Pretreatment Technologies

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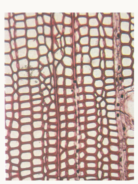
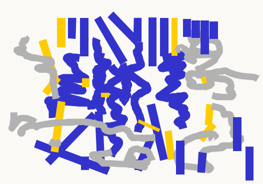
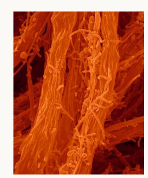
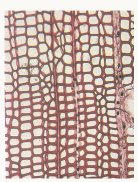


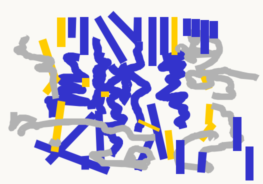


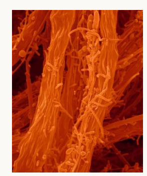



Outline

1. Cellulosic Biofuels – 30,000 ft view
2. Pretreatment : Keystone of Biological Route
3. Pretreatment Technologies: Overview
4. Process Considerations
5. Conclusions
6. Questions

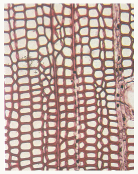



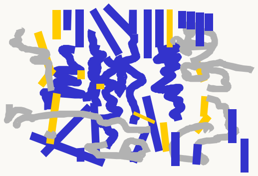


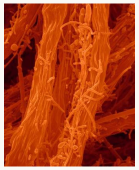



Biofuel Production Strategies

- Biochemical Conversion
  - Conversion by living system
  - Fermentation
  - Biogas, Ethanol, etc
- Thermochemical Conversion
  - Conversion by catalysts and/or heat
  - Pyrolysis, direct combustion, gasification






BIOLOGICAL CONVERSION

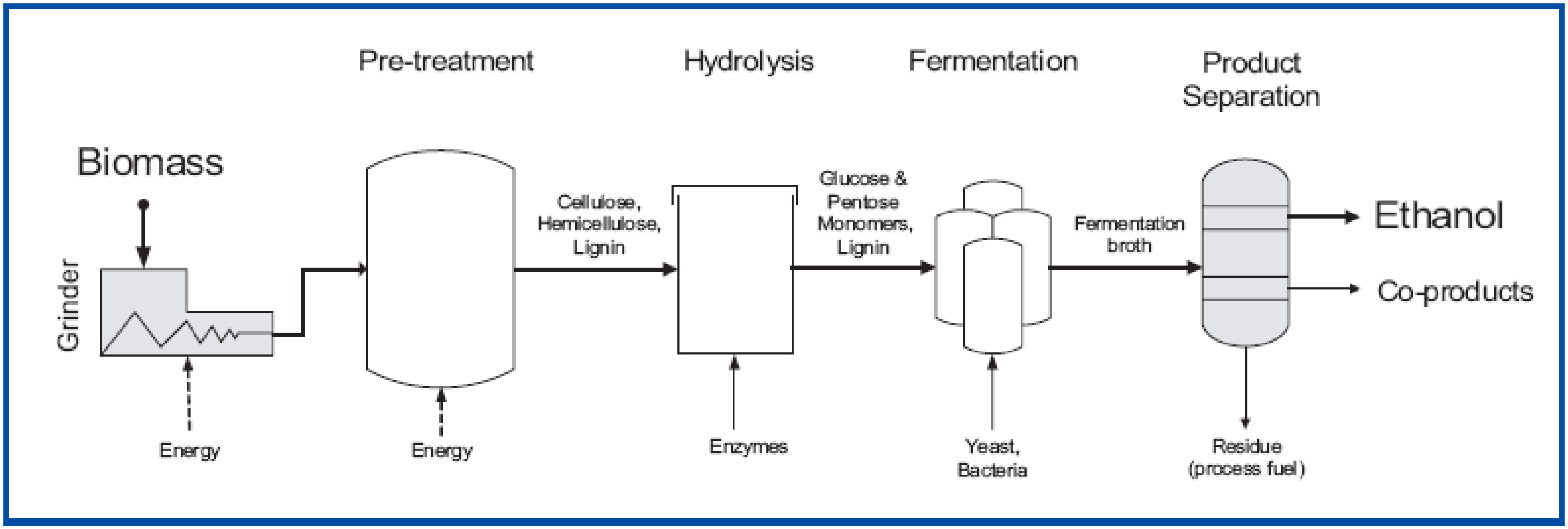
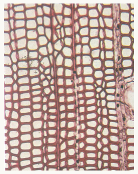
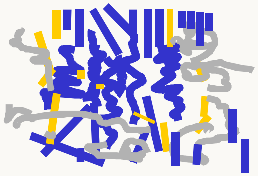
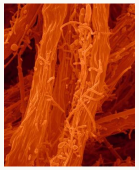


Figure from US DOE

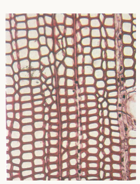



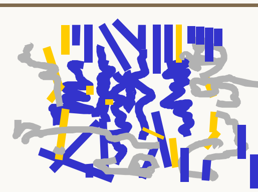


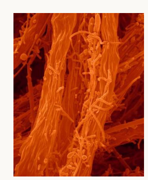



Biological Route from Biomass to Biofuels

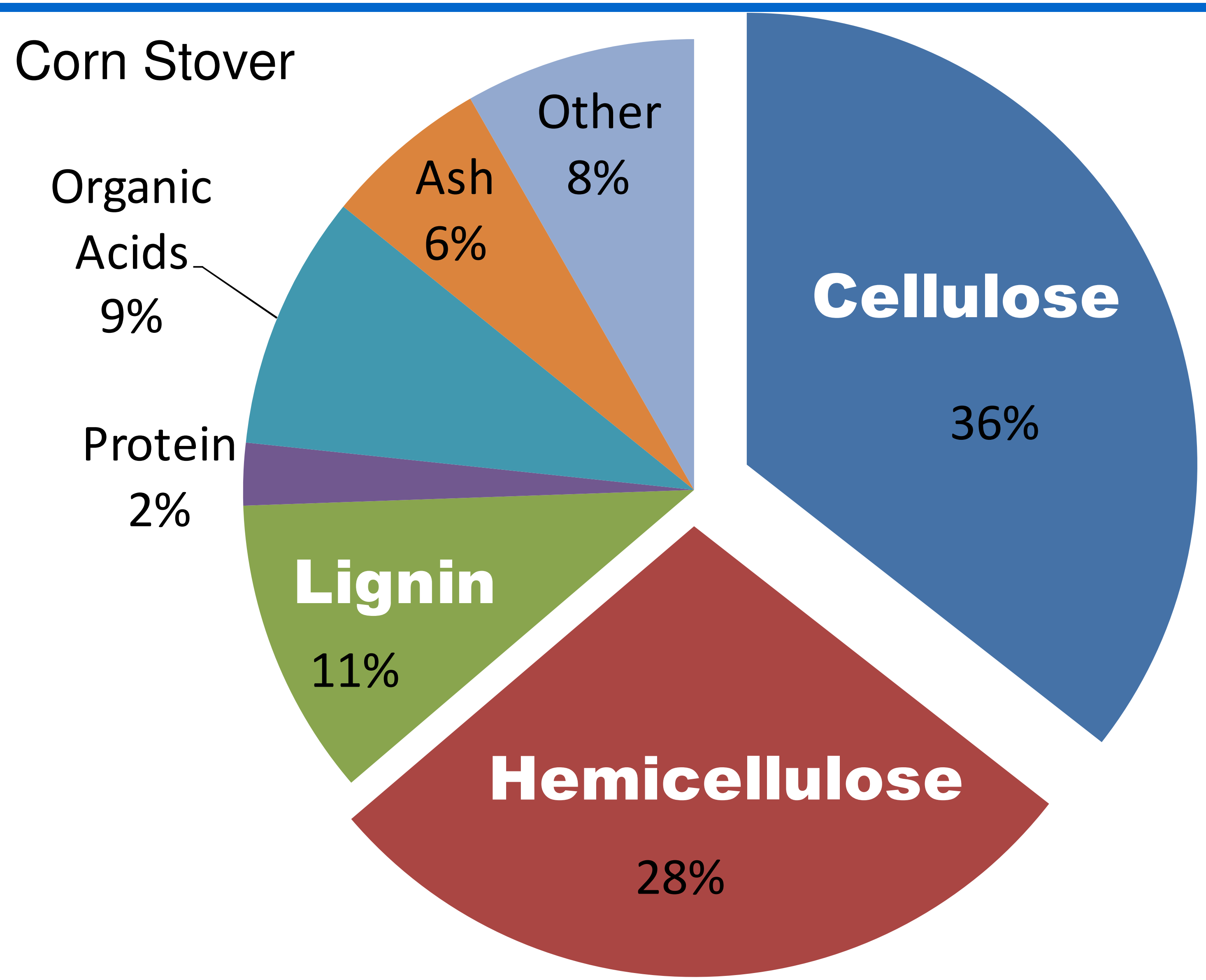
- Use natural or modified biocatalysts to convert **<u>carbohydrates</u>** to **<u>fuel</u>**
- Break long polymers of sugars (cellulose and hemicellulose) into individual sugars
- Ferment sugars to biofuel molecules



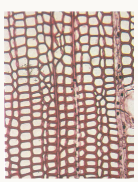


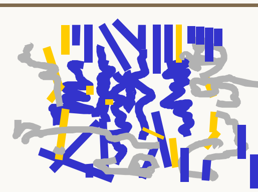

Lignocellulosic Biomass

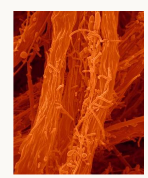


Plant Cell Wall Polysaccharides

- Source of fermentable sugars
  - Hexoses (glucose)
  - Pentoses (xylose)
- Recalcitrant to hydrolysis by consortium of enzymes
- Materials handling (viscosity)
- Source of inhibitors of enzymes and fermentation
  - Present in biomass (phenolic acids, acetate)
  - Derived from biomass during processing (furfural, HMF)

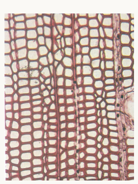



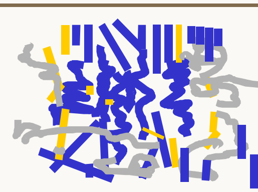


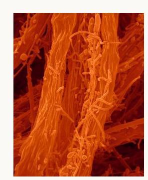



Biological Route: Fuels

- Ethanol
  - Various microbes (yeast and bacteria)
  - Current king of biofuels (corn, cane, beet)
- Butanol
  - *Clostridia sp.* - bacteria
  - Mixed solvent fermentation (butanol, acetone, ethanol)
- Others
  - Organic acids upgraded via thermochemistry (Mixalco)
  - Amyris Biotechnologies
  - LS9, GEVO, etc.

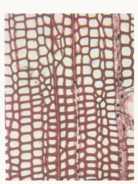



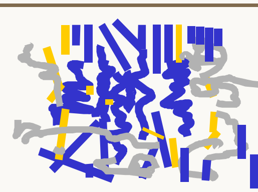


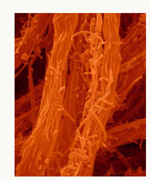



Pretreatment: Keystone of the Biological Route

- Overcoming recalcitrance of biomass to hydrolysis (saccharification)
- Multiple technologies, varying mechanisms
- Increase **rate** of hydrolysis (release of sugars)
- Increase **yield** of sugars
- Commodity chemical – yield, yield, yield!

