DOE Bioenergy Technologies Office (BETO) 2023 Project
Peer Review

Sulfur Profiling in Pine Residues and Its Impact on Thermochemical Conversion

April 5, 2023
Feedstock Technologies

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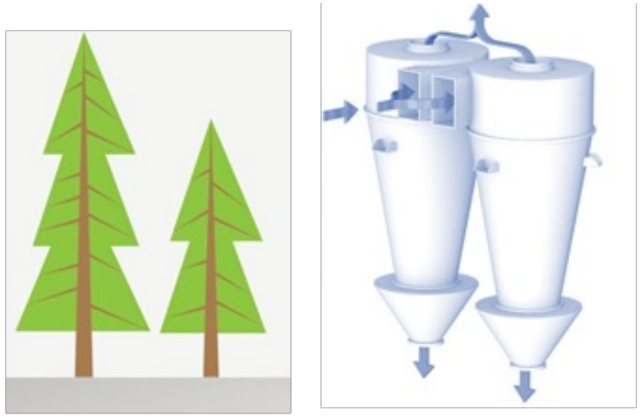
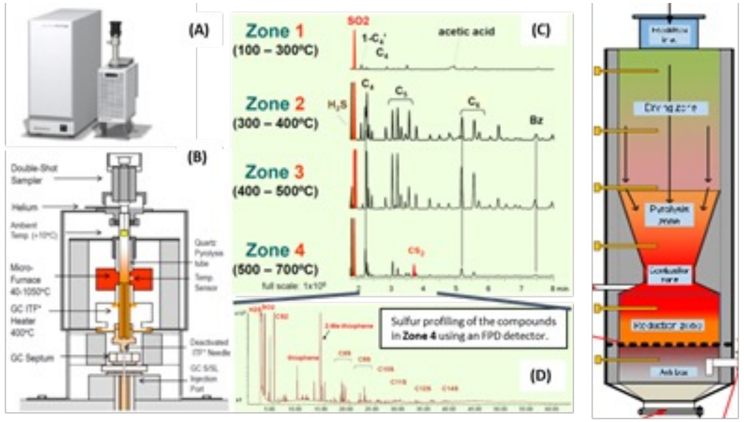
Project Overview



Feedstock preprocessing and sulfur mitigation



Sulfur profiling of the compounds in **Zone 4** using an FPD detector.

Sulfur profiling during thermochemical conversion

- Sulfur profile library of a pine residue collection
- Effective biomass preprocessing/sulfur removal strategy
- Predictive model guides process design & implementation

- Timeline:

	From	To
BP1	**10/1/2019**	**09/30/2020**
BP2	**10/01/2020**	**09/30/2022**
BP3	10/01/2022	01/31/2024
BP4	02/01/2024	01/31/2025

- Address MYP Program Barriers ADO-B ”Feedstock Supply Chain Infrastructure” and Ft-E “Feedstock Quality” through 2019 FOA AOI 2a

Problem definition: Sulfur contents vary largely in biomass feedstocks

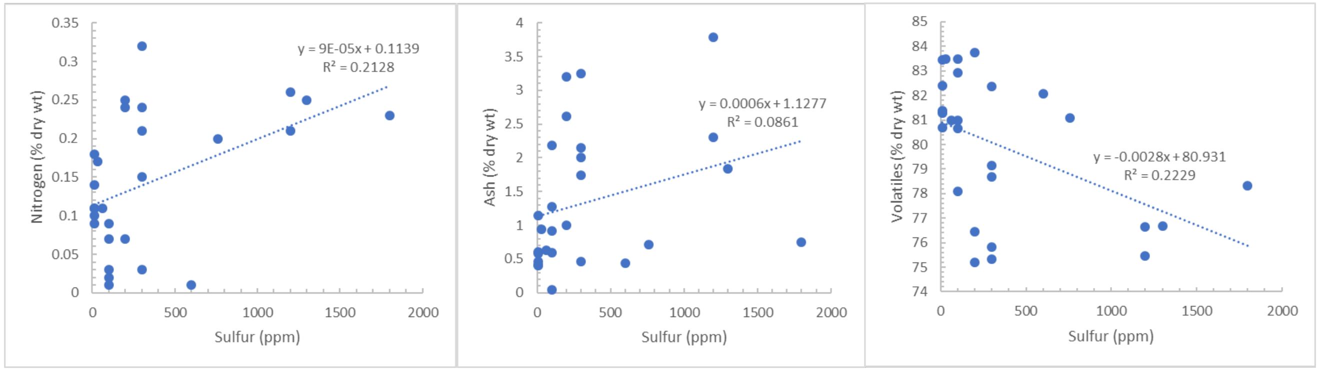
Table 1 Sulfur content of different biomass types based on ultimate analysis.

Biomass Type	Sulfur Content (% dry weight)	Reference
Rice Straw	0.14	1, 2
Wheat Straw	0.39	1
Corn Stover	0.07	4
Switchgrass	0.08	1
Softwood	0.02	5
Hardwood	0.02	5
Bana grass	0.1	6
Bagasse	0.05	6
Carinata	0.32	7
Rape	0.06	7
Peanut shell	0.54	8
Municipal solid wastes	0.1-1.0	8

Table 2. Total sulfur for twenty-six samples of forest residue based on ultimate analyses (RRBH study)

Order of Magnitude of Sulfur Content	No. of Samples
0.001% (one-thousandth percent)	11
0.01% (one-hundredth percent)	11
0.1% (one-tenth percent)	4

Figure 1. No clear correlation was found between sulfur content and nitrogen, ash and volatiles.



- The root cause (origin) of the sulfur variation is not clear

Problem definition:

- **The form and fate of sulfur during thermochemical conversion of biomass are poorly understood**
- **Lack of effective biomass preprocessing/sulfur mitigation methods**

  - Scarce quantitative data reported on the transformation of sulfur during thermochemical conversion of biomass
  - The reaction pathway of organic sulfur and inorganic sulfur is dependent on temperature and atmosphere and possibly the interactions with other biomass constitutions
  - Distribution of sulfur species in the gas and solid products is not clear
  - Effect of sulfur species (other than H_2S) on conventional and Mn/Mo/Zr improved catalyst is not well understood

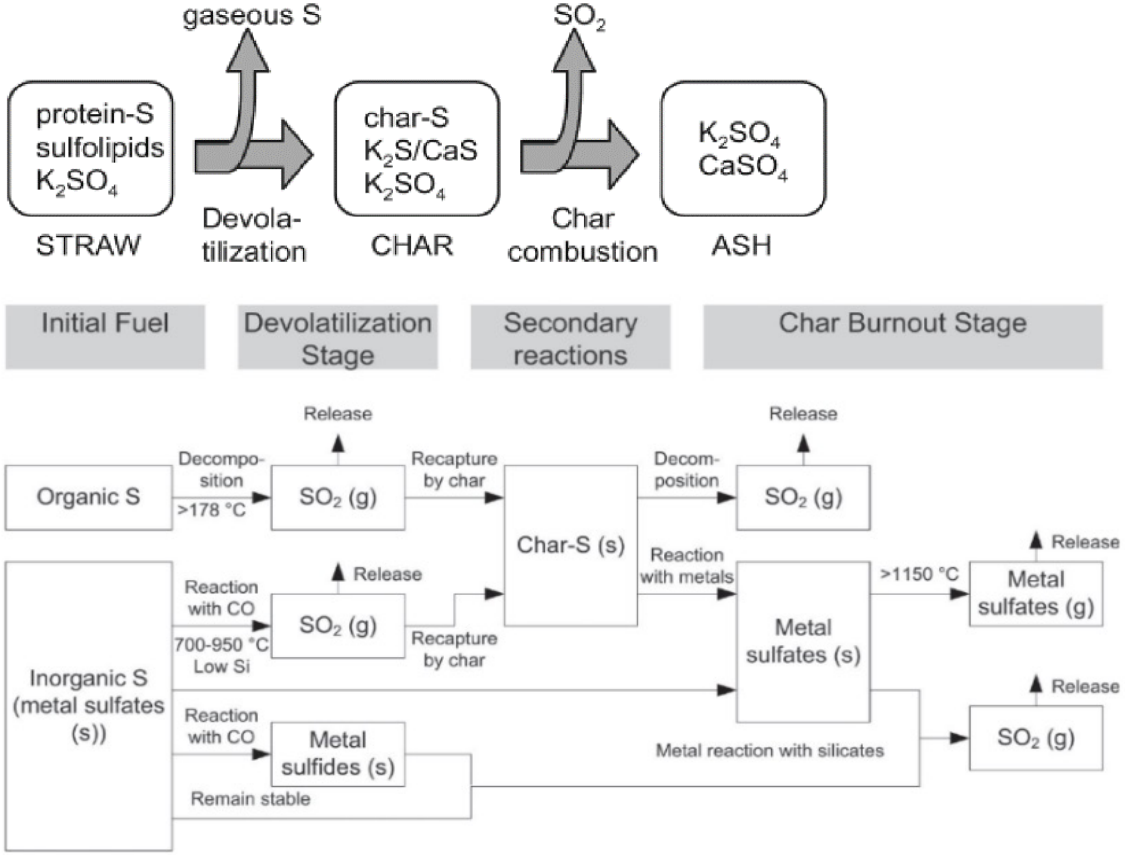
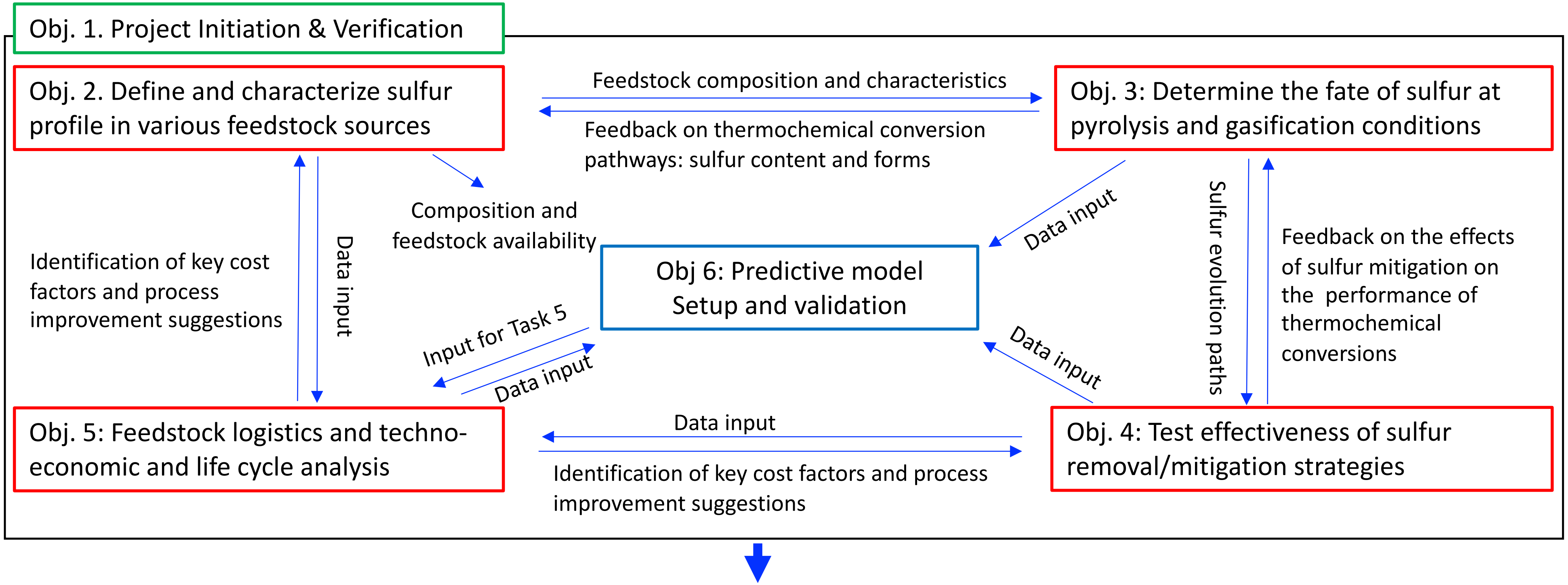


