Producing Ethanol from Wood

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Cellulosic Ethanol

- The presentation will focus on production of ethanol or other chemicals from cellulosic sources.
- These include wood, agricultural residuals, and dedicated fuel crops.

Cellulosic Ethanol

- Grasses, trees and agricultural plants all consist of three primary classes of polymers:
  - Lignin
  - Cellulose
  - Hemicellulose

Cellulose

- Cellulose – 40-60% of biomass.
- A straight chain polymer consisting of glucose (sugar) monomers.
- Cellulose is partially crystalline.
  - The crystalline regions are chemically and biologically robust.

Hemicellulose

- Hemicellulose, 15-25% of typical lignocellulosic biomass.
- A group of straight chain and branch chain polymers assembled from various sugars: xylose, mannose, galactose, arabinose and glucose.
- Hemicellulose is amorphous and readily hydrolyzed.

Lignin

- Lignin, 10-25% of most biomass.
- Lignin is a cross linked phenolic polymer that is chemically and biologically robust.
- Although chemists drool over the phenolics they can get from lignin, it typically fractures into so many different monomers and oligomers that it has little value beyond fuel.

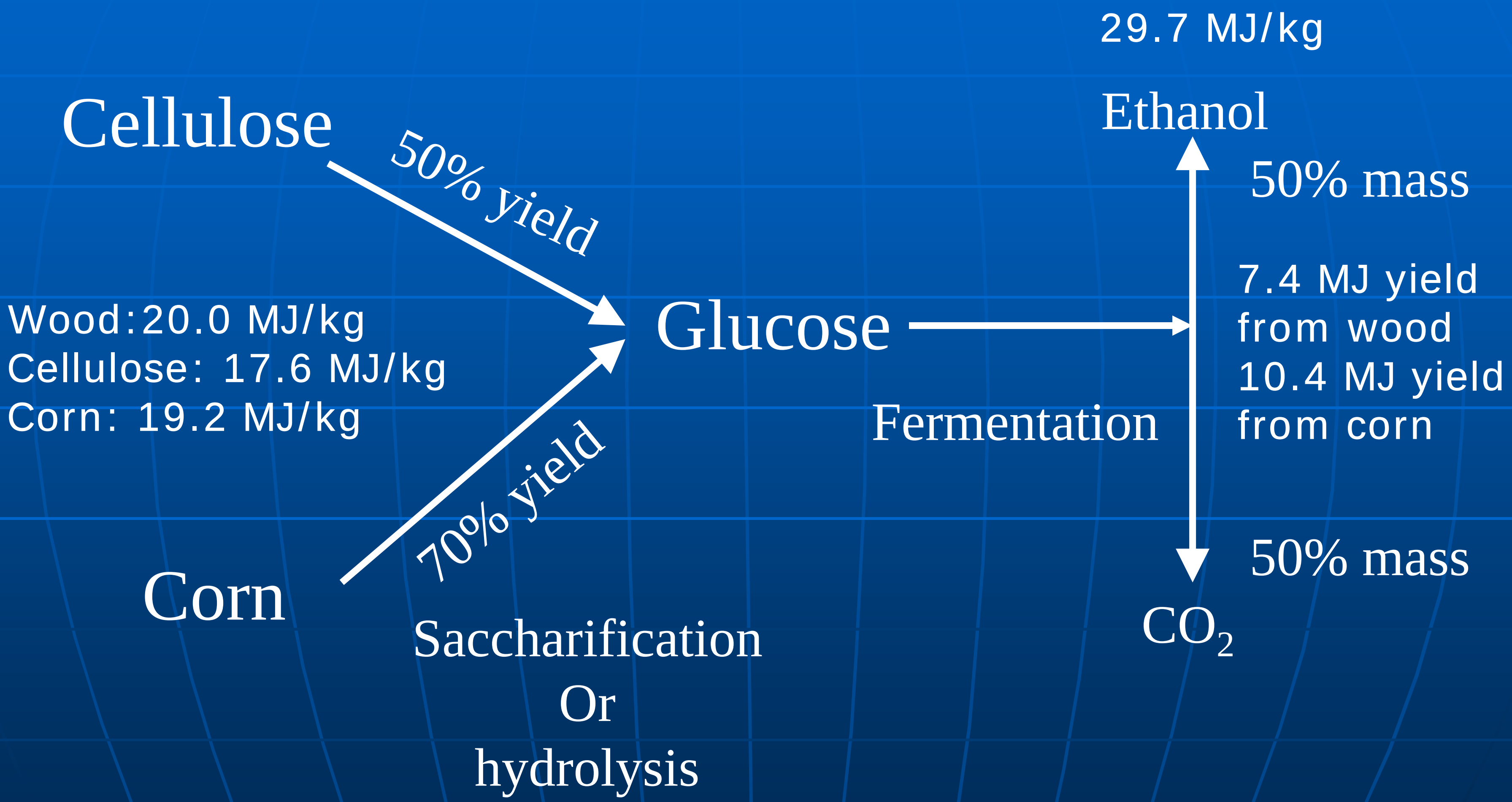
Cellulosic Ethanol

- Cellulose can be depolymerized to glucose
  - 50% yield using dilute acid,
  - 100% yield using strong acid, or
  - 100% yield using enzymes.
    - High yields with enzymes take about 4 days.
- Hemicellulose can be depolymerized in nearly 100% yield, but Xylose and Arabinose are difficult to ferment to alcohol.

Corn

- Corn kernels have a similar ligno-cellulosic composition for the shell, but the inside is starch, food for the seedling.
- Starch is also a polymer of glucose molecules, but they are linked differently.
- This difference makes starch an almost universal food source, and very easy to convert to ethanol

