Ash Reduction Strategies to Provide On-Spec Feedstocks for Biofuel Conversion Processes

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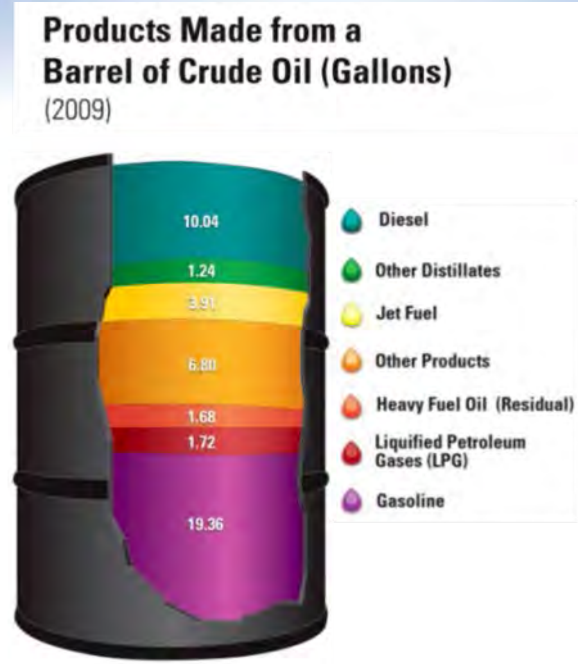
Idaho National Laboratory

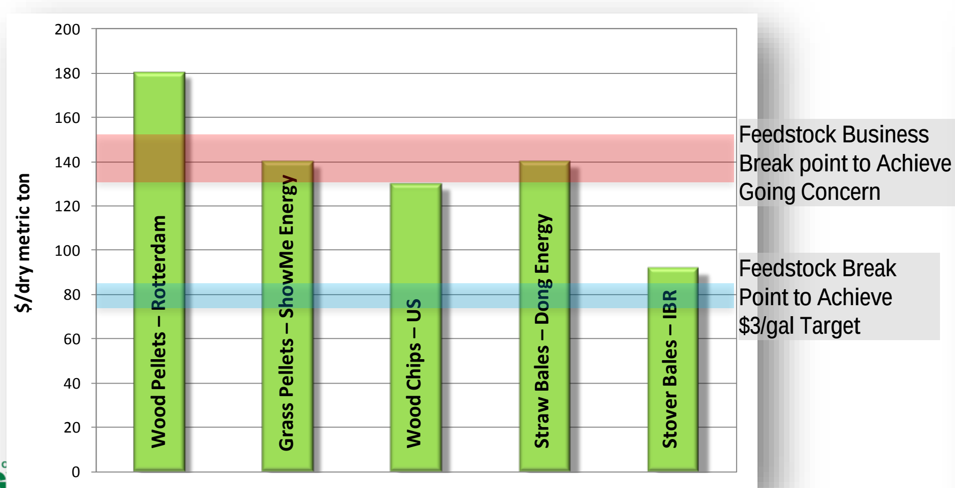
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

National Challenge

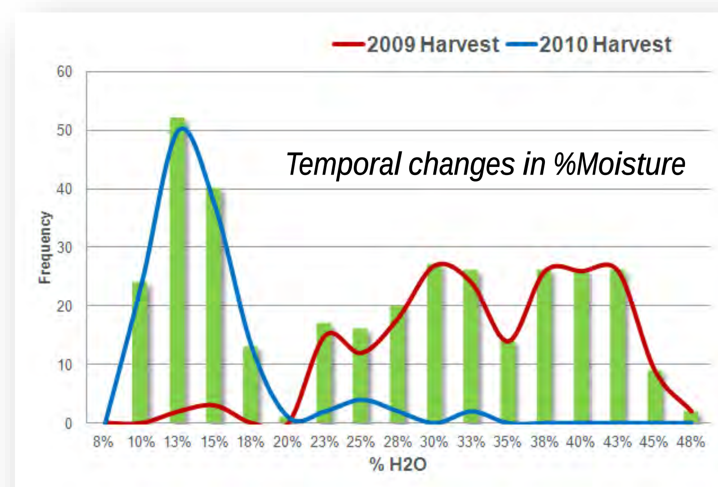
- Replacing the whole barrel
  - US spends $1billion/day on oil imports
  - Reducing dependence on oil requires replacing the whole barrel
  - Climate change mitigation by replacing fossil fuels
- Feedstock costs represent up to one-third current biofuel production costs