Figure 2. Possible reaction paths and release mechanisms of sulfur during thermochemical conversion [3]

1-Approach



Obj. 1. Project Initiation & Verification

Obj. 2. Define and characterize sulfur profile in various feedstock sources

Feedstock composition and characteristics

Feedback on thermochemical conversion pathways: sulfur content and forms

Obj. 3: Determine the fate of sulfur at pyrolysis and gasification conditions

Identification of key cost factors and process improvement suggestions

Data input

Composition and feedstock availability

Obj 6: Predictive model Setup and validation

Data input

Sulfur evolution paths

Feedback on the effects of sulfur mitigation on the performance of thermochemical conversions

Input for Task 5

Data input

Data input

Obj. 5: Feedstock logistics and techno-economic and life cycle analysis

Data input

Identification of key cost factors and process improvement suggestions

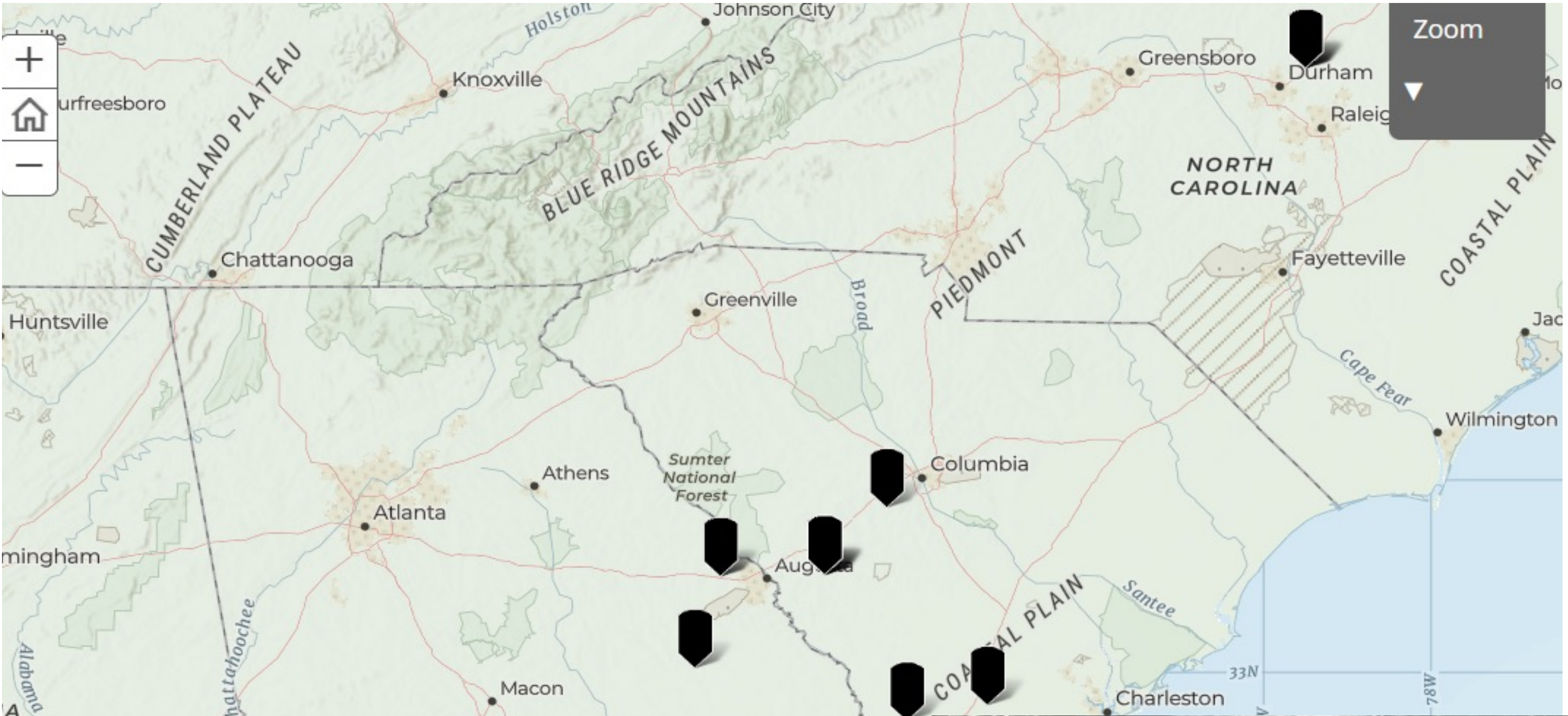
Obj. 4: Test effectiveness of sulfur removal/mitigation strategies

Project outputs:

- A comprehensive sulfur profile library of a representative pine residue collection
- Mechanistic understanding of the fate of sulfur during thermochemical conversion processes
- Effective biomass preprocessing/sulfur removal technologies that remove >50% of the sulfur from pine residues
- A set of TEA/LCA models that help selecting suitable sulfur mitigation technologies based on feedstock properties
- Validated predictive model that can guide design & implementation of pyrolysis and gasification processes

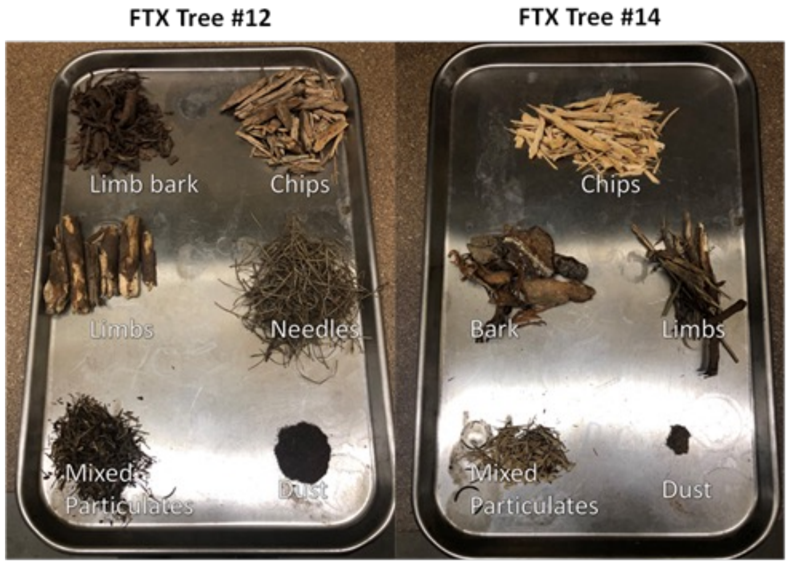
Sample collection

- NCSU samples: 4
- FTX samples: 11
- Auburn sample: 1
- RRB samples: 2



Sample preparation

Sample air-dried or oven-dried and stored in drums



Manually separated anatomical fractions

Bags of milled samples

Milled and sieved for characterization

Subtask 2.3 Ultimate, Proximate and Sulfur analyses

Subtask 2.4 Air Classification and Bioleaching tests

* We followed ASTM D6323 to obtain homogeneous subsamples; this ensures representative samples being distributed to the whole project team.

Representative feedstock factors

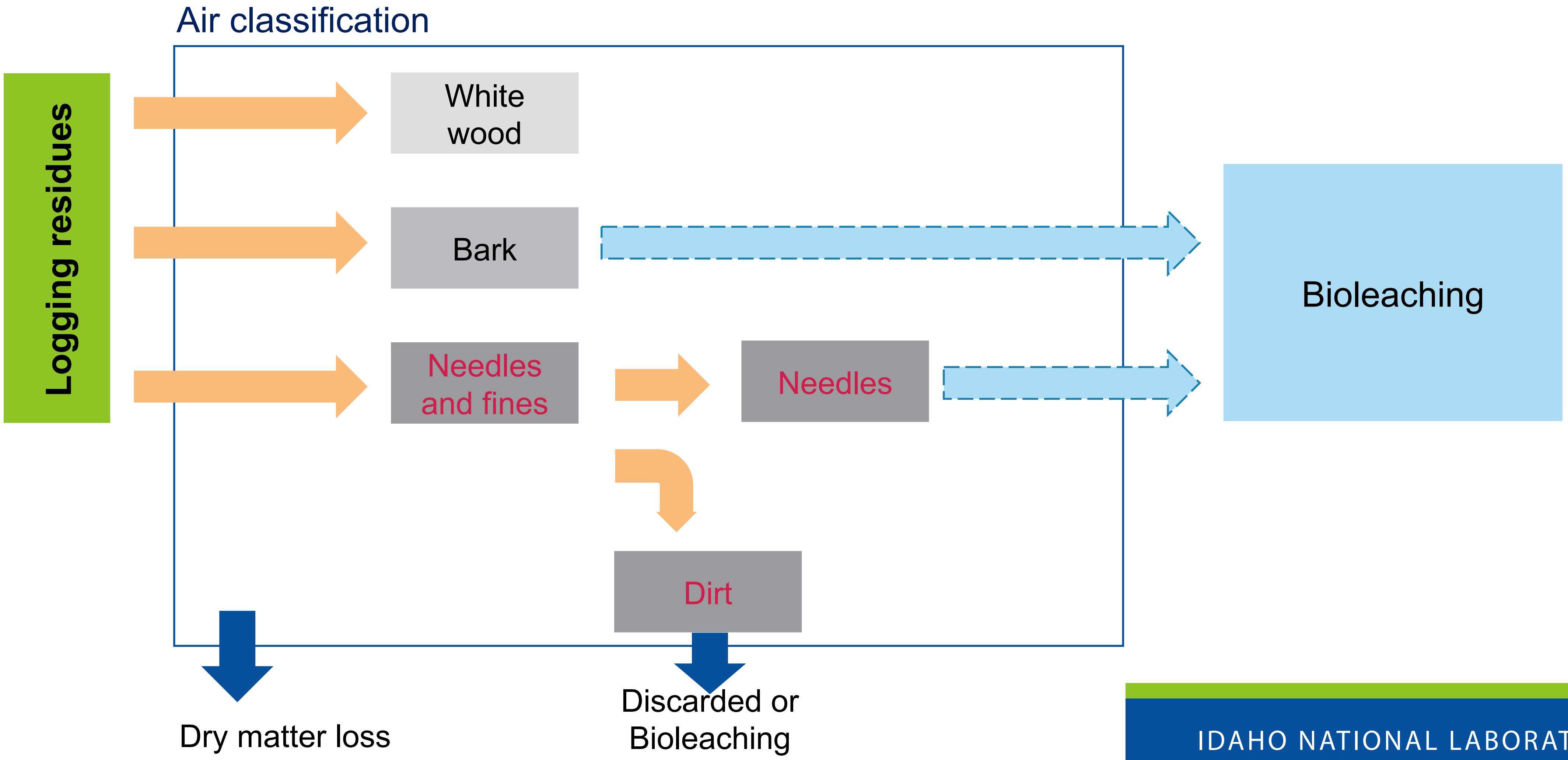
- The collected samples cover the age, location, harvesting practice, species/genetics, and anatomical fraction factors.