Process



29.7 MJ/kg

Ethanol

Cellulose

50% yield

50% mass

7.4 MJ yield
from wood
10.4 MJ yield
from corn

Wood:20.0 MJ/kg
Cellulose: 17.6 MJ/kg
Corn: 19.2 MJ/kg

Glucose

Fermentation

70% yield

50% mass

Corn

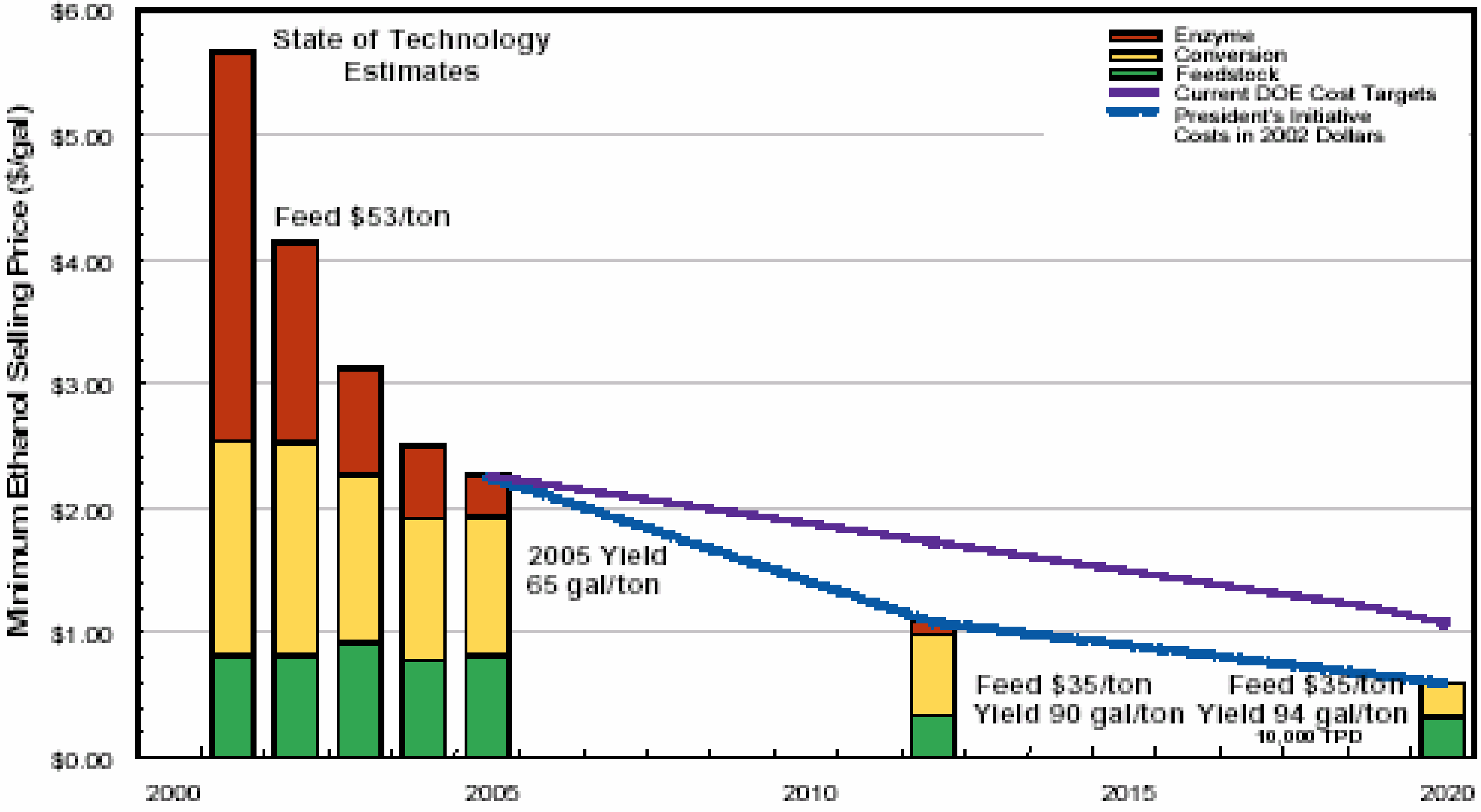
CO_2

Saccharification
Or
hydrolysis

Other fermentation products

- Acetic acid
- Lactic acid
- Butanol
- 1,2 propandiol
- 1,3 propandiol

DOE Target Ethanol Price



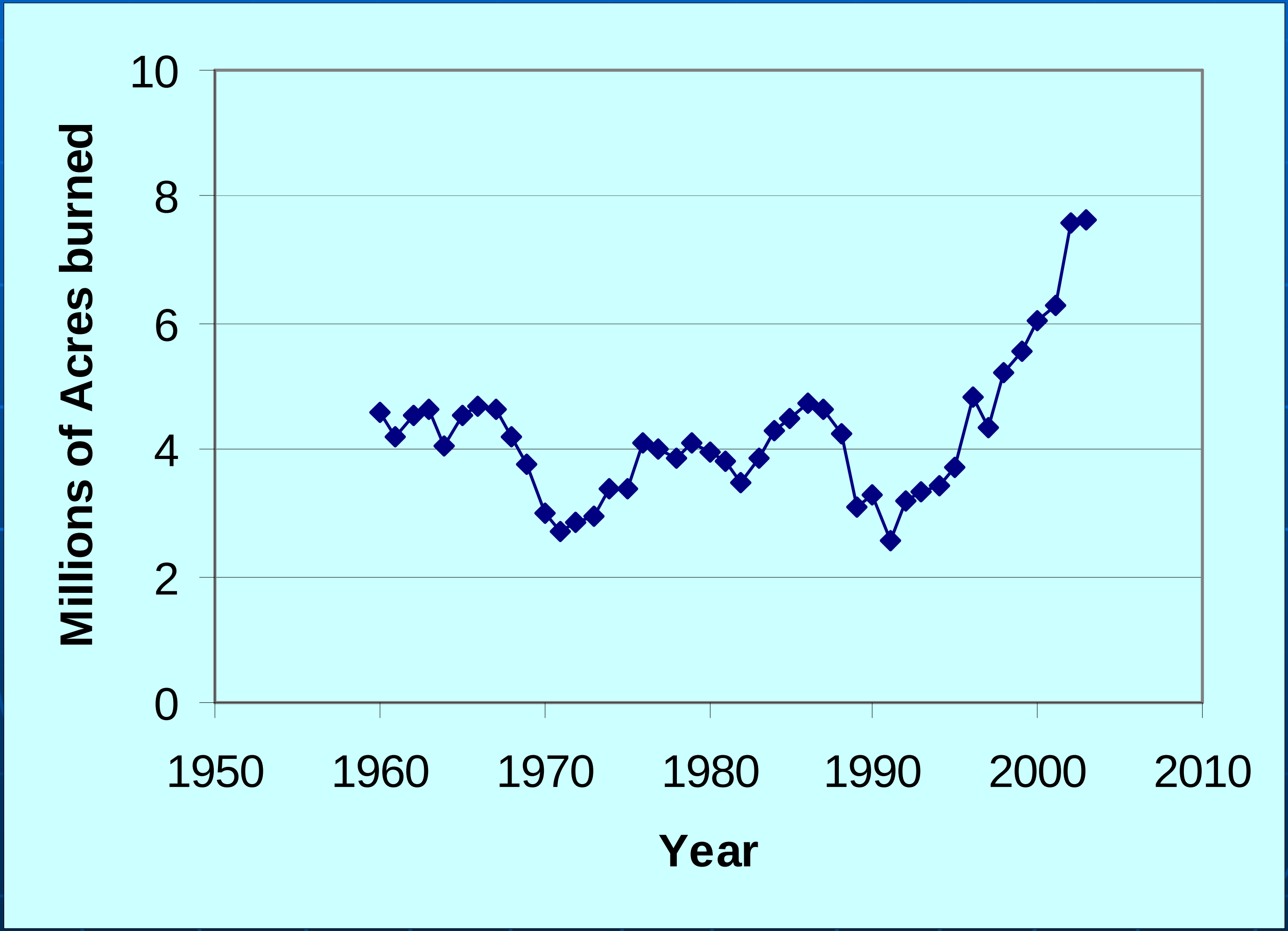
Why – take your pick

- Strategic:
  - more control over fuel and energy,
  - less dependence on potentially unreliable foreign sources of petroleum
- Economic:
  - Petroleum costs are high and a major source of the US trade imbalance
  - Financial benefit to US farmers and rural America.

More why’s:

- Environmental
  - Fossil fuels (coal>petroleum>gas) are a major source of atmospheric CO_2 which is a contributor to global warming.
  - Combustion of biomass is regarded as greenhouse gas neutral because the amount of CO_2 given off in combustion is the same as the amount sequestered in photosynthesis

A Fourth Reason: Forest Service



A perspective

- *“As we know, there are known knowns, there are things we know we know.*
- *We also know there are known unknowns.*
  That is to say we know there are some things we do not know.
- *But there are also unknown unknowns, The ones we don't know we don't know.”*
  - Donald Rumsfeld, former US Secretary of Defense.

My Goal: Sort it out.

- What do we know we know:
  - Demonstrated technologies that have been reproduced by multiple researchers or put into large scale practice.
- What we know we do not know:
  - Scientific questions that are still being actively researched.
- What do we not know with certainty:
  - Research claims and progress

The good news!

- We know how to make ethanol from lignocellulosics when and if we need it.
- We did it for WWI
- We built a plant to do it at the end of WWII
- The Germans and Russians have also built and operated plants

The bad news

- We (US) do not have a plant capable of producing significant volumes of cellulosic ethanol operating today.
- We do not know if we can produce ethanol from cellulose profitably at current oil prices – whatever that is.
- We do know that we (the US) do not control the price of oil.
    - Until we control fuel costs politically, or supply dictates a higher real cost – we are unlikely to have profitable commercial alternatives.

