NC STATE UNIVERSITY

Emerging Forest-based Products and Processes

Richard A. Venditti
Forest Biomaterials
(formally Wood and Paper Science)

North Carolina State University

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Center on Global Change
Duke University

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- PhD, Chemical Engineering, Polymer Physics, 1994 Princeton University
- Taught at NCSU in Forest Biomaterials Department for 17 years
- Research (papers)
  - Separation (Solid-Solid) Processes, Recycling (45)
  - Novel materials from wood (plastics, gels, foams) (50)
  - Biofuel production (10)
  - Life Cycle analysis (0)
- On sabbatical, Duke University, January-July, 2011, hosted by Robert Jackson and the Center for Global Change
  - Goal: learn LCA, energy/environment, others
  - Goal: interact with all those interested, develop collaborations

Outline

- **Challenges in biofuels**
- **Forest Biomaterials Biofuels Research**
- **Examples of biofuels research**
  - **Biomass procurement analysis**
  - **Harvesting products as byproducts from wood**
  - **LCA of biofuel production**
- ***Summary***

Sustainable Biofuel Industry?

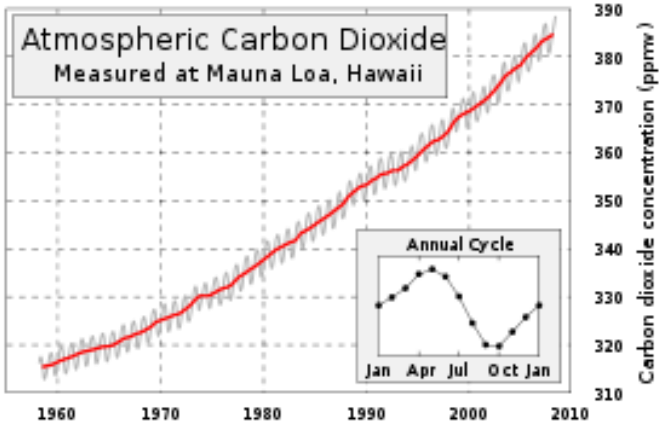
- ***One should expect that, within a few thousand years of its entering the stage of industrial development, any intelligent species should be found occupying an artificial biosphere which completely surrounds its parent star.*** **--Freeman Dyson, 1978.**

- ***The notion that science will save us "is the sedative that allows civilization to march so steadfastly towards environmental catastrophe"*** **--Kenneth Brower, Science, 2010.**

- **Biofuels?**

Global Carbon Cycle and Forests?

- ***Atmospheric concentration of CO2 has increased by 31% since 1750 (to 390 from 280 ppm) and by 1.5 ppm/yr for 1980-2000 (IPCC 2001)***



- **Forests are significant in global GHG (Landsberg & Gower, 1997):**
  - **Cover 65% of the total land**
  - **Contain 90% of the total vegetation carbon**
  - **80% of total soil carbon in terrestrial ecosystems**
  - **Assimilate 67% of the total CO2 removed from the atmosphere by all terrestrial ecosystems**

Global Carbon Cycle and Forests?

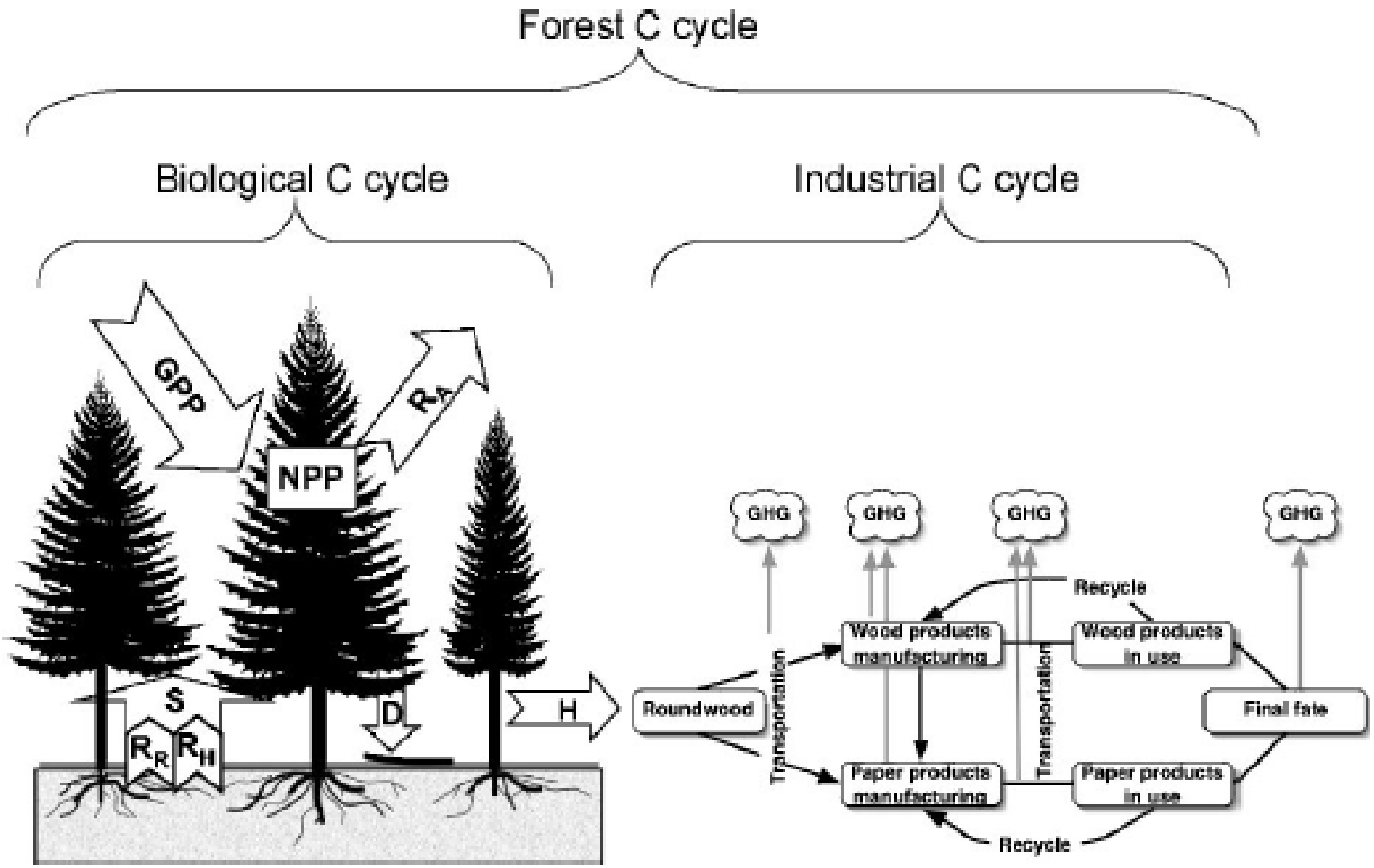


Figure 1 Conceptual diagram of the forest C cycle. The forest C cycle is comprised of a biological cycle (i.e., forest ecosystem) and an industrial cycle (i.e., forest products).

- Gower 2003

Global Carbon Cycle and Forests?

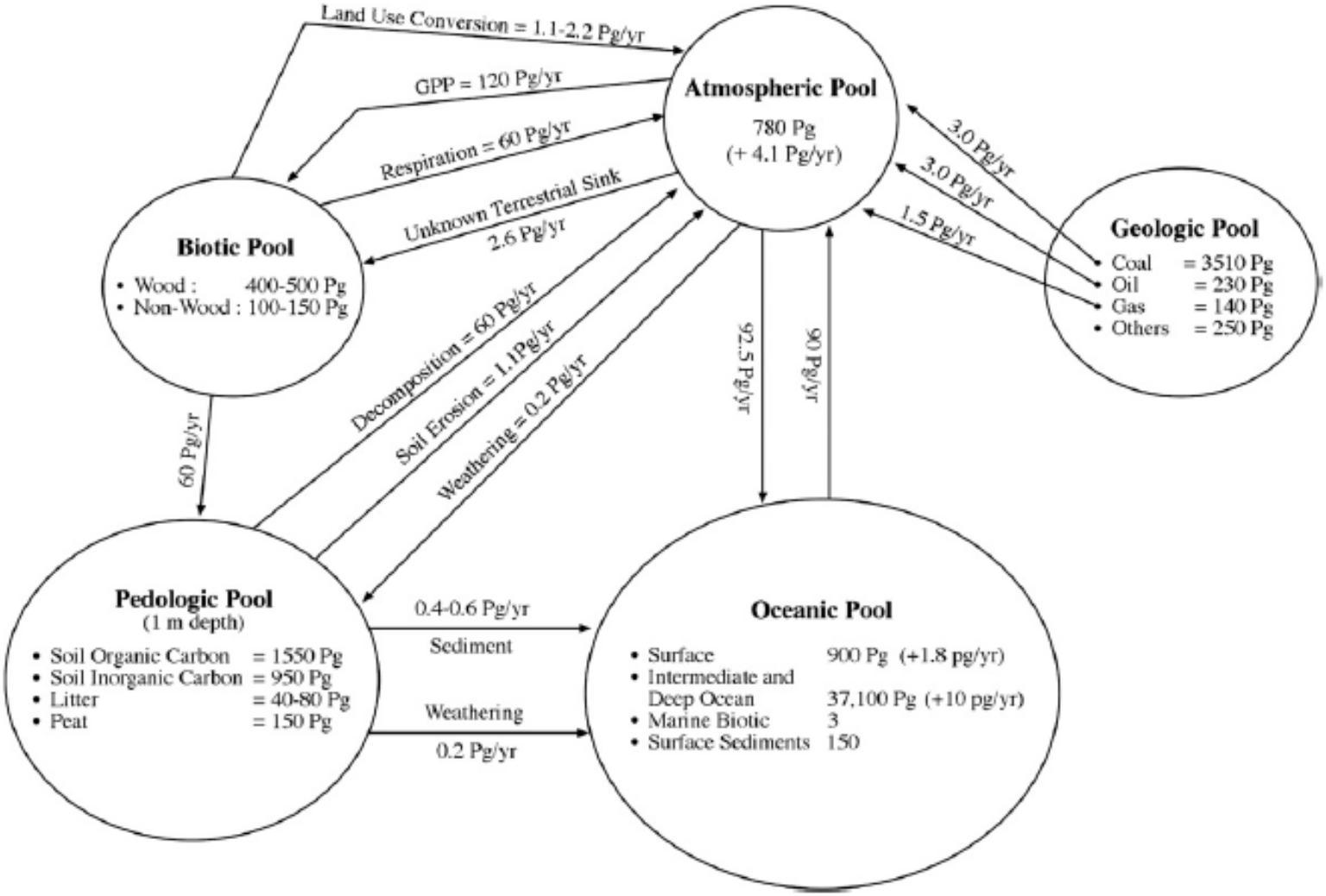
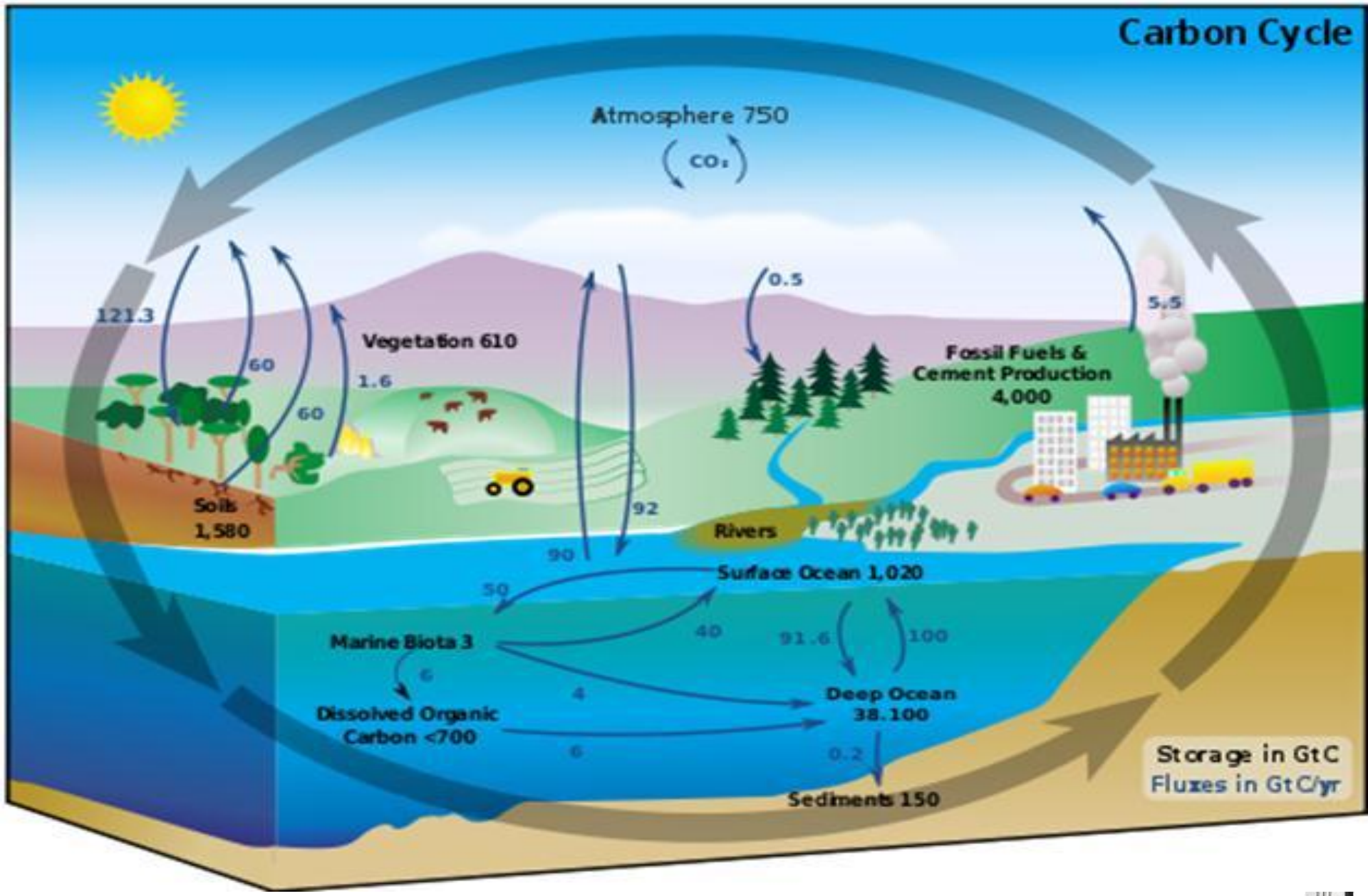


Fig. 1 Estimates of the global pools and fluxes between them.[1,4,5,7,152]



- *The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons ("GtC" stands for GigaTons of Carbon and figures are circa 2004). The dark blue numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen.*