Feedstock Cost Challenge

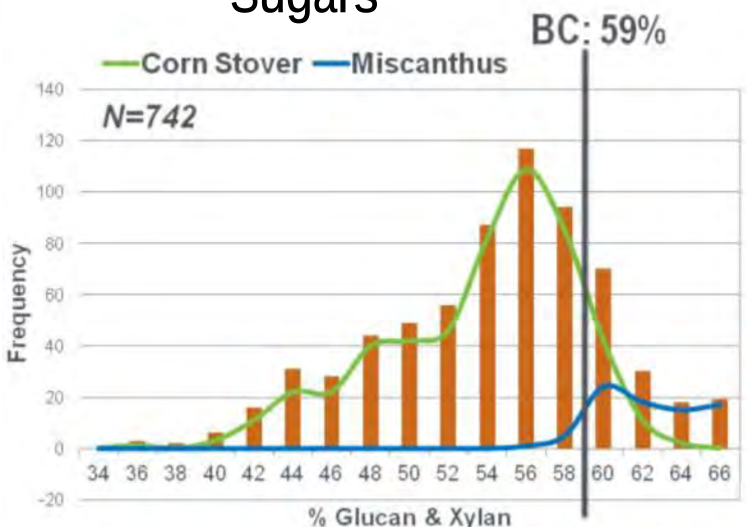


Feedstock Quality Challenge

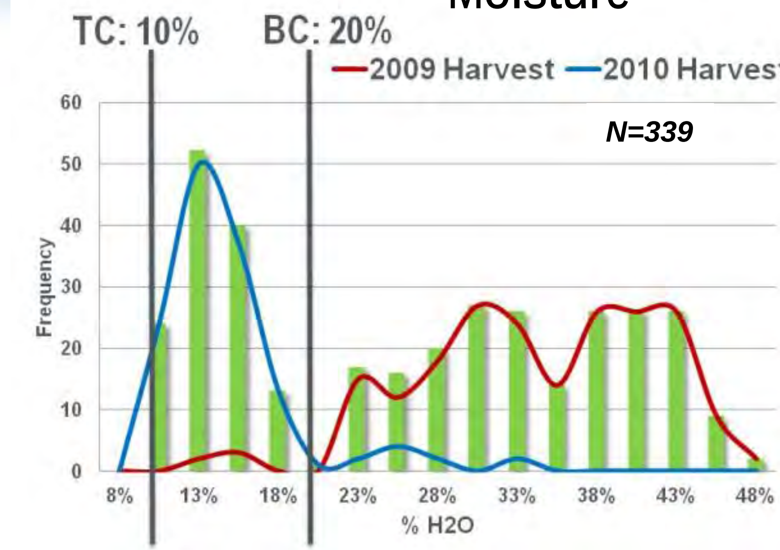


Feedstock Quality Challenge

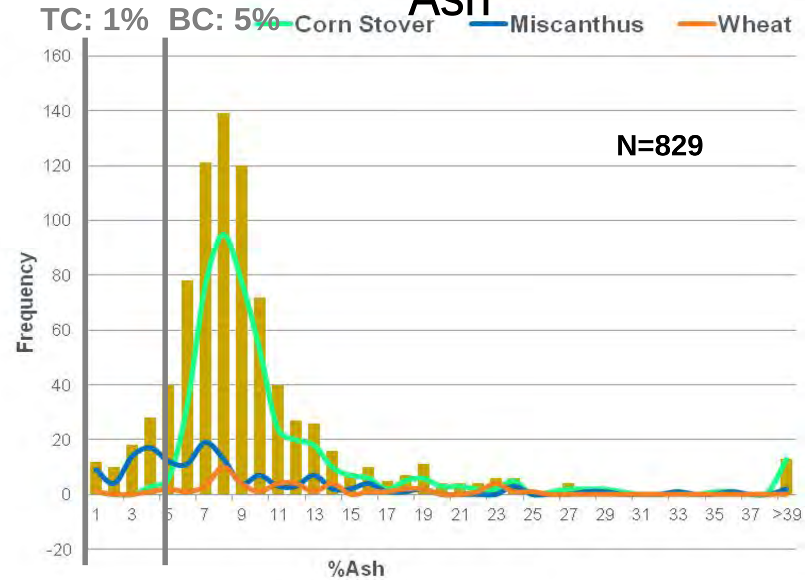
Sugars



Moisture



Ash



- Conversion specs shown (vertical lines) represent DOE biochem (BC) and thermochem (TC) pathway quality assumptions
- Distributions represent variability in biomass properties relative to spec
- Distributions likely greater if broader range of resources are considered
- Illustrates challenge associated with diversity

Least Cost Formulation

What is it?

- Standard practice in the animal feed industry
- Identify the least cost resources necessary to achieve a performance target

Feedstock Least Cost Formulation

- Costs: Access costs (aka grower payment), logistics costs, and quality
- Performance:
  - Composition
  - Yield
  - Degradation Products

Feed Reference No. QuickFinder

110

Feed No	Ingredient Name	As-Fed Diet Composition	$/Cwt As-Fed
145	COTTONSEED HULLS	15	
405	Corn Grain Cracked		
404	Corn Hominy	53	
510	Distillers Gr. Dehy - Inter.	30	
812	Limestone	2	

As-Fed Total	100	
Dry Matter Total	90.5	
Predicted DMI: lbs/hd/d, %BW	14.44	2.35
Estimated DMI: lbs/hd/d, %BW	14.44	2.35
DMI Adjuster	100	% Predicted DMI

NUTRIENT PROFILE

	DIET DM COMP*	DIET PROVIDED	ANIMAL REQ.		Percent Requirement
Dry Matter %	90.5		--------		
NDF %	39.1		--------		
eNDF (%DM)	6.7				
TDN %	82.0				
ME (Mcal/lb)	1.35				
NEm (Mcal/lb)	0.91	5.34	5.34	Mcal	100%
NEg (Mcal/lb)	0.61	5.55	4.92	Mcal	113%
CP %	15.9	2.29	2.07	lbs	111%
DIP (%CP)	40.4	0.926	1.027	lbs	90%
Fat %	7.3				
Ca %	0.88	0.127	0.083	lbs/d	154%
P %	0.56	0.082	0.044	lbs/d	186%
Mg %	0.28	0.041	0.014	lbs/d	282%
K %	0.67	0.097	0.087	lbs/d	112%
Na %	0.14	0.020	0.012	lbs/d	174%
S %	0.15	0.022	0.022	lbs/d	100%
Co ppm	0.09	0.57	0.656	mg/d	86%
Cu ppm	11.16	73.20	65.615	mg/d	112%
I ppm	0.03	0.17	3.281	mg/d	5%
Fe ppm	228	1492.78	328.074	mg/d	455%
Mn ppm	16.81	110.31	131.229	mg/d	84%
Se ppm	0.12	0.79	0.656	mg/d	121%
Zn ppm	20.45	134.20	196.844	mg/d	68%

***Values are not valid if numbers are missing from an ingredient's profile in the feed list**

PERFORMANCE INDICATORS

Calf Weight (lbs)	615
Desired Rate of Gain (lbs/d)	3.00
Energy Predicted Rate of Gain (lbs/d)	3.49
As-Fed Feed Cost per lb gain	0.000
Dry Matter Feed Conversion (Feed:Gain)	4.1