Supply and Cost (bbl)

Source	Cost	Reserve (Billion bbl)	Annual (billion bbl)
ME	$10	800	7.5
South Amer.	$25	100	2
Oil Sand	$25 $50 New	175	0.4
Corn Ethanol	$50		0.2
Cellulosic Ethanol	$85 (est)*		2

NREL, $45/ton, 75 g/t

Supply and demand

- US requires about 7.5 billion bbl of oil annually. (Energy Information Administration, 2005)
- US imports about 5.5 billion bbl annually
- Cellulosic sources can displace about 1.6 billion bbl with existing technology.
    - Basis – 1 billion annual tons available, 70-75 gallons per ton.

The known technologies

- Dilute acid hydrolysis.
  - Basis for plants in WWI and WWII
  - Madison process (1945, FPL/UW) produces 64-68 gallons of ethanol per ton of softwood.
- Enzyme hydrolysis
  - Time is money. The question is not what yield is possible (100 – 120 gal/t), it is what is economically achievable (65-75 gal/t)*.

NREL stated 65 gal/t for 2005 with a target of 75 gal/t for 2008

DOE Commercial Demonstrations

- Abengoa Bioenergy: 79 gal/ton
- Bluefire Ethanol: 68 gal/ton
- Iogen: 71 gal/ton
- Broin (Poet): 83 gal/ton

Supply

- Known supply is about 1 billion tons of harvestable biomass in the US annually (USDA billion ton report).
  - Approximately 2/3 agricultural residuals and annual fuel crop potential.
  - Approximately 1/3 forest product residuals, logging slash and forest thinning to manage fire risk.

Supply potential

Fuel crop	Growth ODt/ha/a	Fuel Value GJ/ODt	Energy GJ/ha/a
Wheat	7 + 7	12.3 (straw)	123
Switchgrass	8	17.4	139
Poplar	10-15	17.3	216

McKendry, *Biomass Tech*., 83: 37(2002)

Known impediments

- Transportation
- Yield (time)
- Xylose and arabinose

Known knowns

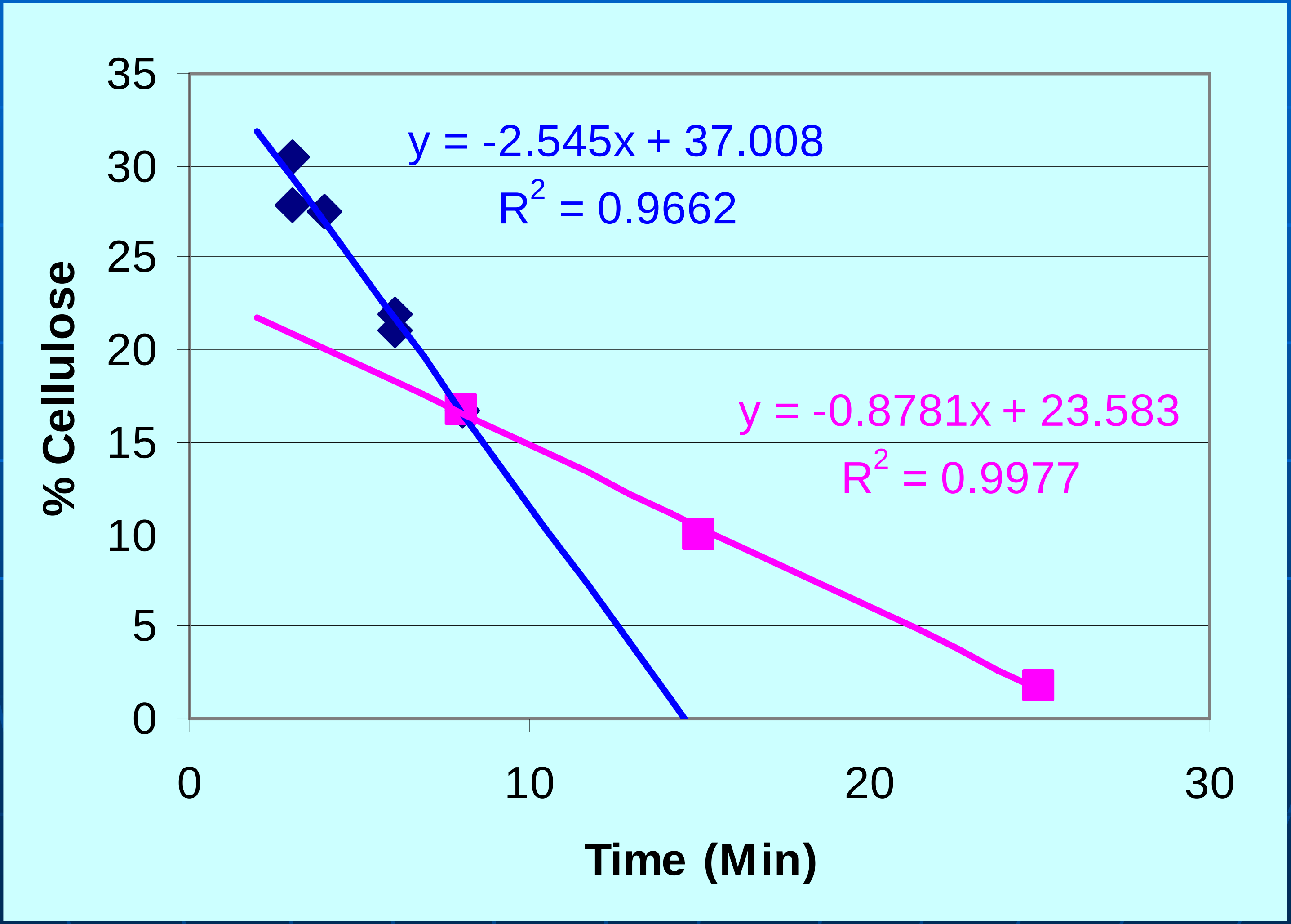
- It costs a lot of money to move water and air.
  - Biomass typically 30 to 50% water
  - Bulk density (OD basis)
    - 40-80 kg/m^3 for chopped corn stover
    - Without compaction, corn stover will require 40 semi-trailer loads per harvester per day.
    - Birrell estimates that at $35/ton, farmers will lose money hauling more than 15 miles.
    - 176 kg/m^3 for wood chips
    - 900 kg/m^3 for coal

Birrell: Iowa State University, Dept Ag and Biosystems Engineering

More Knowns: Dilute Acid

- Two rates for carbohydrate hydrolysis
- Amorphous carbohydrates hydrolyze much faster than crystalline cellulose
- Cellulose crystallinity is thought to be a primary barrier to increasing yield.