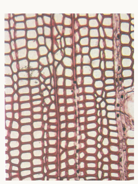



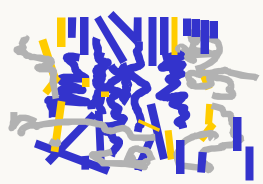


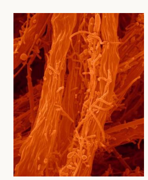


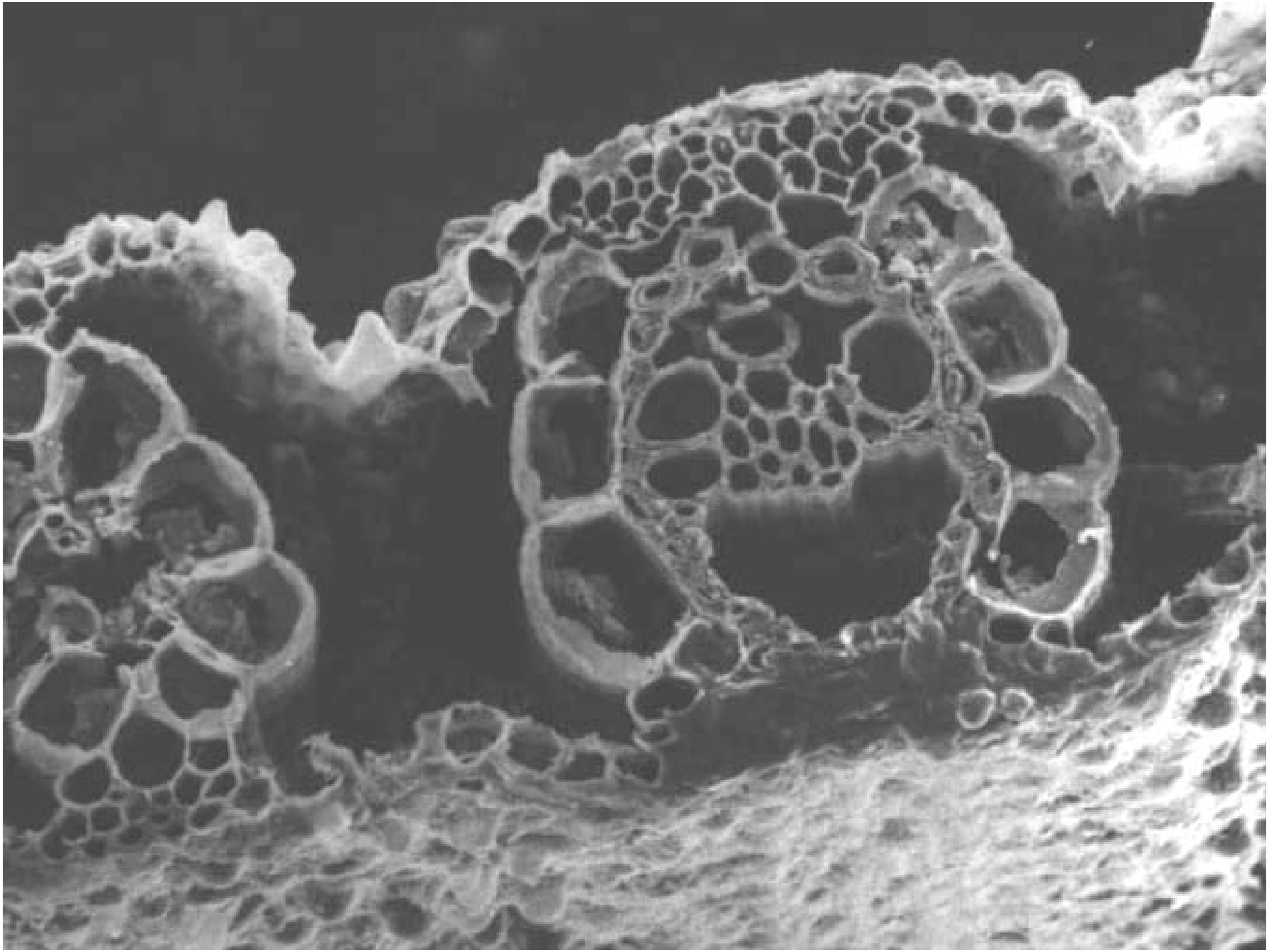

Pretreatment
Keystone of Biological Route

- Affects chemical makeup of feedstock
- Affects physiochemical interactions between feedstock constituents
- Affects fermentation performance
  - Inhibitors generated by pretreatment (furfural, HMF)
  - Inhibitors inherent to feedstock (acetate, phenolics, etc.)