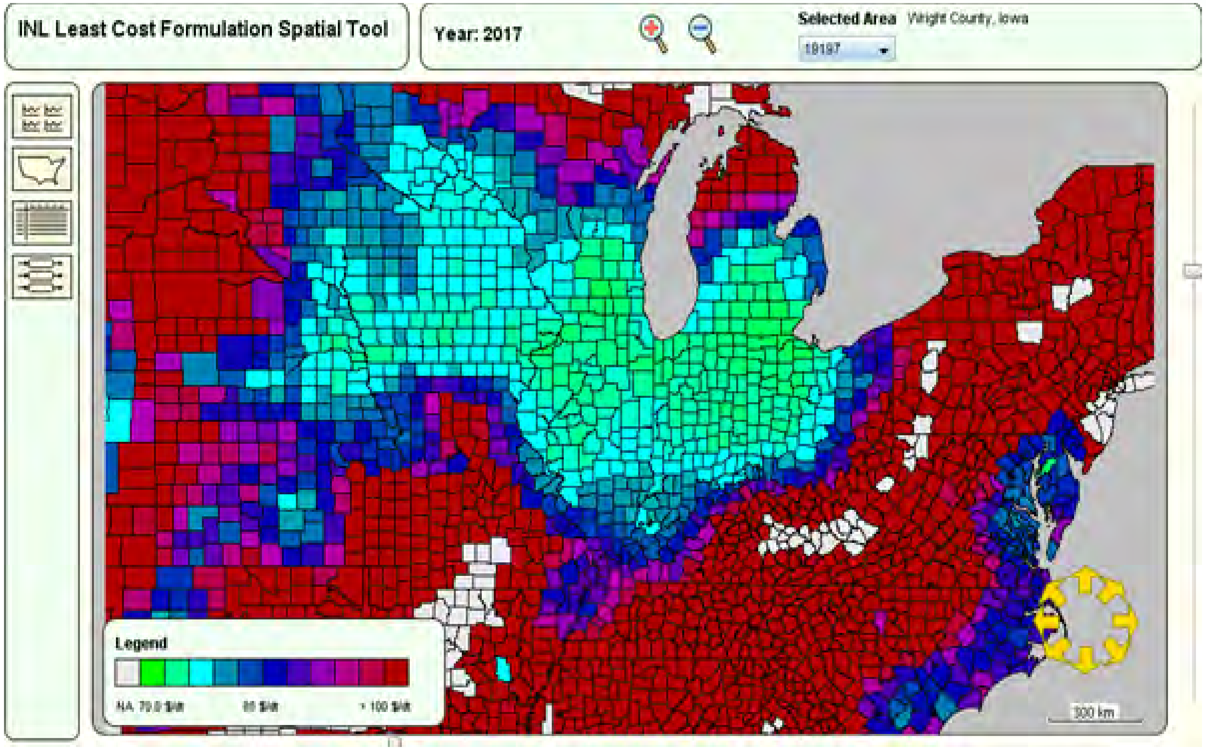
BALANCE ISSUES

MAKE SURE ENOUGH FIBER IS IN THE DIET FOR RUMEN HEALTH

Current Ca:P 1.56 :1

HIGH FAT WARNING, LOWER HIGH FAT INGREDIENT

Formulation Case Study



Material	Ash(%)
Corrugated Cardboard	3.3
Glossy cardboard	12.7
Office paper	11.0
Glossy paper	25.1
Corn Stover	n.m.
80:20 corn stover/MSW	5.5

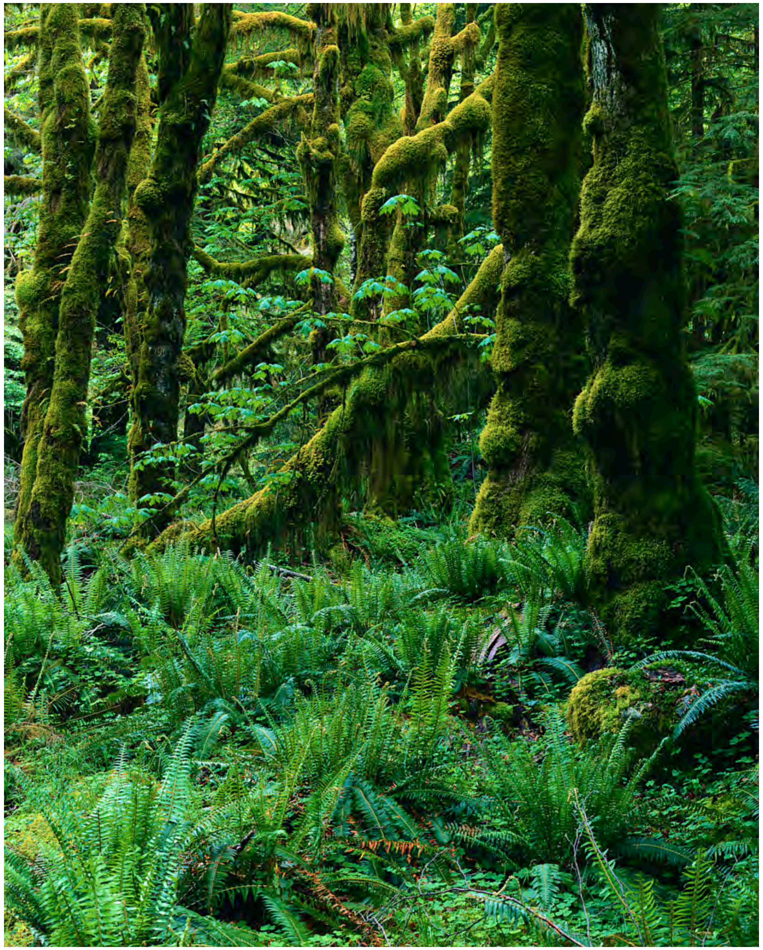
- Least cost formulation only allows 20% MSW blend due to high ash components
- Limits the benefit of using low cost materials
- Need methods to reduce undesirable components such as ash

Why Is Ash A Quality Issue?

- Biomass contains both introduced soil ash and endogenous ash
- Endogenous ash is comprised of structural and non-structural physiological ash
- Ash is comprised of metals and heteroatoms that may be
  - Inert… e.g., SiO_2 in biochemical conversions
  - Destructive to conversion products… e.g., K, Na, Ca, Mg in pyrolysis
  - Fouling agents for conversion catalysts… e.g., N, S, P for several processes
  - Sources of pollutants… e.g., N, S in combustion and gasification
  - Damaging to equipment… e.g., SiO_2, K, Na in combustion and gasification
- This increases processing costs and/or reduces product yields
- Knowing the chemical form, function and plant tissue location of specific ash components aids in identifying effective reduction methods

Ash – Form, Function and Distribution

- Mineral nutrients
  - Macronutrients – Ca, K, S, Mg, N, P
  - Micronutrients – Zn, Fe, Mn, Cu, Cl
  - Beneficial elements – Na, Si
- Physiological functions
  - Vascular transport – K^+, Na^+
  - Counterions – Ca^{2+}, Mg^{2+}
  - Heteroatoms - S^{2-}, N, PO_4^{3-}, SO_4^{2-}
  - Alleviating biotic and abiotic stresses – SiO_2
- Tissue locations
  - Actively growing tissues
    - K^+, Na^+, Ca^{2+}, Mg^{2+}, S^{2-}, SO_4^{2-}, N, P
  - Structural or inactive tissues
    - SiO_2, S^{2-}, SO_4^{2-}, N, P, Ca^{2+} (as oxalate crystals)



Ash Reduction Methods

- <u>Mechanical methods</u>
  - Screening to separate rocks and soil from biomass
  - Classification by density or color to separate plant tissue fractions
  - Fractional milling to separate size fractions with higher ash
  - Triboelectrostatic separation of finely ground biomass to reduce silica
- <u>Chemical methods</u>
  - Simple washing to remove soil
  - Leaching with water/acid to remove alkali metals/alkaline earth metals
  - Limited structural disruption with hot water or acid to remove cell-bound nitrogen and sulfur
  - Dissolution of silica with alkali

Anatomical Fractionation of Corn Stover

	Ash Content	% of Plant Mass
Leaves	10.56%	20%
Sheath	7.72%	10%
Nodes	4.76%	10%
Husk	3.45%	10%
Internode	3.92%	30%
Cob	1.62%	20%

To meet an ash spec of 5%, additional treatment only required on 30% of total biomass