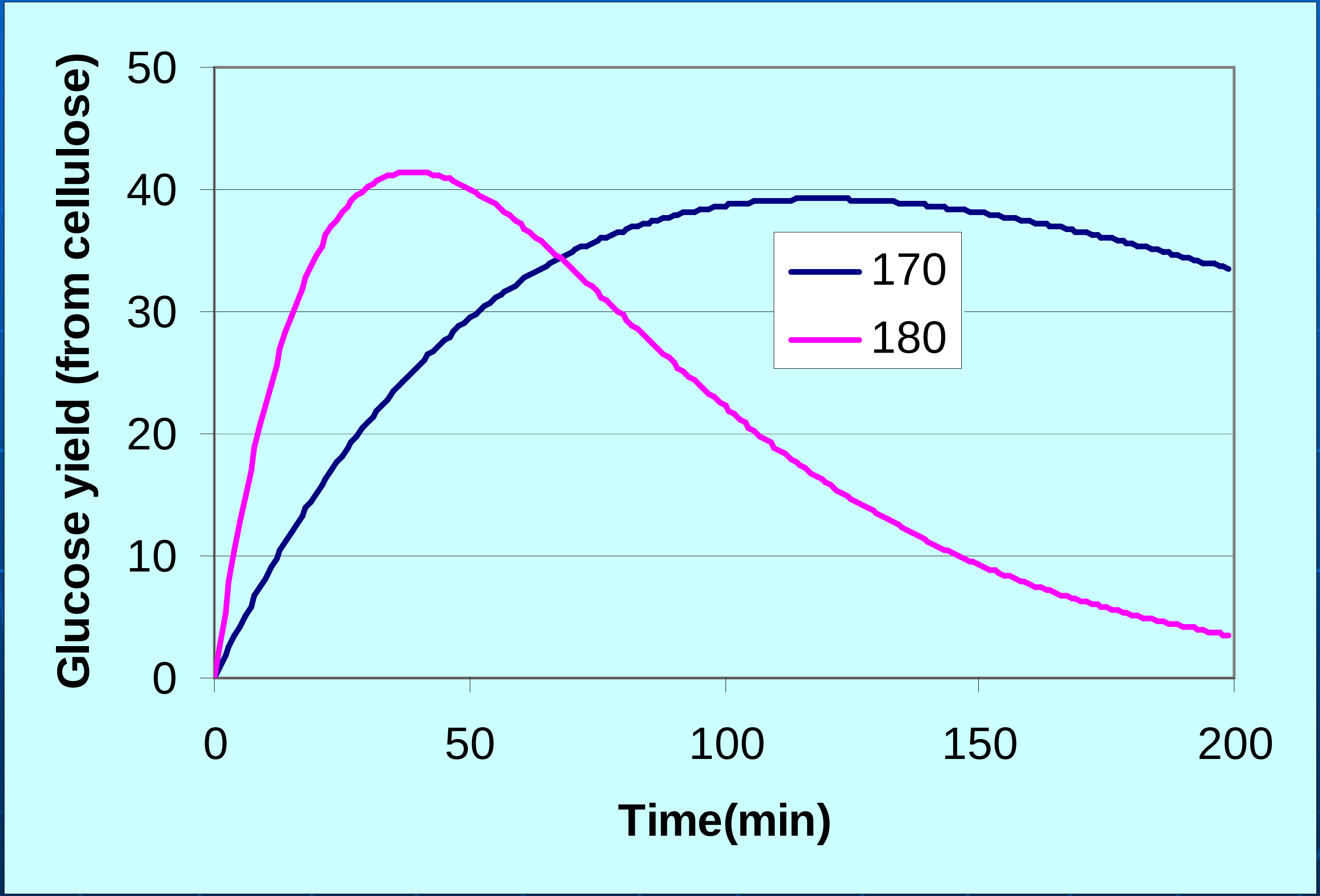
Dilute Acid Hydrolysis



More knowns: acid hydrolysis

- Competition between the rate of hydrolysis and the rate of decomposition
- Lignin and particle size are also limitations to rate and yield.
- Higher temperatures, higher acid concentrations and shorter reaction times used to improve yield. (WWI → WWII)

Yield of glucose from cellulose



Conner et al, J Wood Chem and Tech, 5(4): 461(1985). 40% is ~ 50 gal/mt

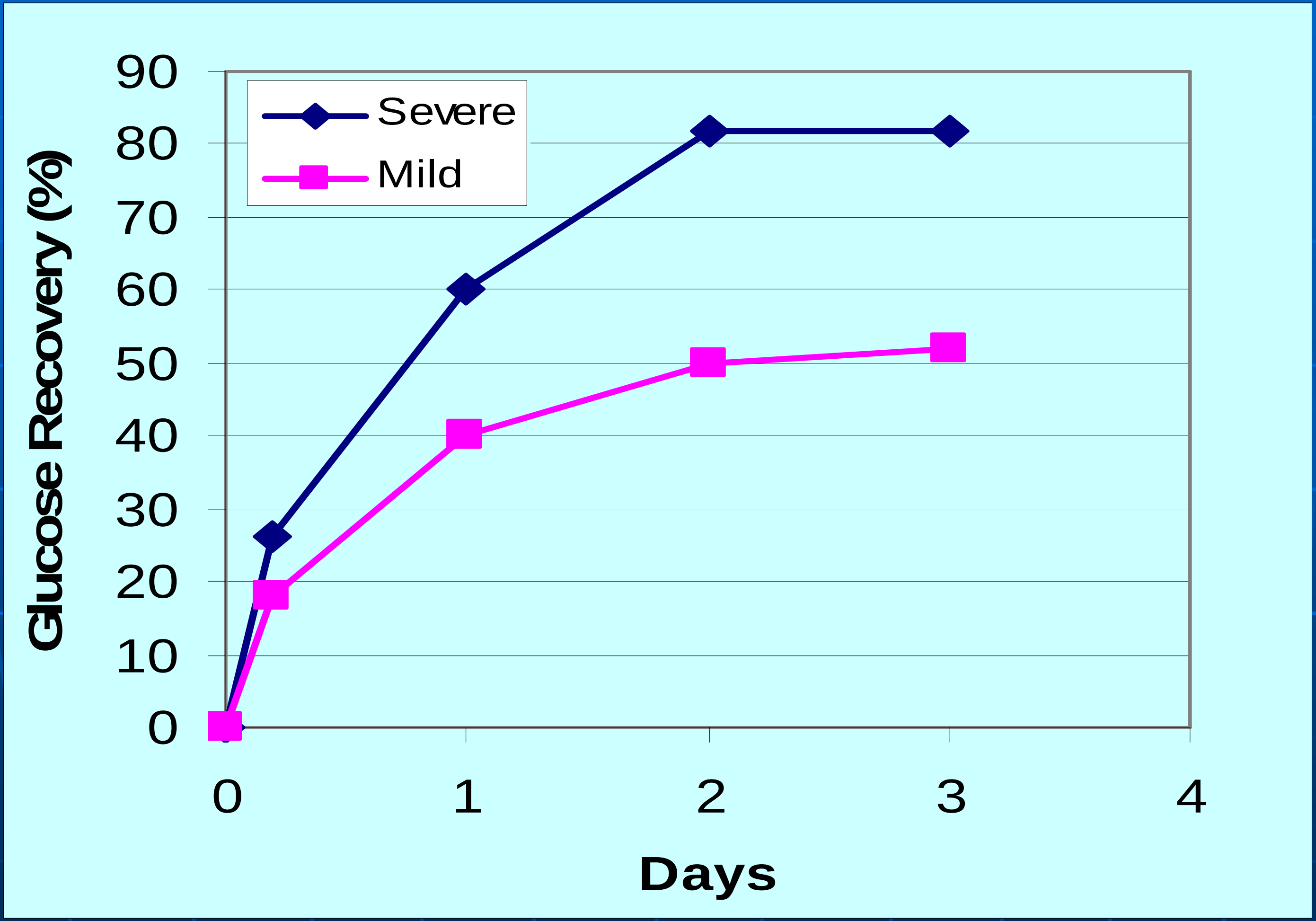
More Knowns

- Enzyme methods have been under investigation since WWII
  - Sources: fungi, bacteria and other organisms
- The process requires several enzymes
  - Endo, Exo and Beta glucosodases
- Like dilute acid, enzymes readily saccharify the amorphous carbohydrates but slow down on crystalline cellulose.

More known knowns

- Enzyme processes require pretreatment
- Amorphous material is hydrolyzed to sugars in about 24 hours. Two to five days for the rest.
- Fermentation and hydrolysis can be carried out simultaneously.