Factor description	No. of Levels	Details
Species/genetics	4	4 genetic lines, (2 Piedmont region families and 2 Coastal region families) , 9-10 years old
Age	5	5-30 years, 5 years apart, all from Sandhill region
Growth location (soil type)	3	Sandhill, Piedmont, Coastal plain and others
Harvesting practices	2	Whole tree (precommercial thinning) and tops/branch/bark fractions (logging residues)
Anatomical fractions	2-5	Chips, limbs, barks, needles, particulates

- Link to ArcGIS Story Map site: https://arcg.is/95WK8

Mechanical separation

A mechanical separation process using **air classification** was designed and applied to remove fractions with higher sulfur contents.



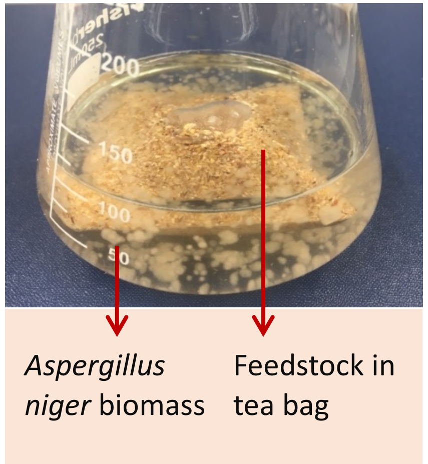
Air classification process overview

Note
Screen Chute Exits the
other side of the Machine

Bioleaching

- Leaching procedure:

Aspergillus niger strains:
NRRL 2001, NRRL 3122, NRRL 567

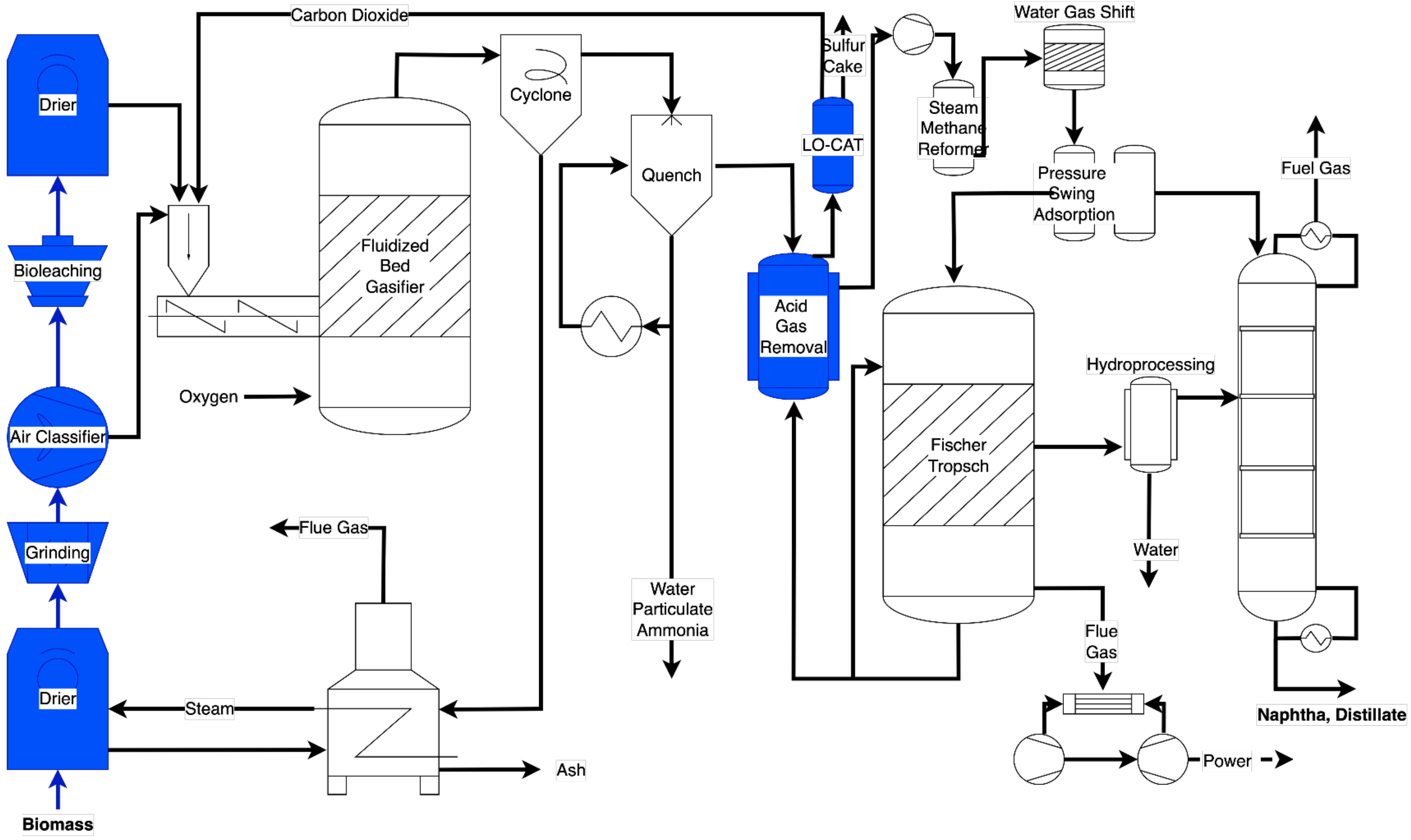


Leached pine biomass

Filtered leachate

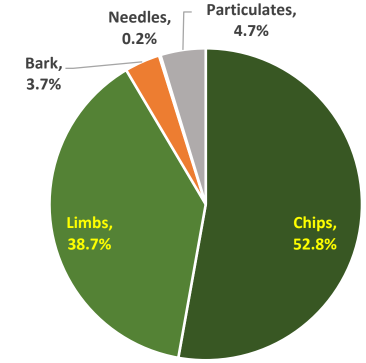
Elemental composition via ICP-OES

Baseline Techno-Economic Analysis (TEA)