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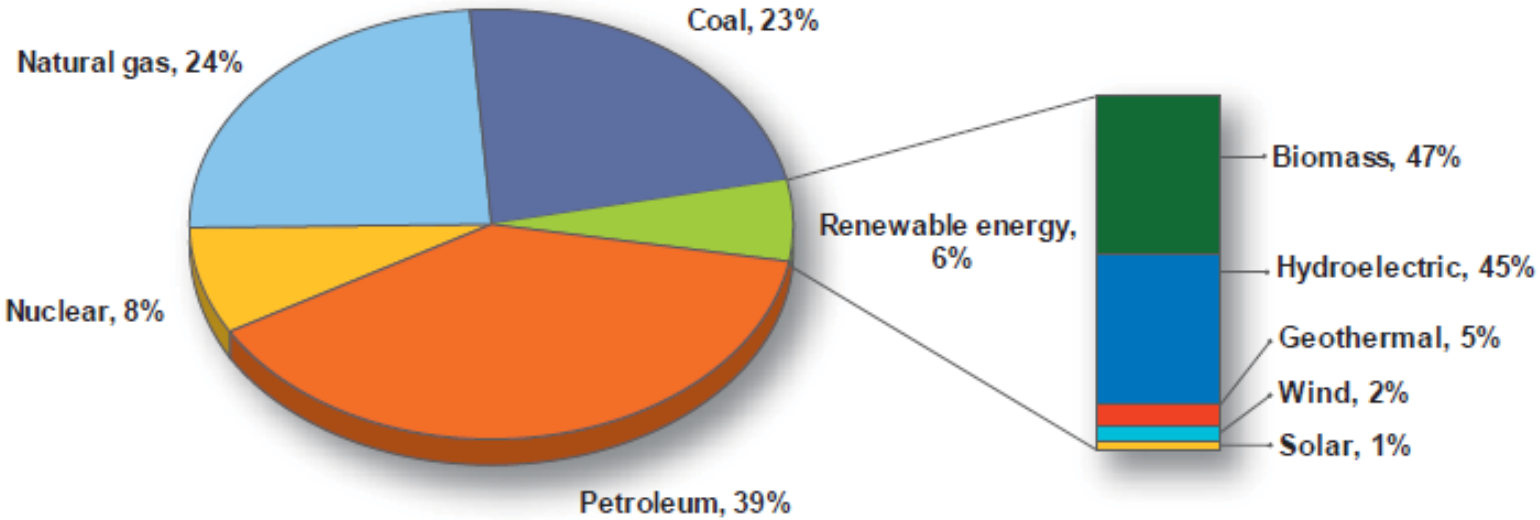
State of Biofuels relative to US Energy Demands



Biomass Consumption	Million dry tons/year
Forest products industry	
Wood residues	44
Pulping liquors	52
Urban wood and food & other process residues	35
Fuelwood (residential/commercial & electric utilities)	35
Biofuels	18
Bioproducts	6
Total	**190**

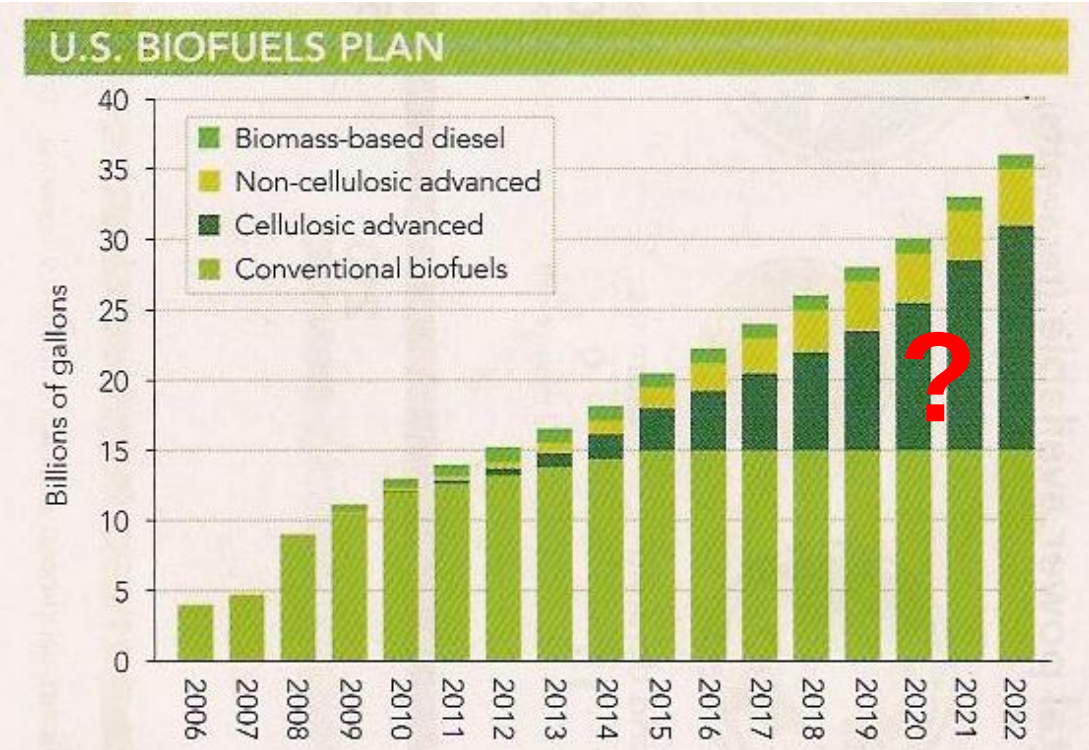
- Forestlands and agricultural lands contribute 190 million dry tons of biomass - 3% of America's current energy consumption.

- Biomass as a Feedstock for a Bioenergy Industry, USDA, 2005.

Figure 2: Summary of biomass resource consumption

2007 Energy Independence and Security Act

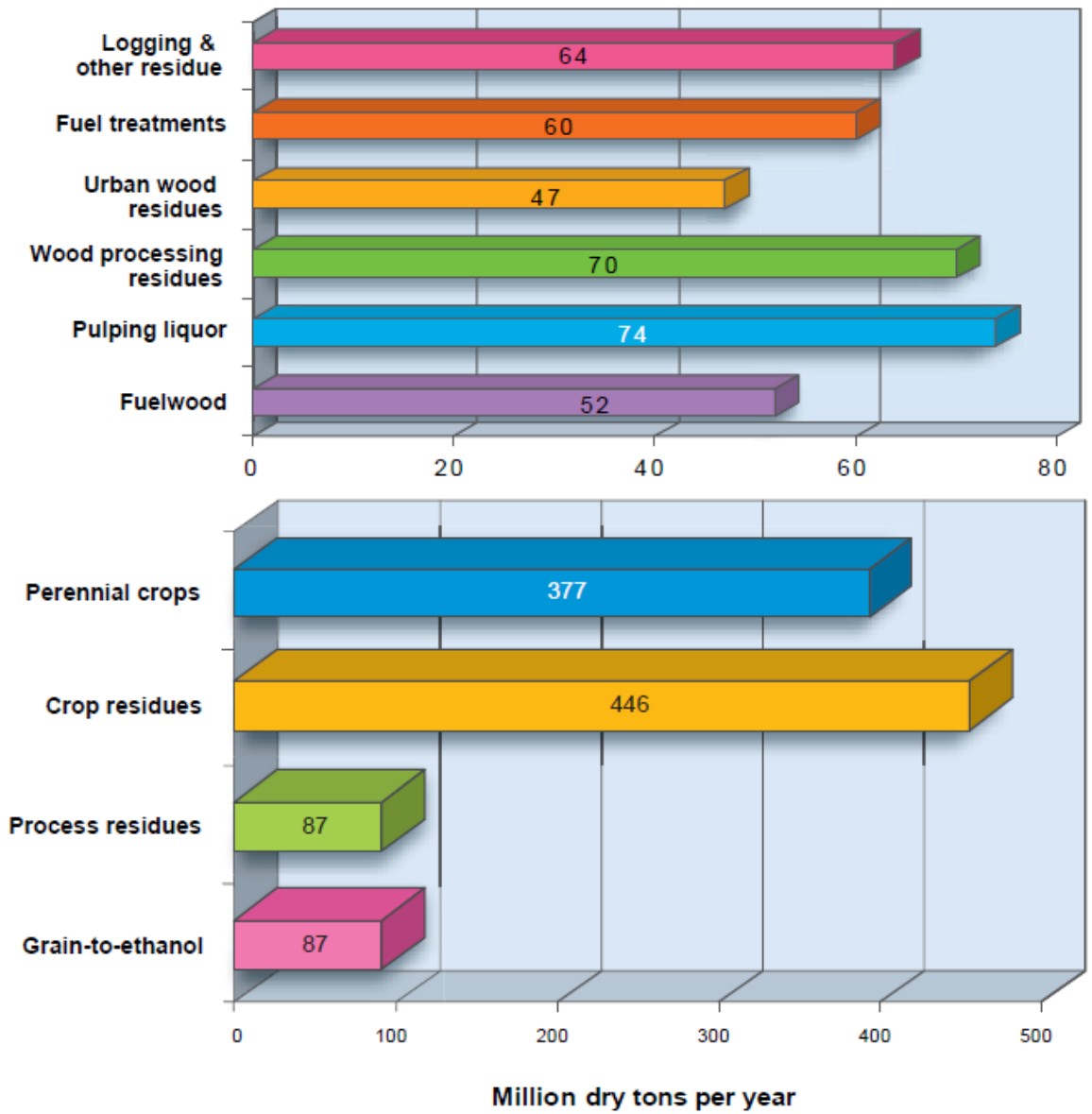
- Replace 30% of petroleum consumption by 2022
- 36 Billion Gallons of Renewable Fuel
- 15 Billion Gallons from Corn Ethanol
- 16 Billion Gallons from Cellulosic Biofuels
- R. F. Service, *Science*, 329, pp 784-785, 2010.



Growing gap. Energy legislation from 2007 mandates an increasing share of cellulosic ethanol (dark green). But the industry is already falling behind.

Challenges: Quantities

- To replace 30% of petroleum consumption in the US, it is estimated that 1 billion OD tons of biomass/yr needed
- 368 million OD tons/yr forest matl out of 8.4 billion tons standing, 1/20
- 998 million OD tons agricultural out of the 1.2 billion tons available per yr, 1/1
- Figures are optimistic: light economics, including assumed yield increases, no till, changing crops and land uses



Biomass as a Feedstock for a Bioenergy Industry, USDA, 2005.

Challenges: Quantities

- International Energy Agency estimates a 50% reduction of GHG by 2050 to require a factor of 4 increase in bioenergy production, up to 20% of the world primary energy
- If one type of material was used to fulfill this, the corresponding volume required is shown
- In contrast the global volumes handled currently:
  - Total of rice, wheat, soybeans, maize, others is 2.75 bcm
  - Coal 6.2 bcm/yr
  - Oil 5.7 bcm/yr

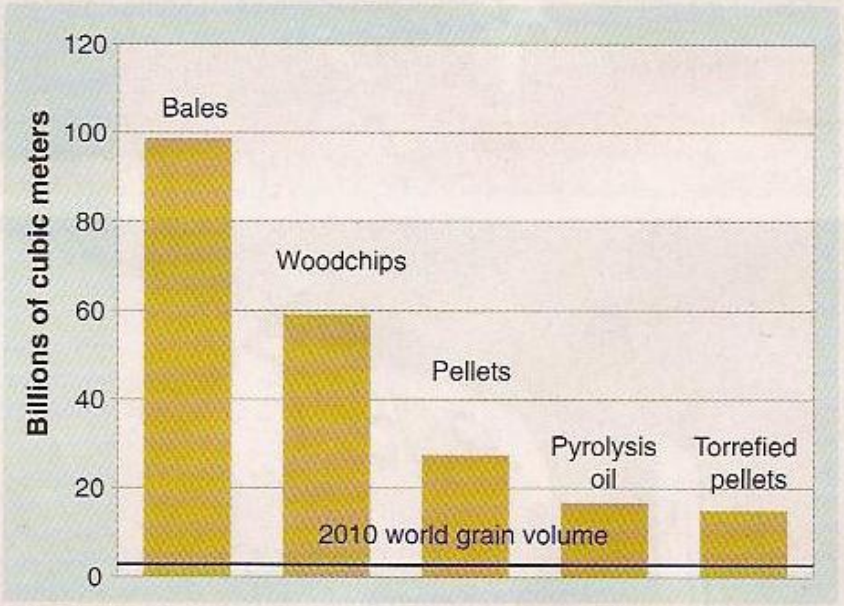


Fig. 1. Global biomass volumes required to achieve a 50% reduction in greenhouse gas emissions by 2050. A wide range of densification options are possible, but even the most effective will still require several times the biomass-handling capacity that the commodity grain system uses today.

- T. L. Richard, *Science*, 329, pp 793-795, 2010. Assumptions: 15 billion mT, 60% conversion efficiency, 17 MJ/kg dry matter, 150 and 225 kg/m3, baled grass and wood chip density.

Challenges: Low Energy Density

Table 3.5. Density and volumetric energy content of various solid and liquid fuels

Fuel	Density (kg/m^3)	Volumetric Energy Content (GJ/m^3)
Ethanol	790	23.5
Methanol	790	17.6
Biodiesel	900	35.6
Pyrolysis oil	1280	10.6
Gasoline	740	35.7
Diesel fuel	850	39.1
Agricultural residues	50–200	0.8–3.6
Hardwood	280–480	5.3–9.1
Softwood	200–340	4.0–6.8
Baled straw	160–300	2.6–4.9
Bagasse	160	2.8
Rice hulls	130	2.1
Nut shells	64	1.3
Coal	600–900	11–33

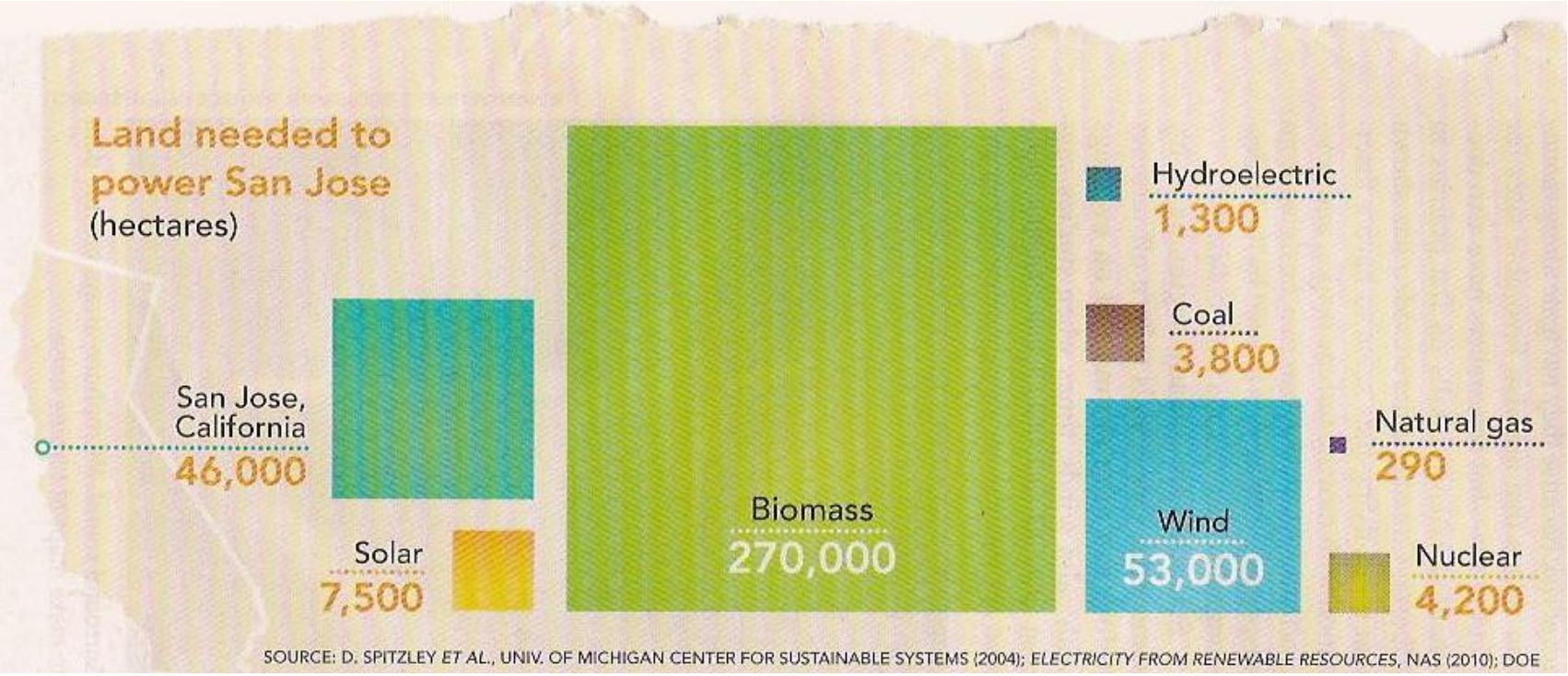
10x

Sources: K. Grohmann, C. E. Wyman and M. E. Himmel, 1992, "Potential for Fuels from Biomass and Wastes," in *Emerging Technologies for Material and Chemicals from Biomass*, R. M. Rowell, T. P. Schultz and R. Narayan, eds., ACS Symp. Series 476 (Washington, D.C.: American Chemical Society); E. D. Larson, P. Svenningsson and I. Bjerle, 1989, "Biomass Gasification for Gas Turbines Power Generation," in *Electricity*, Johansson, Bodlund and William, eds (Lund, Sweden: Lund University Press).