Enzymatic Saccharification

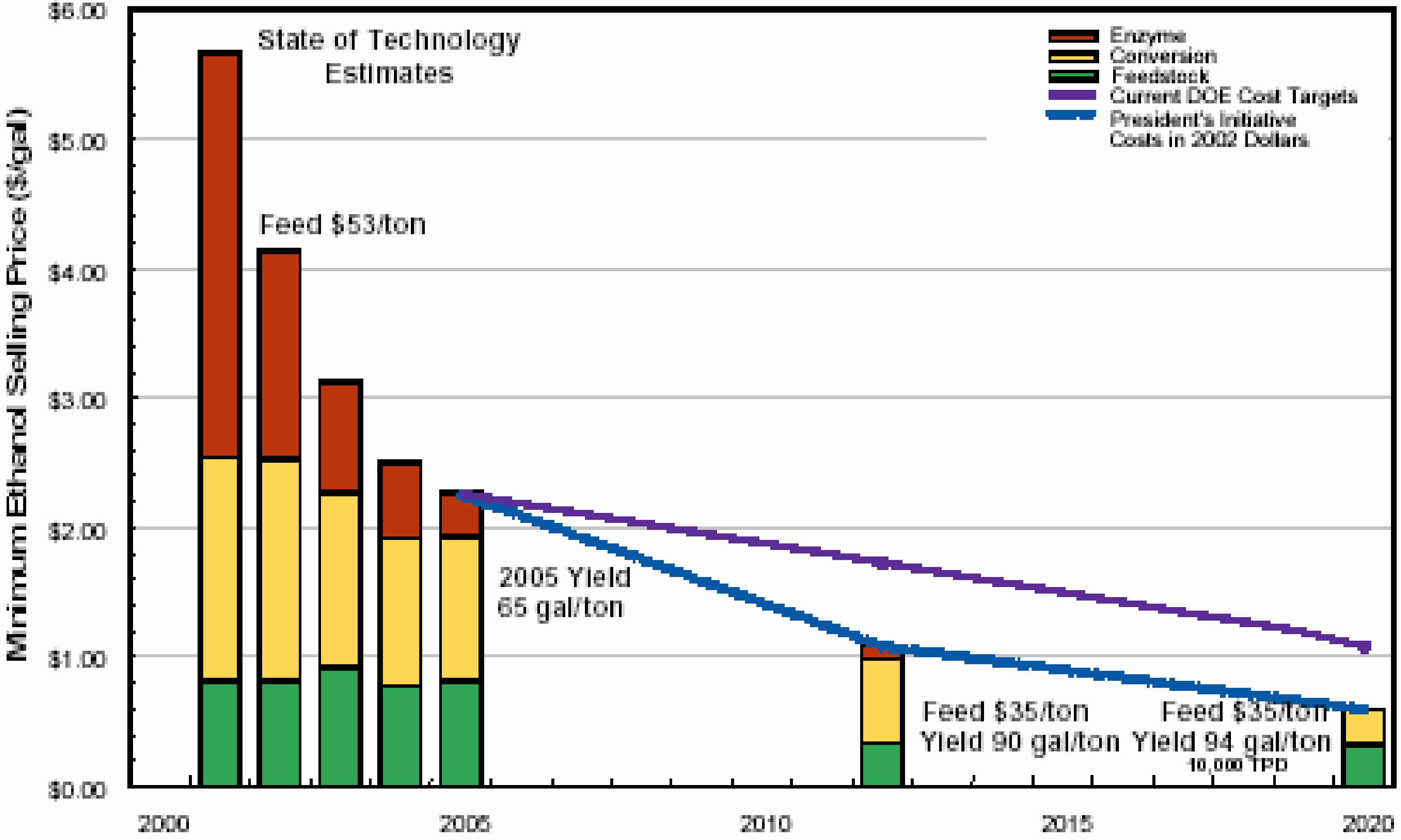


Boussaid et al., App. Biochem. Biotech: 84-86: 693(2000)

Known Unknowns

- The price of crude oil on October 1st, 2007!
- The potential to increase the yield from dilute acid methods.
- The potential to speed up enzymes.
  - It is unlikely that biologists will find a significantly more efficient organism. Such an organism has the capacity to lay waste to all plant life on earth.

Unknown – Ethanol Cost in 2008



Known Unkowns

- A major cost of biomass is harvest and transportation.
  - Will they be able to produce single pass harvest systems that collect and separate grain and stalk?
  - Will the high stalk volume make this impracticable?
  - Can biomass bulk density be increased (cost effectively) to reduce transportation costs?

More Known Unknowns

- The ability to ferment five carbon sugars under commercial conditions
  - There are about five candidate organisms under investigation
- Exactly how much of that 1 billion annual tons is available?
  - Within a reasonable transportation distance.
  - Cost.
  - Social license to provide (many Forest Service projects get delayed or derailed by litigation.)

Known Unknowns

- We must expect that people will be resourceful once biorefineries are established.

The unknown unknowns

- Obviously, we do not know
- To the extent that people believe the 6 DOE supported plants have proven technology: might I suggest that
  - We do not know at this point if any of these proprietary systems will be profitable.
  - (The Iogen plant claims about 70 gal/ton with a retention time of 5 days.)

FPL Research

- Coproduct ethanol/fuels with traditional forest products
- Pretreatment technologies
- Fermentation of five carbon sugars
  - 20% of hardwoods, 30% of corn stover
- Materials handling and behavior
- Cellulose crystallinity
- Lignin