Air Classification – Corn Stover

Fines

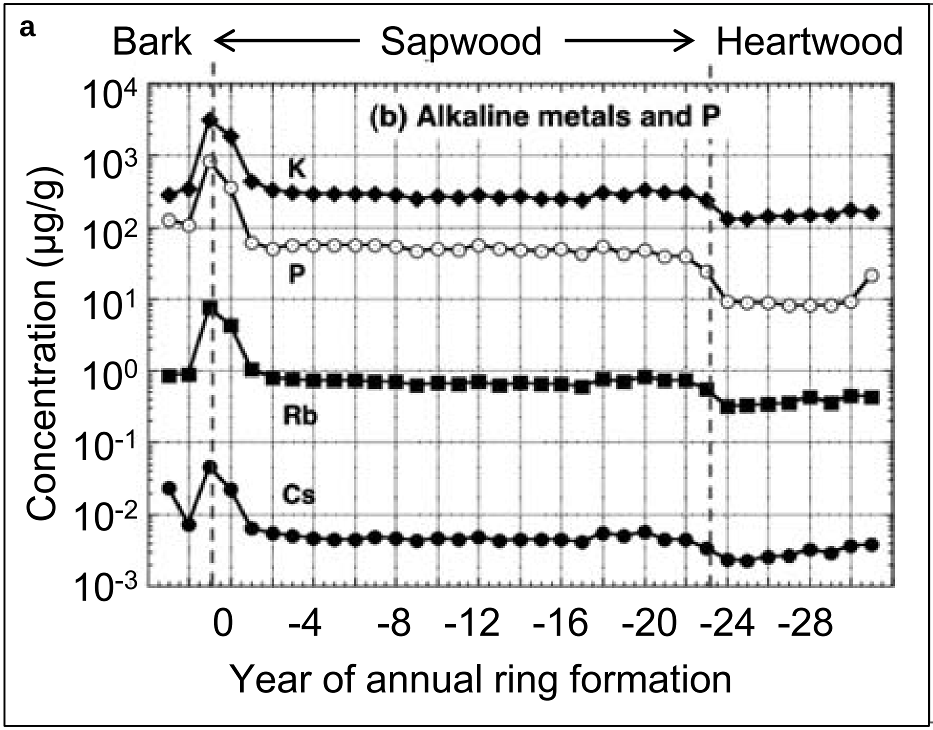
Light Fraction

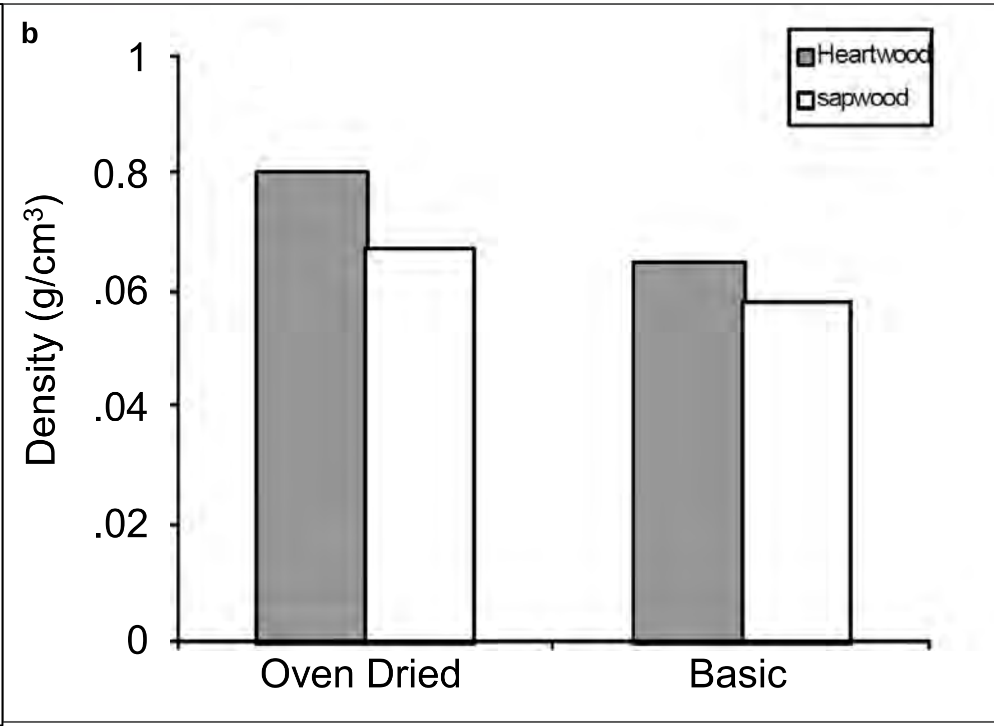
Heavy Fraction

Leaves

Cobs

Potential for Air Classification of Heartwood & Sapwood





- Density differences between dried heartwood and sapwood show potential for air classification of these tissues
- Radial distribution of ash components shows large differences among tissues

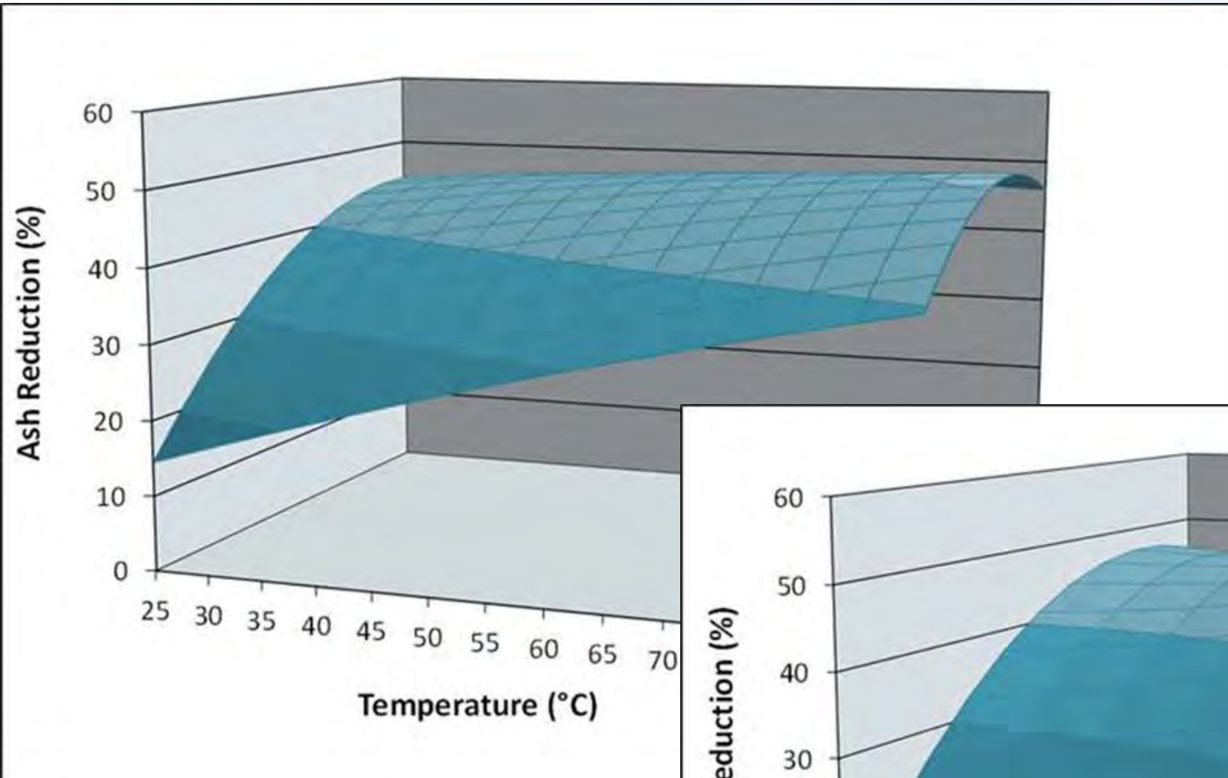
a Yoshida, S. *et al.*, *Radiat Prot Dosimetry*, 146(1-3):326-329, 2011.
b Ayobi, E. *et al.*, *Middle-East J Sci Res*, 8(3):669-673, 2011.