Note: GJ = Gigajoules.

- **R. C. Brown, *Biorenewable Resources, Engineering New Products from Agriculture*, Blackwell Pub, 2003.**

Challenges: Land Mass Required



- **A Cho, *Science*, 329, pp 786-787.**
- **San Jose population: ~1 million, California Dept of Finance. January, 2010.**

Challenges: Solids Handling

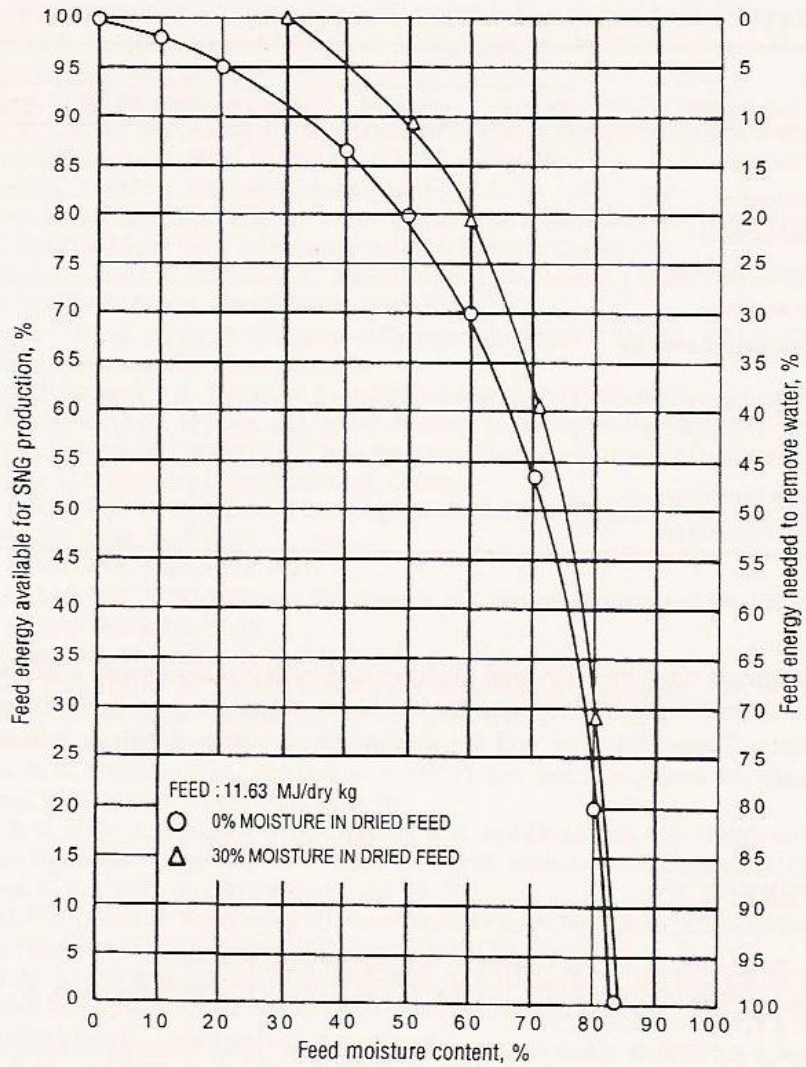


FIGURE 3.7 Effect of feed moisture content on energy available for SNG production. (Example of use: Reduction of an initial moisture content of 70 wt % by thermal drying to 30% requires the equivalent of 37% of the feedstock energy content and leaves 63% of the feedstock energy available for SNG production.)

- **Transport, communition, measurement, and dosing problematic**
- **Storage conditions important**
  - **Moisture and temperature sensitive**
  - **Break down through the action of a naturally occurring microorganisms, such as bacteria, fungi, etc.**
- **Low bulk density**

- **D. L. Klass, *Biomass for Renewable Energy, Fuels and Chemicals,* Academic Press, 1998.**

How the current forest products industry might fit in.

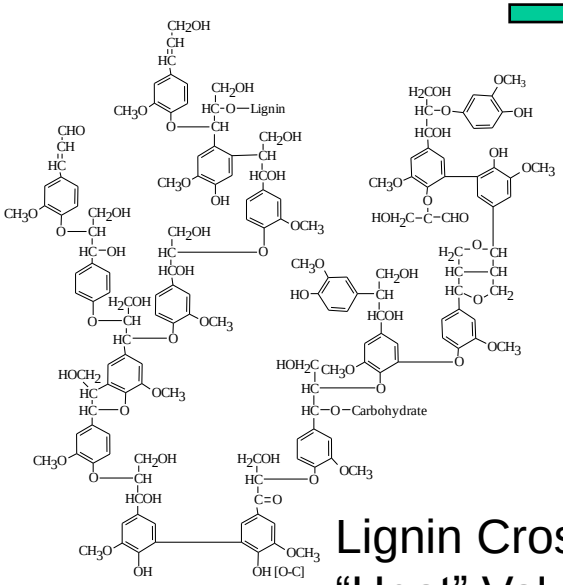
Biomass as a Feedstock for a Bioenergy Industry, USDA, 2005.