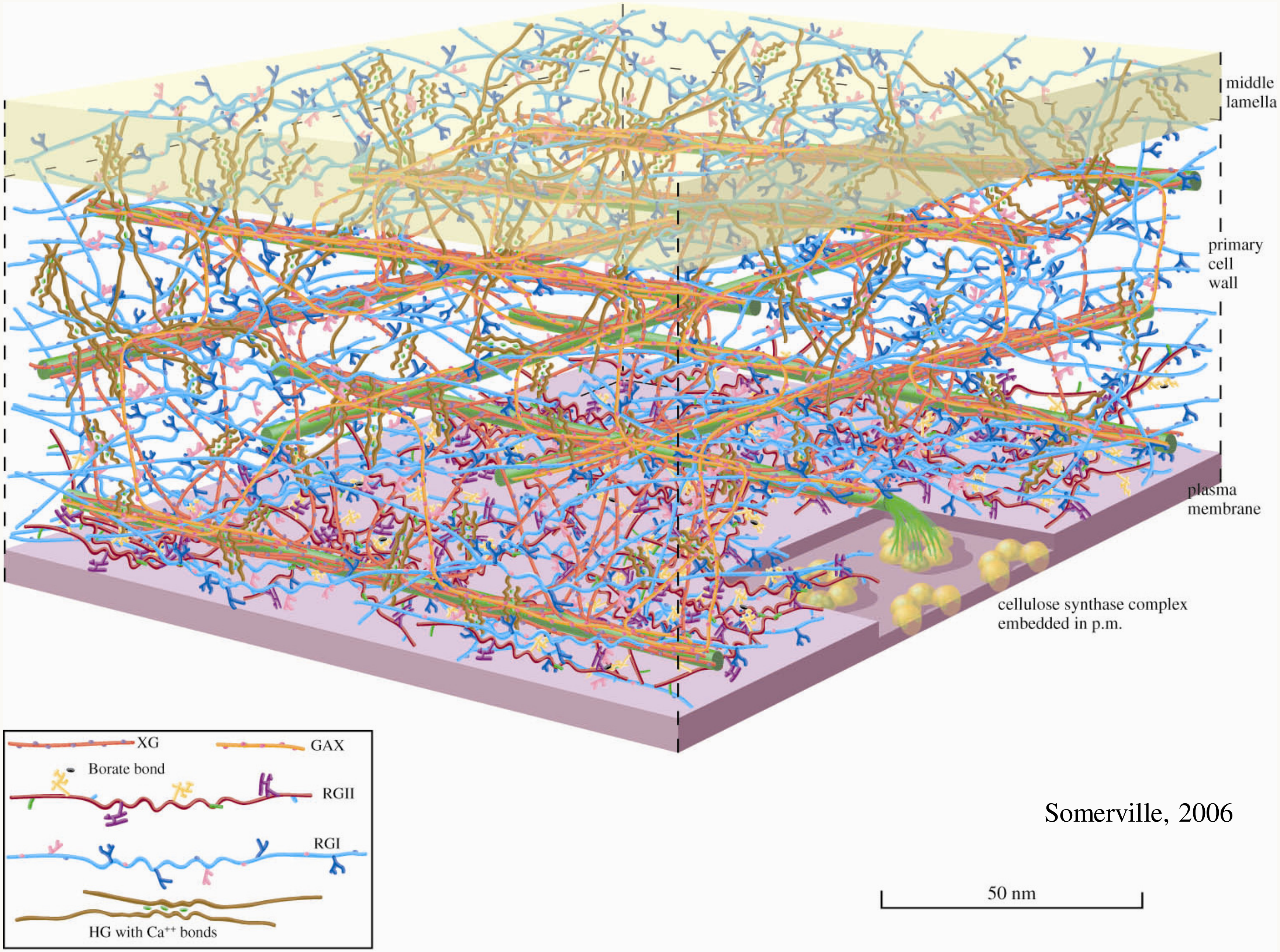







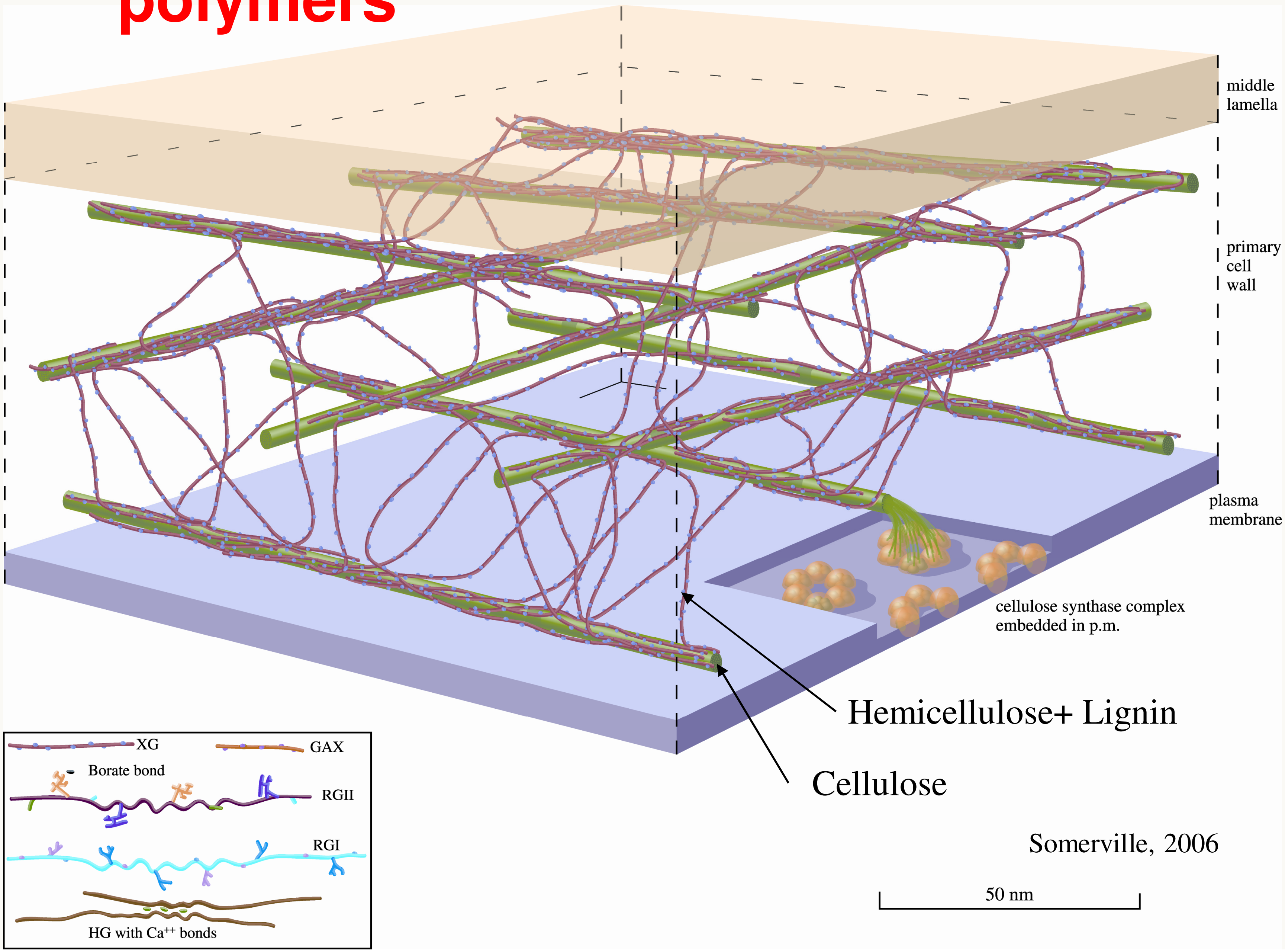



Scale model of a cell wall

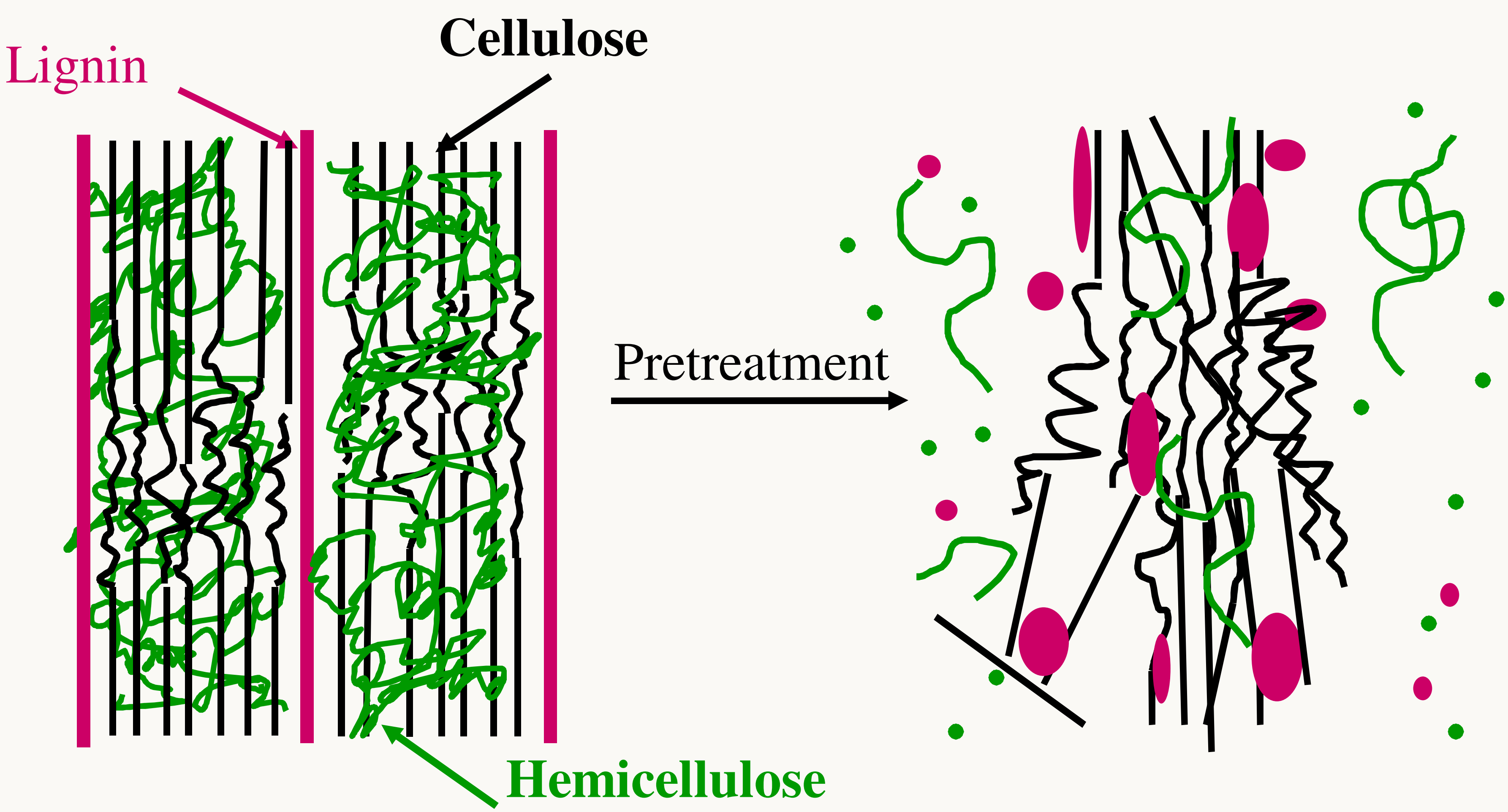


Somerville, 2006

Cellulose is occluded by other polymers



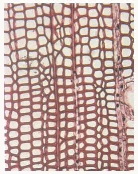
Simplified Impact of Pretreatment on Biomass

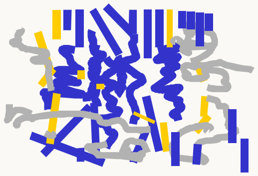


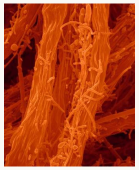
Mosier, N.; Wyman, C.; Dale, B.; Elander, R.; Lee, Y. Y.; Holtzapple, M.; and Ladisch, M. R. "Features of Promising Technologies for Pretreatment of Lignocellulosic Biomass," *Bioresource Technology* 96(6):673-686 (2005).

Overcoming Biomass Recalcitrance

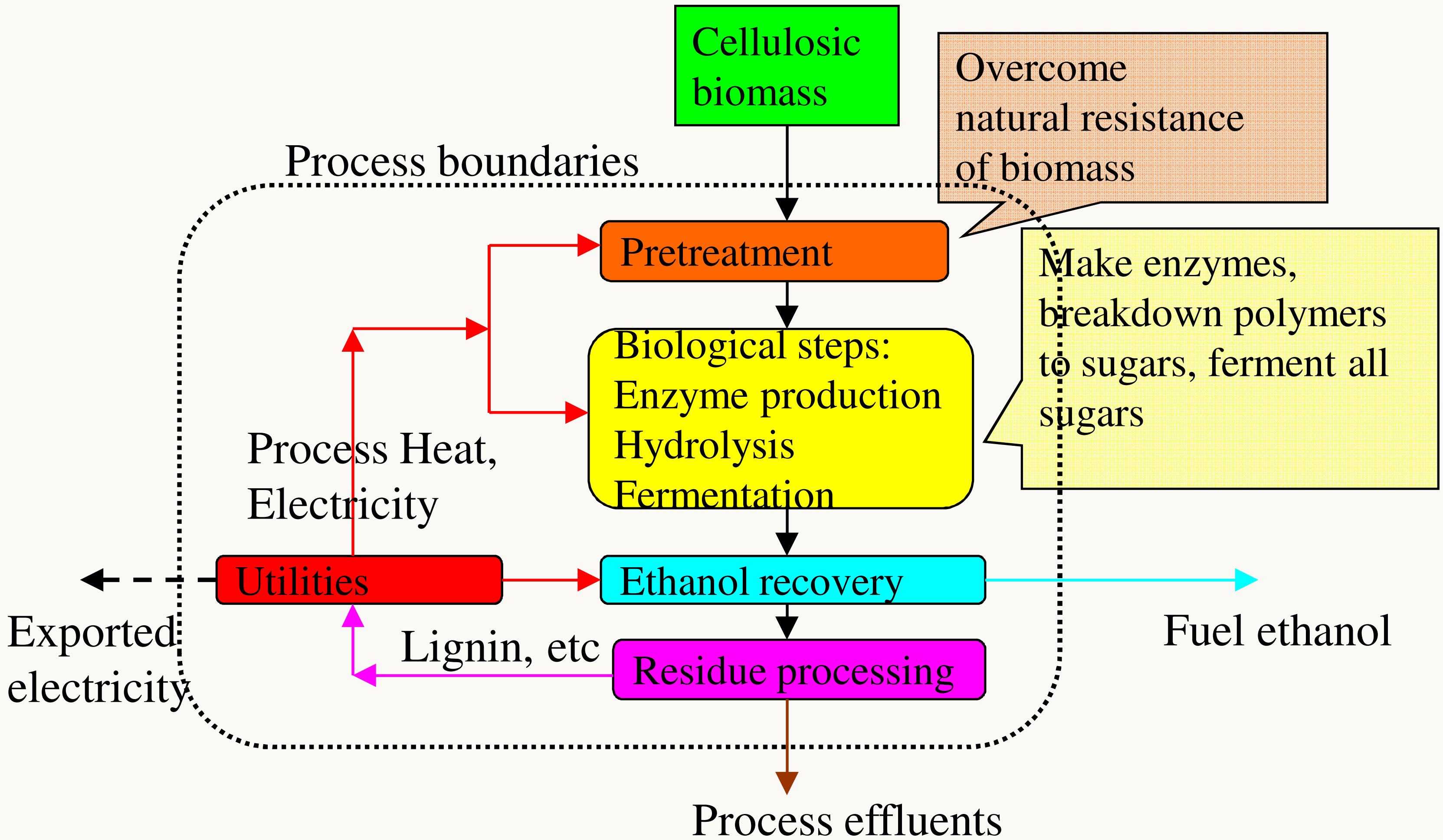
- Remove or rearrange lignin
- Remove or rearrange hemicellulose
- Alter cellulose crystallinity / accessibility to enzymes – <u>improve reactivity</u>
- Current technologies use a combination of chemicals and energy (thermal)



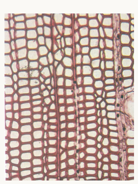
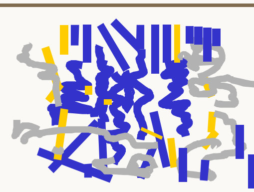
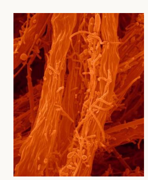



Enzymatic Conversion of Cellulosic Biomass to Ethanol



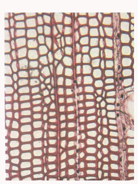
Factors Affecting Enzymatic Hydrolysis

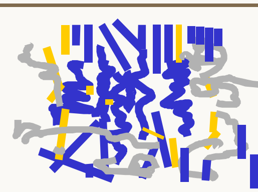
- Accessible beta bonds
  - Higher accessibility of surface improves rate of attack by endo and exoglucanase
- DP of pretreated cellulose
  - Lower DP favors higher ratio of exo to endo glucanase
- Lignin content
  - Blocks enzyme accessibility
  - Adsorbs enzyme non productively
- End-product inhibition
  - Reduces rates and yields
  - Cellobiose and glucose particularly strong inhibitors