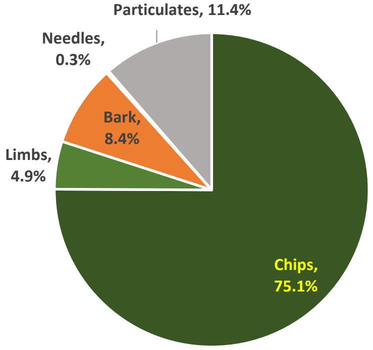


2 – Progress and Outcomes

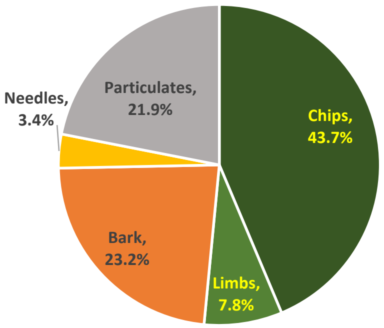
Weight ratios of anatomical fractions



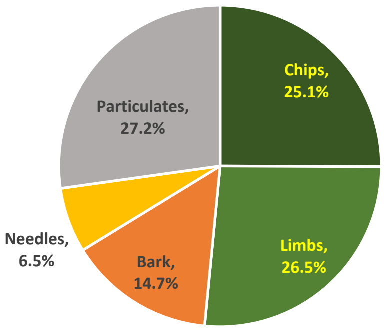
FTX #10, Piedmont, 26-Yr



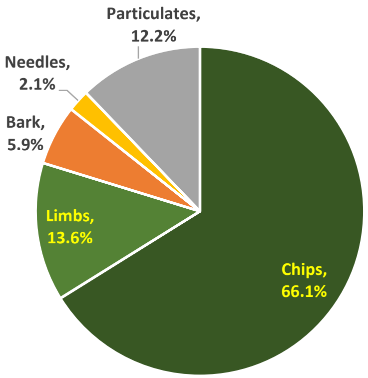
FTX #13, Piedmont, 33-Yr



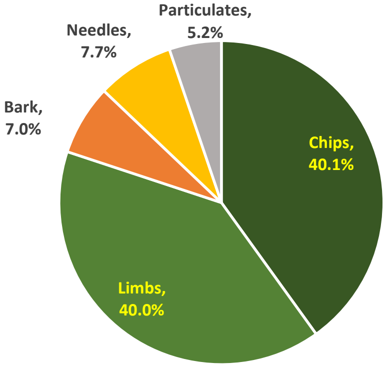
FTX #12, Coastal Plain, 22-Yr



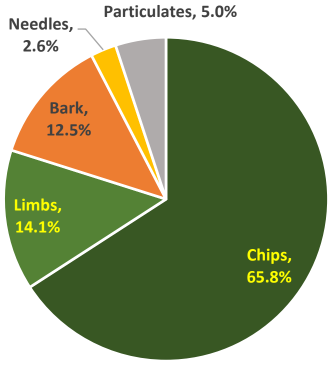
FTX #15, Coastal Plain, 31-Yr



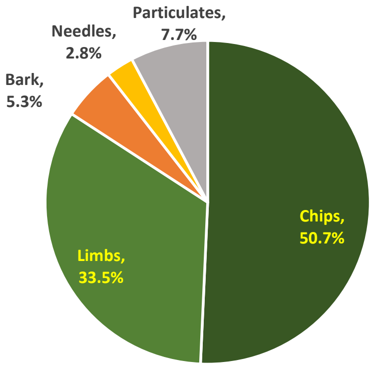
Auburn, Blackland prairie, 34-Yr



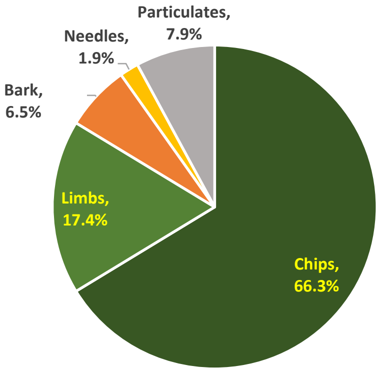
FTX #16, Sandhill, 5-Yr



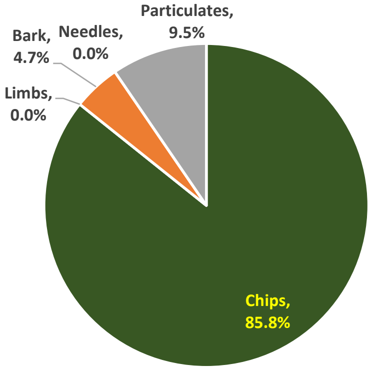
FTX #17, Sandhill, 10-Yr



FTX #19, Sandhill, 16-Yr



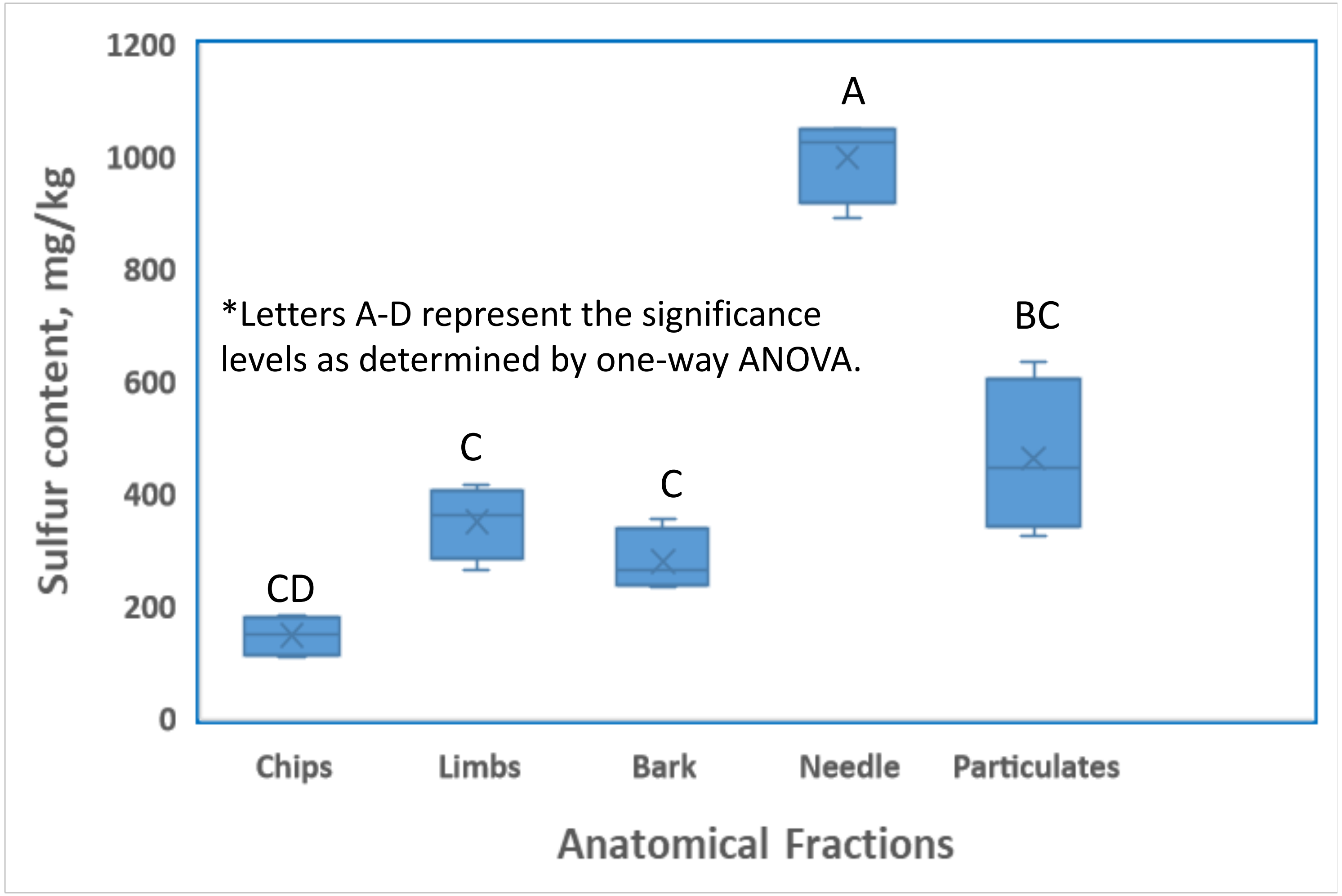
FTX #21, Sandhill, 26-Yr



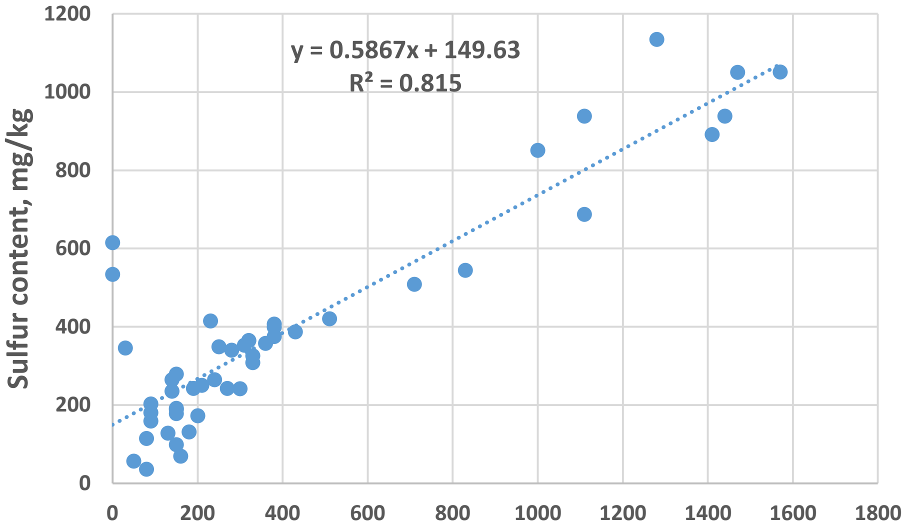
FTX #23, Sandhill, 32-Yr

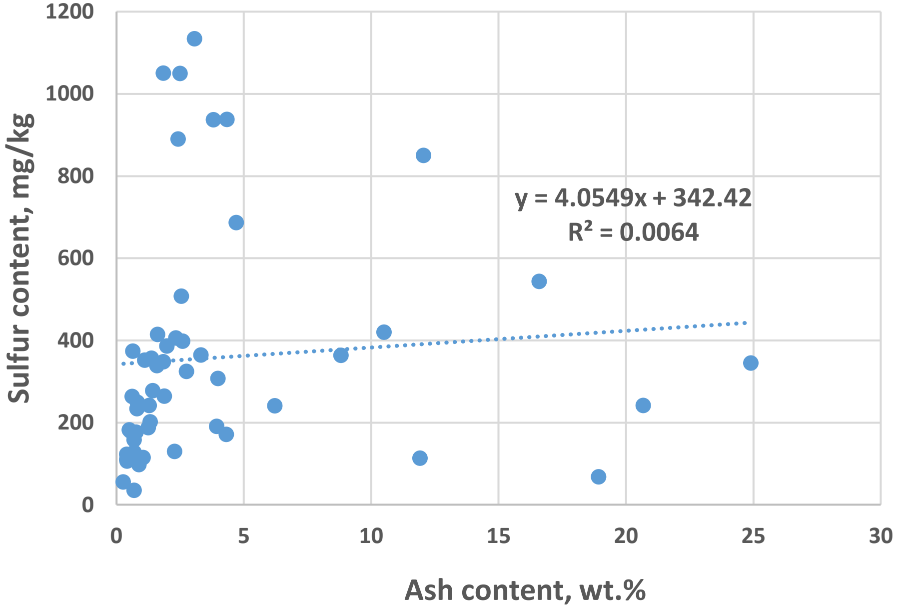
- Overall large variation across soil type, age, and harvesting practices.
- Coastal plain samples contain large fractions of bark, needles and particles.

Sulfur content vs. anatomical fraction



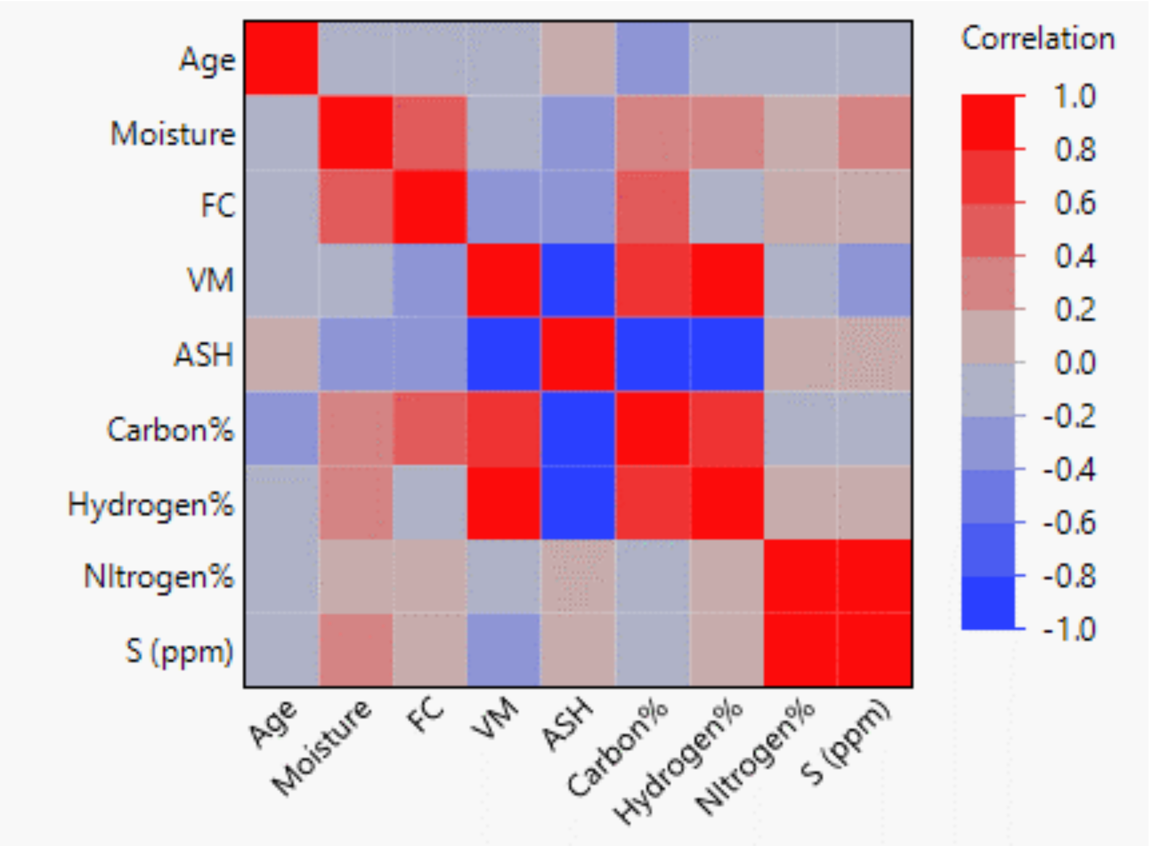
*Letters A-D represent the significance levels as determined by one-way ANOVA.