Chemical Components of Wood

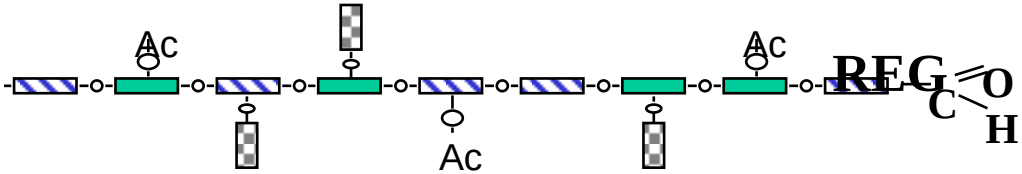
WOOD

- **LIGNIN** — SW 25%, HW 21%
- **CELLULOSE** — 45%
- **HEMICELLULOSE** — SW 25%, HW 30%
- **EXTRACTIVES** — 2-5%

Cellulose:
DP=4000
"Polymer" Value

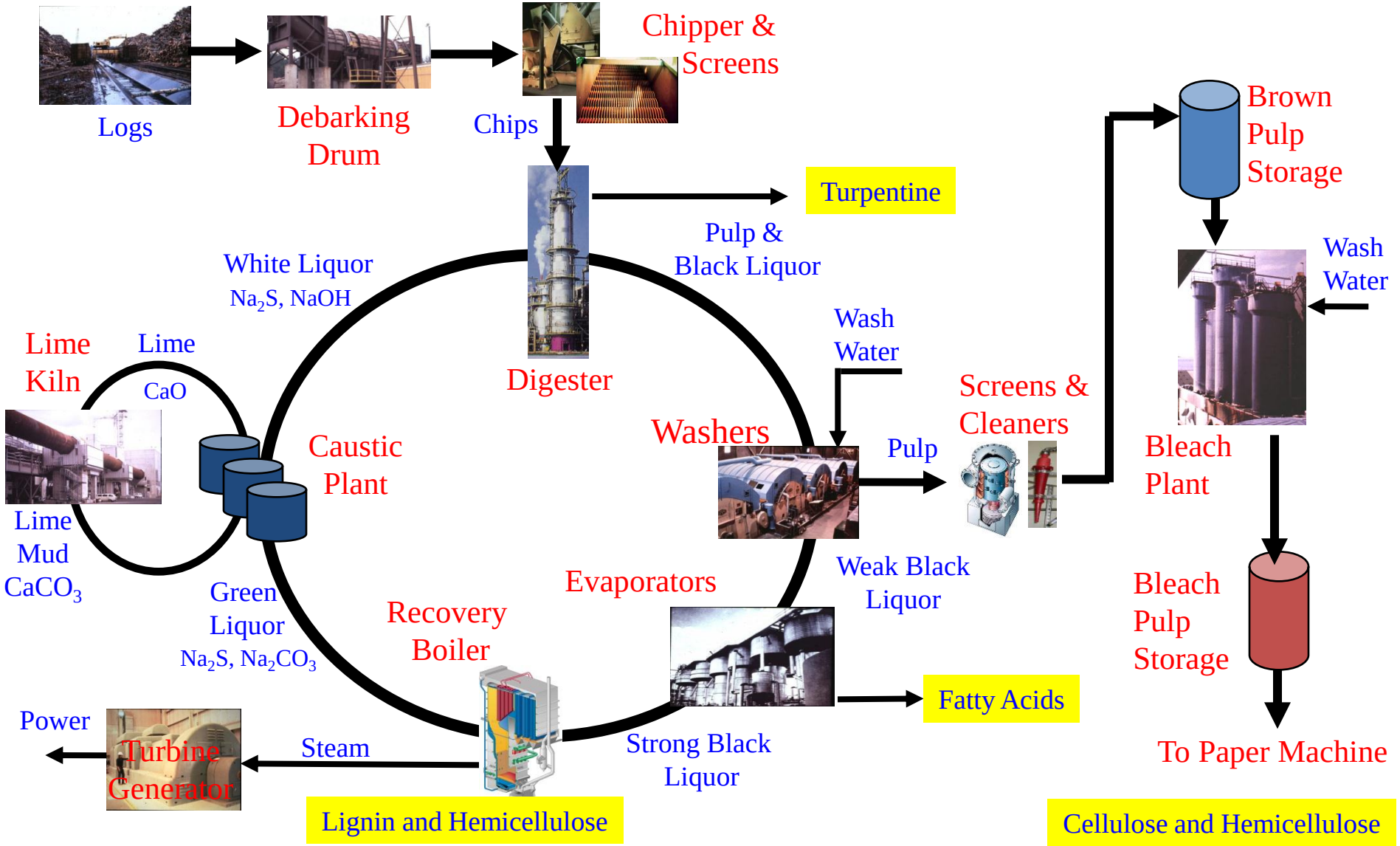


Lignin Crosslinked
"Heat" Value

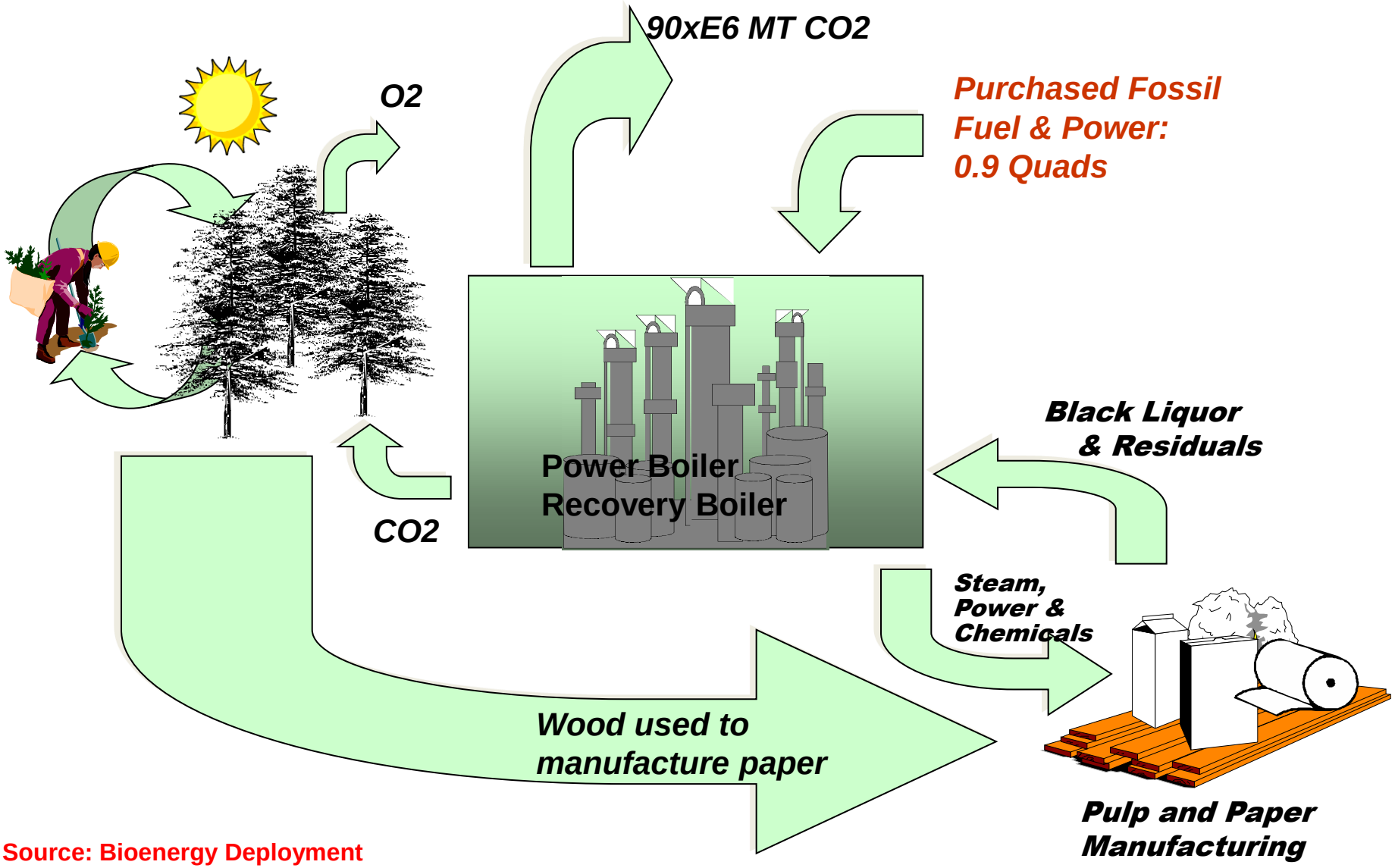


Hemicellulose: DP=150
"Sugar" Value

Current: wood to paper process

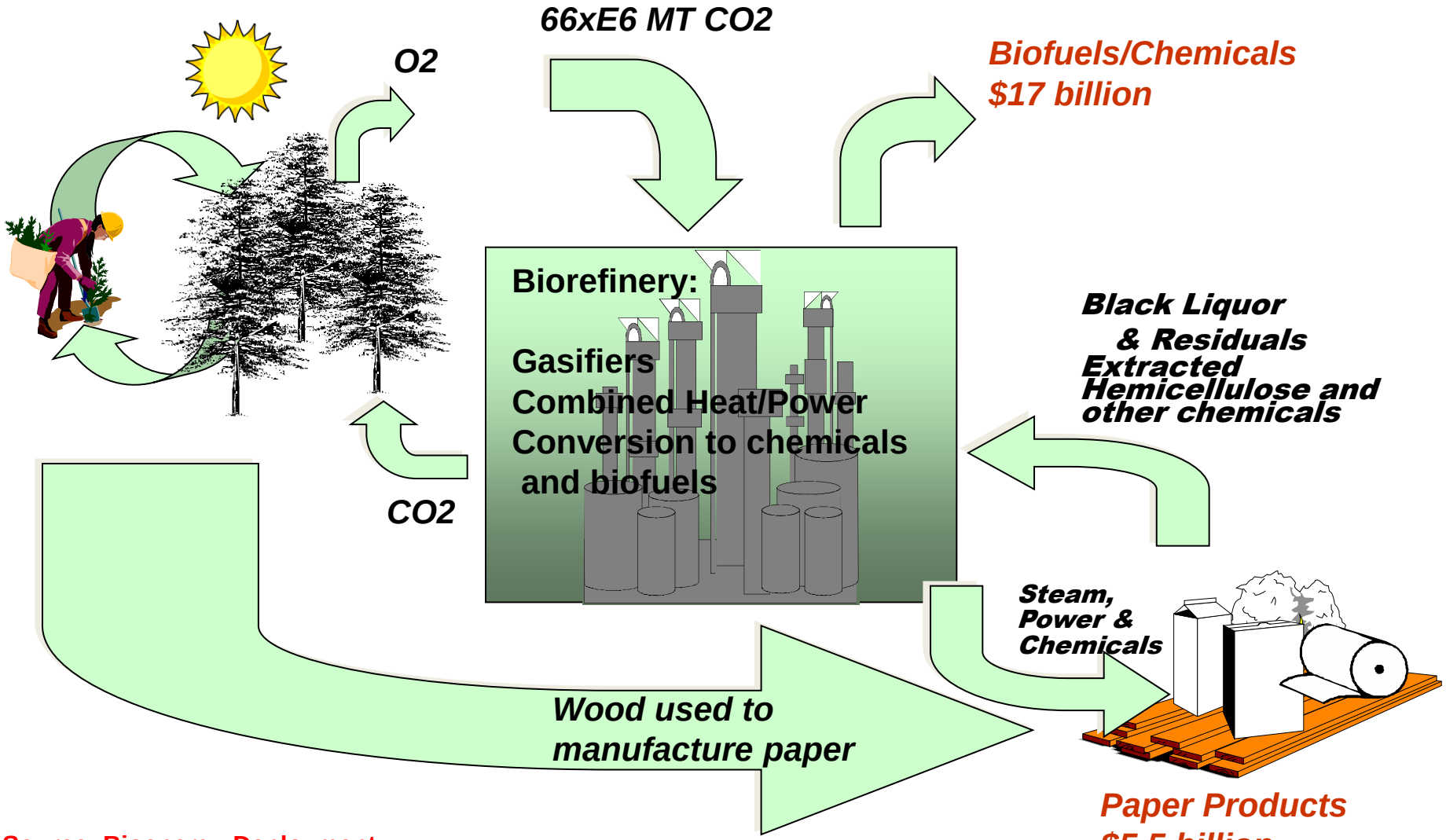


Current Wood Processing Industry



Source: Bioenergy Deployment

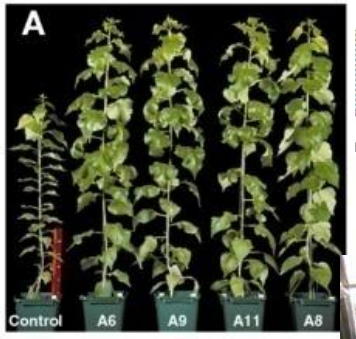
Proposed: Biorefinery Industry

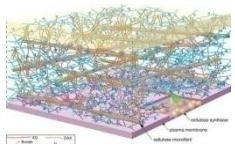


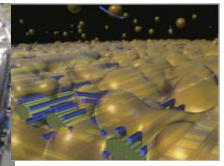
Source: Bioenergy Deployment

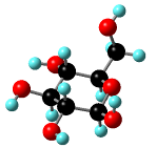
Bioenergy Program

Department of Forest Biomaterials









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Faculty in Bioenergy Science and Technology

Dimitris Argyropoulos
Professor
Wood Chemistry

Med Byrd
Associate Professor
Process Development

Hou-min Chang
Professor Emeritus
Wood Chemistry

Vincent Chiang
Professor
Forestry Biotechnology

John Heitmann
Professor
Enzyme Biotechnology

Martin Hubbe
Professor
Surface Chemistry

Hasan Jameel
Professor
Process Engineering

Stephen Kelley
Dept Head & Professor
Polymer Chemistry

Adrianna Kirkman
Professor
Process Simulation

Lucian Lucia
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Wood Chemistry

Sunkyu Park
Assistant Professor
Bioenergy Process

Richard Phillips
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Bioenergy Economics

Orlando Rojas
Associate Professor
Surface Chemistry

Daniel Saloni
Assistant Professor
Process Development

David Tilotta
Associate Professor
Wood Chemistry

Richard Venditti
Professor
Process Engineering

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Bioenergy Projects

- Bioethanol Pilot Plant
- Wood-to-Ethanol Research Consortium
- Value Prior to Pulping (VPP)
- Ethanol from Transgenic Hardwoods
- Ethanol from Coastal Bermuda Grass
- Enhancing Wood Penetration for More Efficient Hydrolysis and Optimized Saccharification
- Opportunities with Dissolved Wood for the Forest Biorefinery
- Validation of Therminator Syngas Cleanup
- Advanced Technology for Low Cost Ethanol from Engineered Cellulosic Biomass
- Economics and Feasibility of North Carolina Biomass Conversion
- Producing Ethanol from Biomass by Extracting Value Prior to Extraction
- Low Cost Conversion of Industrial Sludges to Ethanol
- Integrated Torrefaction-Gasification for the Production of Biofuels
- Economic Analysis of Pine Biomass Varieties for Ethanol Production
- Life Cycle Analysis for the Production of Transportation Fuels
- Fast Pyrolysis of Forestry Biomass

Wood to Ethanol Research Consortium (1)

- Paper industry in US has idled about 25% of its production, about 50 million tons/yr of wood processing (potential of 4 billion gallons of ethanol)
- Concept: Repurposing a kraft pulp mill into a ethanol mill
- Develop cost effectiveness by reusing existing asset: a pulp mill is about $1 Billion in capital

BE&K A KBR Company

Catchlight Energy A Chevron | Weyerhaeuser Joint Venture

ARBORGEN

NIPPON PAPER GROUP

AMERICAN PROCESS

ANDRITZ

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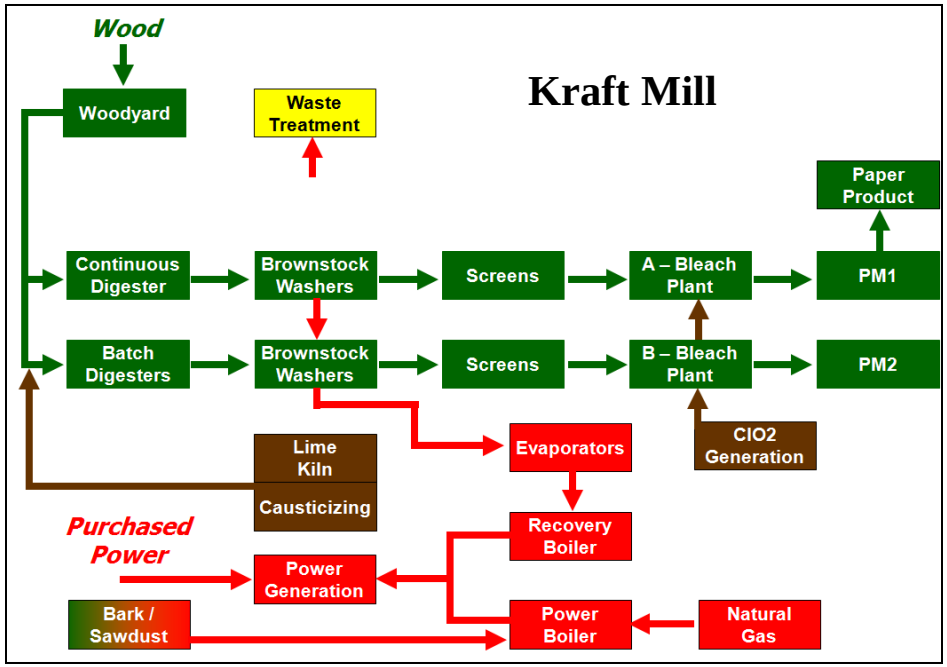
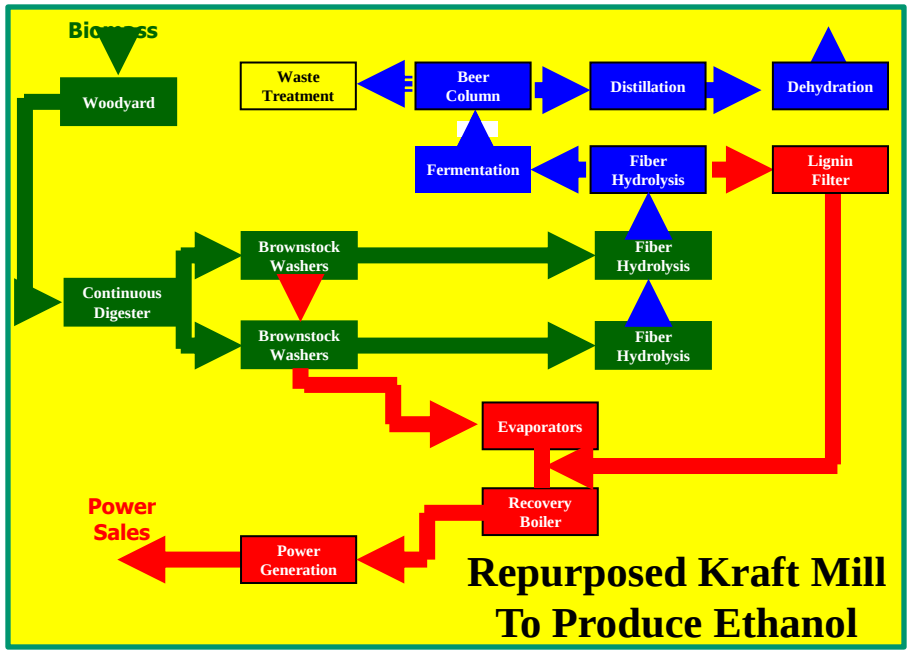
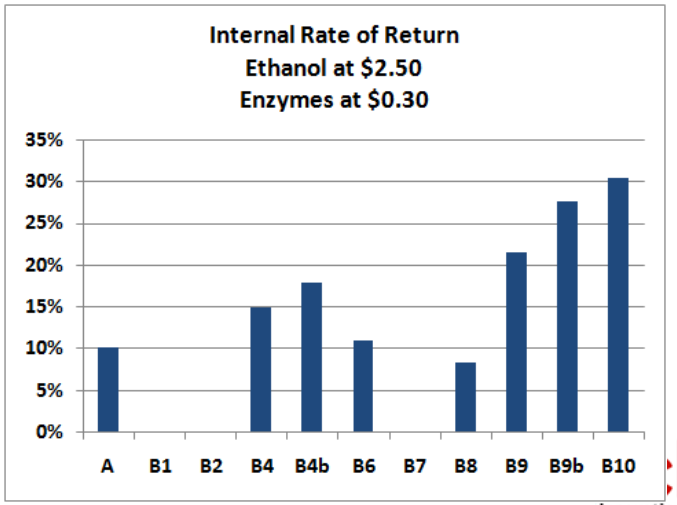
Wood to Ethanol Research Consortium (2)



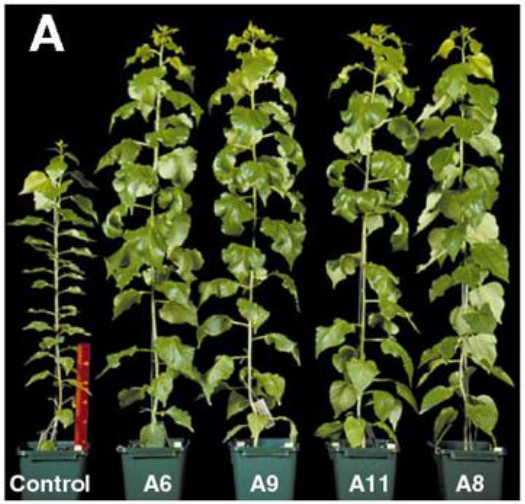


80% of sugars in wood can be converted by enzymatic hydrolysis when wood is pretreated with green liquor.



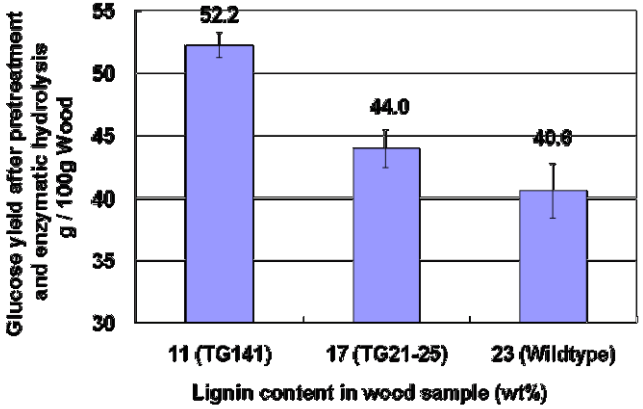
Ethanol from Transgenic Hardwoods

- Challenge: bioconversion of wood to ethanol, wood is recalcitrant to enzyme hydrolysis, low sugar yields
- Must pretreat wood with alkali, acid…
- Evaluate potential for simplifying pretreatments for low/modified lignin hardwood (aspen)



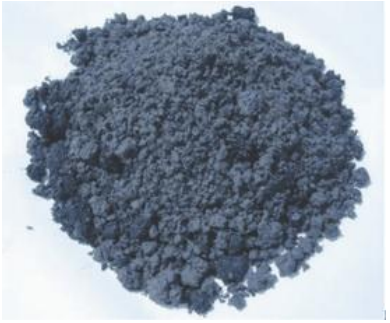
Samples	Lignin	S/G	Glucan
Wildtype	23	2.2	44
TG96	24	6.4	45
TG141	11	2.6	54

Figure 1. Effect of lignin content on glucose yield from wildtype and transgenic woods

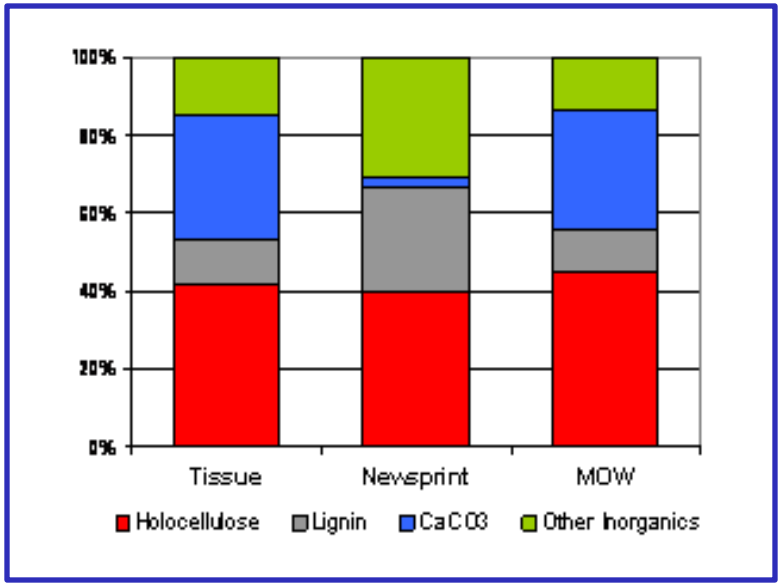


Low Cost Conversion of Industrial Sludges to Ethanol

- **Biofuels Center of North Carolina**
- **Demonstrate an effective technology to convert industrial papermaking sludge as a cost effective feedstock for the efficient biochemical biomass conversion to ethanol**



Papermaking Sludges



Negative feedstock cost
Contains $CaCO_3$ and inorganics

A closer look at three Biofuels projects:

1. Integrated biomass supply and financial models
2. Extraction of hemicellulose for higher valued products
3. Thermoconversion of Biomass to Liquid Fuel

1: Integrated Biomass Feedstock Supply and Financial Models

Ronalds Gonzalez, Hasan Jameel, Richard Phillips

Biorefinery

- Dilute acid
- Thermochem
- GL
- ZeaChem
- Plant location
- Complete financial analysis

Freight

- $/BDT
- Bulk density

Storage

- $/BDT
- Sugar/Biomass loss

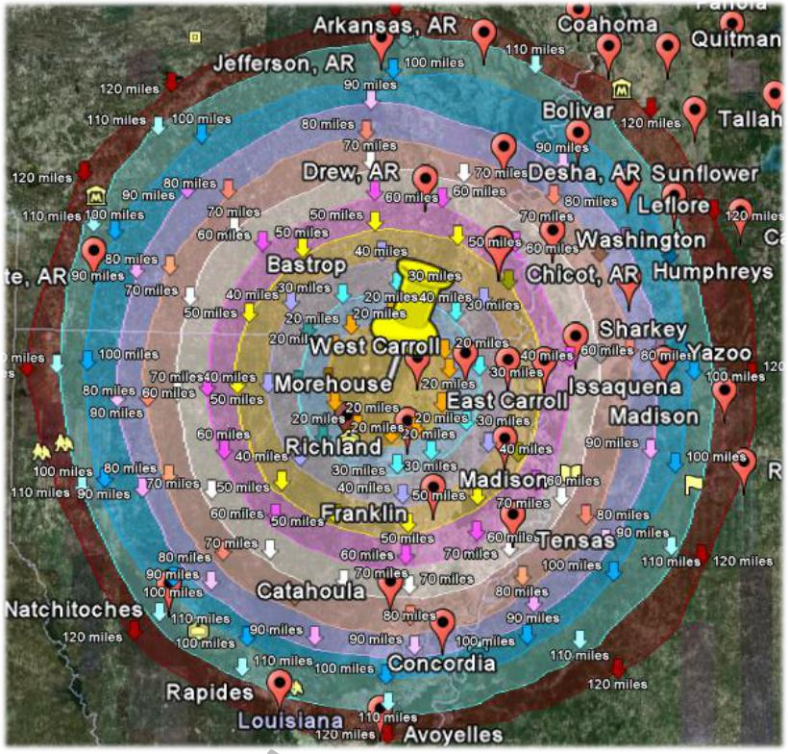
Integrated Supply and Financial Models

- Land available to grow biomass?
- What are the strategies for conversion of land use?
- Whole tree chemical composition?

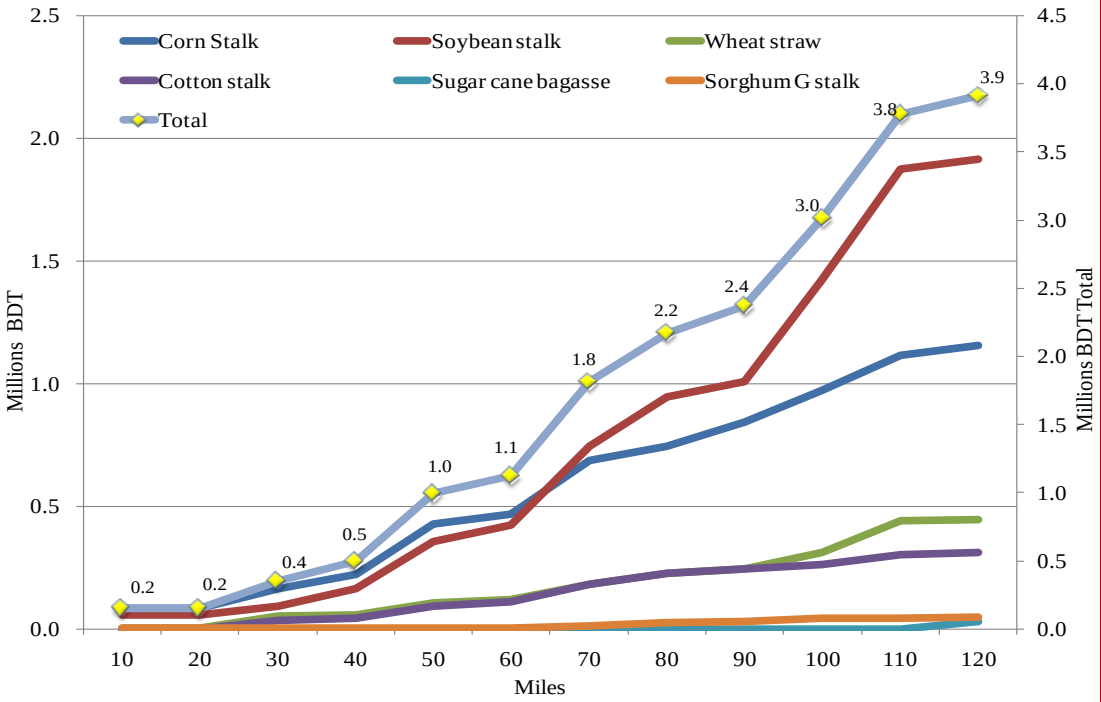
Harvesting

- Biometrics
- $/acre; $/BDT
- Ton Carbohydrate/acre

SUPPLY CHAIN ASSESSMENT



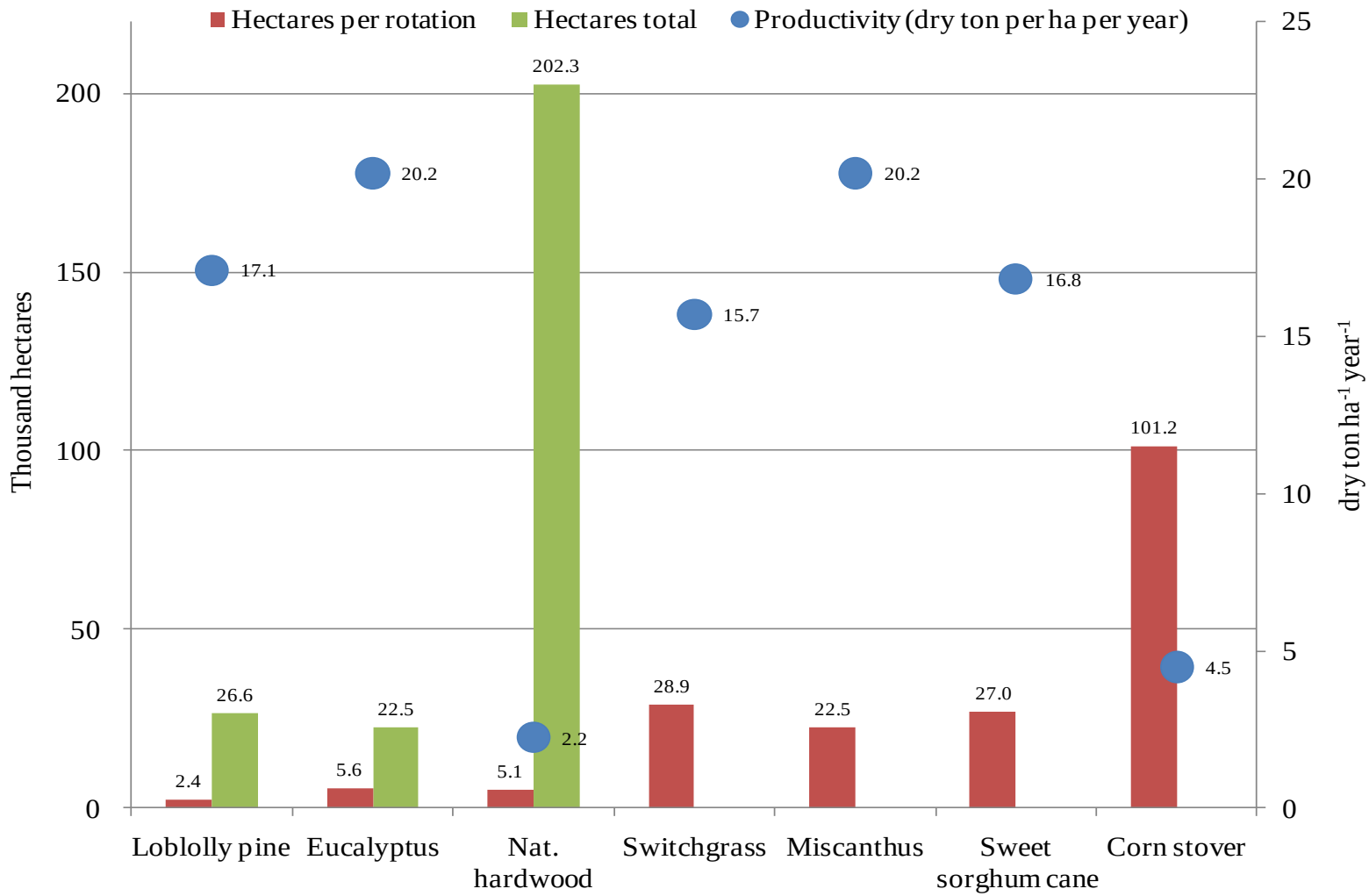
- Integrated feedstock supply
- Biomass availability – curve supply
- Delivery costs, economic analysis
- Supply chain and logistic analysis



Cellulose to ethanol

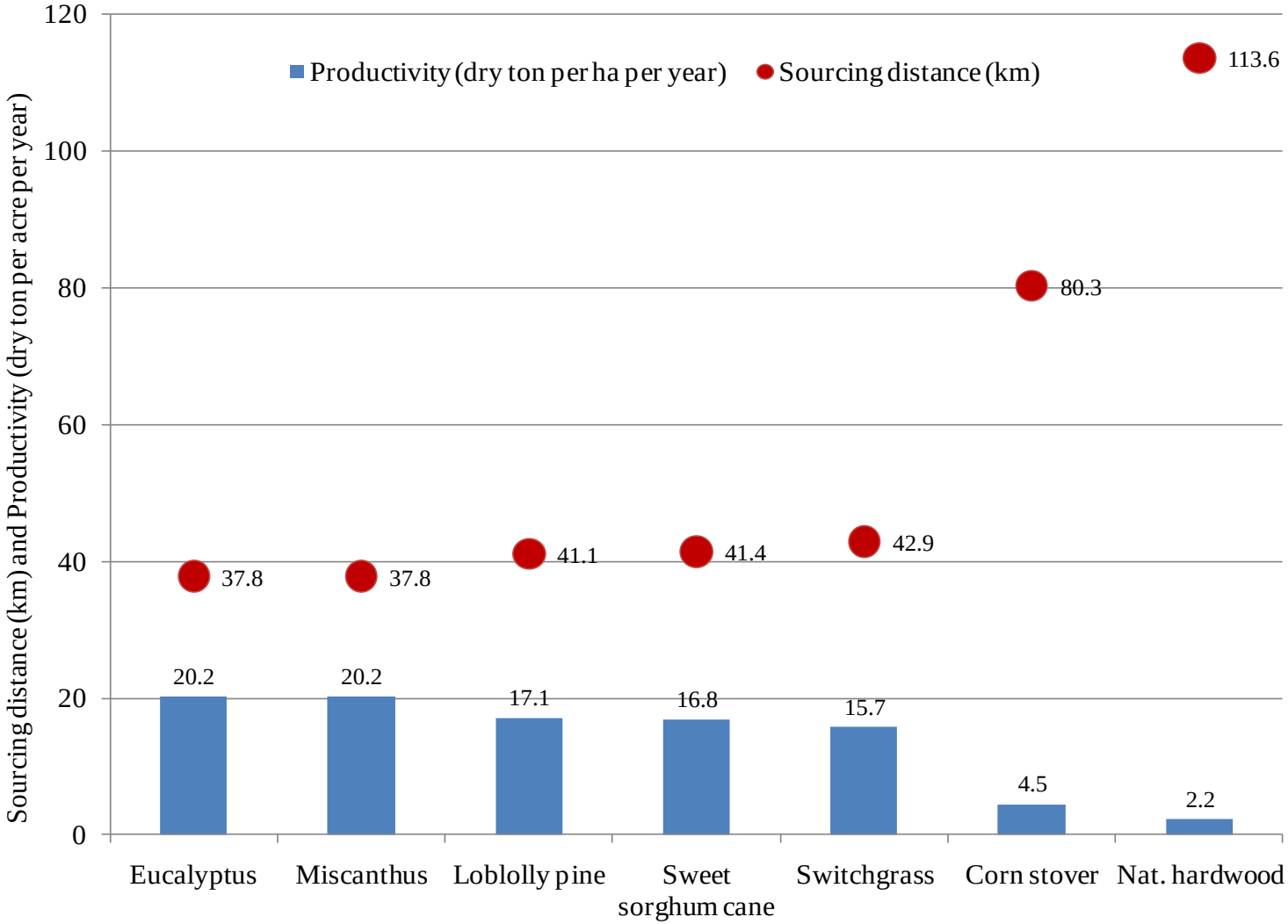
Biomass to Cellulosic Ethanol in Southern U.S.: Supply Chain and Delivered Cost

BIOMASS PRODUCTIVITY AND REQUIRED LAND



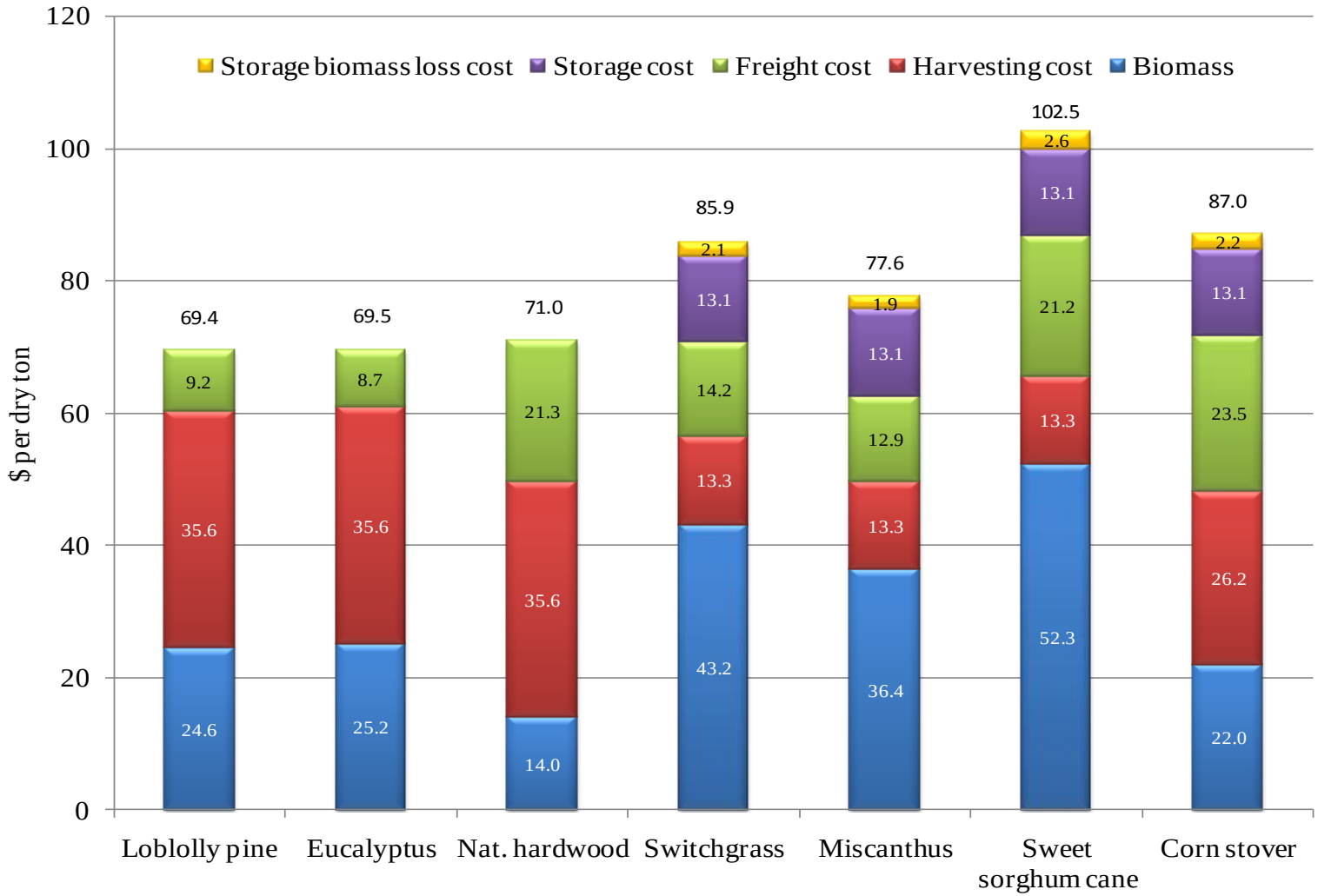
Biomass productivity and hectares required for production to supply 453,597 dry ton yr^{-1}