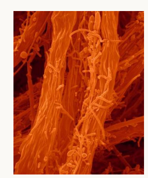
      

Pretreatment Goals

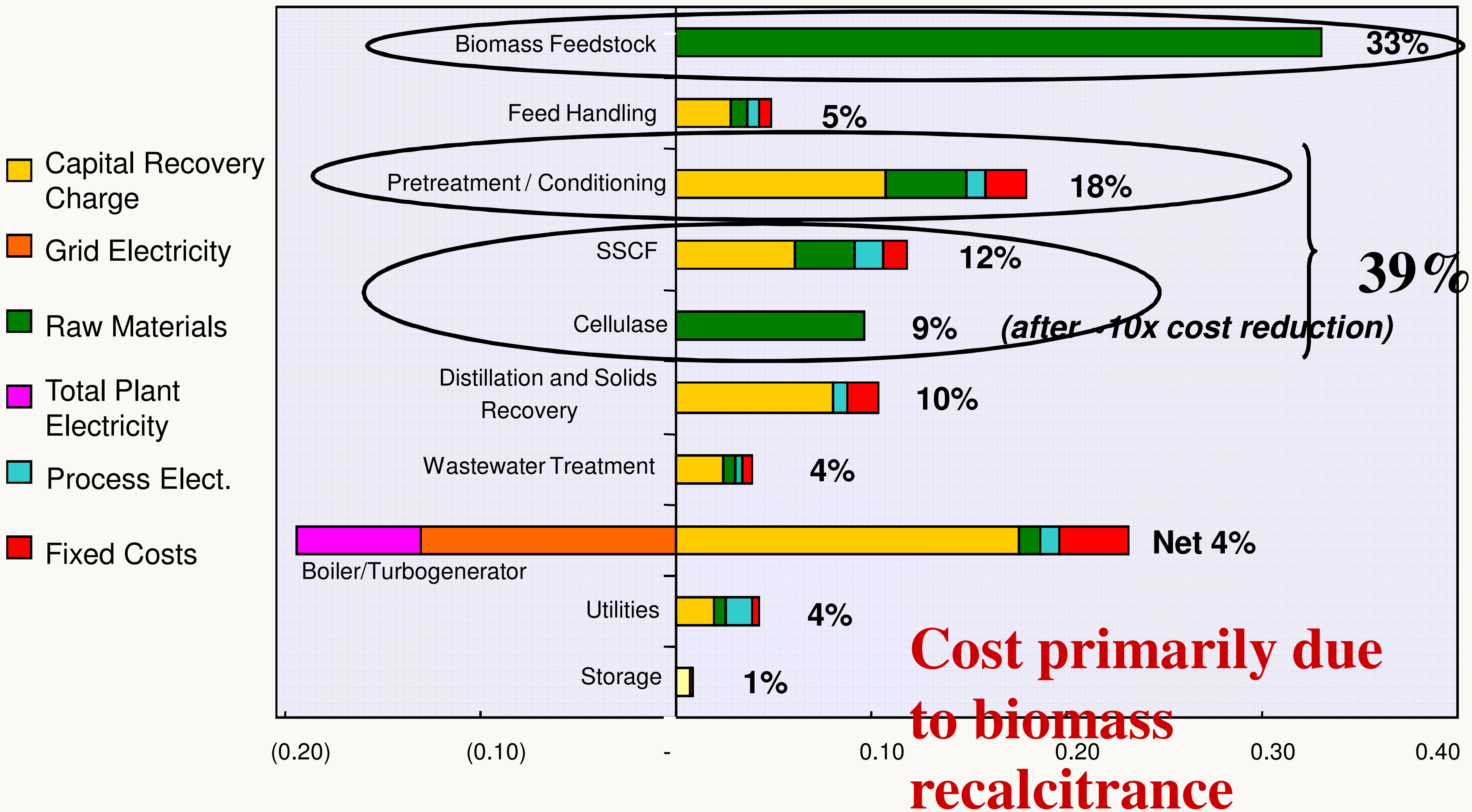
- Need to open up structure to make cellulose accessible to enzymes - high digestibility
- High sugar yields from hemicellulose are also vital
- Low capital cost – pressure, materials of construction
- Low energy cost
- Low degradation
- Low cost and/or recoverable chemicals
- A large number of pretreatment technologies have been studied to improve cellulose digestion



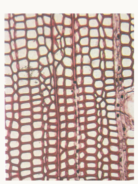


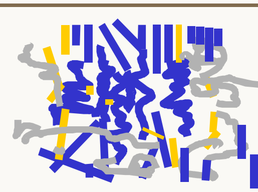

Key Processing Cost Elements

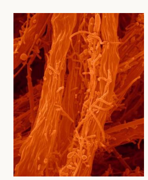


Importance of Pretreatment

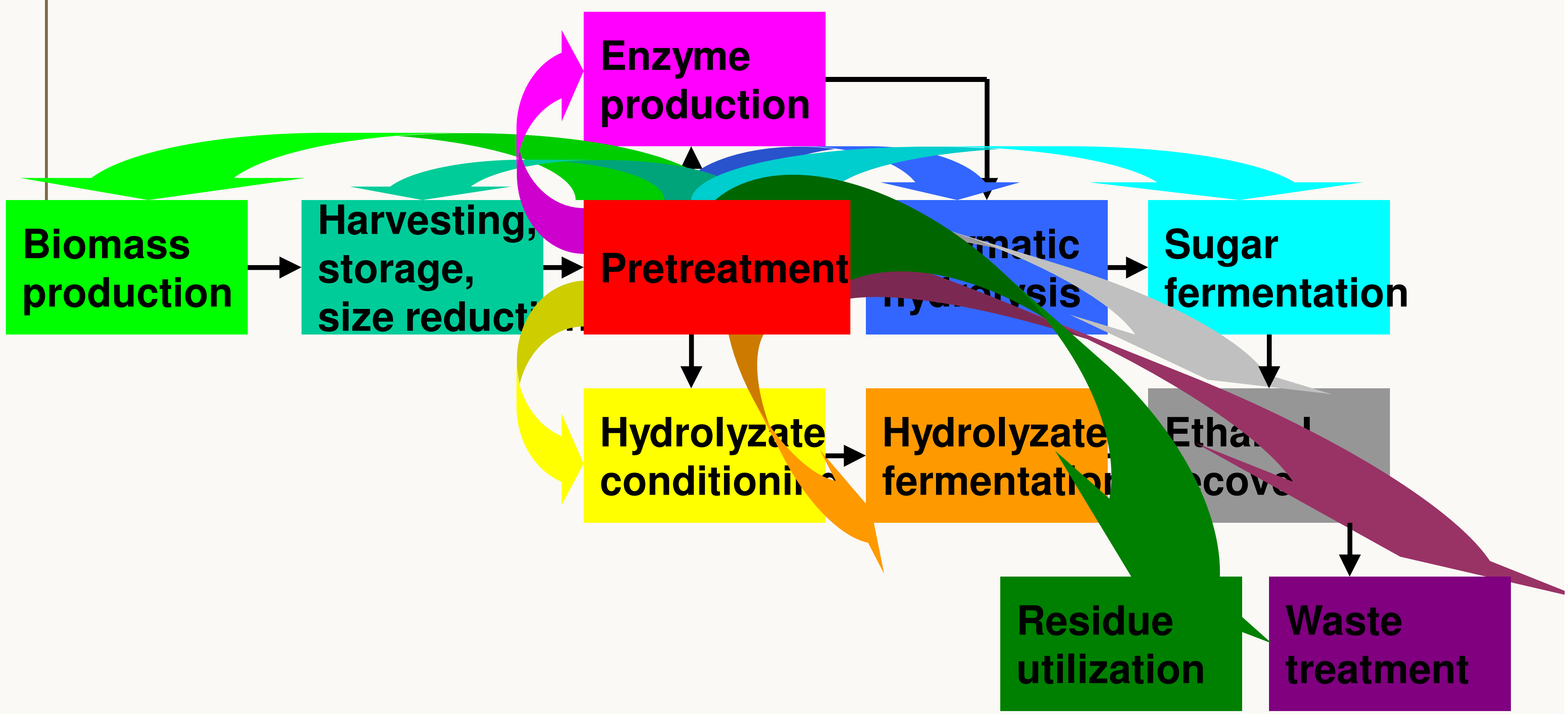
- Although significant, feedstock costs are low relative to petroleum
- In addition, feedstock costs are a very low fraction of final costs compared to other commodity products
- Pretreatment is the most costly process step: the only process step more expensive than pretreatment is no pretreatment
  - Low yields without pretreatment drive up all other costs more than amount saved
  - Conversely enhancing yields via improved pretreatment would reduce all other unit costs
- Need to reduce pretreatment costs to be competitive

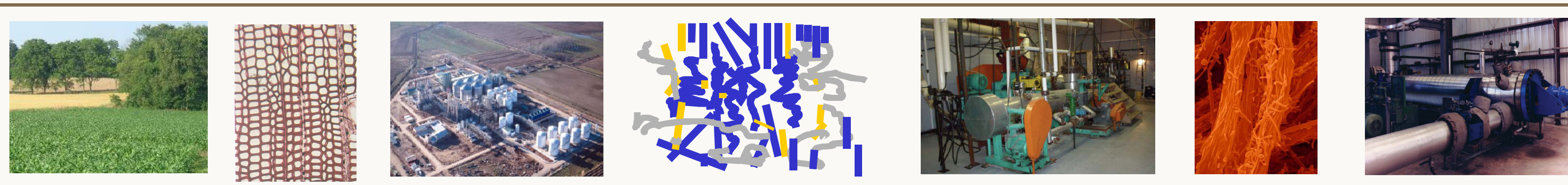







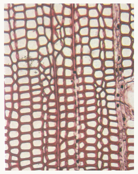

Central Role and Pervasive Impact of Pretreatment for Biological Processing

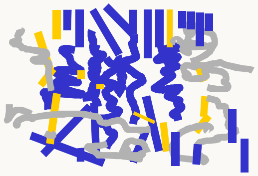


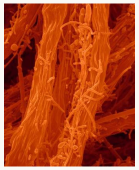


Distinguishing Features of Pretreatment

- Additives - none, acid, base, solvent, enzymes
- System - physical, chemical, thermal, biological
- Operation - batch/plug flow, continuous, flow through, countercurrent
- Solids concentration
- Heat up method and time
- Cool down method and time
- Long on invention, short on fundamentals

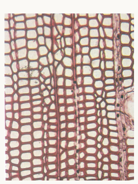



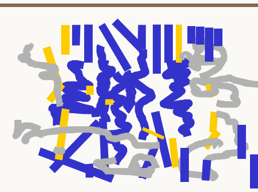


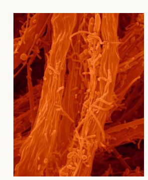



Pretreatment Classes

- Physical
- Biological
- Chemical

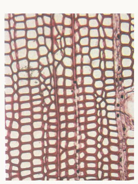


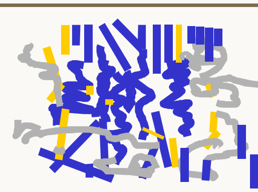


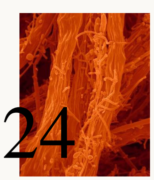

Physical Pretreatments

- Size reduction
  - Hammer mills
  - Knife mills
  - Extruders
  - Disc refiners
  - Planer
- Mechanical decrystallization
  - Ball mills
  - Roll mills
  - Dry mills
  - Colloid mills
- Thermal
  - Freeze/thaw
  - Pyrolysis
  - Cryomilling
- Radiation
  - Gamma rays
  - Microwaves
  - Electron beam
  - Lasers