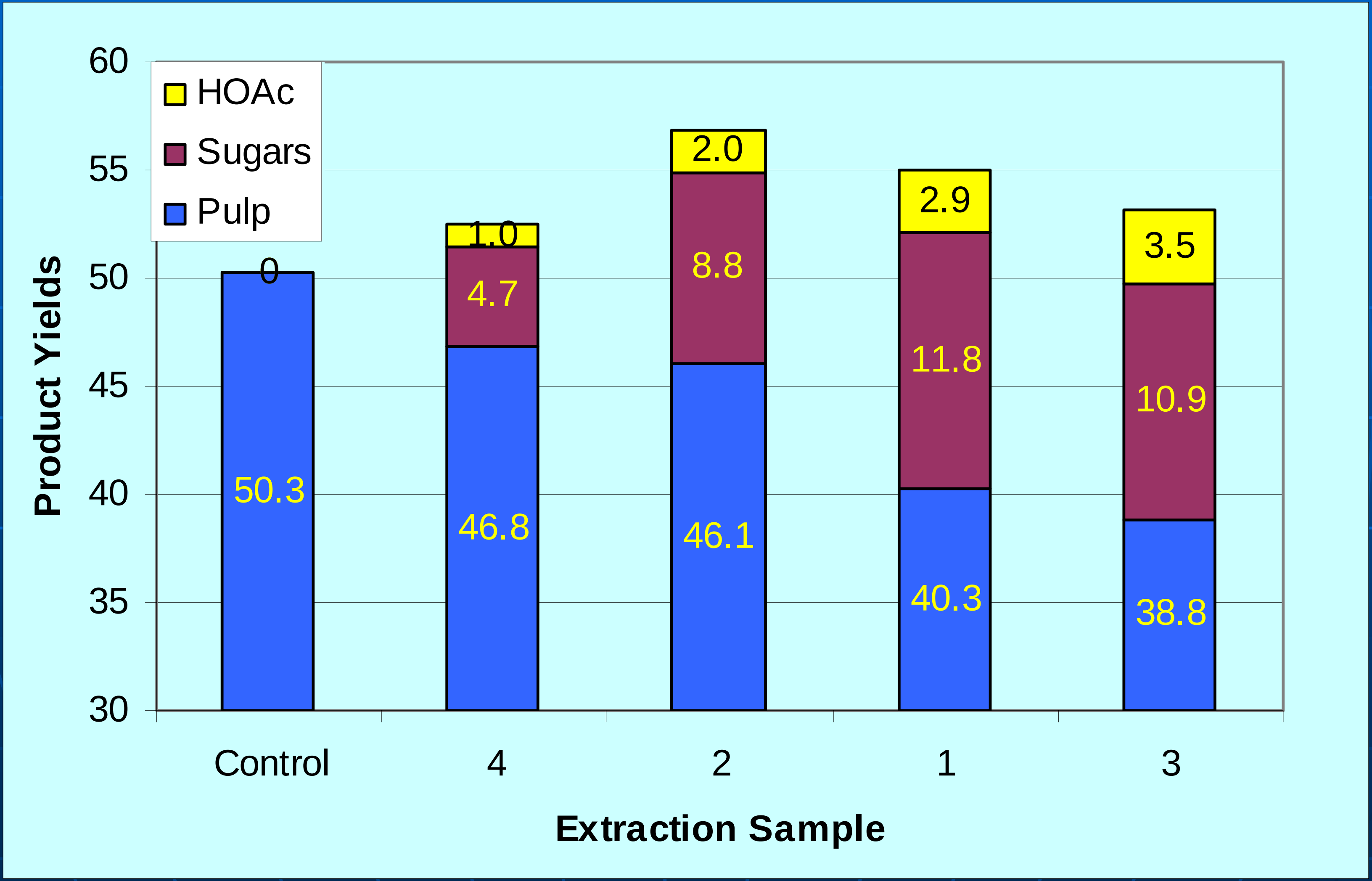
Value Prior to Pulping

FS-PI	Kenealy, Rudie, Jeffries
Objective	Recalcitrance
Funding	DOE, AF&PA partners and WI Department of Commerce
Cooperators	SUNY Syracuse, U. Maine North Carolina State University Georgia Institute of Technology U. Florida

Ethanol as Coproduct

- Kraft pulping dissolves ~80% of the hemicellulose in the wood.
- Can we extract this in pretreatment
- Not impact pulp yield
- Not reduce pulp properties

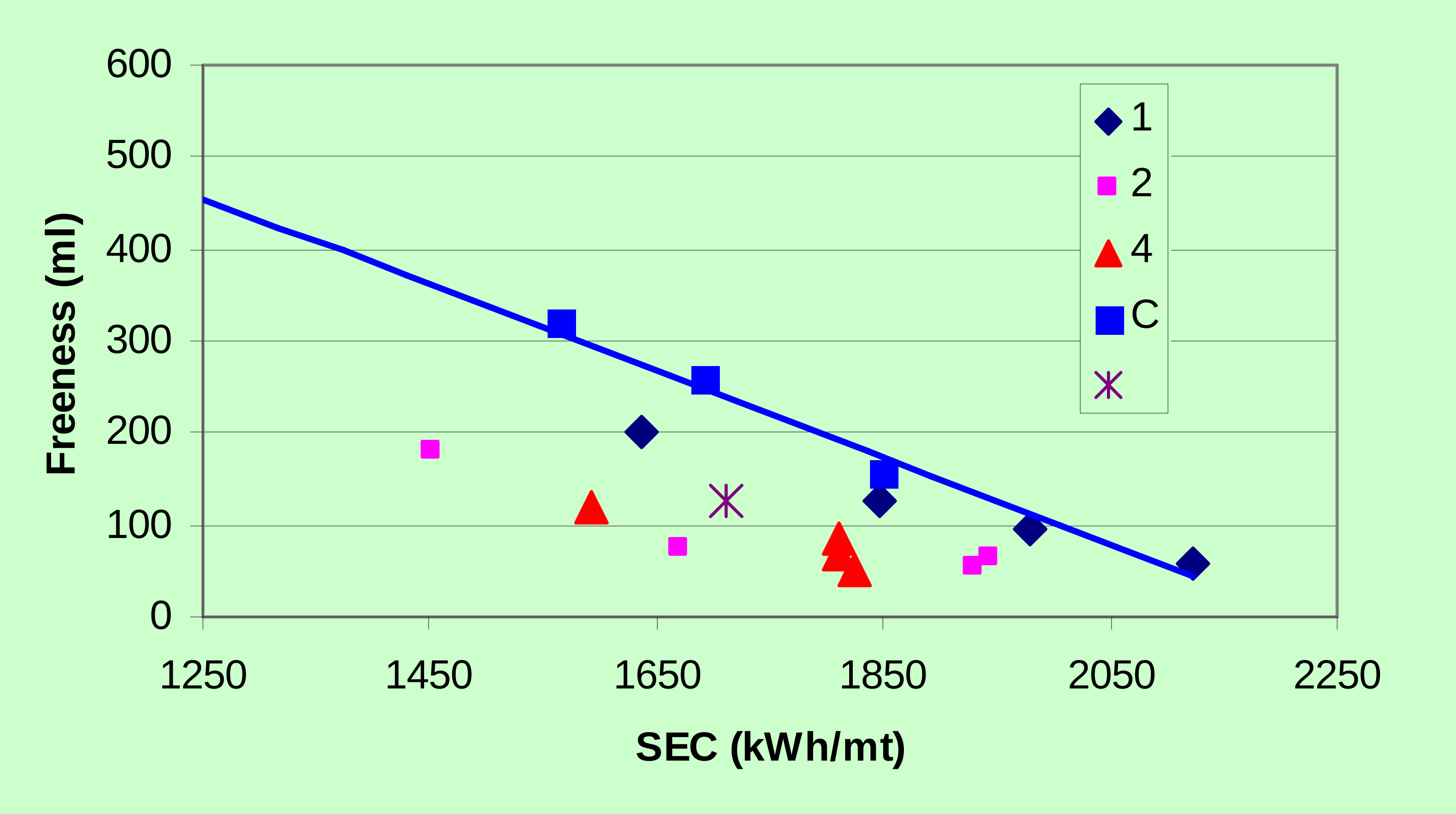
Product Yields (Starting wood basis)



Prehydrolysis with oxalic acid

FS-PI	Kenealy
Objective	Energy savings: TMP Recalcitrance (VPP)
Funding	DOE 04 and 07 (VPP) FS-RFP (07)
Cooperators	Biopulping International University of Georgia

P-TMP Specific Energy



Coproduct Fiberboard

FS-PI	Kenealy, Houtman
Objective	Recalcitrance
Funding	USDA-SB (07)
Cooperators	Biopulping International

Coproduct Fiberboard

- Extract sugars prior to thermomechanical pulping when producing wood fiber for fiberboard.
  - Better moisture resistance
  - Equal strength
  - Lower density?

