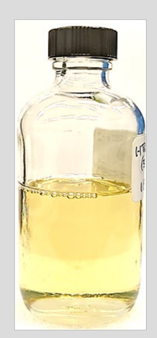


Utilization of cost-advantaged biomass and waste resources to produce clean, domestic biofuels will be a key factor in decarbonizing transportation in the United States. This study investigates how the distribution of anatomical fractions (stem wood, bark, needles, branches) from loblolly pine trees of different ages impacts pyrolysis and hydrotreating processes, including product composition, carbon efficiency, economics, and sustainability. Commercially sourced 13- and 23-year-old loblolly pine residues were chosen to represent available resources; whole tree thinnings, and tops and branches from merchantable timber, respectively. Fast pyrolysis experiments were carried out on the whole samples, separated anatomical fractions, and whole samples that were air-classified to remove loose bark, needs, and soil contaminants. Select samples were processed to hydrocarbon blendstocks, and technoeconomic and life cycle analyses were conducted for the end-to-end process.

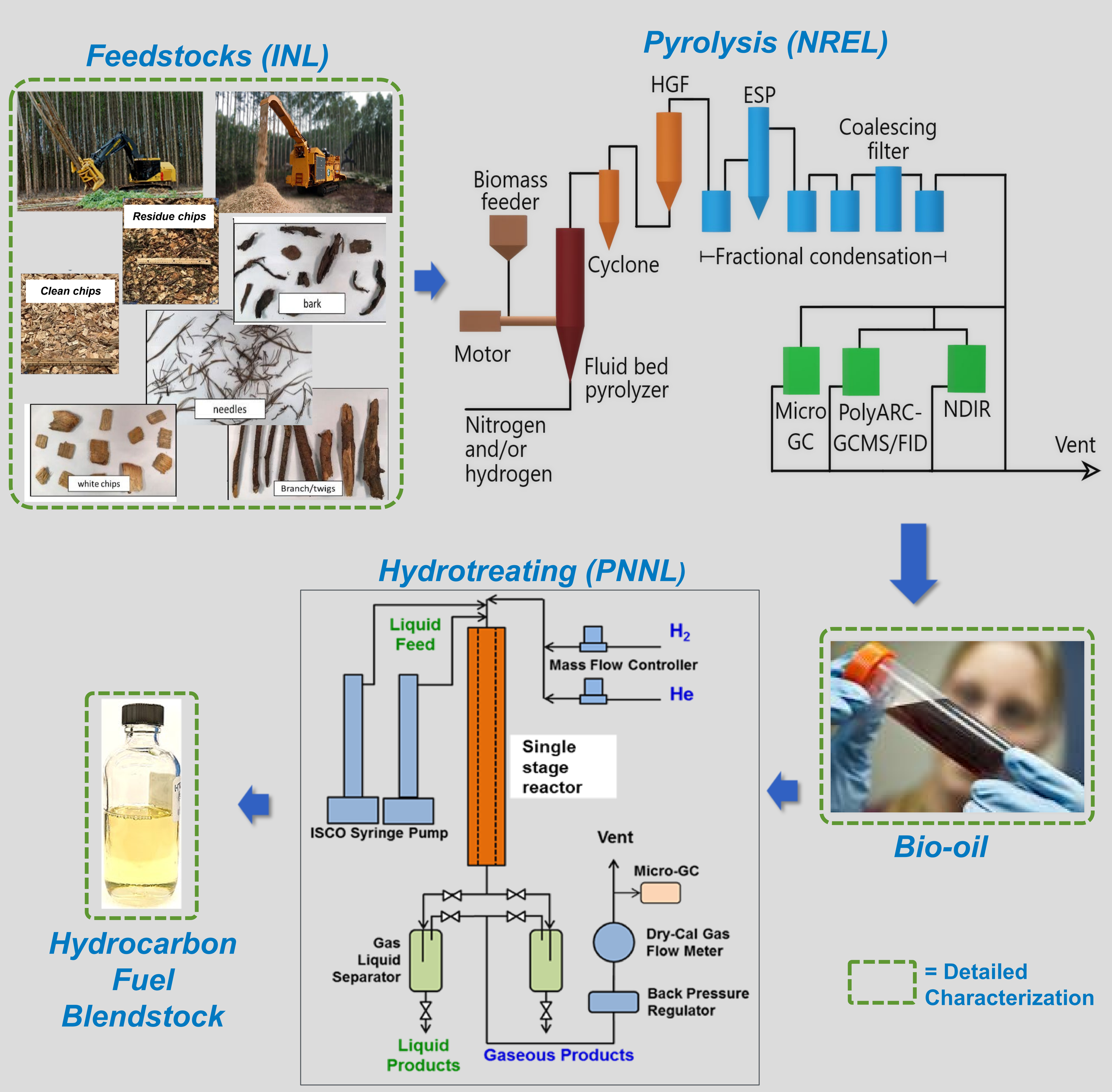
Methods

- **Feedstock:** Commercially sourced Loblolly pine
  - "Residues" = 23 yr. tops and branches
  - "Thinnings" = 13 yr. whole trees
  - Anatomical fractions were hand separated
  - Residues were also air classified at two fan speeds

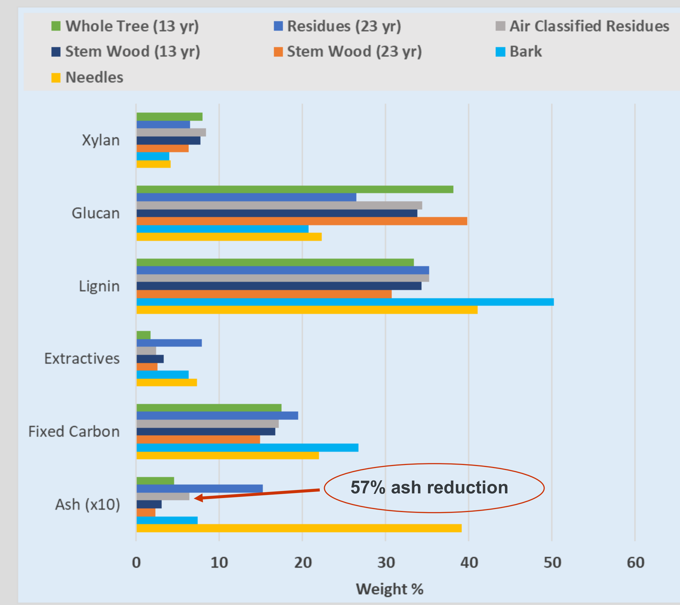
- **Fast pyrolysis:** 2" ID fluidized bed reactor (2FBR)
  - Temperature: 500 °C
  - Feed rate: 0.3 kg/h
  - Product collection: fractional condensation

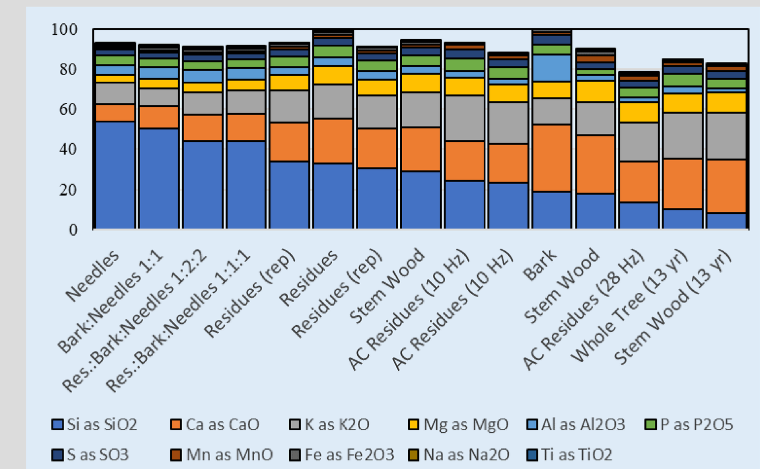


- **Hydroprocessing:** 40 mL/h fixed trickle bed reactor
  - Two-step process
  - *Stabilization:* Ru/TiO_2, 140 °C, 1800 psi, LHSV 0.23 h^{-1} in H_2
  - *Hydrotreating:* sulfided $NiMo/Al_2O_3$, 400 °C, 1800 psi, LHSV 0.22 h^{-1} in H_2 + DTBDS (sufiding agent)