BIOMASS PRODUCTIVITY AND SOURCING DISTANCE



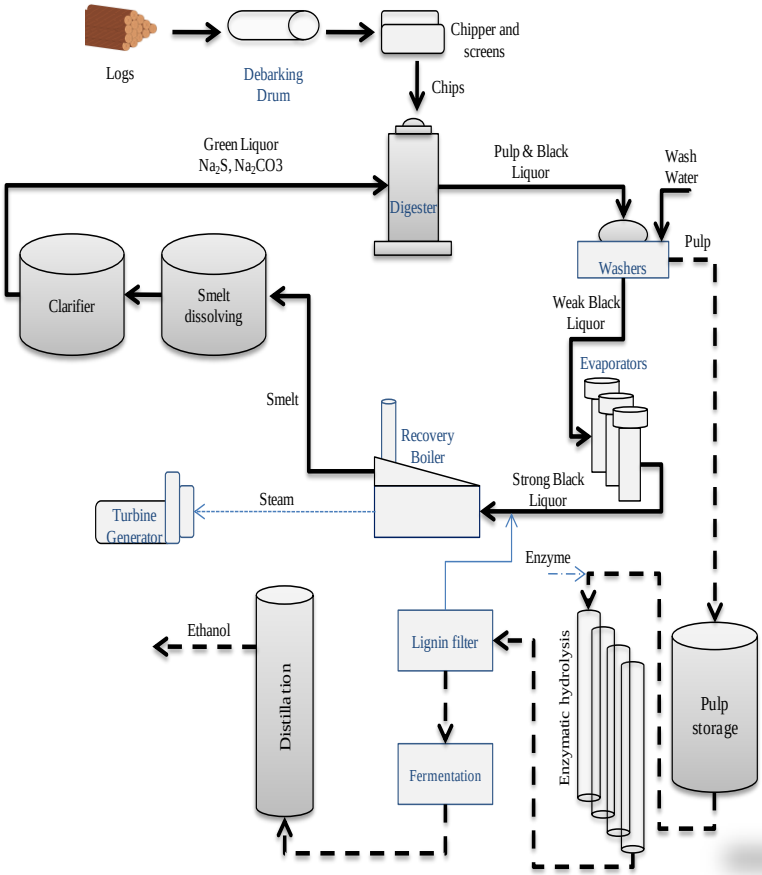
Sourcing distance (km) and productivity (dry ton ha^{-1} yr^{-1}) for the different feedstocks

BIOMASS DELIVERED COST

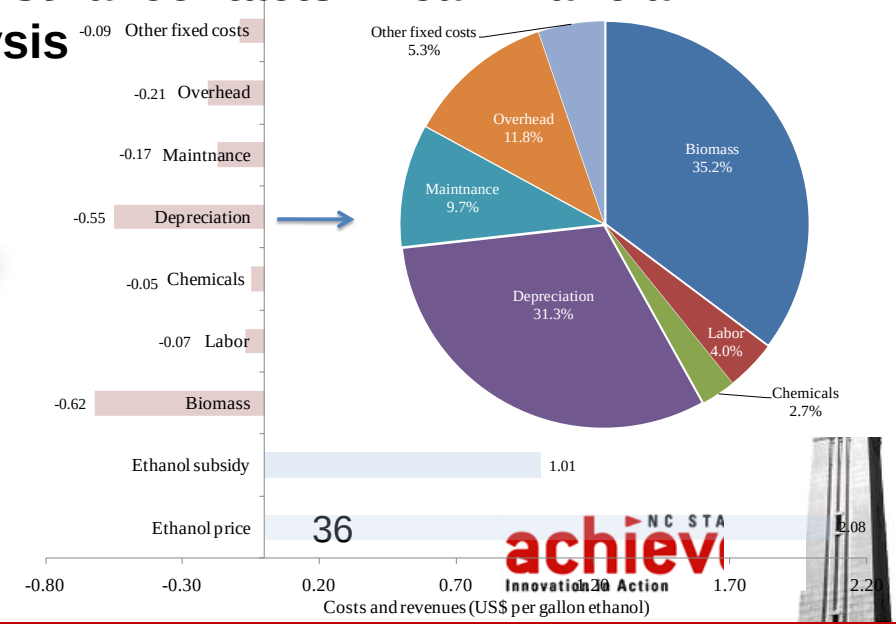


Biomass delivered cost for each of the feedstock, considering 5% covered area and annual supply of 453,597 dry ton year^{-1}

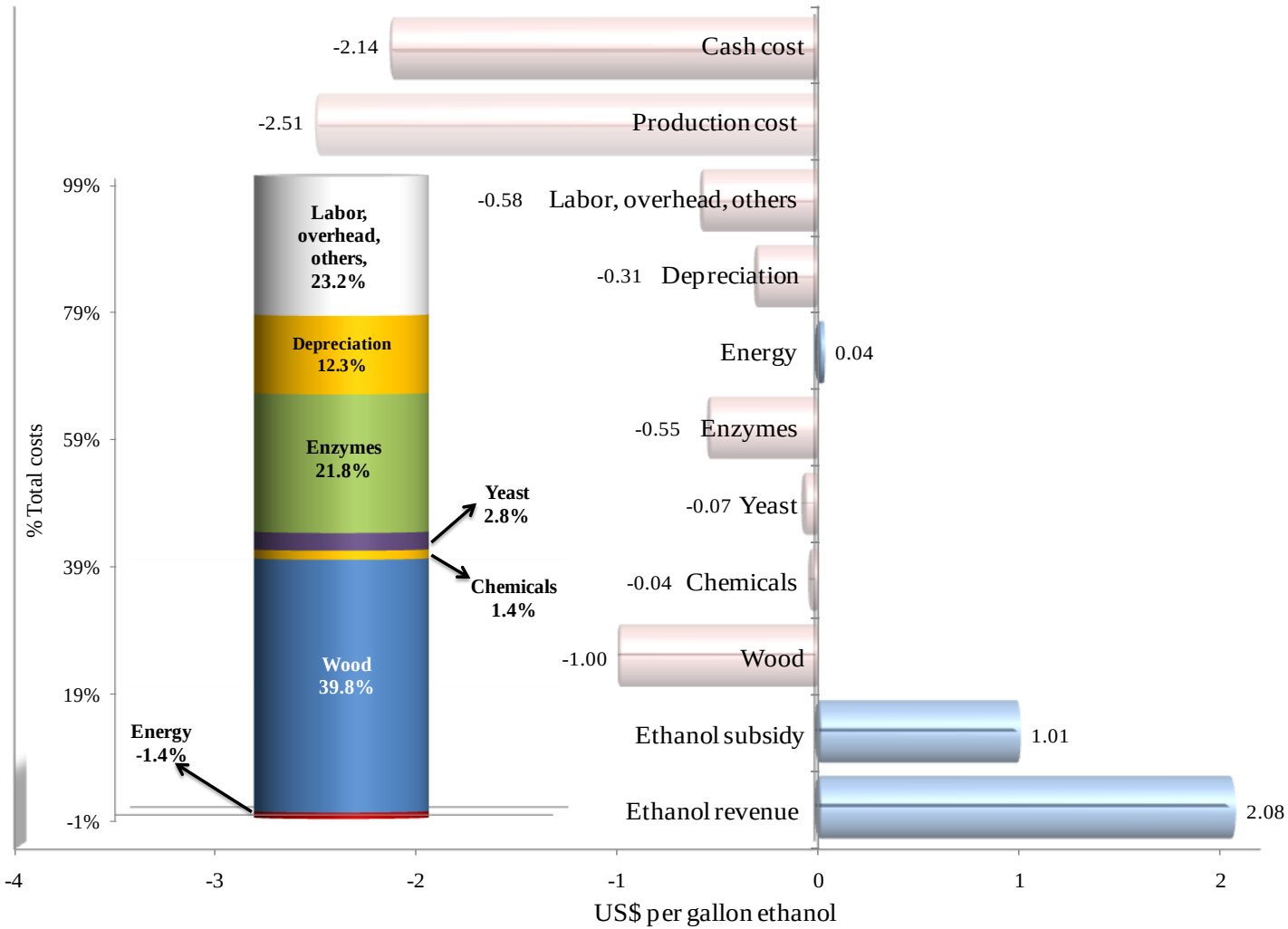
PROCESS SIMULATION – CONVERSION ECONOMICS



- Conversion simulation
- Lab demonstration, pretreatments
- Integrated analysis feedstock – final product
- CAPEX & OPEX
- Industrial contacts – real financial analysis



EXAMPLE CASE: COSTS AND REVENUES:



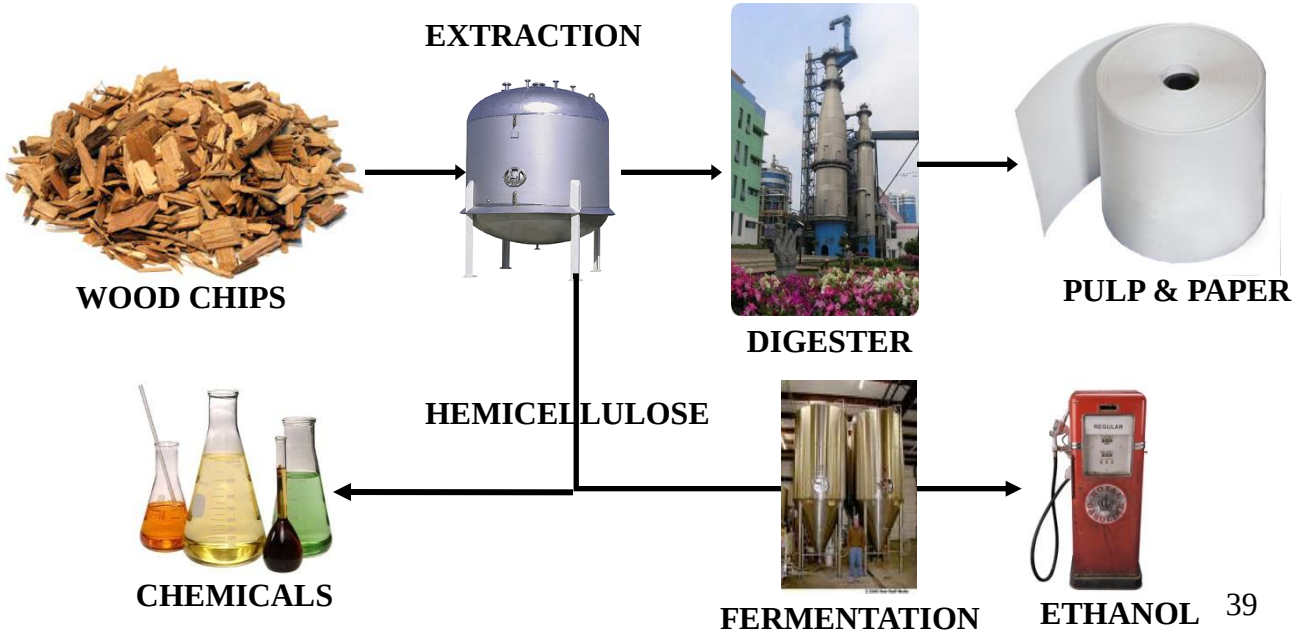
Production costs, cash cost and share cost for ethanol for natural mixed hardwood in the repurposing green liquor scenario.

2: Extraction of Hemicellulose from Wood for Ethanol and Biopolymer Gels

Abdus Salam, Richard Venditti, Joel Pawlak, Khaled El-tahlawy

Value Prior to Pulping or Combustion

- **Extract hemicelluloses prior to pulping or combustion and convert to ethanol or chemicals**
- **Only hot water is required! (Autohydrolysis)**



Hot water extraction of hardwood:

Raw material: 100g

Arabinan: 0.78g
Rhabinan: 0.47g
Galactan: 0.97g
Glucan: 39.22g
Xylan: 16.17g
Mannan: 1.63g

Klason Lignin: 22.36g
ASL: 3.74g
Acetic acid: N/A
Furfural: 0.68g
Others: 13.98g

160 ˚C
1 hour

Pretreated solids: 78.13g

Arabinan: 0g
Rhabinan: 0g
Galactan: 0g
Glucan: 38.40g
Xylan: 7.43g
Mannan: 1.06g

Klason Lignin: 19.95g
ASL: 1.72g
Acetic acid: N/A
Furfural: 0.75
Others: 8.71g

Extract: 15.59g

Arabinan: 0.55g
Rhabinan: 0.14g
Galactan: 0.21g
Glucan: 0.05g
Xylan: 1.10g
Mannan: 0.05g

Klason Lignin: N/A
ASL: 2.36g
Acetic acid: 2.44g
Furfural:1.25g

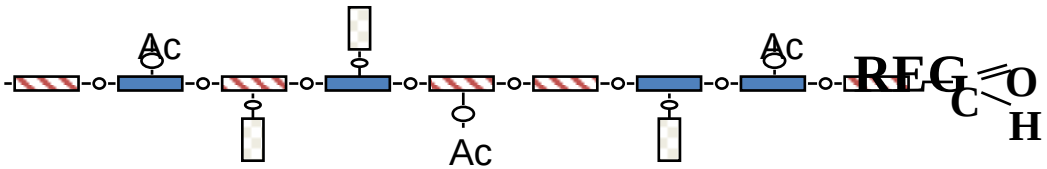
3%
H_2SO_4

Sugar in filtrate: 9.81g

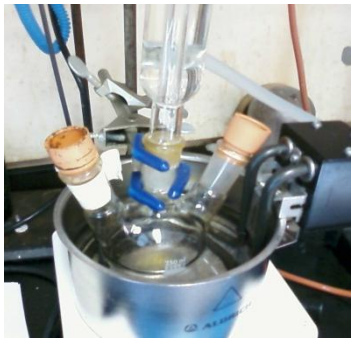
Arabinan: 0.54g
Rhabinan: 0.28g
Galactan: 0.61g
Glucan: 0.25g
Xylan: 7.56g
Mannan: 0.57g

Cross Linking of Hemicellulose Citrate with Chitosan to Make High Value Foams

1.