Air Separation of Needles from Chips

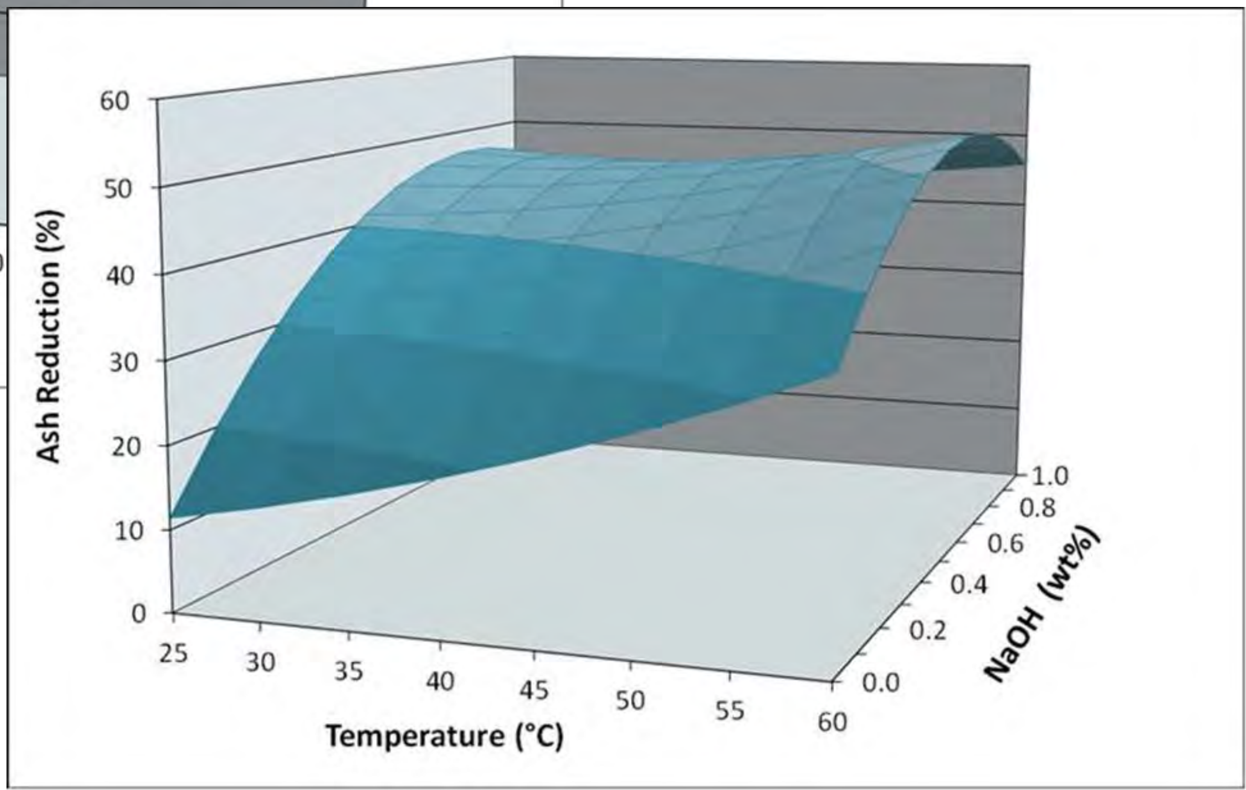
Element		
K	Needle	eaves
Ca	Trunk b	eaves
P	Needle	wood
Si	Needle	eaves
Cl	Trunk w	eaves
S	Trunk w	eaves