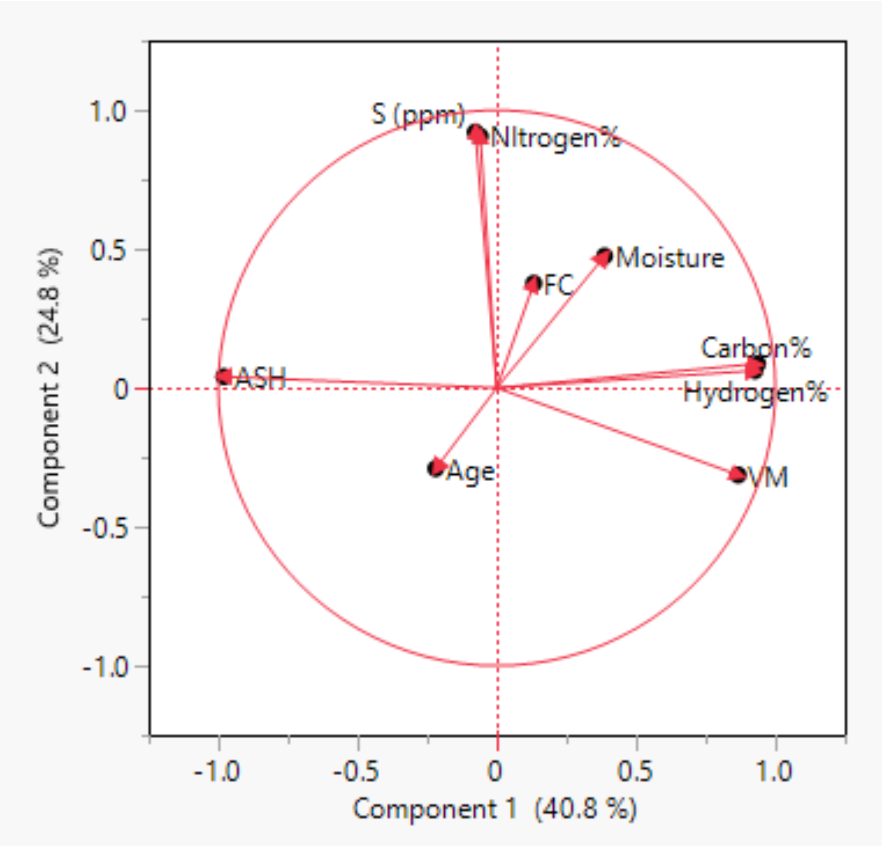


- Sulfur contents vary in different anatomical fractions of FTX and Auburn samples.
- Needles and particulates contain higher sulfur than the other fractions.

Principal component/correlation analyses



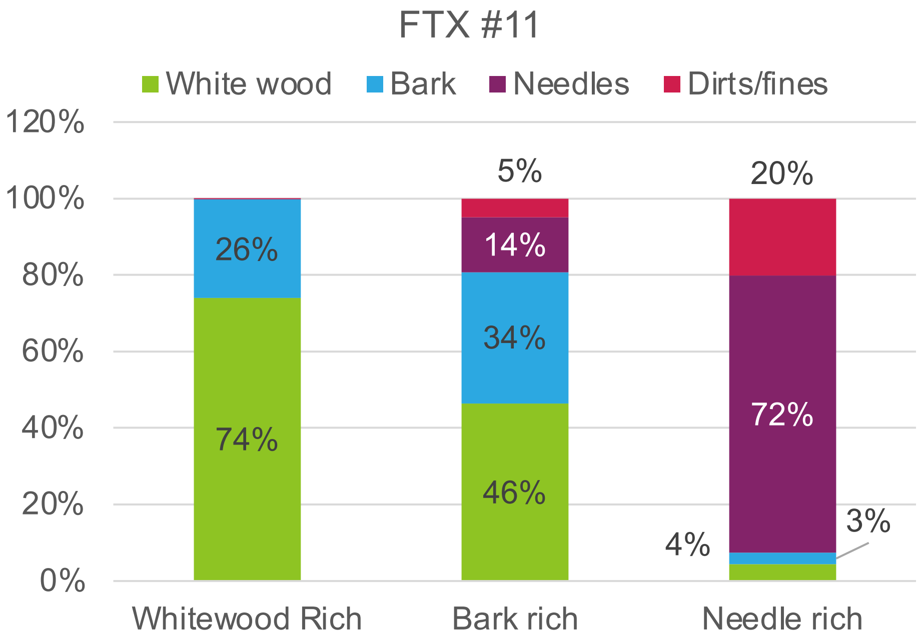
Correlations estimated by restricted maximum likelihood (REML) method



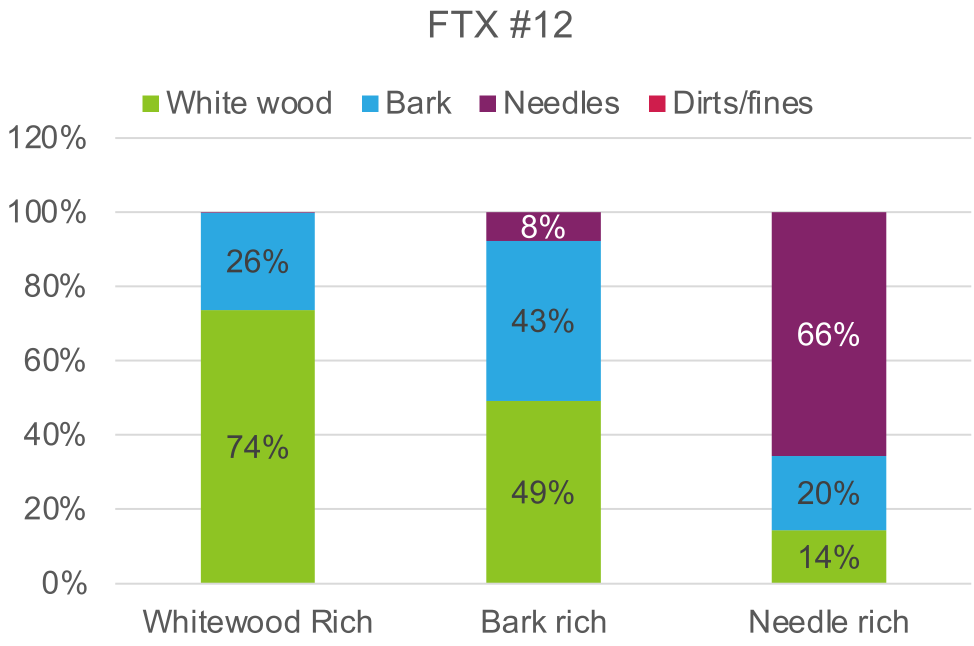
PCA plot estimated by REML method

- Sulfur content strongly correlates with N content (dominant by organic S?)
- Sulfur content has a weak negative correlation with age