Hemicellulose: DP=150
“Sugar” Value



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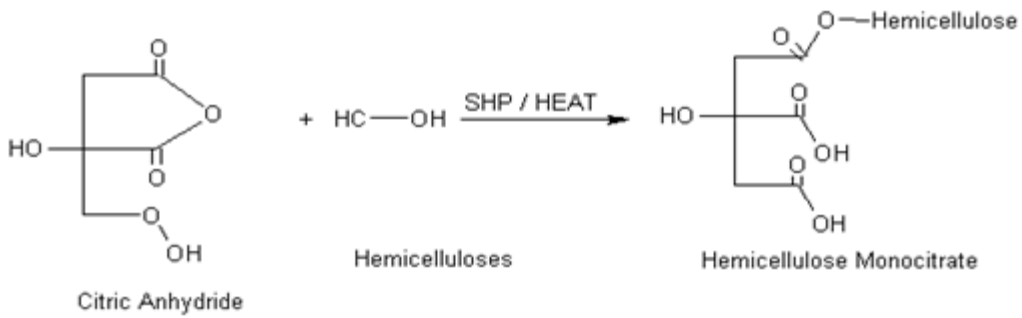
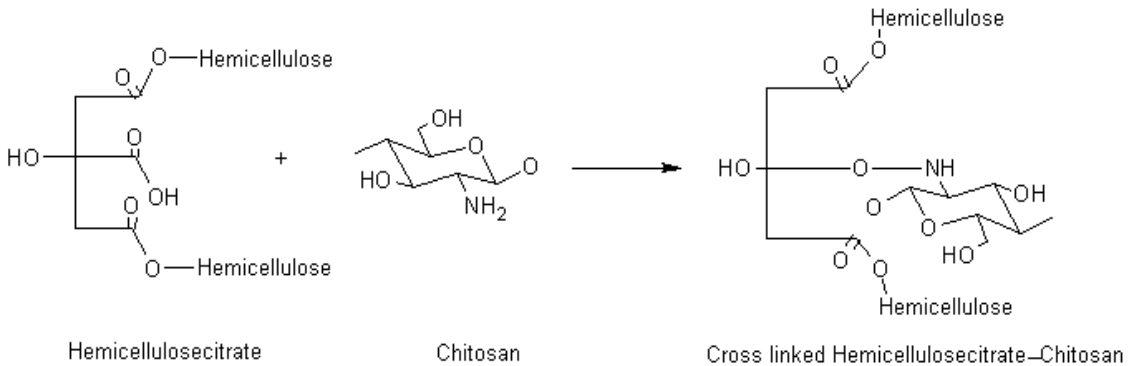
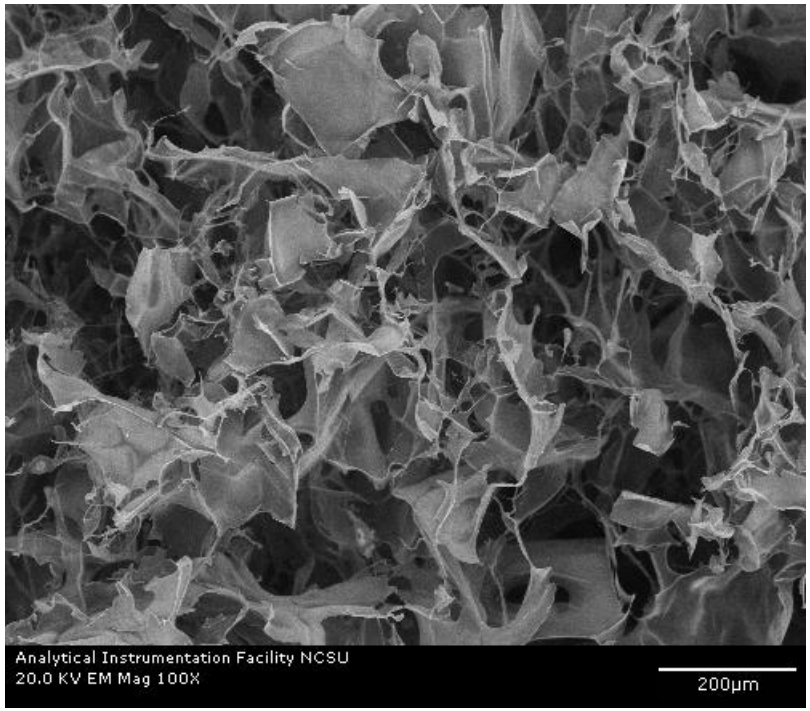


3.



Hemicellulose Citrate Chitosan based elastic foam

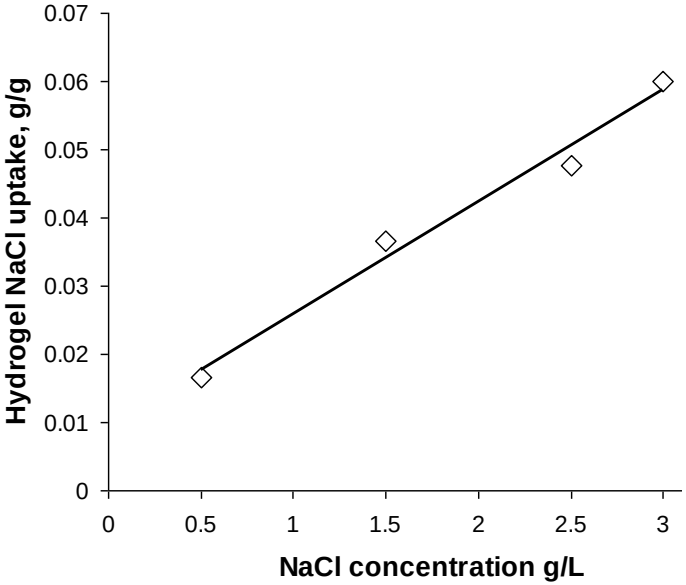


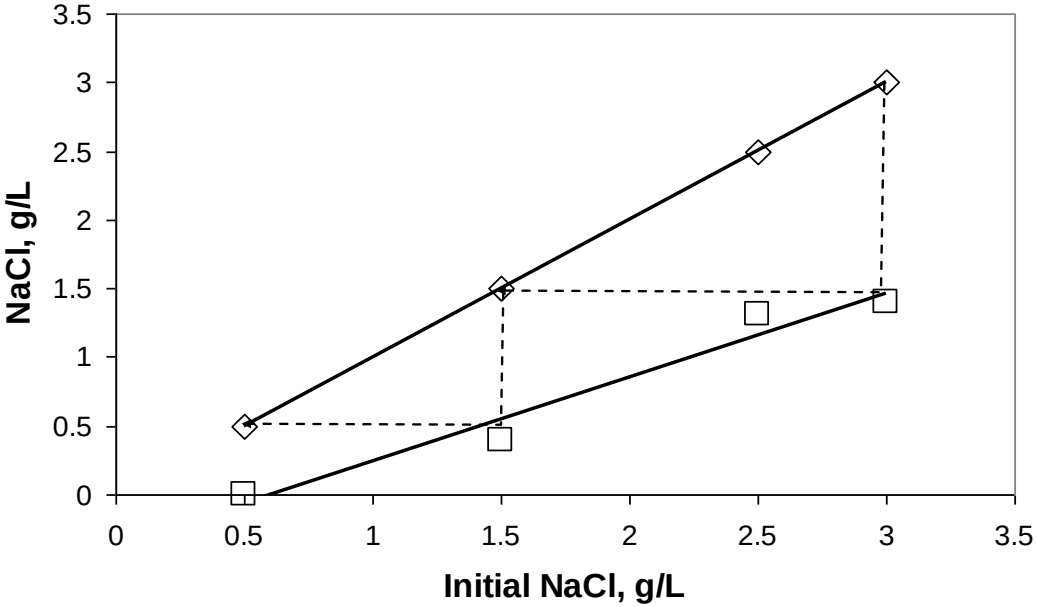
Absorption properties of hemicellulose citrate-chitosan foam (vacuum filtration)

	Water absorption percent with DI water at 1hr	Water absorption percent with 0.9% NaCl at 1hr
Chitosan	640	550
Hemicellulose	120	160
Hemicellulosecitrate	350	380
Hemicellulose/ Chitosan foam	360	390
Hemicellulose citrate Chitosan foam	1520	1780
Commercial Cellulose foam	210	260
Acrylic Acid based Super Absorbent Polymer	14880	1800

Desalination

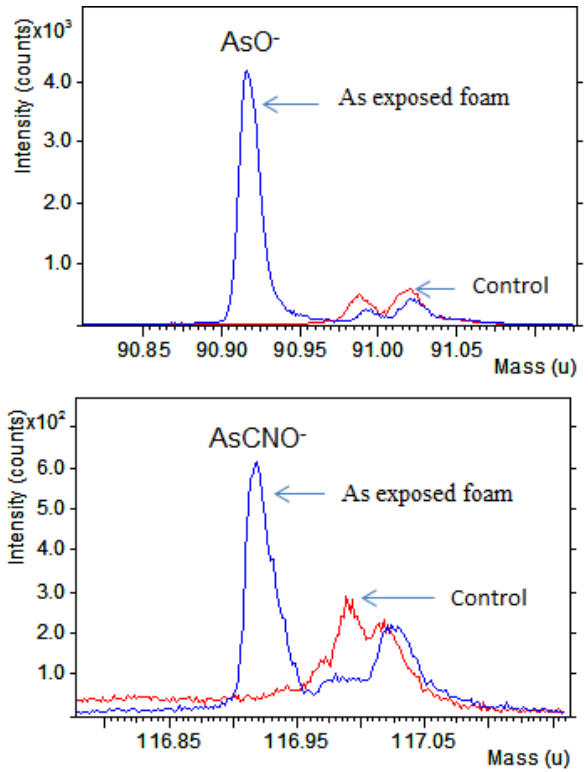
Proposed technology to reduce brackish water from 3000 to 500 ppm salt content with two applications of HCC gel at 1:40 ratio.





Water Remediation Material: Arsenic Removal

Sample	Metal Loading (mg/g)
Hemicellulose citrate-chitosan	1.28
Starch citrate-chitosan	1.84
Starch citrate	1.16
Starch	0.43
Chitosan	0.88
Sorba Tech 450	0.10
LaneRT	0.40
Alumina	0.48
Purolite FerrIX A33E	0.54
Absorbia GTO	0.04

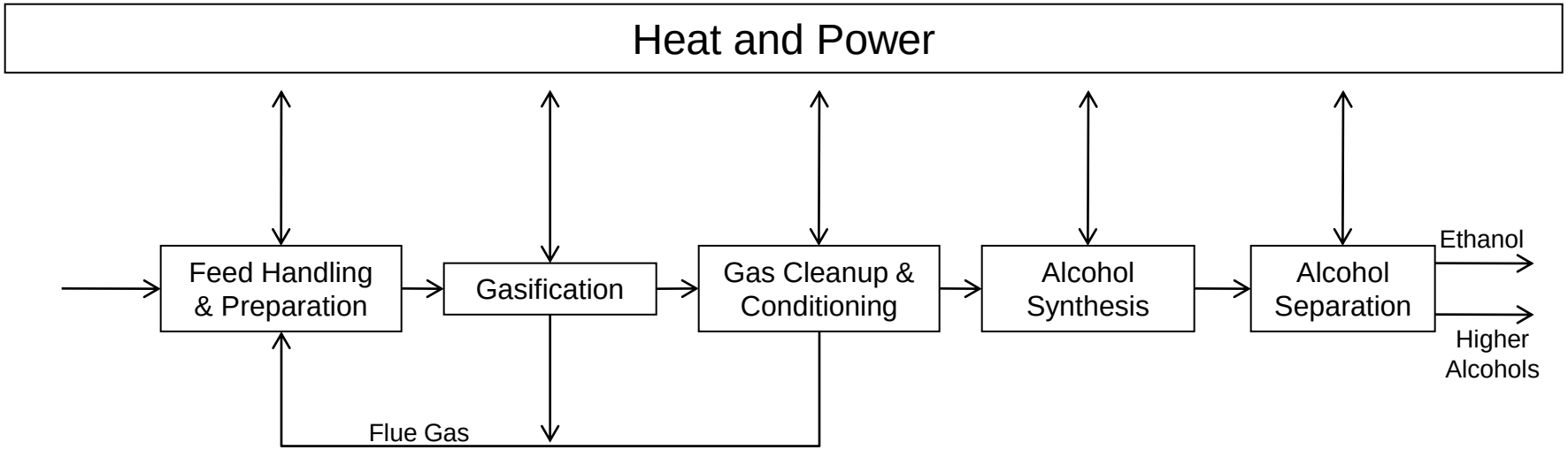


- Arsenic uptake for various materials in a 5 PPM solution. (Absorbent 0.025g, 50ml, 6 minutes).
- TOF SIMS with a Bismuth(+3) primary ion beam.

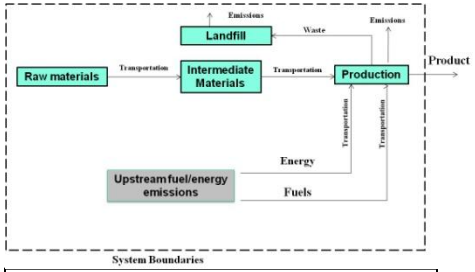
3: Process Model Based LCA of Biofuels Production

Jesse Daystar, Richard Venditti, Hasan Jameel

Thermal conversion of biomass to ethanol

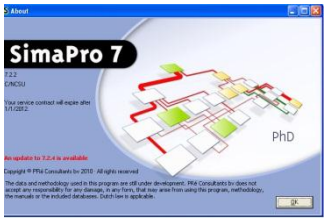


LCA Approach

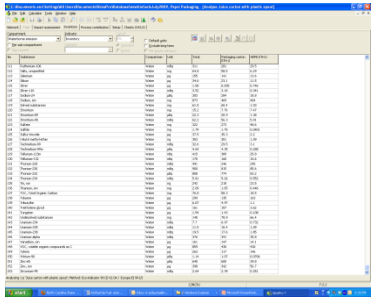


Establish System Boundaries

ASPEN Plus Simulation



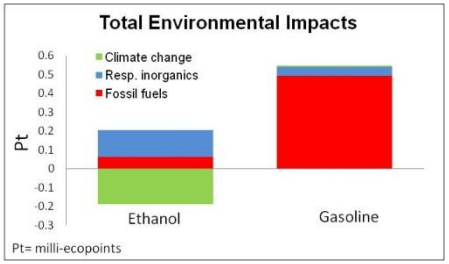
SimaPro



Inventory

Impact Assessment

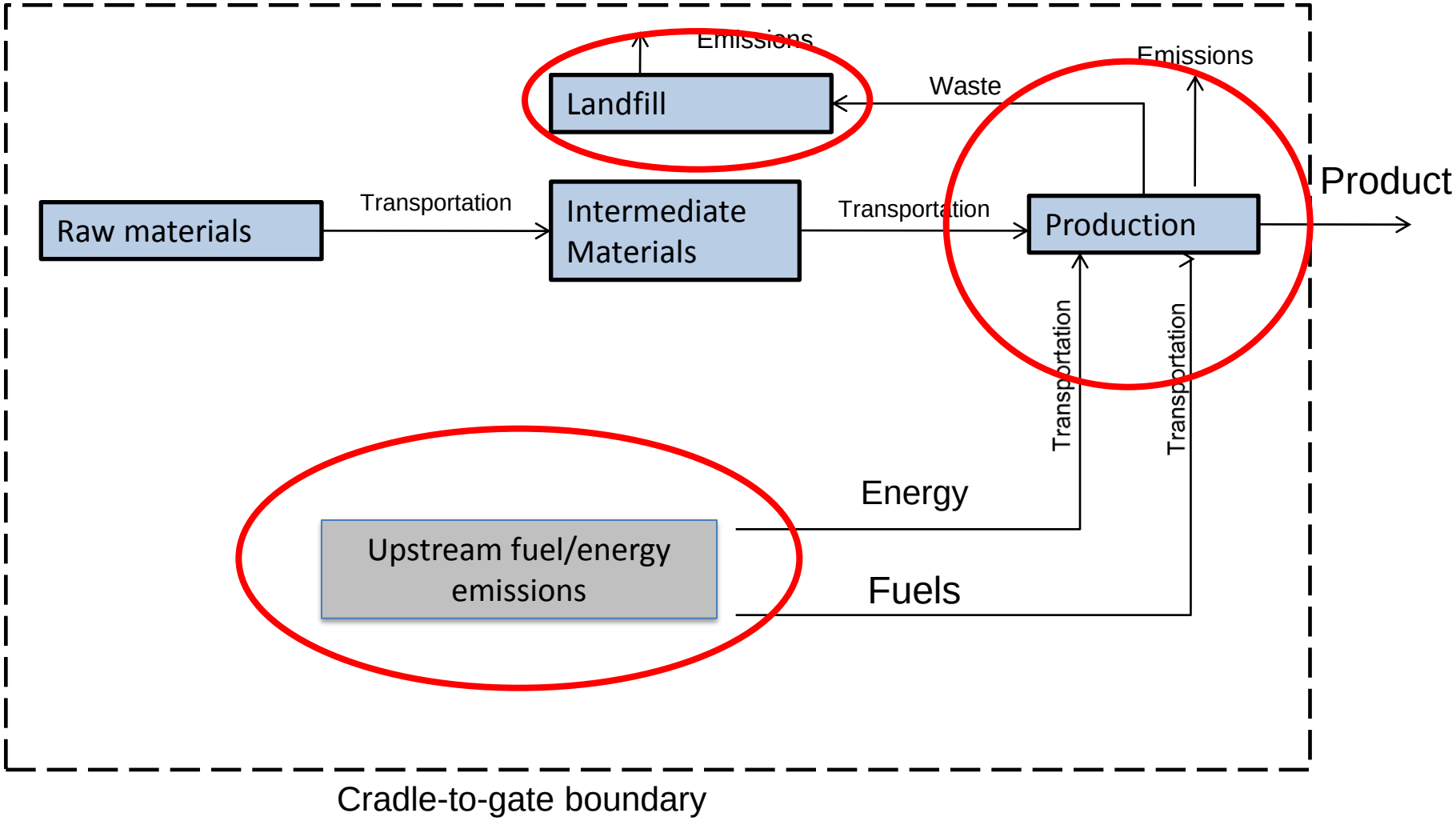
Informed Biomass/Energy Decision Making



Gate-to-Gate Operating Parameters

- Facility size
  - Matches production of the NREL biochemical process model
    - 2,205 dry ton/day
    - 772,000 dry ton/year
    - 1,544,000 wet ton/year delivered
  - Evaluate Various promising feedstocks
- No full scale plant exists currently