Air Classificat
needles in ch

Stover Leaching – Ash Removal

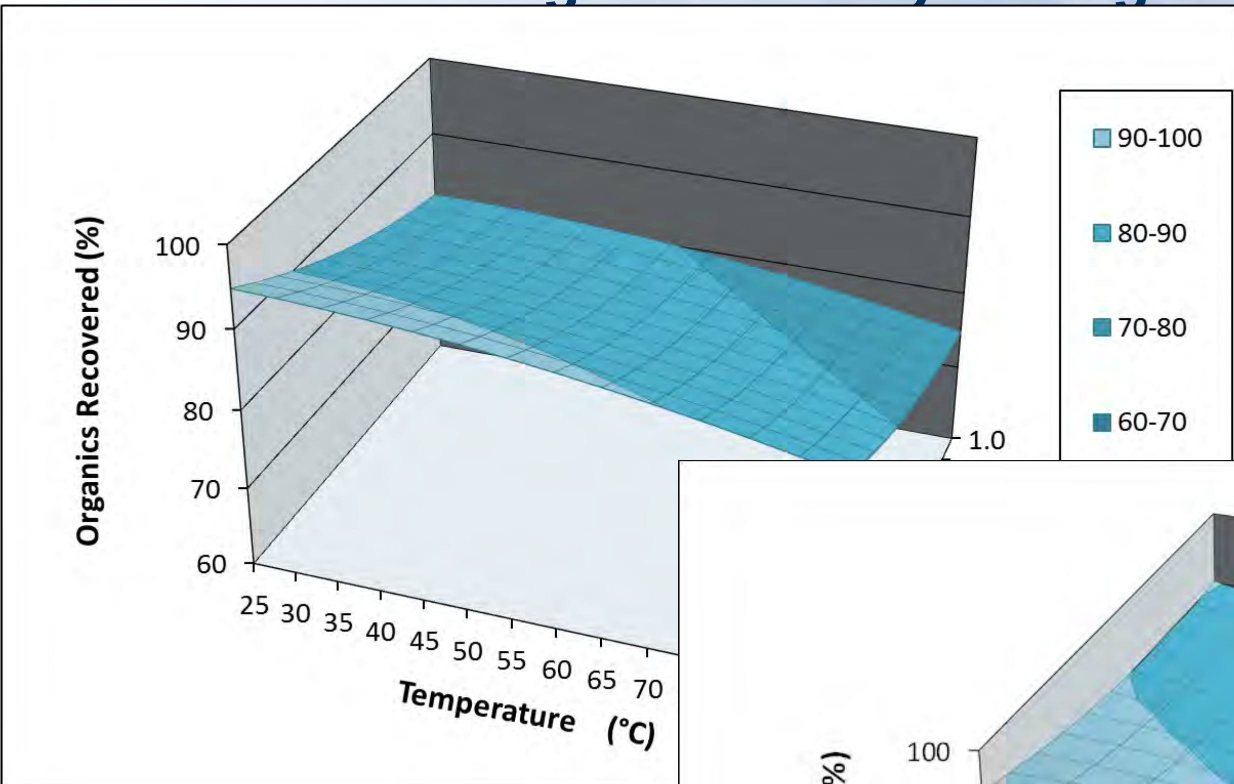


- Power series fits to data
- Equilibrium ash reduction generally increased with temperature & acid concentration

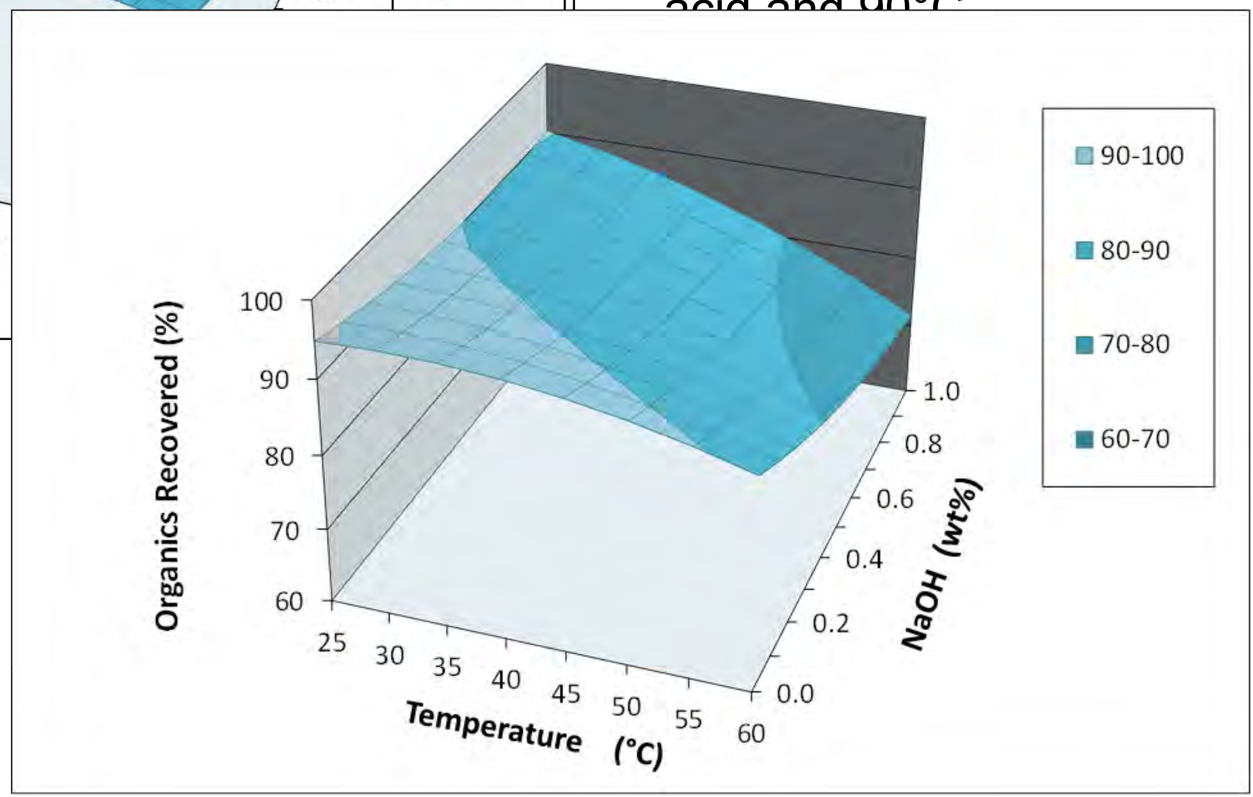


- Similar patterns with alkali leaching
- Overall ash reduction is higher for alkali even at lower temperatures due to silica dissolution

Stover Leaching – Recovery of Organics

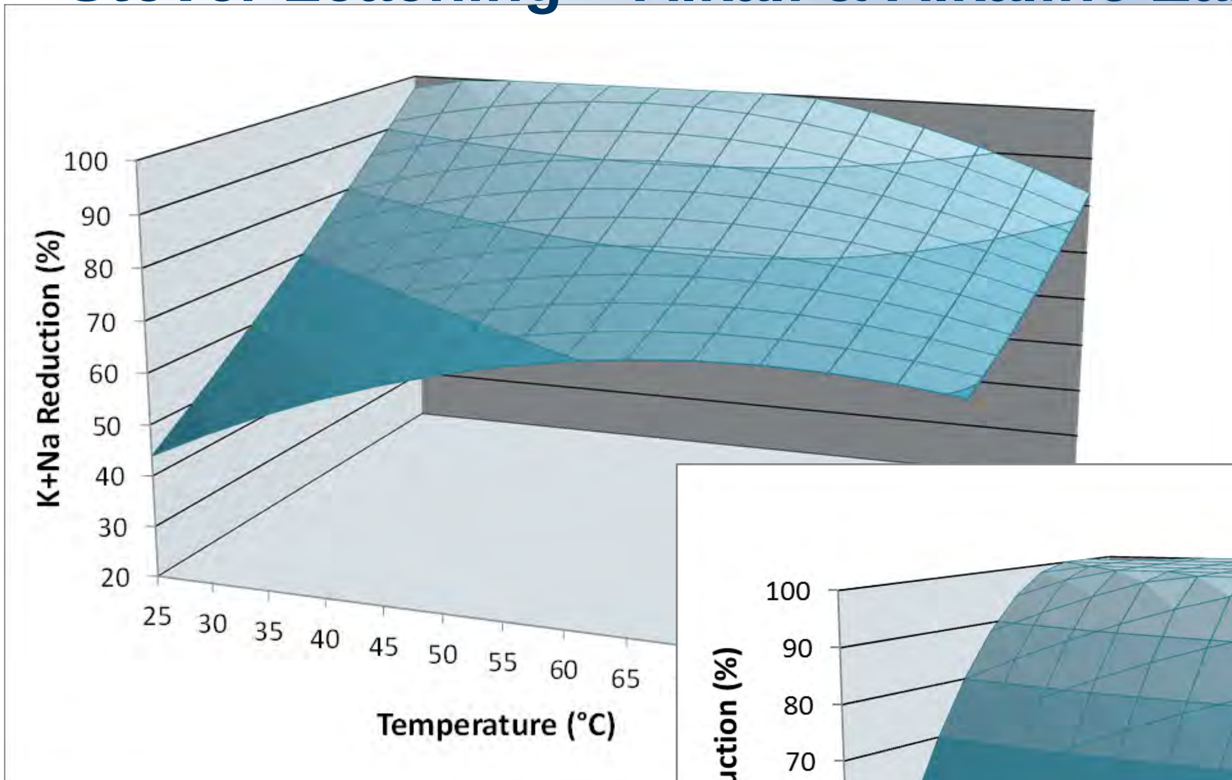


- Losses of convertible material increase with temperature and catalyst concentration
- Approximately 25% of the material was solubilized at 1% sulfuric acid and 90°C