Expensive and limited effectiveness






Biological Pretreatments

	White Rot	Red Rot	Brown Rot

FomesfomentariusFomitopsisannosaPiptoparusbetulinus

PhellinusigniariusLaetiporussuphureus

GadodermaapplanatumTrametesquercina

ArmillariamelleaFomitopsispinicola

PleurotusostreatusGloephyllumsaepiarum

Attacks	White Rot	Red Rot	Brown Rot
lignin	+	+	+
cellulose	+	+	–

Not very effective and require long times

Chemical Pretreatments 1

- Oxidizing
  - Peracetic acid
  - Ozone
  - Hydrogen peroxide
  - Chlorine
  - Sodium hypochlorite
  - Chlorine dioxide
- Concentrated acid
  - Sulfuric (55-75%)
  - Phosphoric (79-86%)
  - Nitric (60-88%)
  - Hydrochloric (37-42%)
  - Perchloric (59-61%)
- Cellulose solvents
  - Inorganic salts
    - *Lithium chloride*
    - *Stannic chloride*
    - *Calcium bromide*
  - Amine salts
    - *Cadoxen*

      (cadmium chloride + ethylenediamine)
    - *Cooxen*

      (cobalt hydroxide + ethylenediamine)

Not cost effective

Chemical Pretreatments2

- Delignification
  - Organosolv
    - *Ethanol*
    - *Butanol*
  - Triethylene glycol
- Cellulose modification
  - Carboxymethyl cellulose
  - Viscose
  - Mercerized

Many too expensive

- Alkaline
  - Sodium hydroxide
  - Calcium hydroxide
  - Kraft pulping
  - Soda pulping
  - Amines
  - Ammonia
    - *Gaseous*
    - *Liquid*
    - *Supercritical*
    - *Aqueous*
    - *Percolation*

Chemical Pretreatment 3

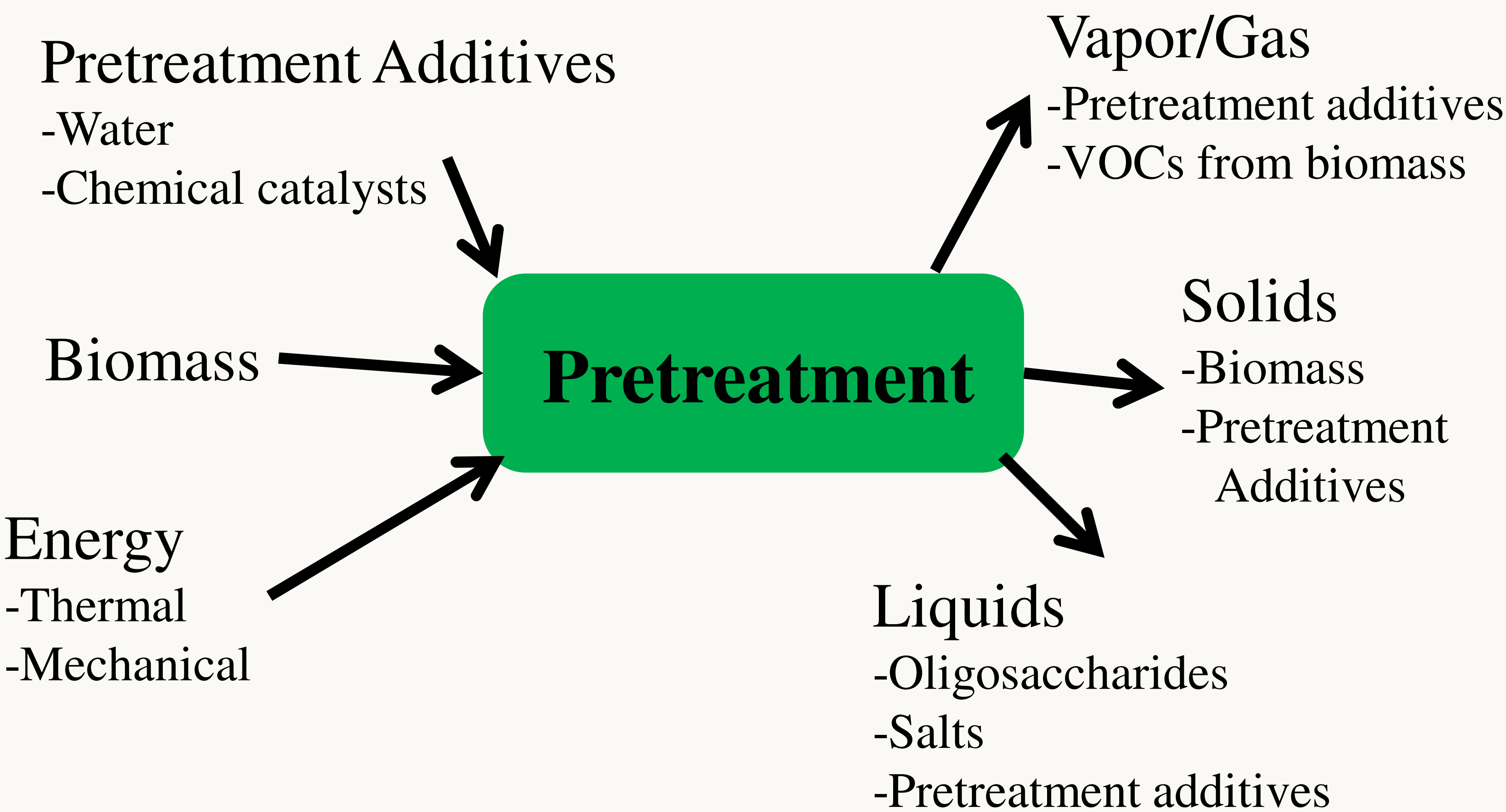
- Acids
  - Sulfite pulping
  - Dilute sulfuric, phosphoric, or nitric acid
  - Autohydrolysis with natural acids
  - Liquid hot water
  - Gaseous
    - *HCl, SO2, NO2, CO2*
- Neutral pH

Pretreatment with dilute acid currently favored

Challenges with Dilute Acid Pretreatment

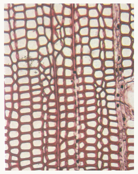
- Cost of acid
- Cost to neutralize
- Need to remove toxics released and produced prior to biological steps
- Expensive materials of construction
- Hemicellulose sugar yield limited to about 90%
- High enzyme dosages in subsequent cellulose digestion step
- Slow digestion of cellulose

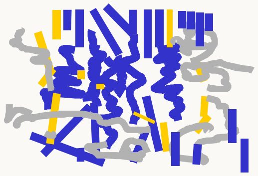
Pretreatment Process

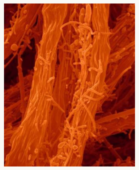


Pretreatment Additives

- Solvents
  - Water
  - Acetone, Ethanol
- Catalysts
  - Acid
  - Alkaline

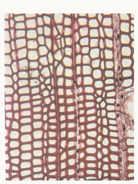



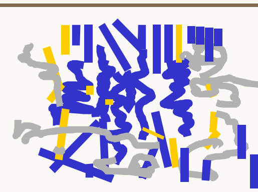


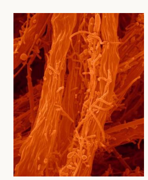



Pretreatment Solvents

- Partial fractionation of biomass (solid into liquid)
- Water
  - Most common solvent
  - Least expensive, compatible with downstream biological processing
- Ethanol, acetone, others

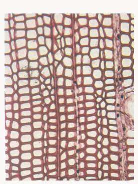



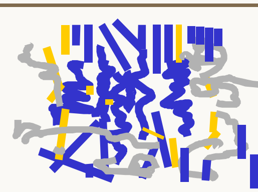


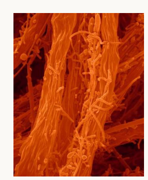



Catalysts

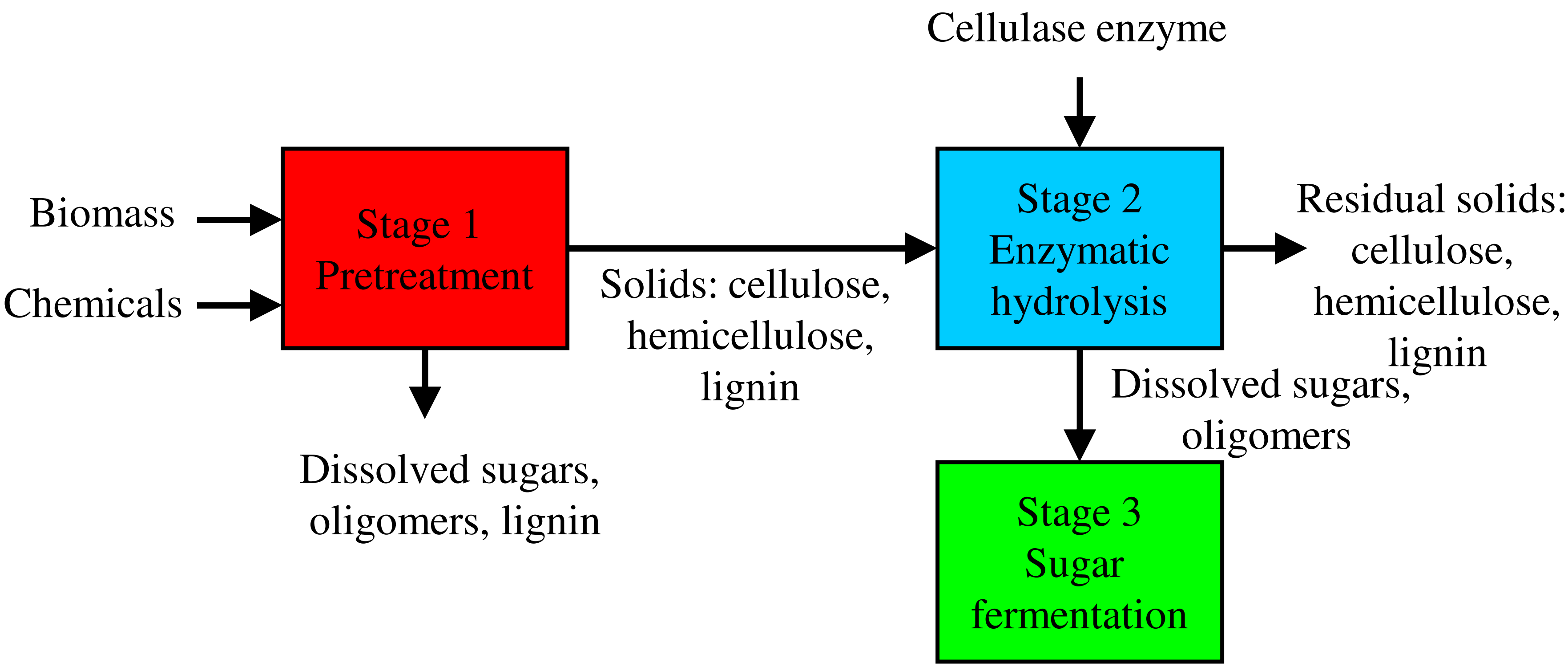
- Aid in hydrolyzing plant cell wall polymers
- Lignin more susceptible to degradation via alkaline chemistry
- Hemicellulosemore susceptible to hydrolysis via acid chemistry
- Cost is key!
  - Acids: Sulfuric, phosphoric, hydrochloric
  - Bases: Sodium Hydroxide, Calcium Hydroxide, Ammonia