Air classification: Resulted fraction enriched streams

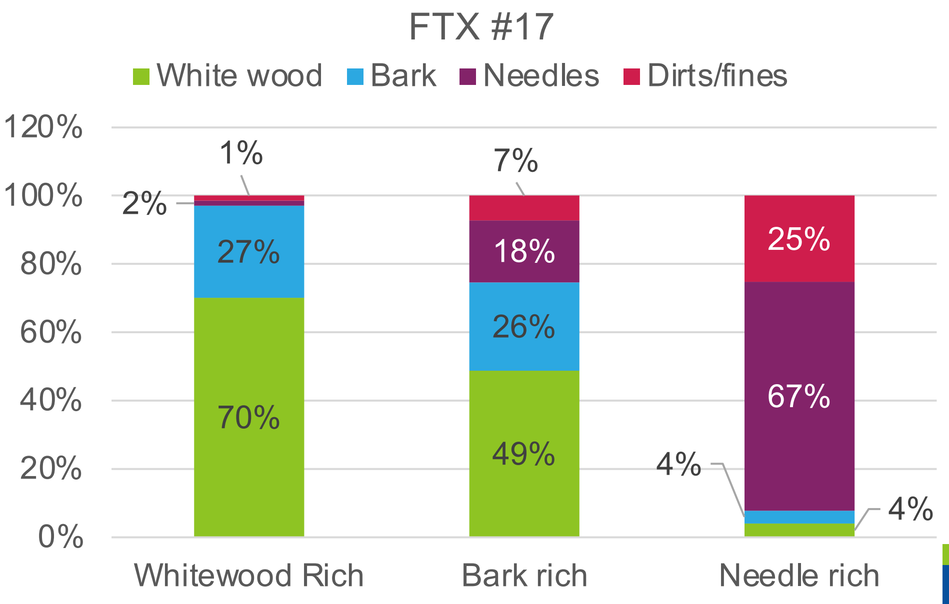


FTX #11



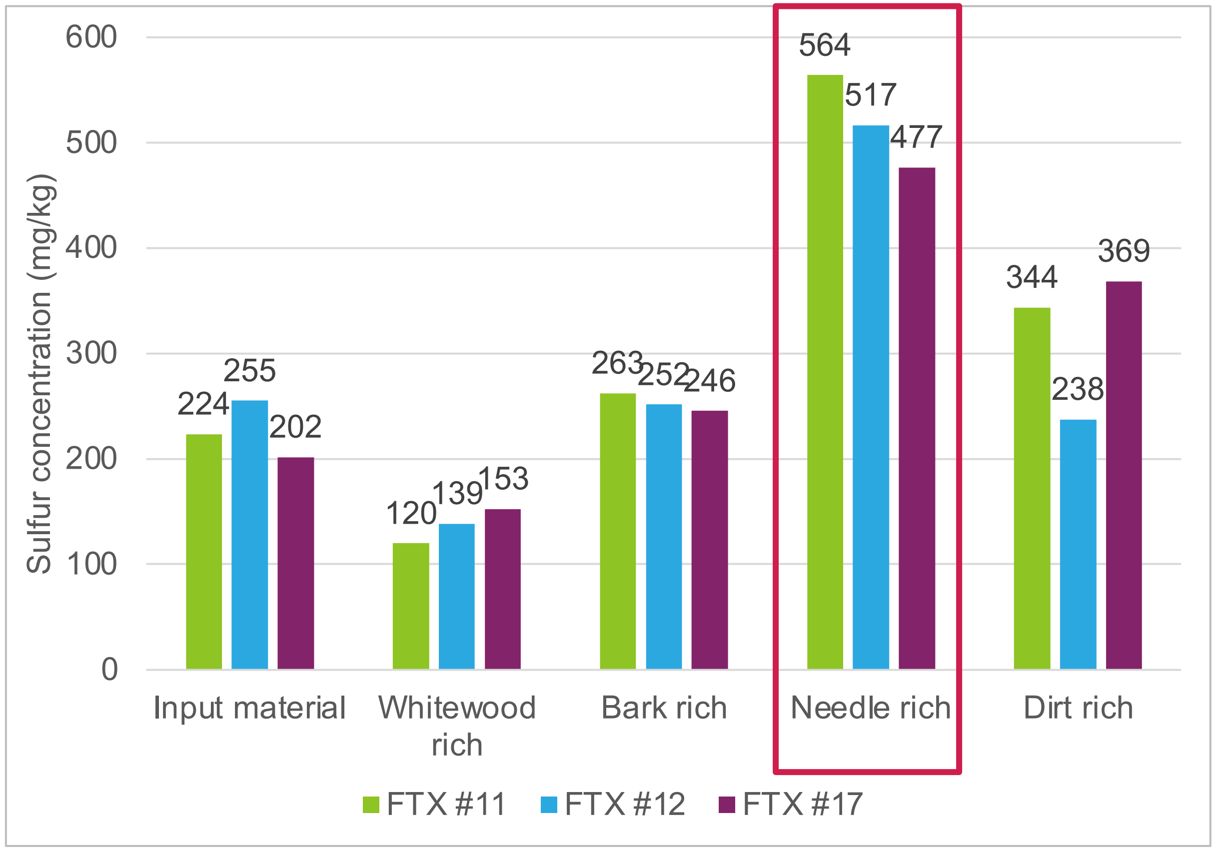
FTX #12

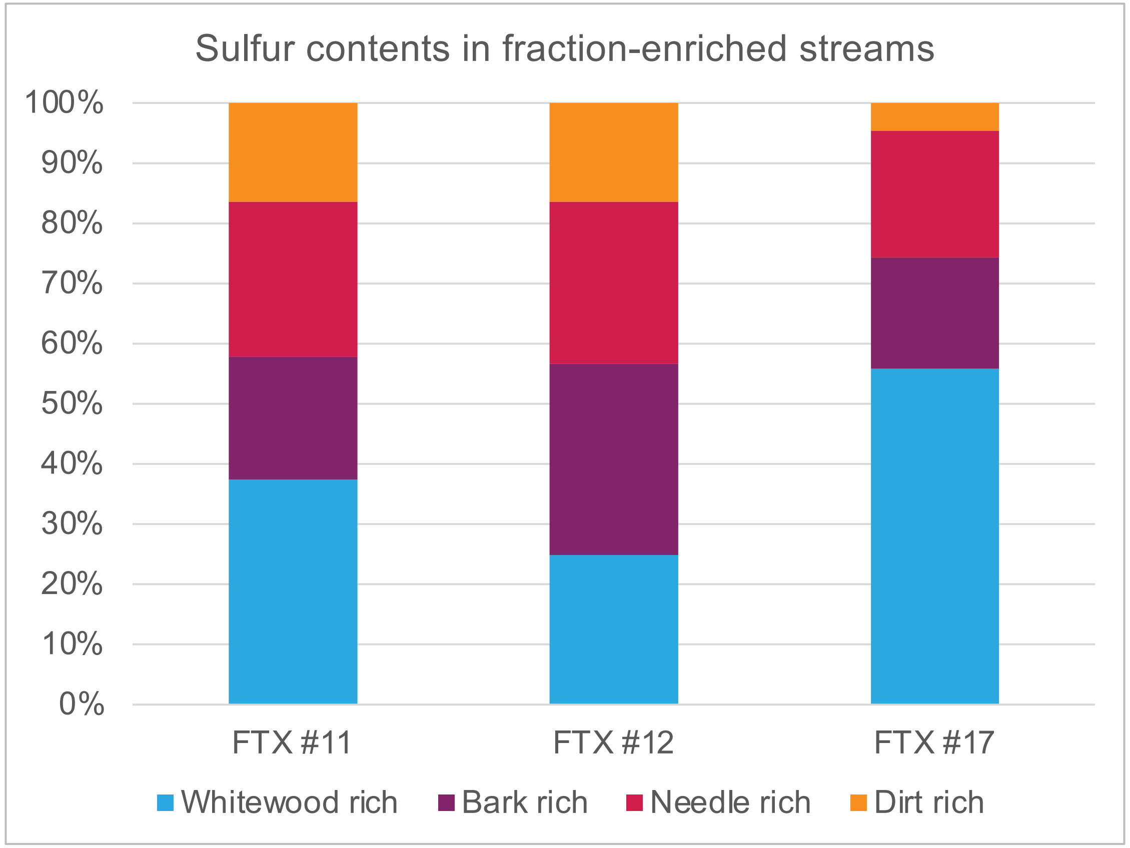
- The purities of whitewood and needle rich streams were about 66%-74%.
- Due to the low moisture content (7%~9%), it was challenging to separate small whitewood from bark.



FTX #17

Sulfur concentration and content in fraction enriched streams

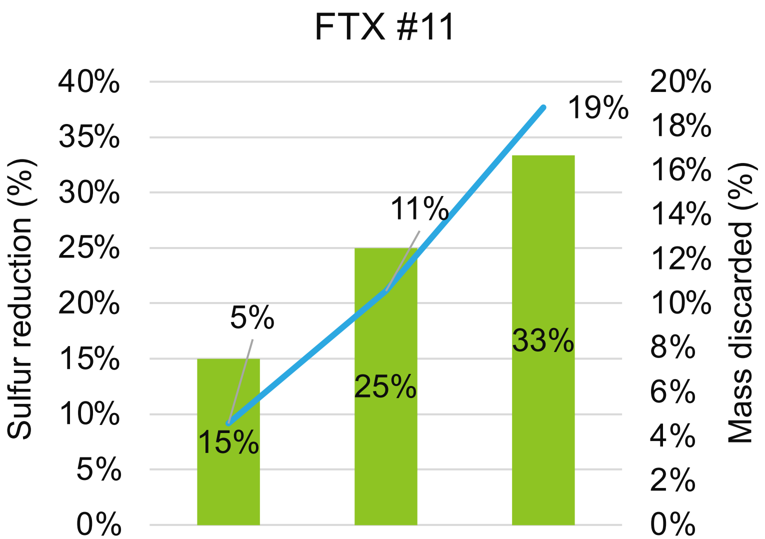



Sulfur contents in fraction-enriched streams

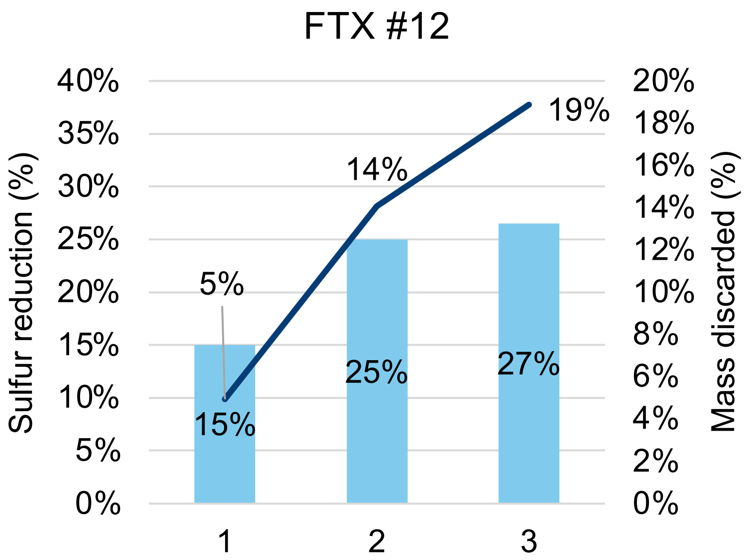
IDAHO NATIONAL LABORATORY

Sulfur reduction from the air classification process

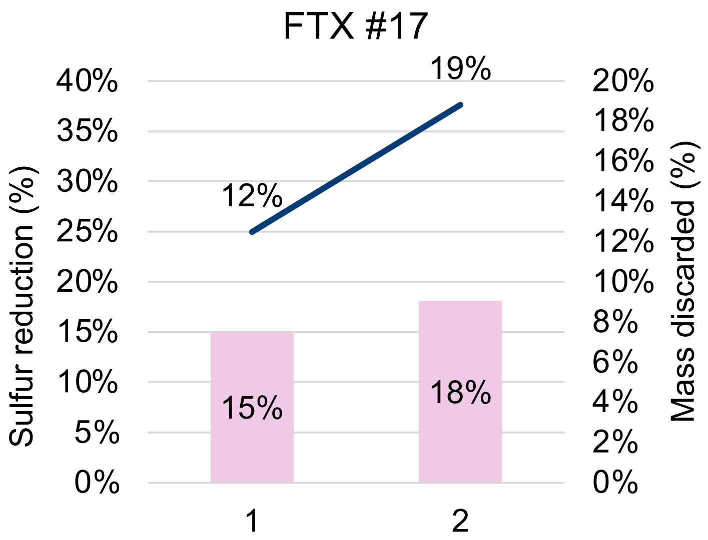
- Sample specific trade-offs between sulfur removal and material reject rate.
- More material needs to be discarded to reduce the sulfur content from pre-commercial harvesting samples.
- The discarded portion can be sent to bioleaching or other value-added markets. For different samples.



Sulfur reduction	15%	25%	33%
Whitewood rich	0%	0%	0%
Bark rich	0%	0%	4%
Needle rich	51%	100%	100%
Dirt rich	0%	18%	100%