Feedstock Analysis

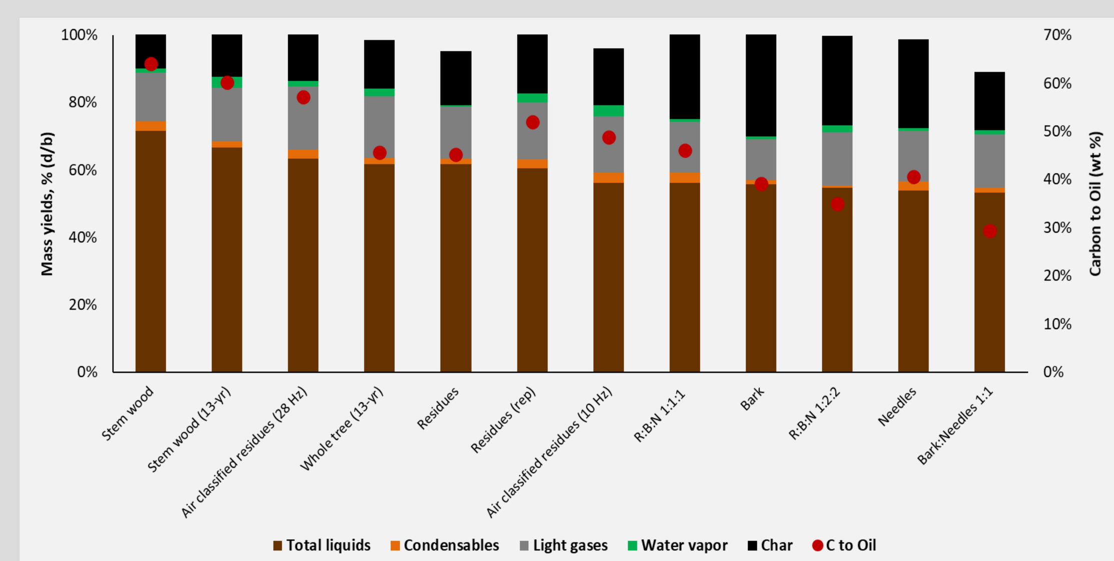




Feedstock Moisture: **2.8-5.9 wt%**

Feedstock Ash: **0.3-3.9 wt%**

Fast Pyrolysis

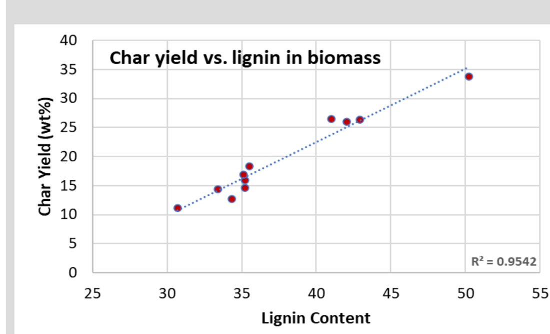


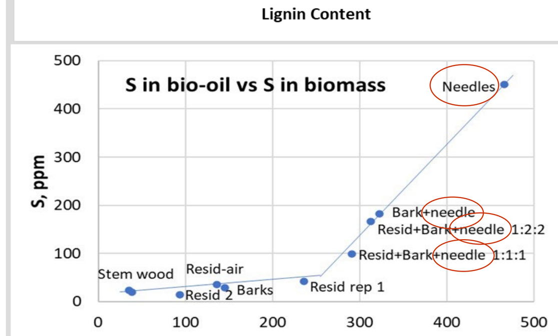
Fast pyrolysis product distributions, ranked by total liquid yield. Condensables were measured by online GC/MS-PolyArc FID. All oils except from bark were single phase.