Understanding Sugar Yields



Biomass Refining CAFI

http://www.eng.auburn.edu/cafi/

CAFI Pretreatments

- Acid
  - Dilute sulfuric acid in water (0.5 -1.0% w/w)
  - 140-220 C (285-428 F)
  - Pressurized to keep water in liquid phase
- Hot Water (Controlled pH)
  - 140-220 C (285-428 F)
  - Pressurized to keep water in liquid phase
  - Water acts as weak acid

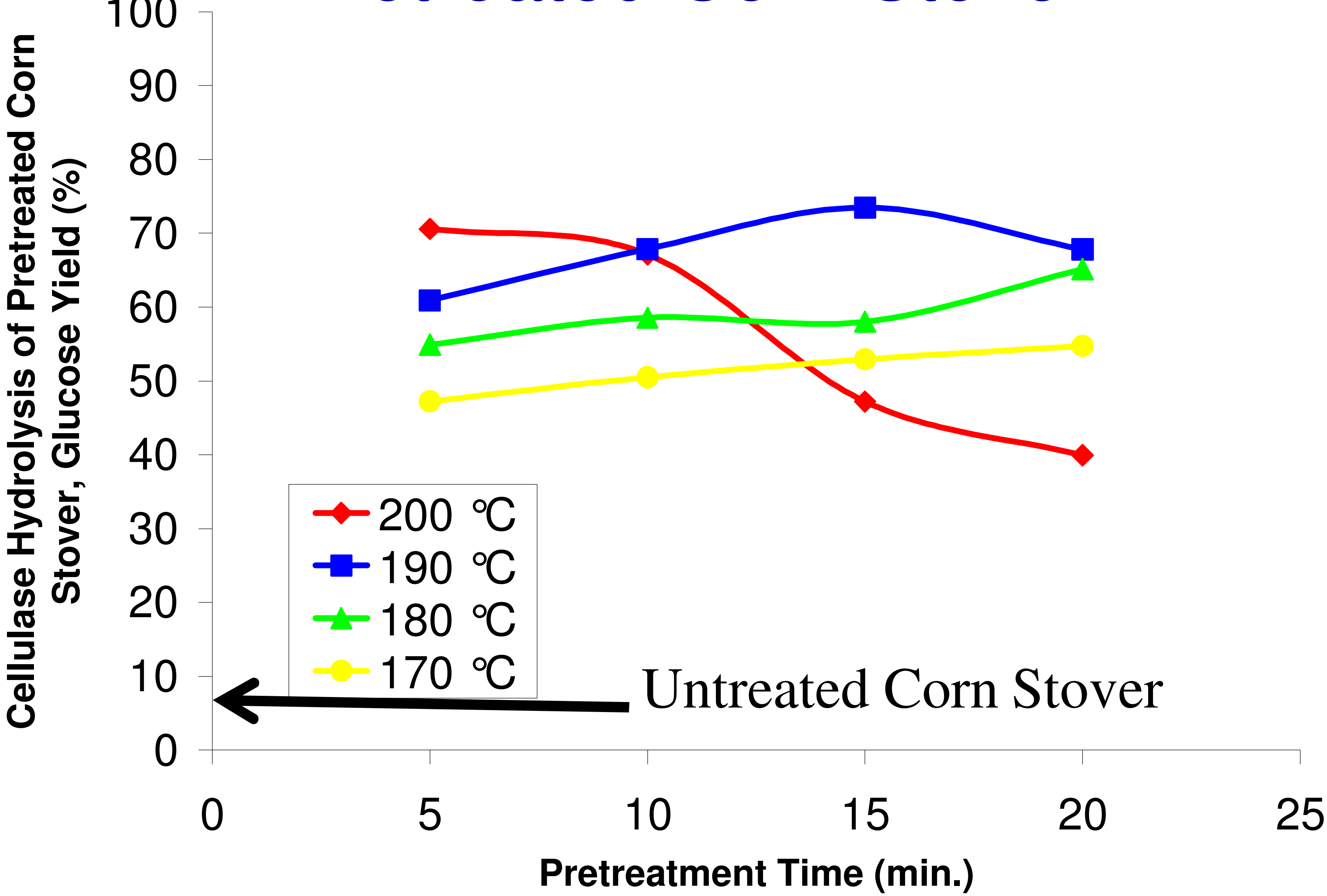
CAFI Pretreatments

- Lime
  - Lime (calcium hydroxide) water slurry
  - Percolation bed
  - Temperatures 20-50 C (70-120 F)
- Ammonia Fiber Expansion (AFEX)
  - Dry-to-dry process
  - Liquid aqueous ammonia under pressure
  - 60-90 C (140-195 F)
  - Vaporize ammonia for recovery

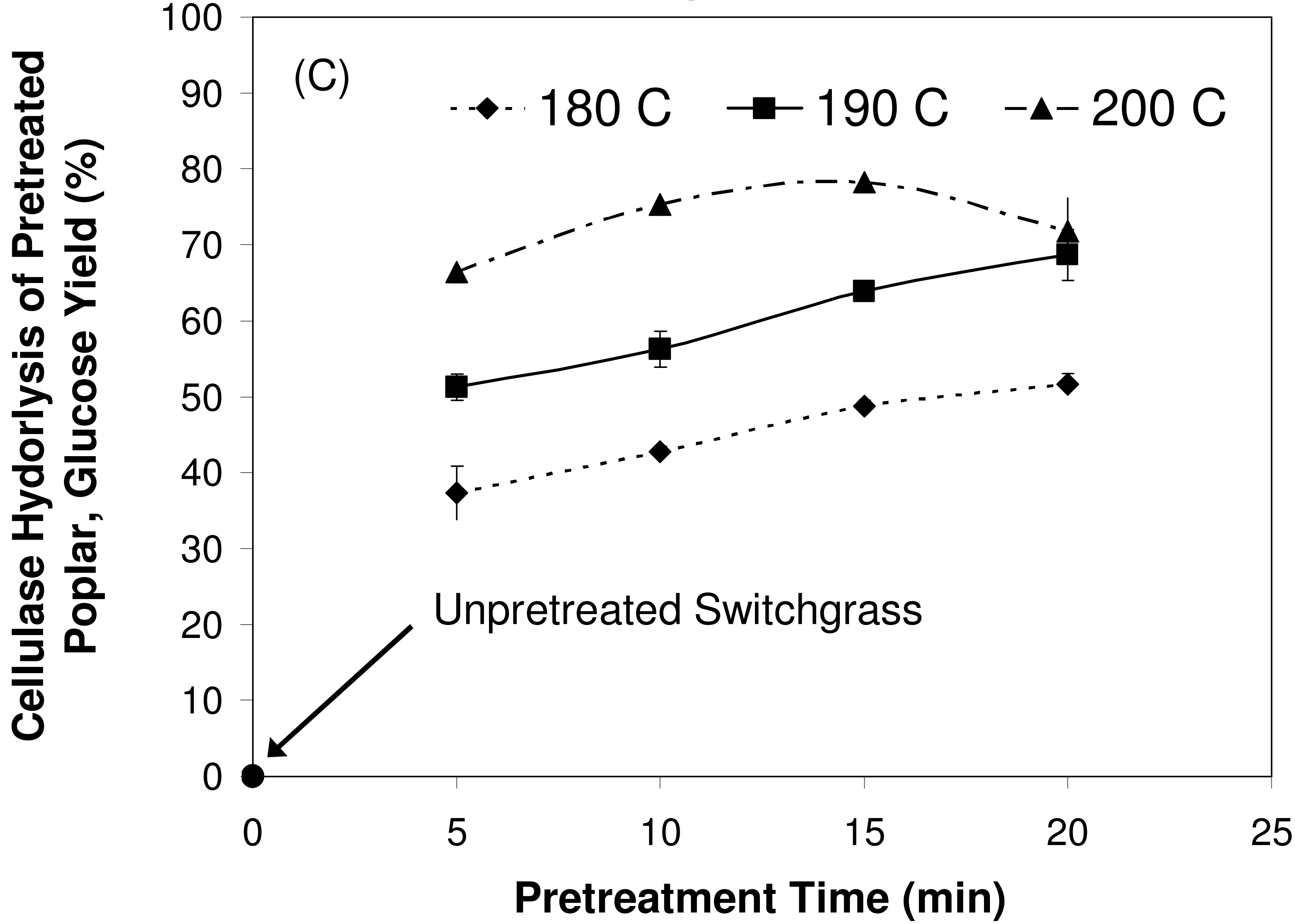
CAFI Pretreatments

- Sulfur Dioxide Steam Explosion
  - Sulfur dioxide 3%, soaked overnight
  - Temperature 190 C
  - 3 minutes reaction time
- Aqueous Ammonia Recycle Pretreatment
  - Ammonium hydroxide 15%
  - Temperature 180 C
  - Reaction time 27.5 minutes