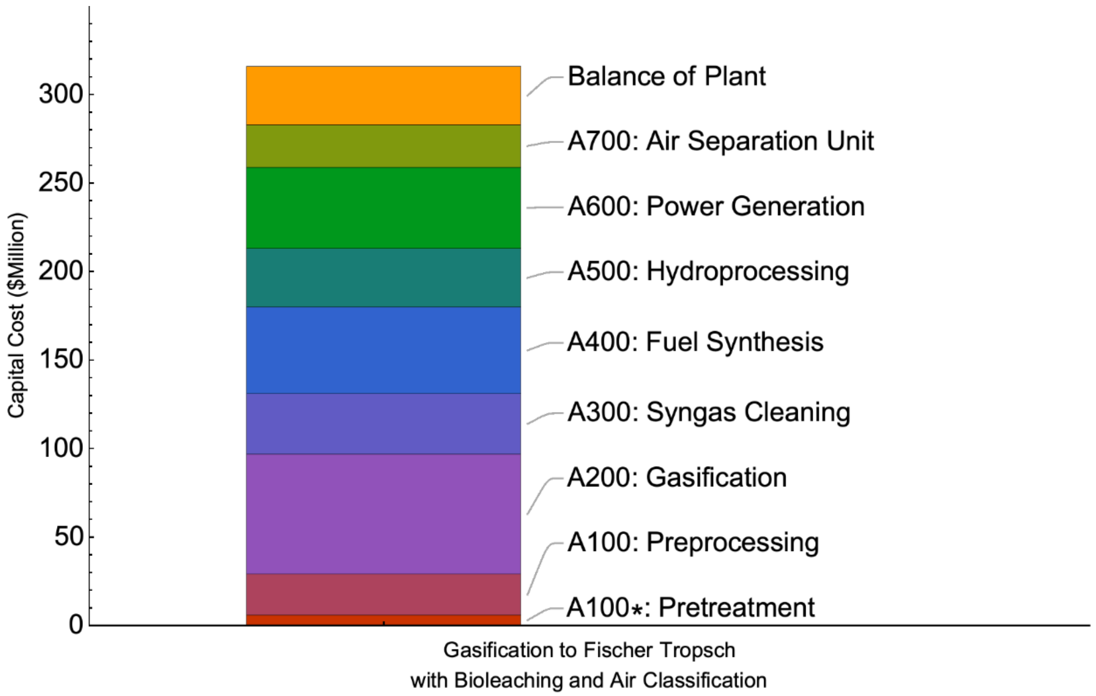


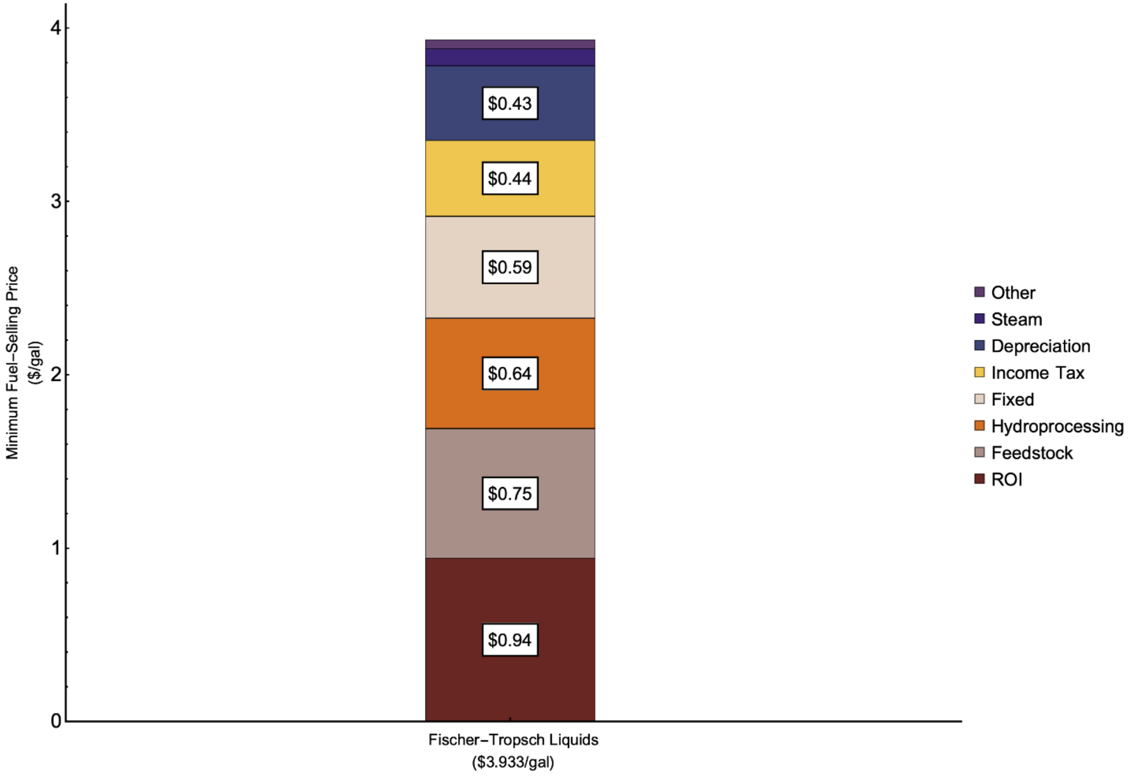
Sulfur reduction	15%	25%	27%
Whitewood rich	0%	0%	0%
Bark rich	0%	9%	26%
Needle rich	43%	100%	100%
Dirt rich	0%	0%	0%



Sulfur reduction	15%	18%
Whitewood rich	0%	0%
Bark rich	12%	57%
Needle rich	100%	100%
Dirt rich	100%	100%

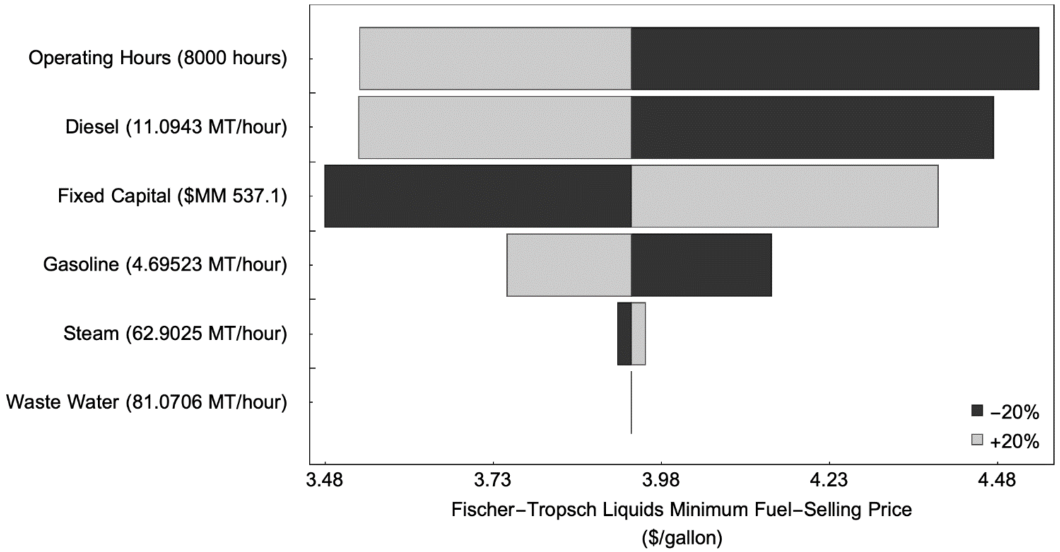
TEA: Capital cost analysis and minimum fuel-selling price baseline

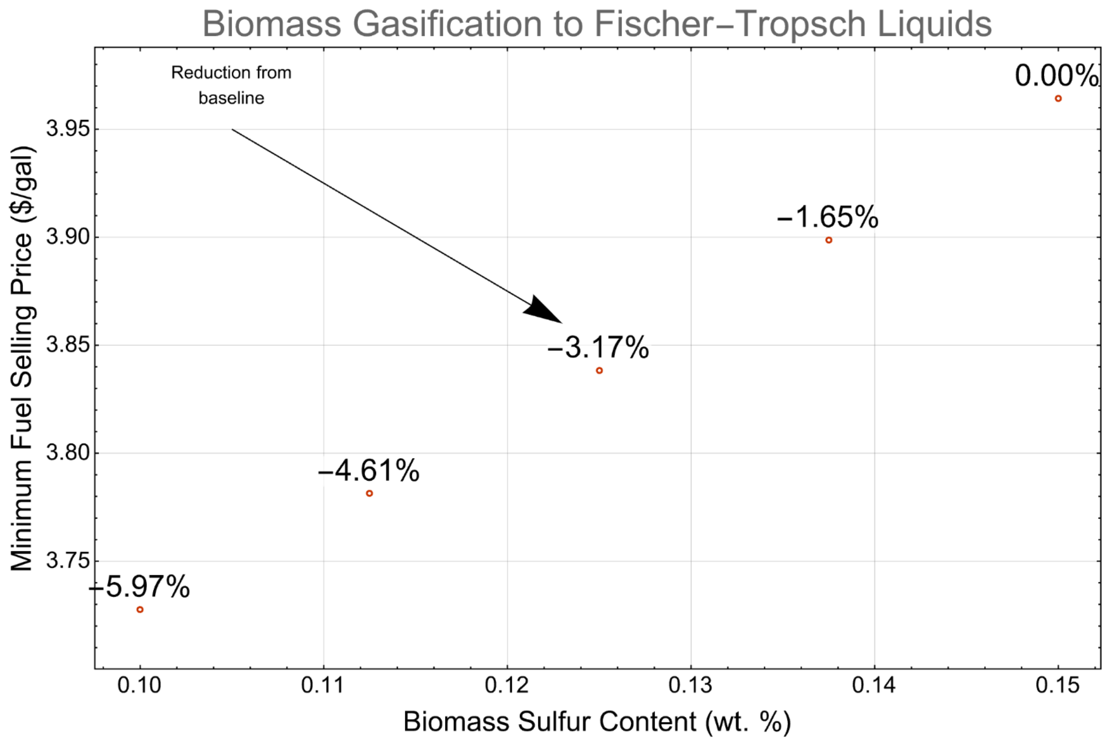


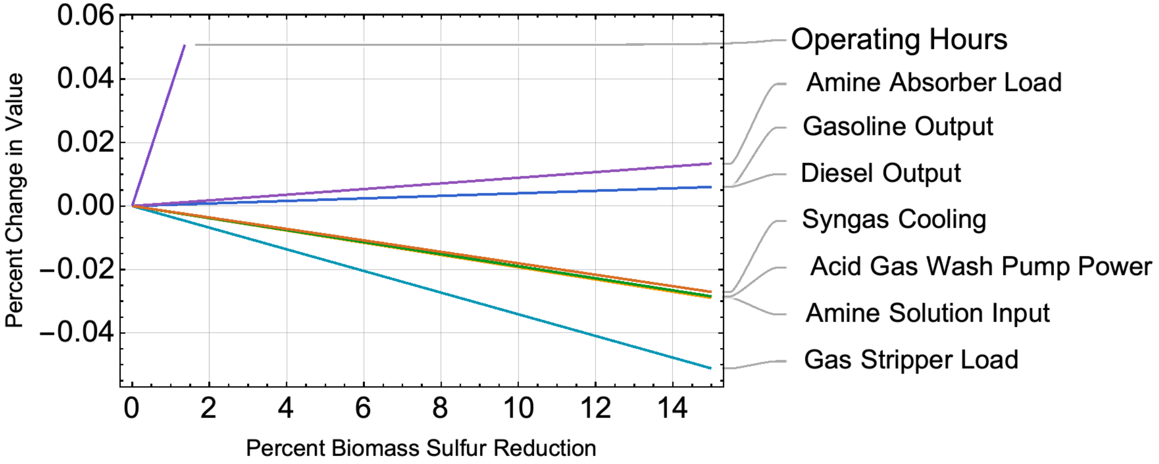


- Potential Capital Cost Reductions Areas: LO-CAT, ZnO Guard Bed, Acid Gas Removal
- The base case minimum fuel-selling price (MFSP) is $3.93/gallon
- Feedstock and hydroprocessing costs contribute more than 15% each to the MFSP