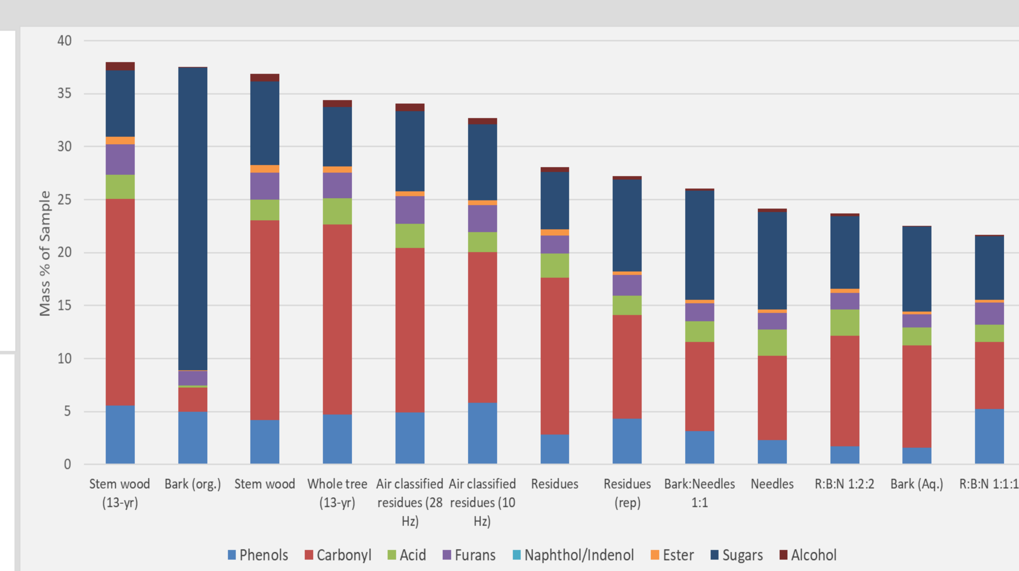
Mass balance: **98 ±2%**

Oil Yield: **53-72% (d/b)**

Carbon to Oil **29-64%**



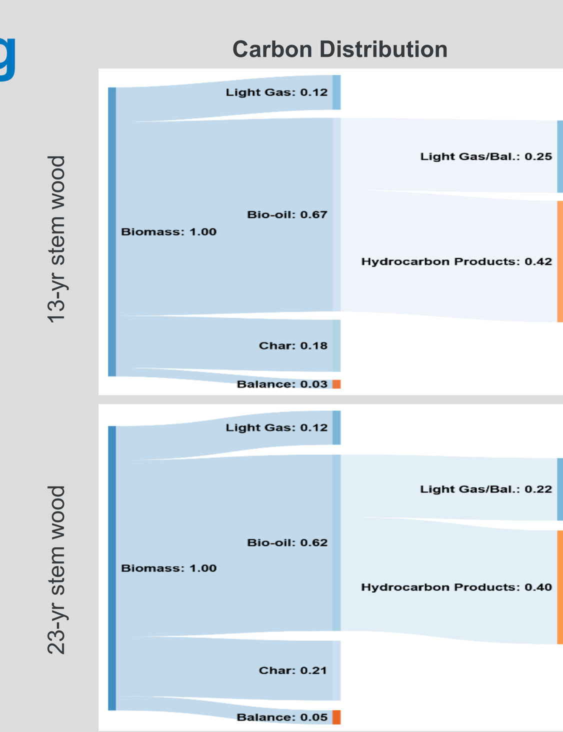




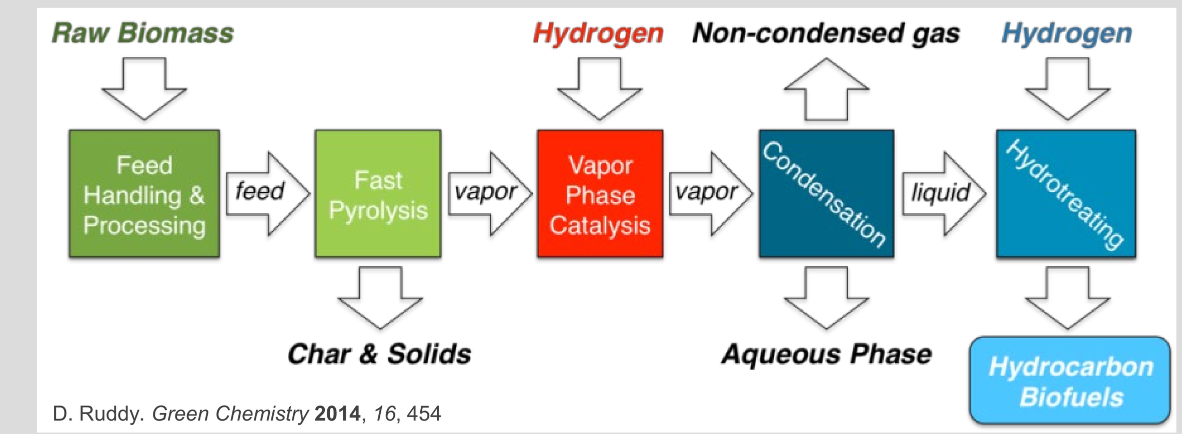
Quantitative GC/MS-FID analysis of pyrolysis oils, ranked by % mass accounted by calibration of 36 compounds (https://www.nrel.gov/docs/fy16osti/65889.pdf).

Hydroprocessing

	Stem wood 13-yr	Whole tree (13-yr)	Stem wood (23-yr)	Residues (23-yr)
Hydrotreating performance				
Hydrotreated oil yield, g/g bio-oil, dry basis	0.419	0.416	0.401	-
Carbon yield to hydrotreated oil, g/g	0.645	0.629	0.637	-
H_2 consumption, g/g bio-oil, dry basis	0.058	0.052	0.065	-
Hydrotreated oil composition				
C, wt.%, dry basis	86.4	86.7	87.1	86.7
O, wt.%, dry basis	<0.1	<0.1	<0.1	<0.1
S, ppm, by ICP	18	8	10	10
Gasoline (IBP-150), wt.%, sim-dist	39.5	43.0	43.9	39.8
Diesel (150-350), wt.%, sim-dist	48.5	46.8	45.4	49.6
Jet (150-250), wt.%, sim-dist	26.7	26.1	24.3	27.4
Heavies (>350), wt.%, sim-dist	12.0	10.3	10.7	10.8