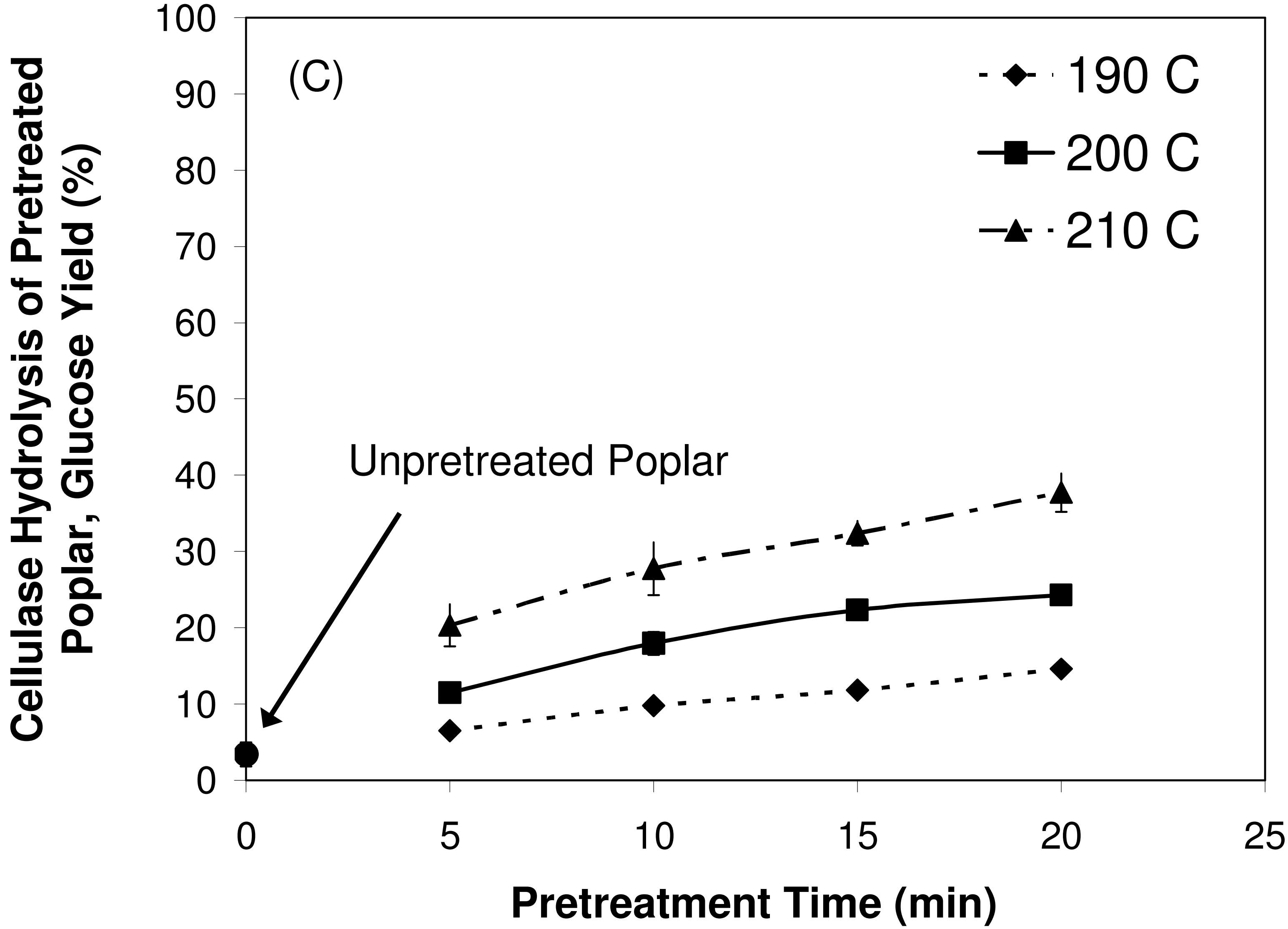
Glucose Yield of Liquid Hot Water (LHW) Pretreated Corn Stover



Glucose Yield of LHW Pretreated Switchgrass



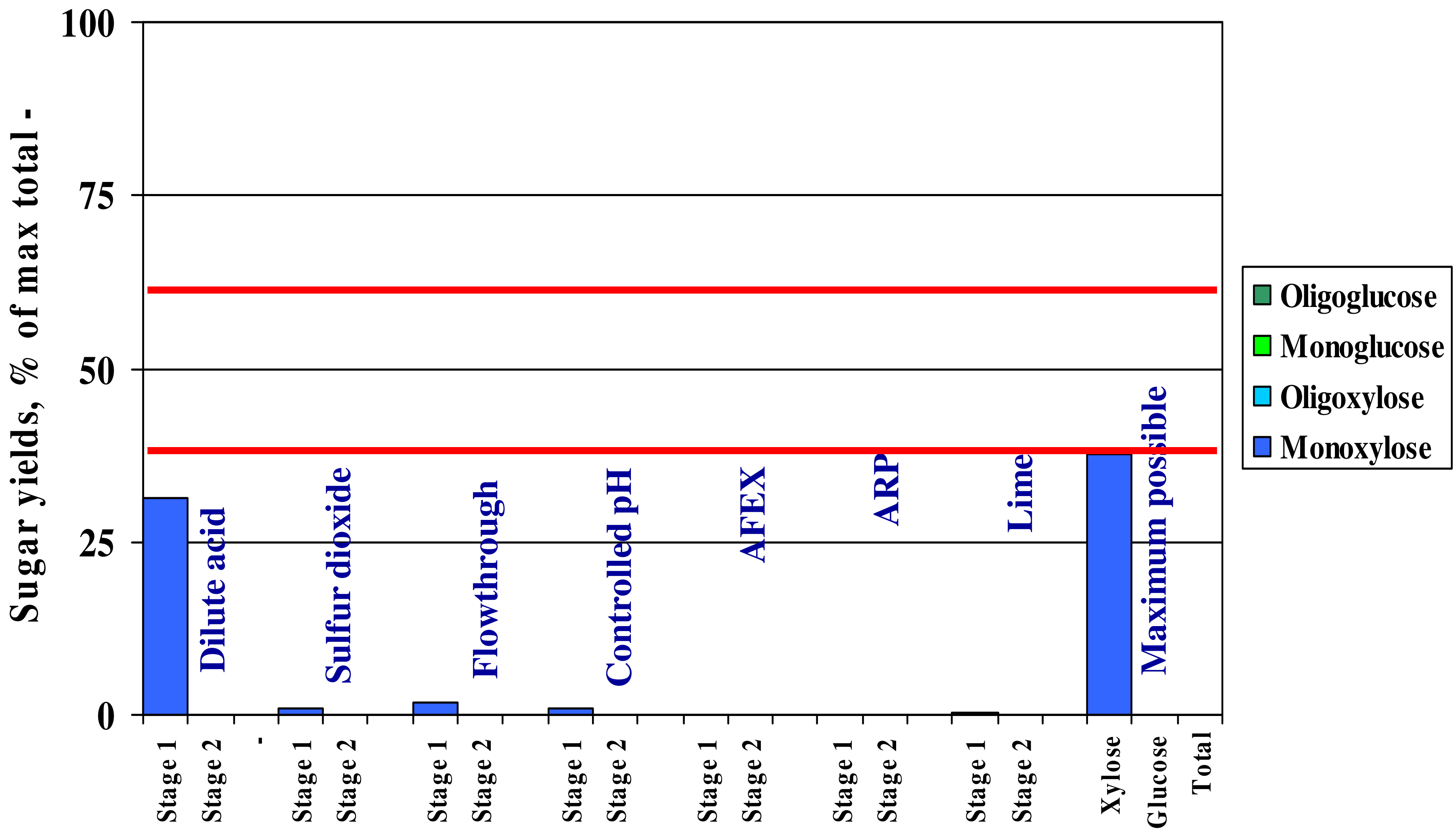
Glucose Yield of LHW Pretreated Poplar



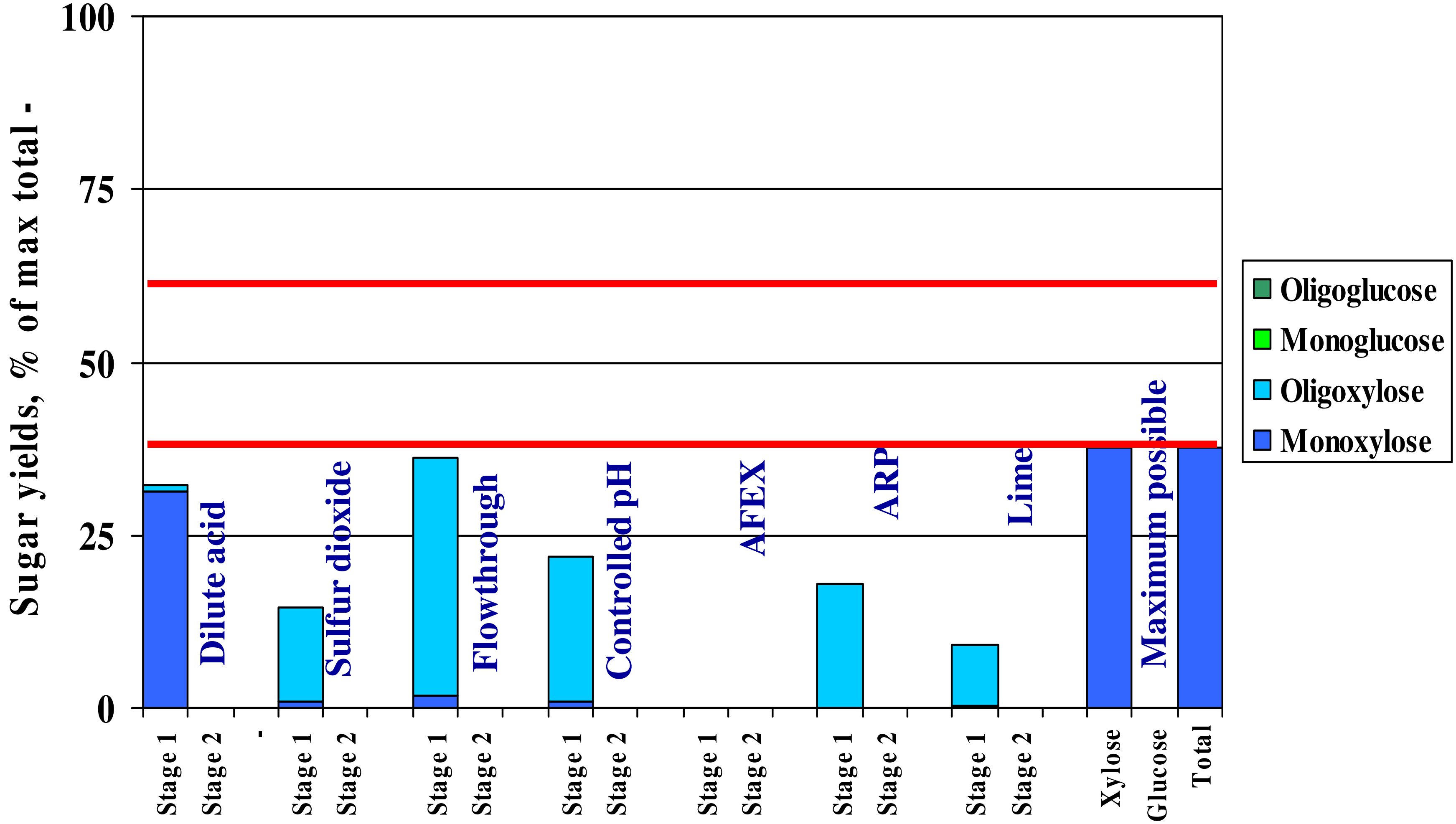
Enzymes Used and Experimental Conditions

- Enzymes from Genencor International
  - Spezyme CP (59 FPU/ml, 123 mg protein/ml)
  - GC-220 (89 FPU/ml, 184 mg protein/ml)
  - β-glucosidase (32 mg protein/ml)
  - Multifect Xylanase (41 mg protein/ml)
- Experimental conditions
  - 1-2% glucan in 100 ml flasks in citrate buffer plus antibiotics
  - Digestion time – 72 hrs
  - CBU : FPU ~ 2.0
  - Enzyme loadings – 3.0, 7.5,15, 50, and 60 FPU/g glucan prior to pretreatment