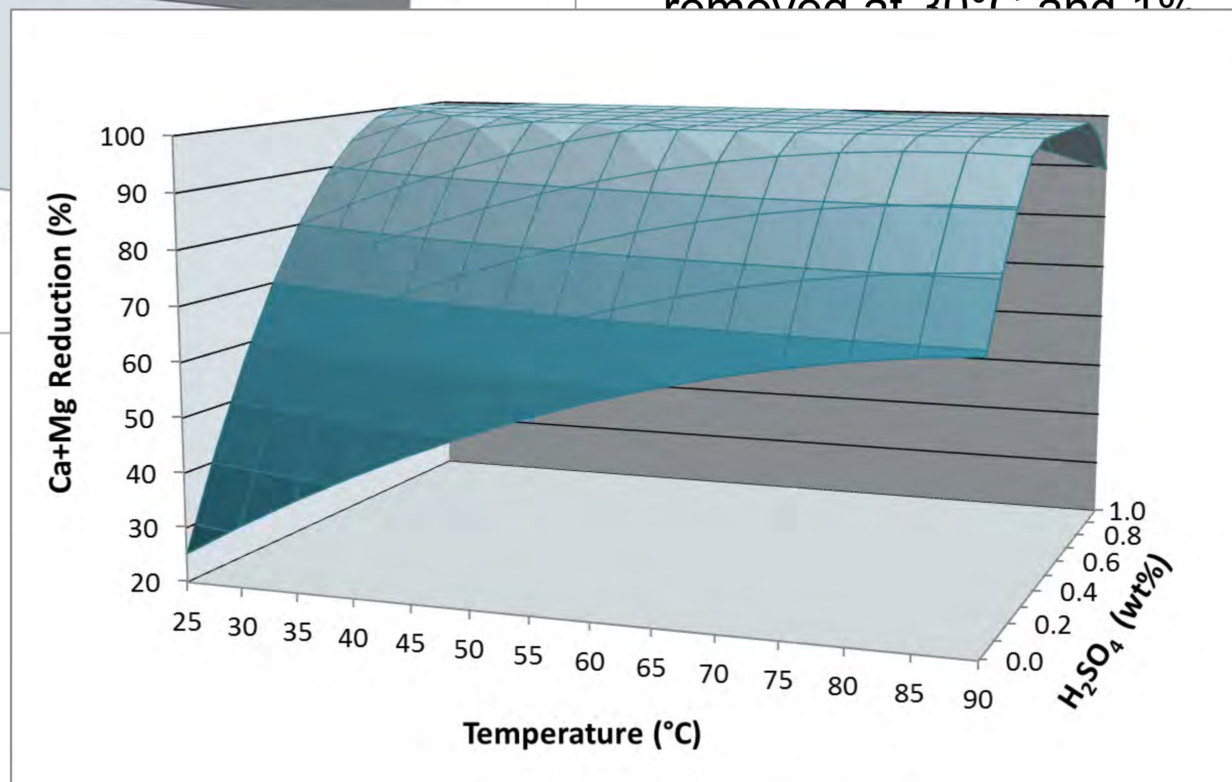


- Alkali leaching results in greater losses of convertible material, especially at higher catalyst concentrations
- Considerable amounts of lignin solubilized

Stover Leaching – Alkali & Alkaline Earth Metals

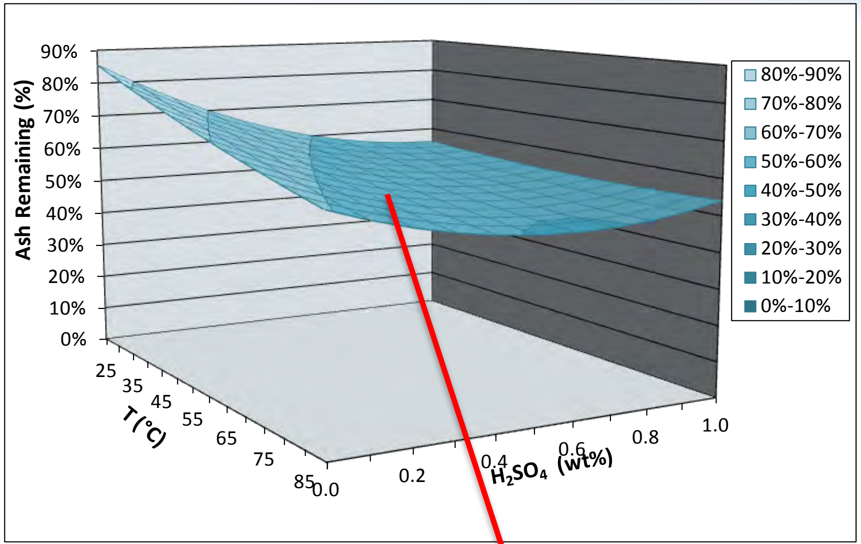


- Acid leaching was especially effective in removing specific ash components including alkali metals
- Essentially all potassium and sodium were removed at 30°C and 1%