Impact of feedstock sulfur content on MFSP: Sensitivity analysis

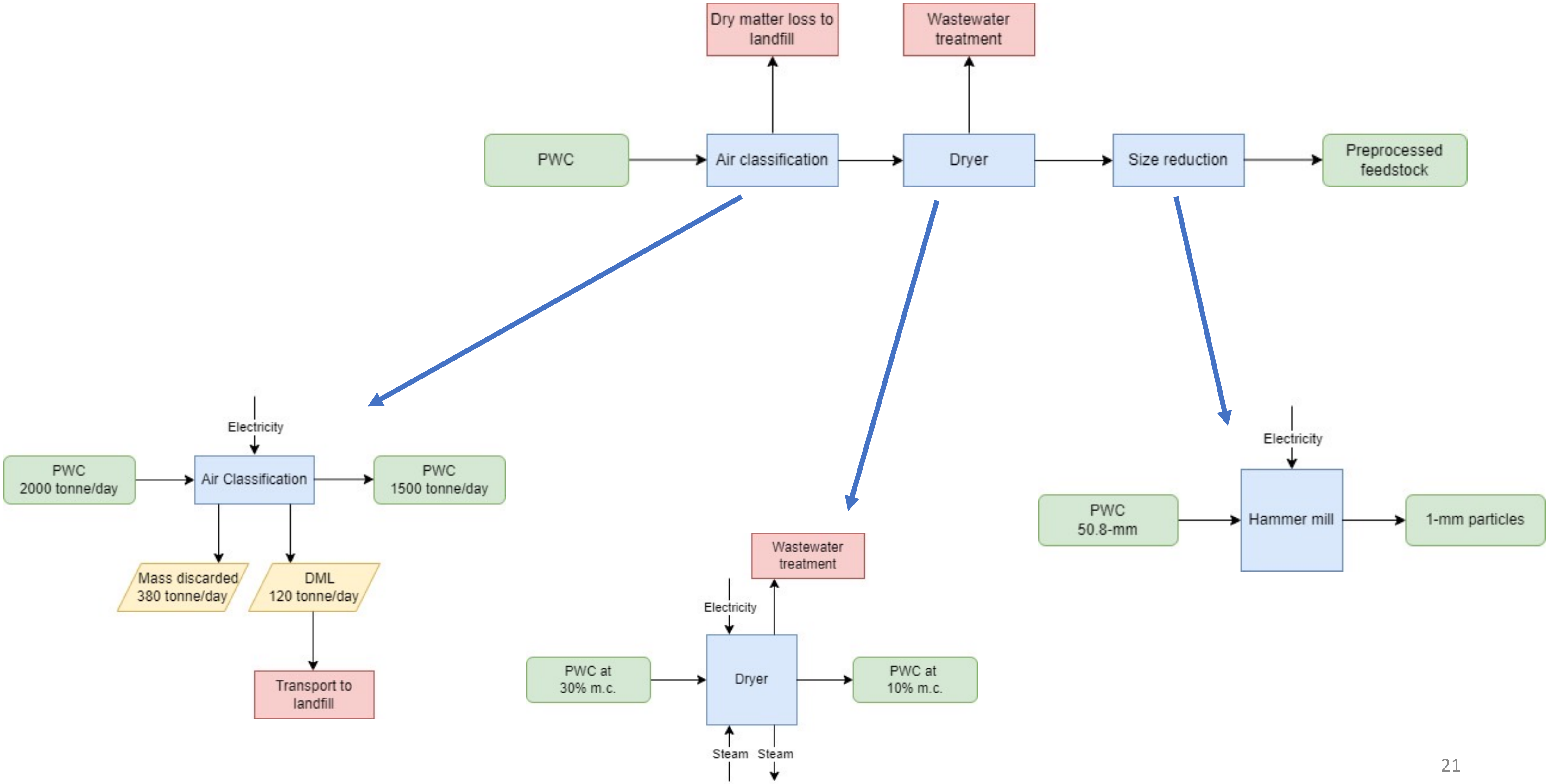




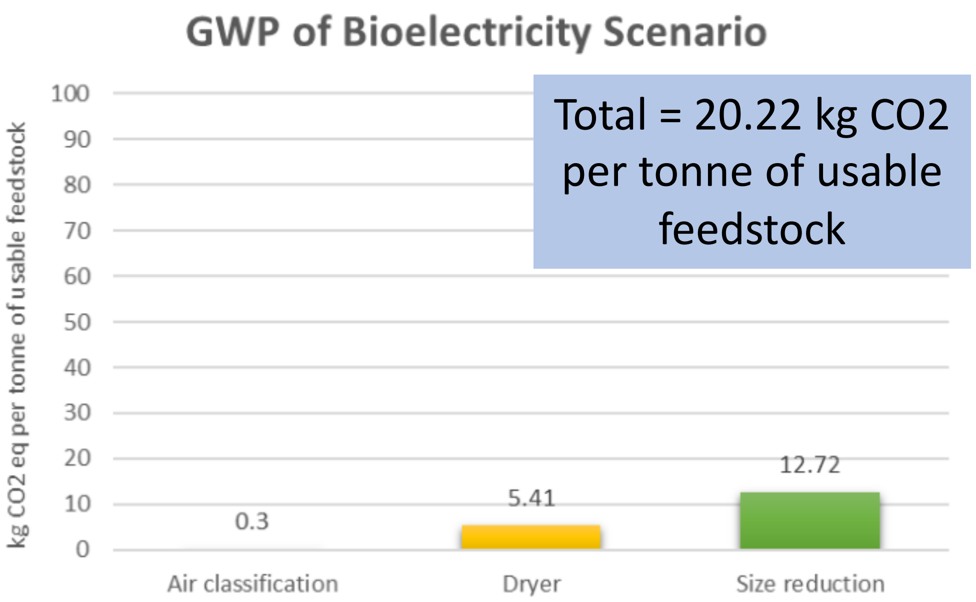


- Operating hours, biofuel output, and capital costs are key cost drivers.
- A 30% reduction in feedstock sulfur content decreases the MFSP by >5%

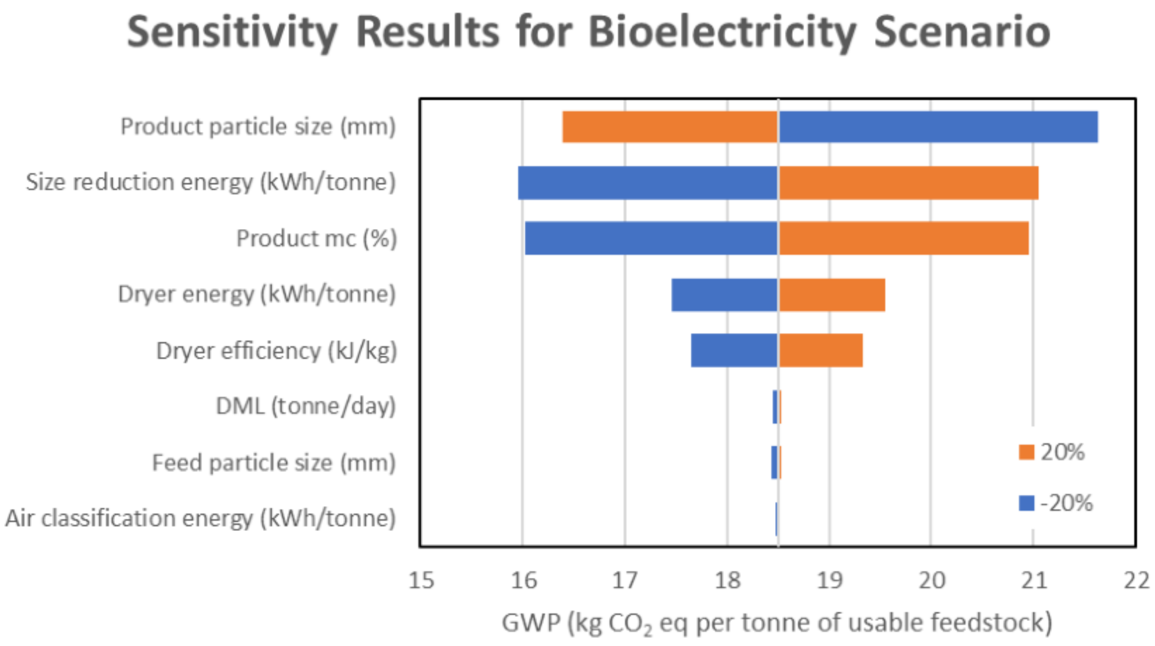
Preliminary LCA on the preprocessing steps



Preliminary LCA on the preprocessing steps



Total = 20.22 kg CO2 per tonne of usable feedstock



- Size reduction is the largest source of impact
- Air classification has relatively small impact
- Assuming best-case scenario, overall GWP can be reduced by ≈ 8 times (bioelectricity vs. grid electricity scenarios)

SimaPro

Argonne GREET LIFE-CYCLE MODEL

3 – Impact

- Identifying the origin of sulfur and developing sulfur mitigation methods are important to the conversion processes.
- Understanding the relationship between the source and nature of sulfur could have implications for feedstock sourcing and harvesting techniques.
- Furthermore, understanding how sulfur is released during thermochemical conversion may have significant implications for process design.
- Reporting these findings to the industry may have a large impact on the future of forest biomass-based pathways to fuels and chemicals.

Summary

- A feedstock library was built with a total of 18 representative pine residue samples and 87 anatomical fractions.
- Correlations model are being set up between sulfur content and feedstock factors
- Air classification and bioleaching technologies show good potentials for sulfur removal thus helps to improve feedstock quality
- Preliminary TEA and LCA results reveal potential cost saving and GHG benefits and suggest directions for future technology development

Quad Chart Overview

Timeline

- *10/01/2019*
- *1/31/2025*

	FY22 Costed	Total Award
DOE Funding	*$423,417*	*$1,641,922*
Project Cost Share *	*$109,822*	*$414,450*

TRL at Project Start: 2

TRL at Project End: 4

Project Goal

The overall goal of this project is to establish a sulfur profile database and correlate the form and fate of sulfur in pine feedstocks to thermochemical conversion performance and to develop effective feedstock preprocessing and sulfur mitigation strategies.

End of Project Milestone

1) Build a model describing the cause of sulfur variability in pine residues and the fate of sulfur during thermochemical conversion 2) identify the impact of sulfur species on activity/selectivity of FTS catalysts; 2) Demonstrate >50% sulfur removal from pine residues using mechanical separation and/or bioleaching; 3) Demonstrate 10% improvement on minimum selling price of produced bio-oils, and 30% improvement in LCA outcome compared to those of baseline.

Funding Mechanism

DE-FOA-0002029, topic area AOI 2a, 2019.

Project Partners*

Idaho National Lab, Kansas State University, Iowa State University, Red Rock Biofuels, Mississippi State University

*Only fill out if applicable.

Additional Slides

Other Project Outcomes

- An ArcGIS Story Map was built to share the project outcomes to the research community.
- Project outcomes from this have been presented during the annual ASABE conference (Edmonson et al., 2022 and Liu et al. 2022).
- One manuscript submitted and one more under internal review/revision (Liu et al.; Hunter et al.).
- Four graduate students (3 females and 2 minority) and 1 postdoc researcher are being trained through this project.
- Engaged industrial partner and industry advisors (RRB, Erudite Process, Forest Concepts)

References

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