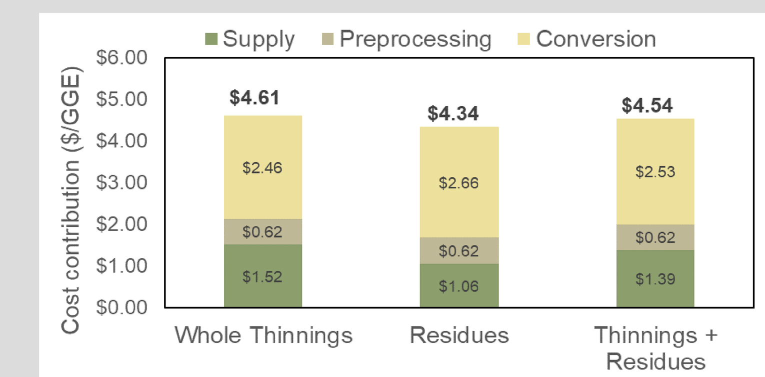


Technoeconomic and Life Cycle Analysis

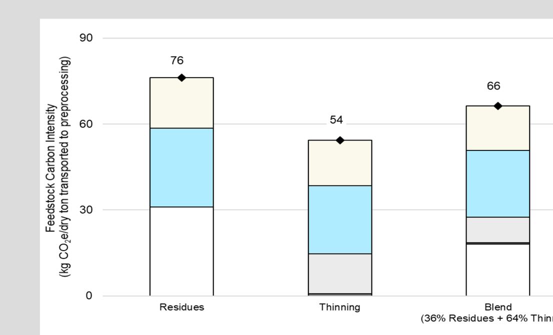


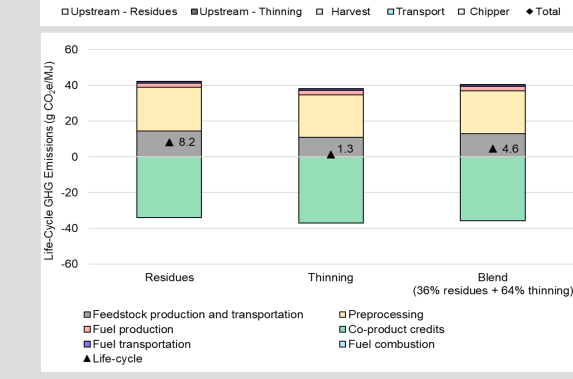
Conceptual design case considered here[1]: Biofuel production via catalytic fast pyrolysis (CFP). CFP yields were extrapolated from data presented here based on previous correlations.[2]

Economics for both feedstocks are similar Residues were the most economical option despite a slightly higher conversion cost, driven by lower supply costs (harvesting costs are allocated to merchantable wood products).



	Whole thinnings	Residues	Thinnings & Residues
Feedstock cost ($/ton)	**$90.13**	**$73.75**	**$85.74**
Supply ($/ton)	$64.00	$46.41	$59.17
Preprocessing ($/ton)	$26.13	$27.34	$26.57





Thinnings have a lower carbon intensity than residues due to reduced collection and transportation requirements and lower upstream emissions.

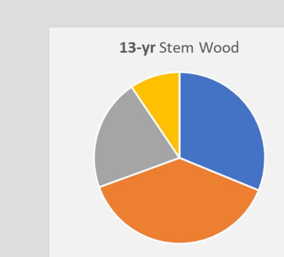
Biofuel produced with all three sources of loblolly pine achieves **>80% reduction in GHG emissions** compared to petroleum equivalents.

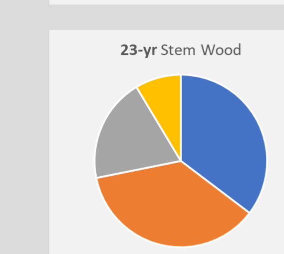
The GHG emissions are dominated by the displacement credits for the co-products **(2-butanone, acetone, and excess electricity)**.

1. Dutta, Abhijit, Maarit K. Iisa, Michael Talmadge, Calvin Mukarakate, Michael B. Griffin, Eric C. Tan, Nolan Wilson, et al. 2020. "Ex Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass to Hydrocarbon Fuels: 2019 State of Technology and Future Research." NREL/TP-5100-76269. National Renewable Energy Lab. (NREL), Golden, CO (United States). https://doi.org/10.2172/1605092.
2. Wiatrowski, Matthew R., Abhijit Dutta, M. Brennan Pecha, Meagan Crowley, Peter N. Ciesielski, and Daniel Carpenter. "A simplified integrated framework for predicting the economic impacts of feedstock variations in a catalytic fast pyrolysis conversion process." *Biofuels, Bioproducts and Biorefining* (2021).

Conclusions

- Higher bio-oil yield was generally correlated with total **volatiles, hydrogen, oxygen, glucan, and mannan**
- Lower bio-oil yield was correlated with **fixed carbon, nitrogen, sulfur, and extractives**
- **Air classification** reduced **ash, extractives, and sulfur**, resulting in an increase in yield and GC-detectable compounds
- **Sulfur contained in needles** appears to disproportionally partition to the oil phase compared to the other fractions
- **Hydrotreating yields** and distribution of **hydrocarbon fuel products** were comparable for thinnings and residues of different ages
- The **minimum fuel selling price** is similar for thinnings and residues
- **GHG emissions** for thinning and residues can achieve **>80% reduction** vs. fossil-derived equivalents, a large driver being **co-product credits**





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Pyrolysis products collected in ESP (left – stem wood, right – R:B:N 1:2:2)

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