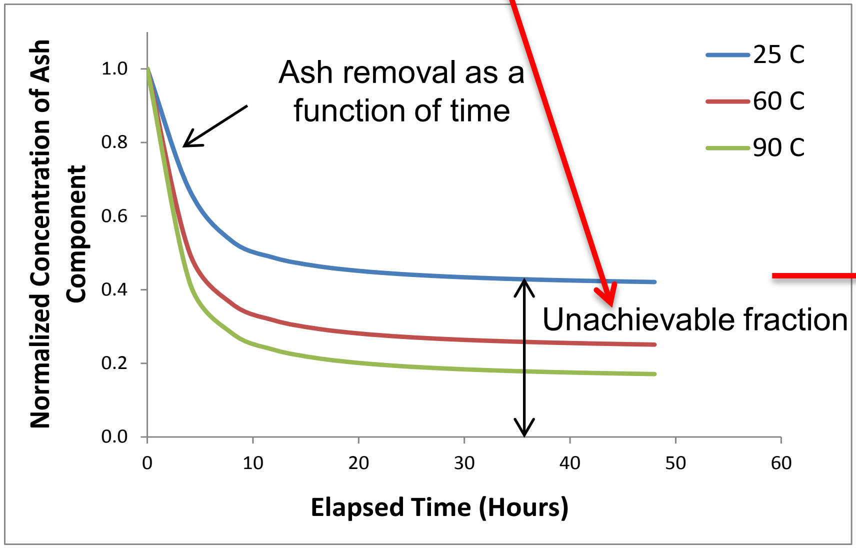


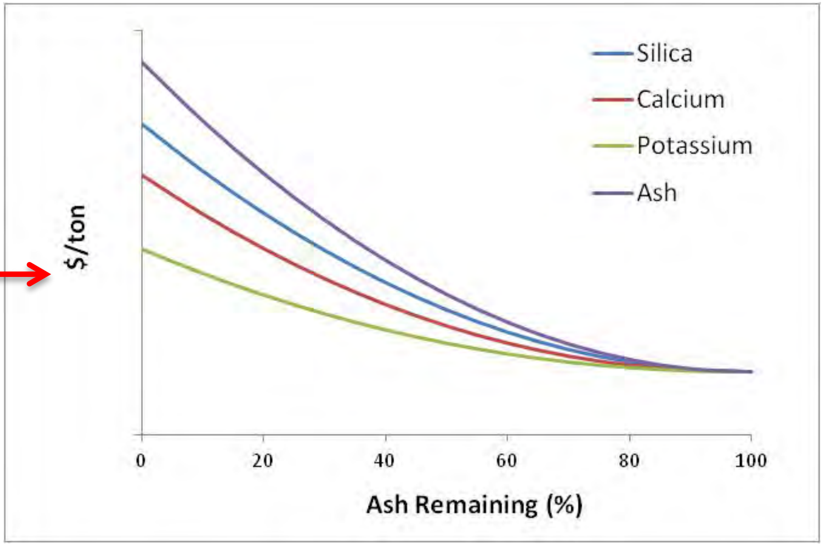
- Acid leaching also effective in removing alkaline earth metals
- 100% removal of Ca^{2+} and Mg^{2+} above 0.5% acid at all temperatures

Data Support Kinetic Models for TEA



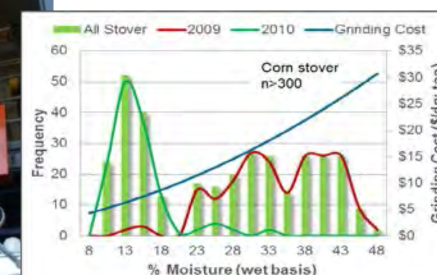
- Maximum achievable ash reduction as a function of T & pH
- Diffusion properties as a function of temperature, particle size and shape, and time
- Process and cost requirements to achieve a given ash reduction (total ash or ash components)





Summary

- A major barrier to replacing the entire barrel of oil is feedstock cost, which represents up to one-third of the final fuel cost
- The cost challenge cannot be solved independently of the feedstock quality challenge
- Least cost formulation together with mechanical and chemical separations can be used to address both challenges
- Air classification is a promising method to separate plant tissues that do not meet an ash specification
- Chemical leaching can improve the quality of low cost feedstocks as well as off-spec tissue fractions



Acknowledgements

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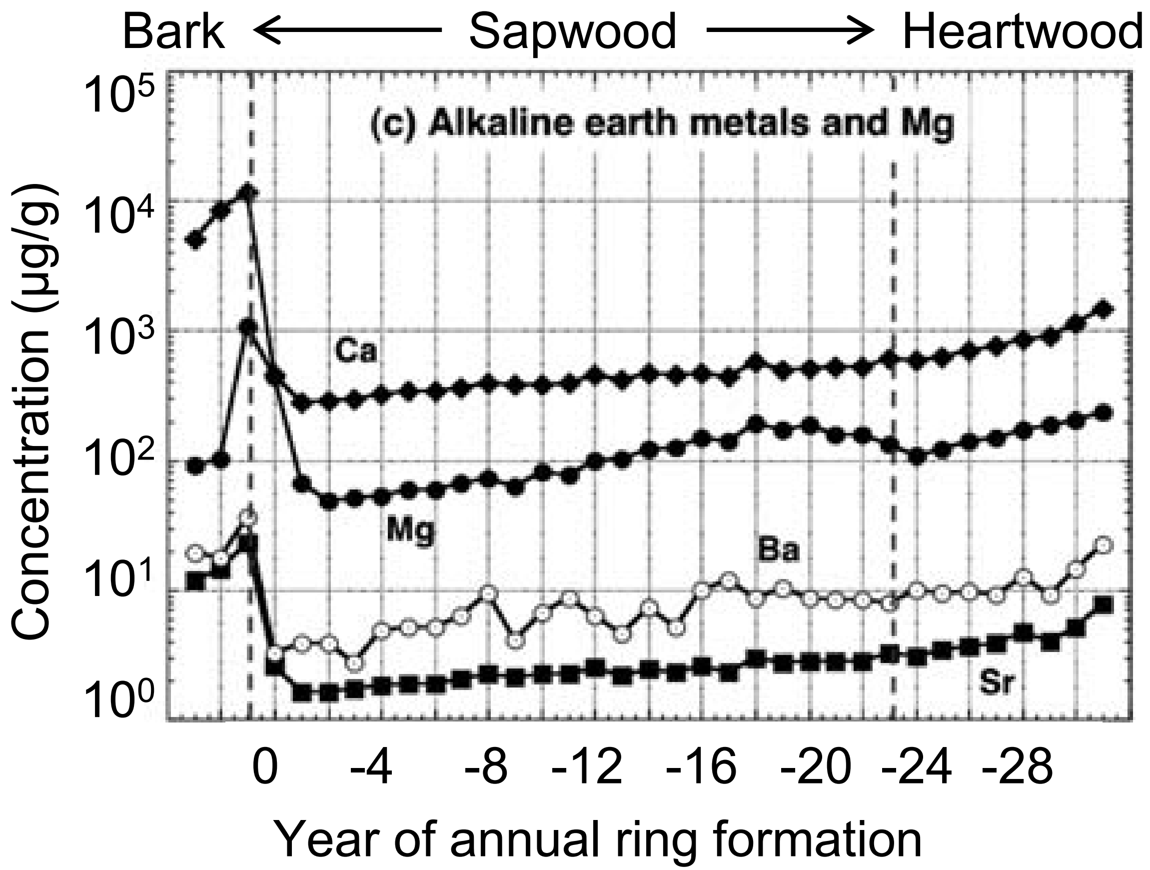
Calcium and Magnesium Distributions in Wood



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