System Boundary: Gate to Gate, circled operations considered



Alcohol Yields
Process Model Results

Forest

Feedstock	Hybrid poplar	Mixed hwd	Loblolly	Eucalyptus
Units:	(gal/OD ton)	Δ %	Δ %	Δ %
Total gallons per OD ton	106	1.8%	5.6%	-3.5%

Energy Crops

Feedstock	Hybrid poplar	Corn stover	Switch grass	Miscanthus
Units:	(gal/OD ton)	Δ %	Δ %	Δ %
Total gallons per OD ton	106	-13.0%	-5.3%	-5.4%

GHG Emissions

Process Model Results

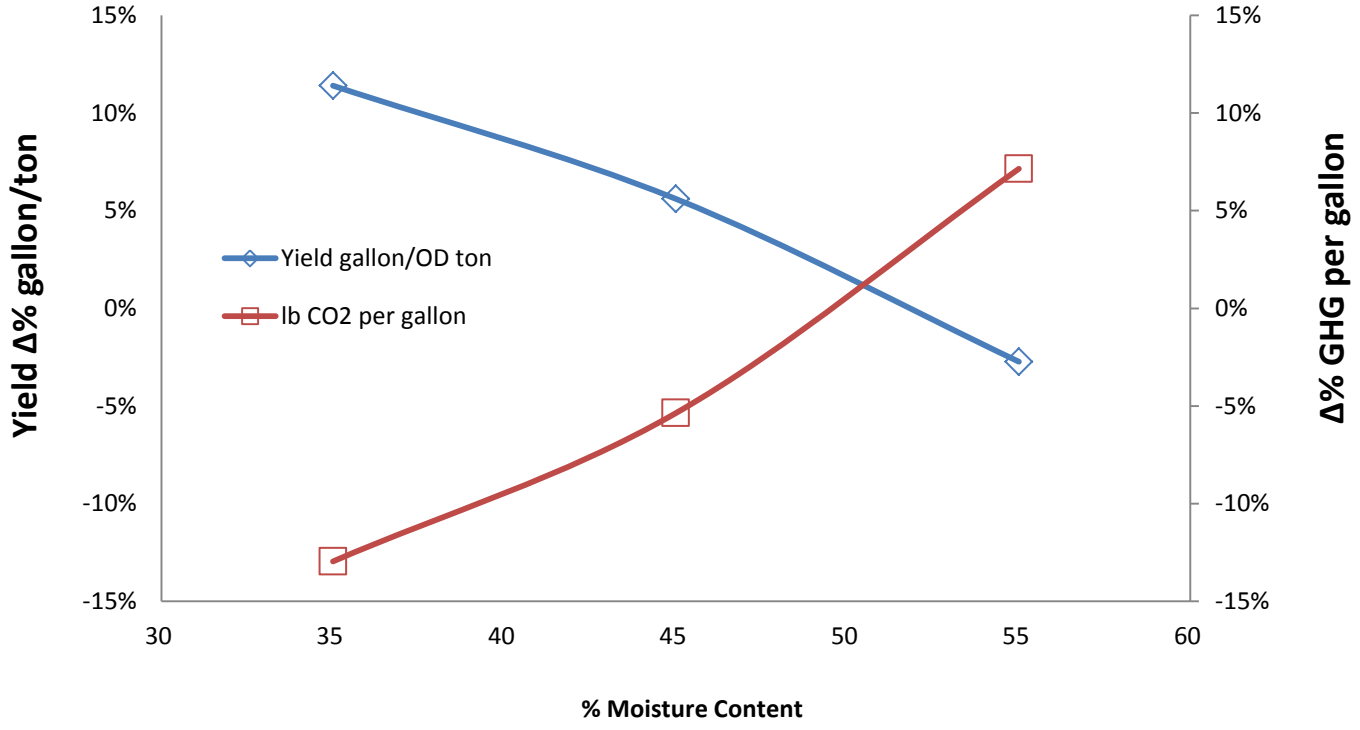
Forest Resources

GHG Emissions	Hybrid poplar	Mixed hardwood	Loblolly pine	Eucalyptus
Units	-	Δ %	Δ %	Δ %
lbs CO_2 eq. /gal eth	23	-4.1%	-5.4%	2.8%

Energy Crops

GHG Emissions	Hybrid poplar	Corn stover	Switchgrass	Miscanthus
Units	-	Δ %	Δ %	Δ %
lbs CO_2 eq. /gal eth	23	-0.3%	-2.8%	-2.5%

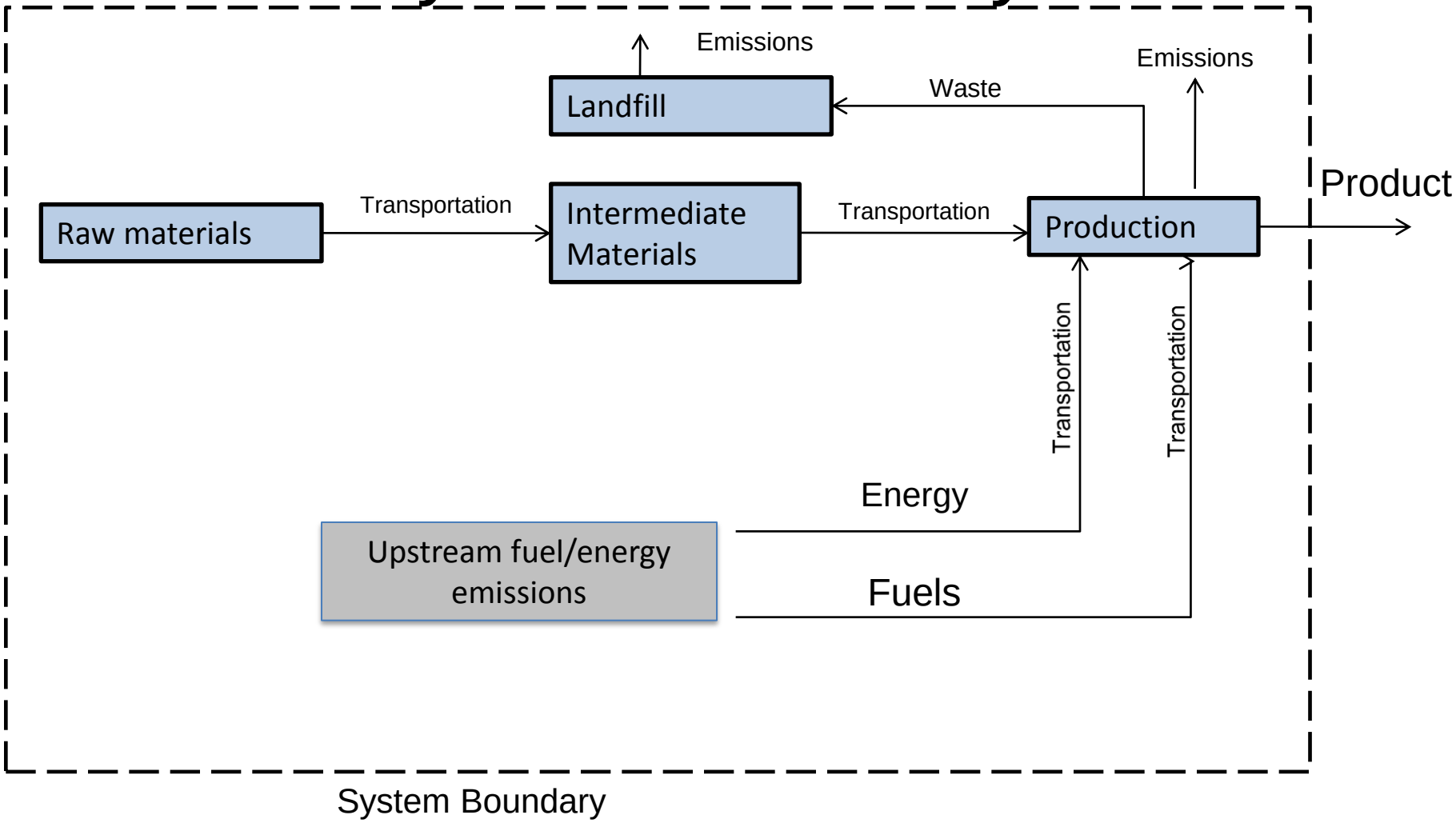
Sensitivity to Moisture Content



Cradle-to-Grave Operating Parameters

- Facility size
  - Matches the NREL biochemical process
    - 2,205 dry ton/day
    - 772,000 dry ton/year
  - Moisture content @50%
    - 1,544,000 wet ton/year delivered
  - Feedstock:
    - Softwood chips: SimaPro data for preliminary analysis

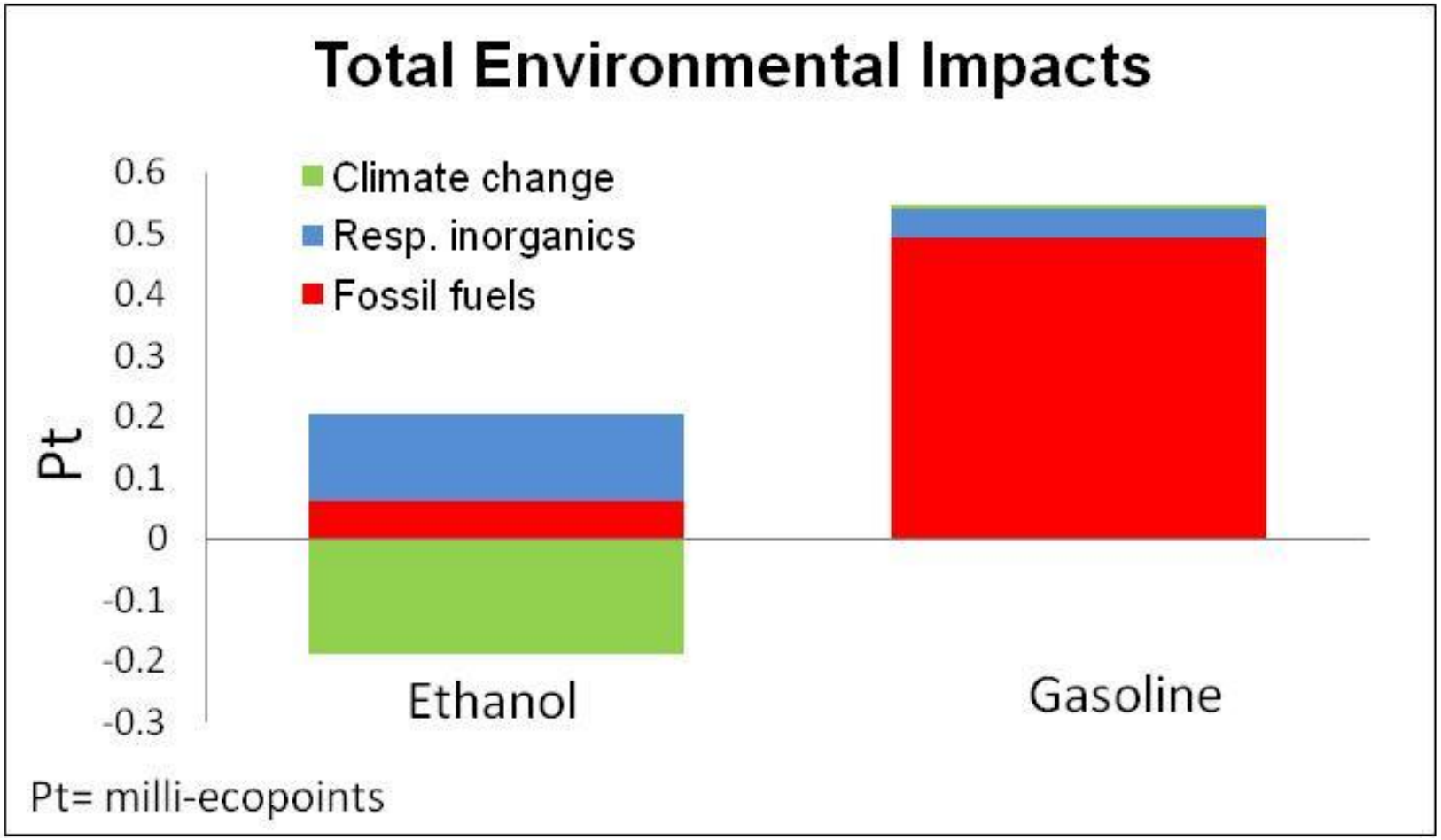
Cradle to Gate System Boundary



GHG Emissions

GHG Emissions by process	tons CO_2 eq / yr	lb CO_2/OD ton wood	Percentage
Hauling	4064	8	1.2%
Feller-buncher	51067	102	15.1%
Pick up truck	91	0	0.03%
Timber jack, Skidder	67664	135	20.1%
Prentice	37024	74	11.0%
450 hp 3-Knife Chipper	168704	337	50.0%
Reforesting emissions (no seedlings)	6227	12	1.8%
Seedlings emissions	1	0	0.0%
Fertilizer emisions	2465	5	0.7%
Total	337307	675	100.0%

Gas vs. Ethanol
Single Score



Pt is the unit of environmental impact in eco-points

Summary

- Enormous challenges exist for the Biofuels industry
- Impacts of a Biofuels industry are not known currently
- Selected biomass sources, technologies and products hold potential and may contribute to the world's needs
- NCSU is active in developing new processes, products and analysis tools for biofuels

Acknowledgements:

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Jesse Daystar, Ronalds Gonzalez, Abdus Salam, Khaled El-tahlway, Yan Pu, Laura Chen, James Lee,

Questions?