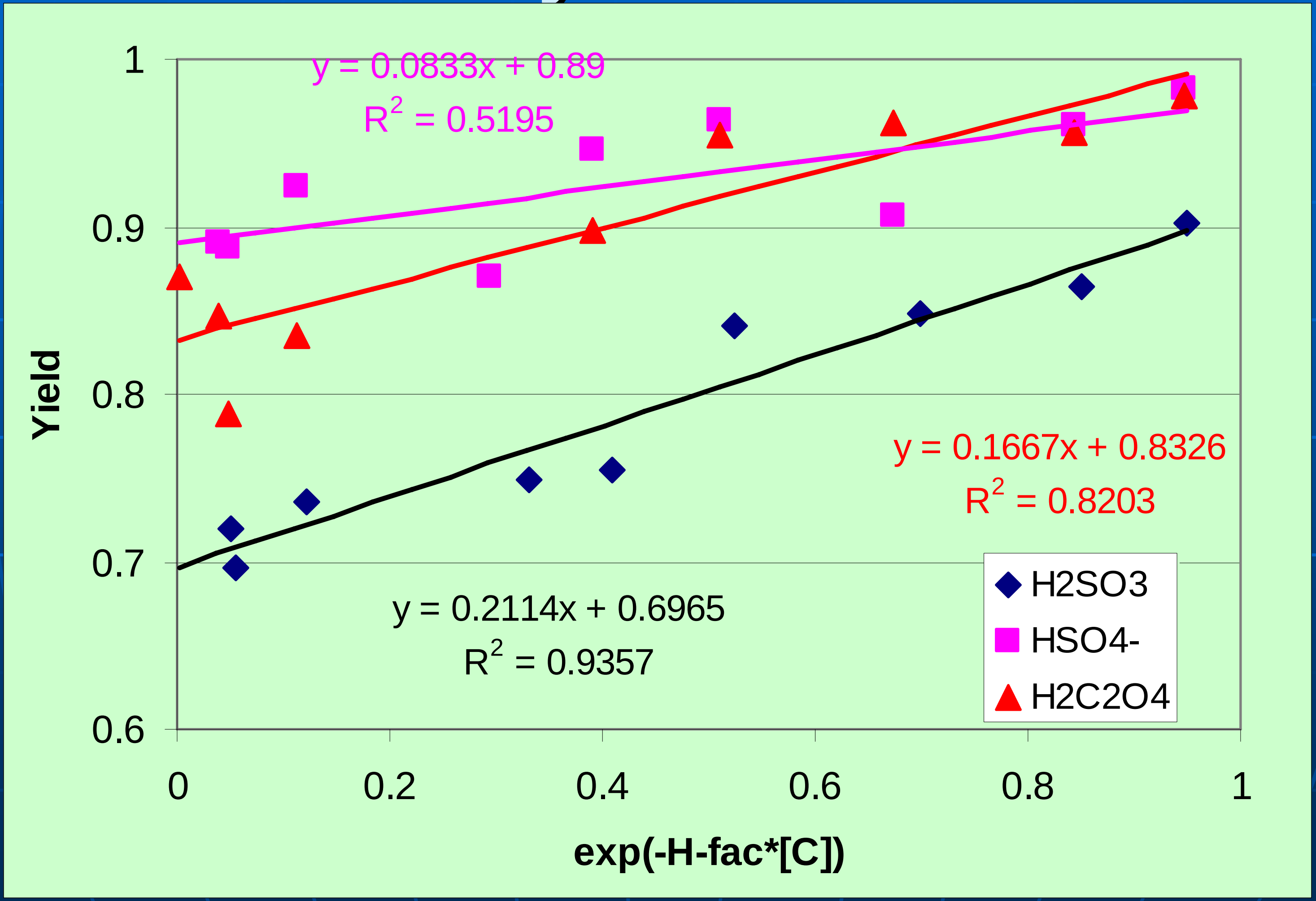
Pretreatment –mineral acids

FS-PI	Rudie
Objective	Recalcitrance
Funding	FS-Research
Cooperators	

Pretreatments

- Oxalic acid is reported to preserve wood brightness in pretreatment.
    - Due to pH?
    - Due to reducing potential?
- Test pH hypothesis with sodium bisulfate and sulfurous acid.
- Test reducing potential with sulfurous acid.

Influence of acid on prehydrolysis yield



Slope is hydrolyzable carbohydrate, intercept is resistant

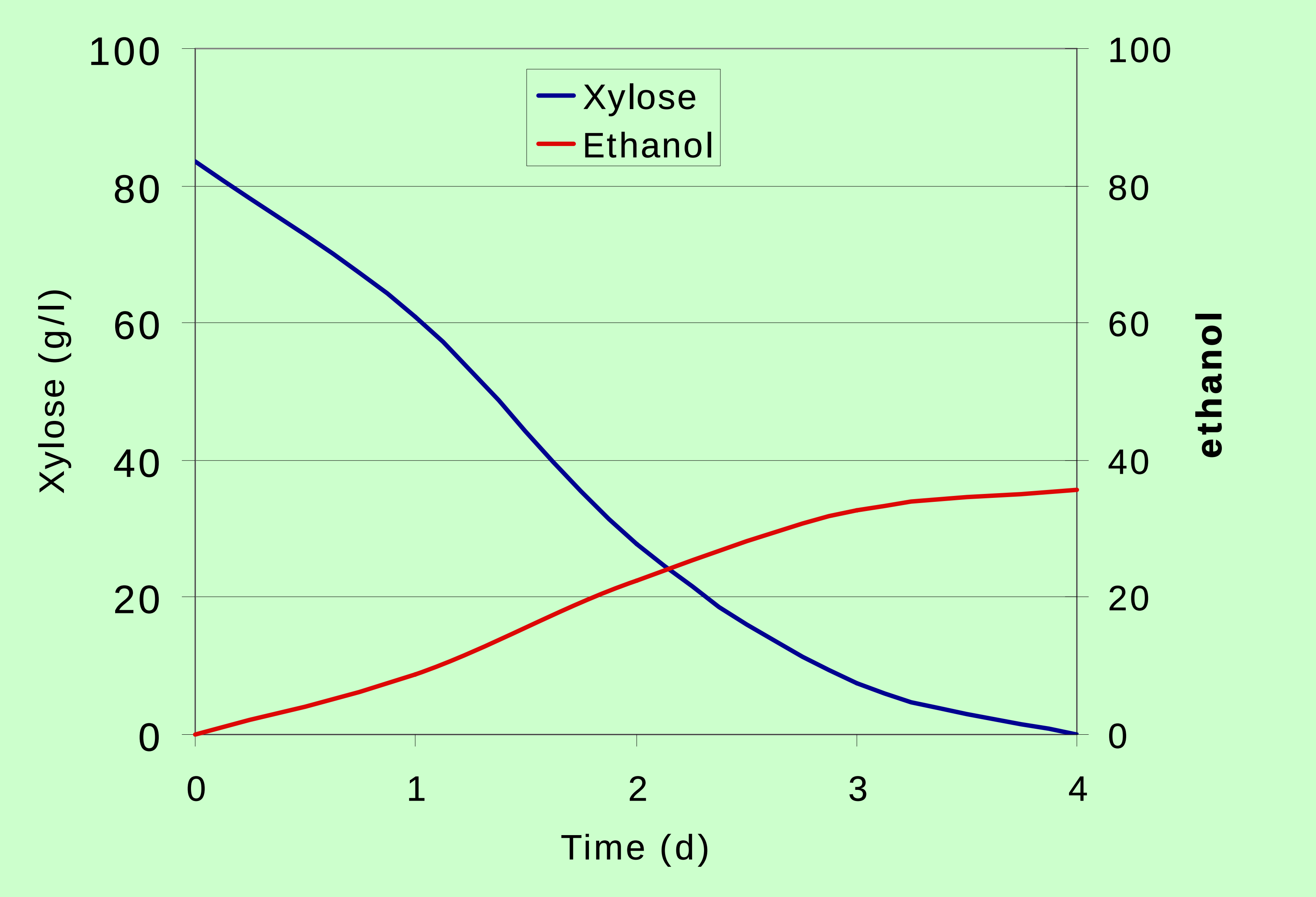
Fermentation of xylose

FS-PI	Jeffries (U.W.)
Objective	Five carbon sugars
Funding	DOE USDA-NRI
Cooperators	Xethanol U Wisconsin

Xylose

- Fermentation of five carbon sugars using *Pichia stipitis*
  - Xylose represents about 20% of the mass of hardwoods and 30% of stover
  - Alcohol tolerance
  - Rate
  - Yield

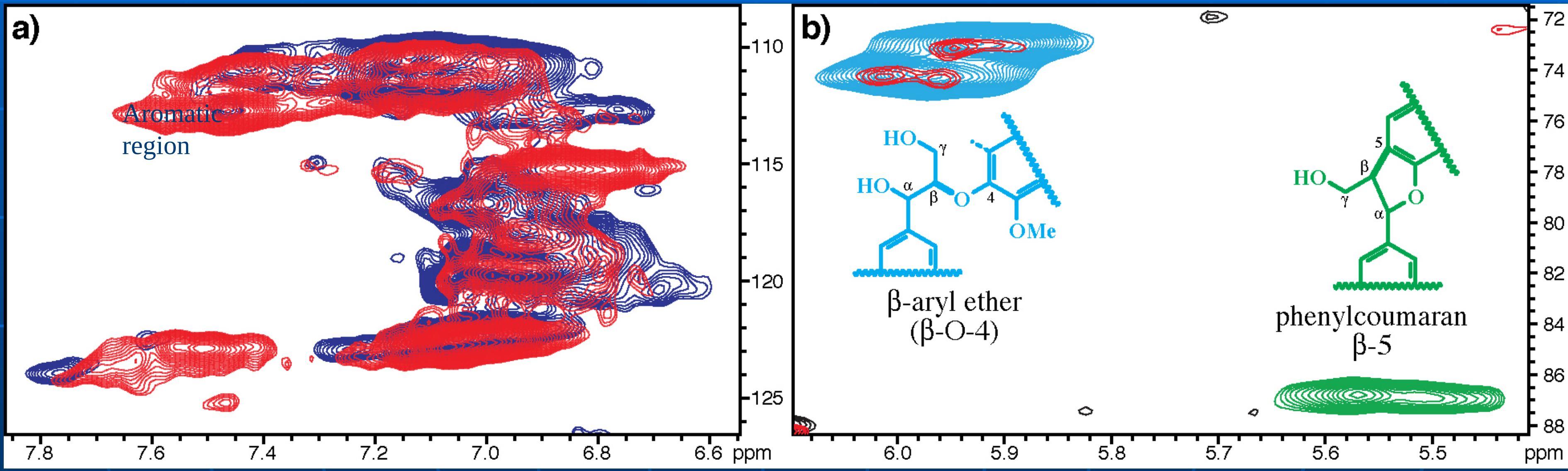
Xylose Fermentation with *P. stipitis*



Nuclear magnetic resonance spectroscopy of bioconverted lignocellulose

FS-PI	Hammel
Objective	Identify roadblocks to bioconversion
Funding	DOE
Cooperators	US Dairy Forage Research Lab (USDA ARS)

Overlaid short-range 2-D ^{1}H-^{13}C NMR spectra of completely dissolved aspen wood, before bioconversion and after 60% weight loss by the brown rot fungus *Gloeophyllum trabeum*

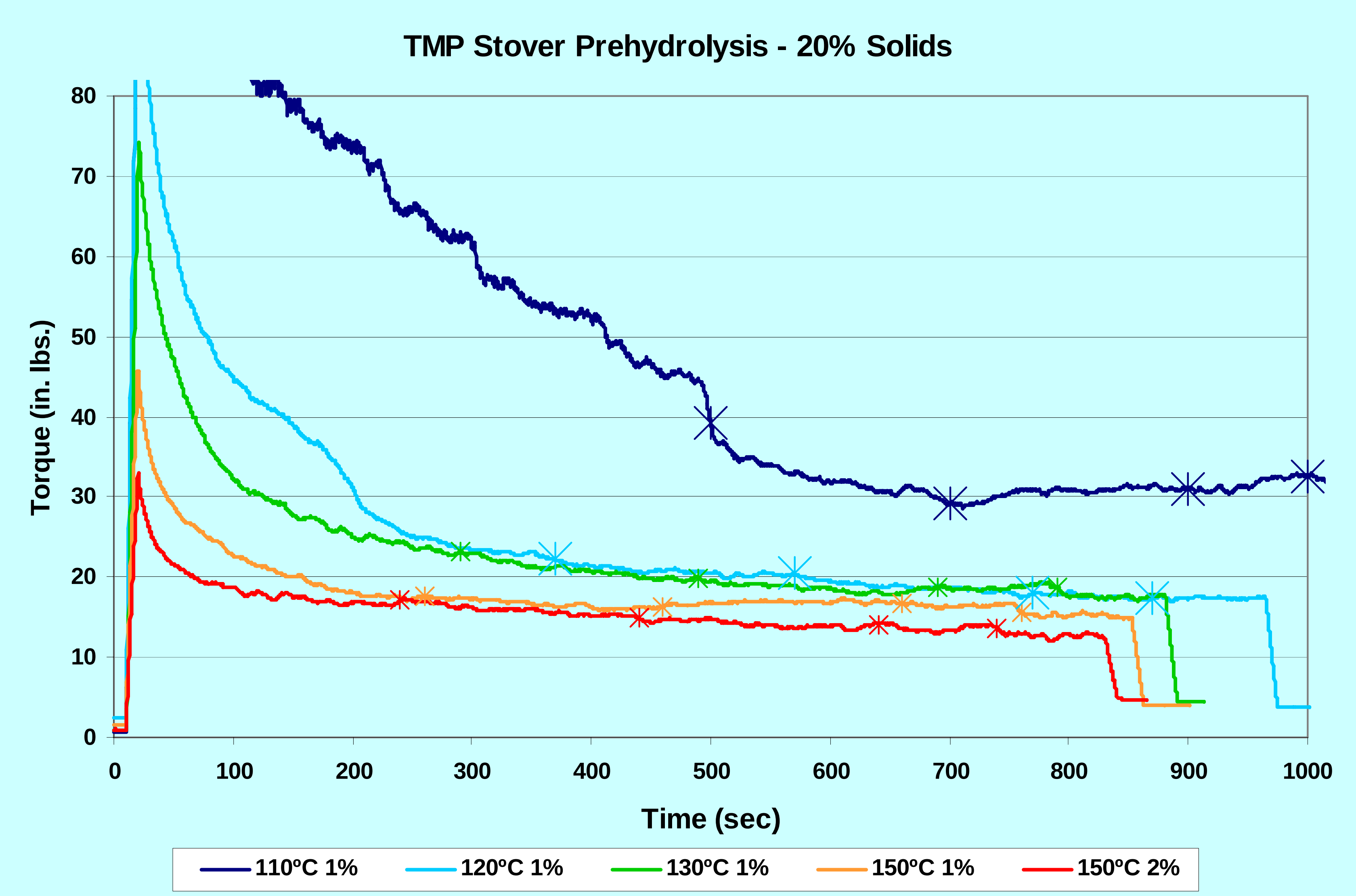


Most of the lignin in extensively brown-rotted lignocellulose has been cleaved.

Rheology and Mass Transport of Biomass Slurries

FS-PI	Scott (Klingenberg, UW)
Objective	Rheology of biorefining
Funding	USDA-NRI (U.W.)
Cooperators	University of Wisconsin

Rheology of Acid-Hydrolyzed Corn Stover
(preliminary data)



Forest Service Research

- Bioenergy and biochemicals offer a market for small trees, brush and slash that needs to be controlled to reduce fire risk.
- Ultimately collection and transportation become the major barriers to success.
- Short term, profitable biorefinery processes are needed.

FPL

- The Forest Service is committed to developing fuels from biomass.
- Long term solutions are technical
  - The barriers have stood for half a century
  - No data says they cannot be achieved.
- Probability of success for current commercial efforts is not known
- Near term may need financial incentives