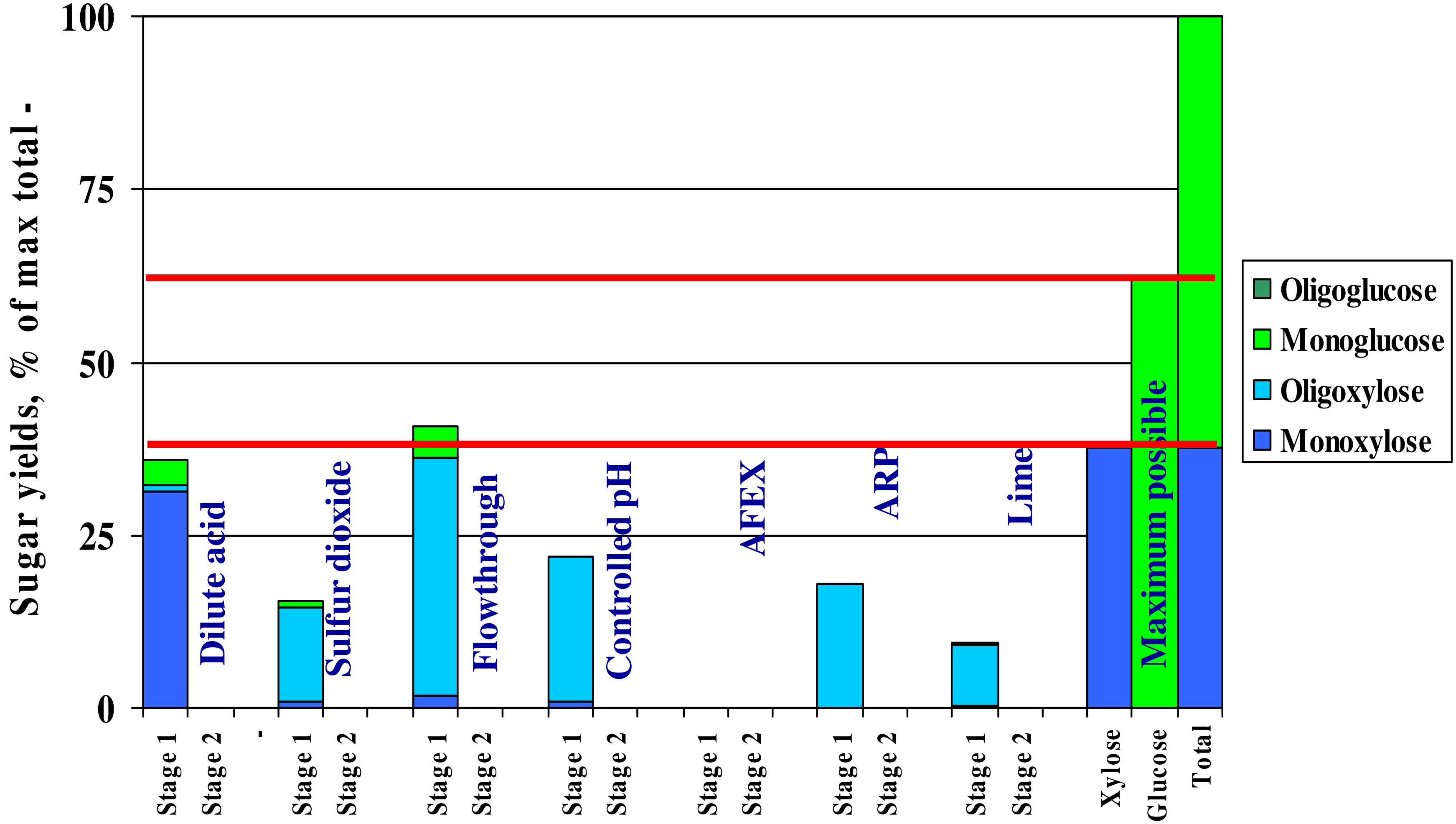
Sugar Yields from Corn Stover at 15 FPU/g Glucan



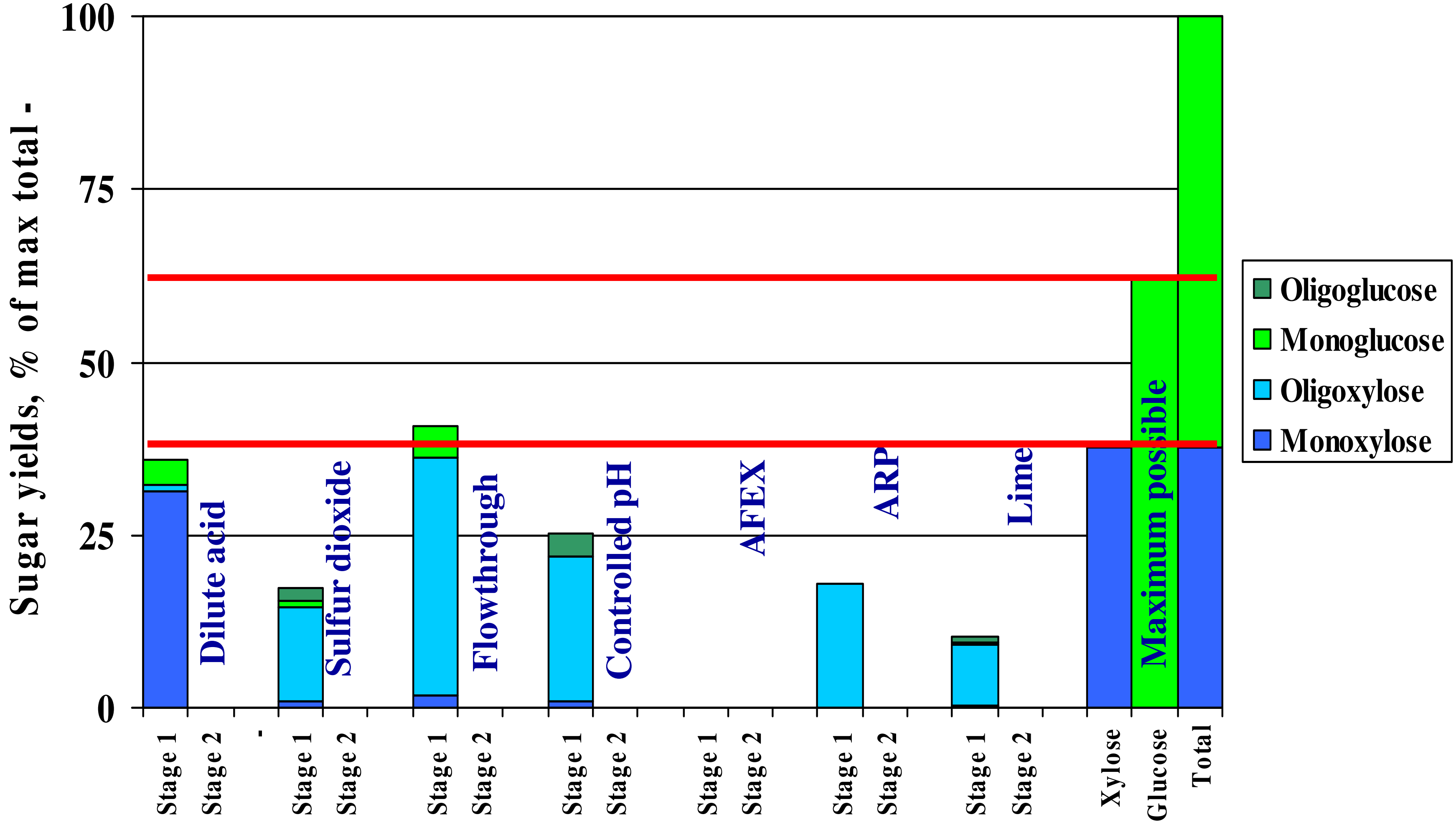
Sugar Yields from Corn Stover at 15 FPU/g Glucan



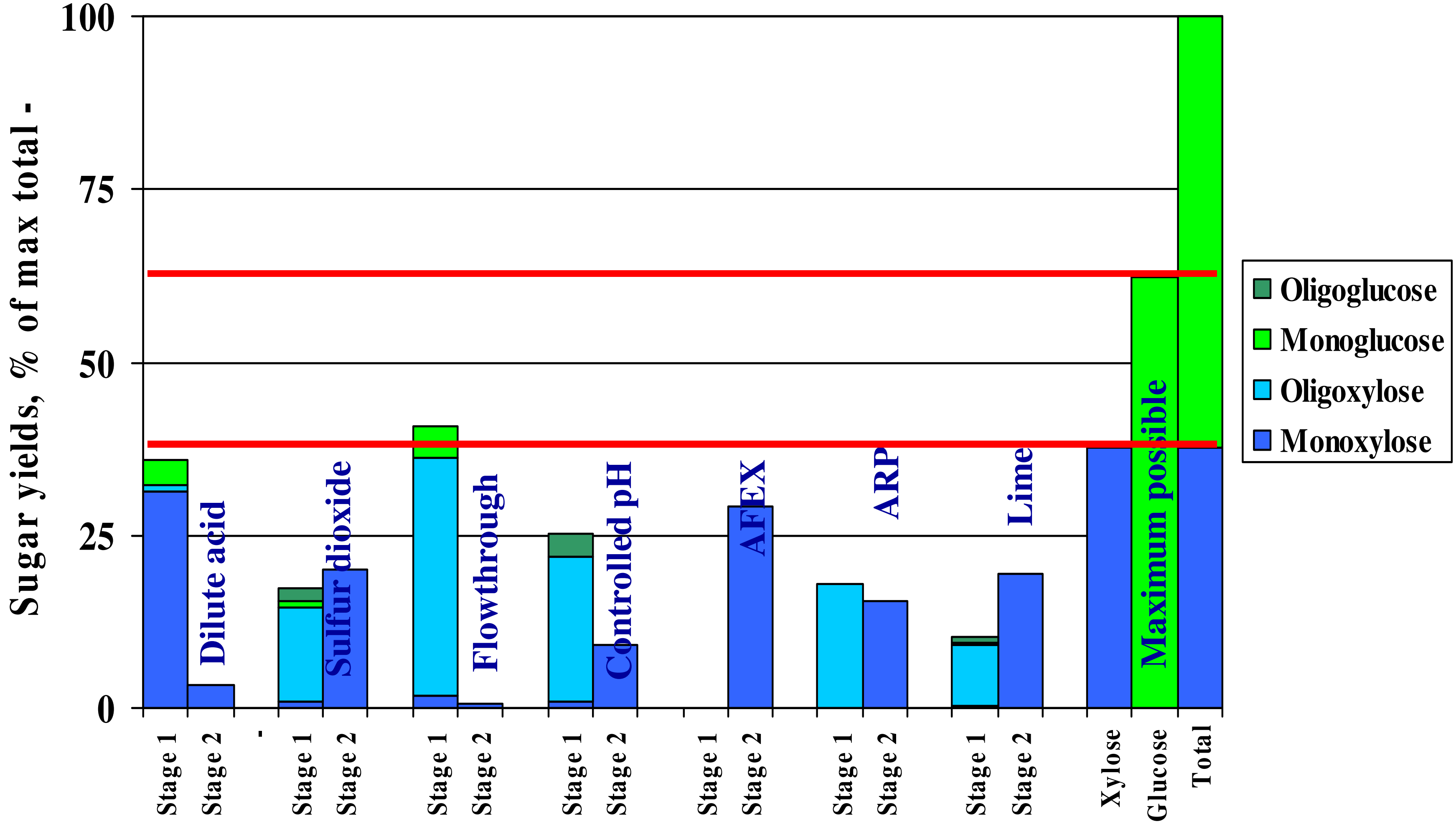
Sugar Yields from Corn Stover at 15 FPU/g Glucan



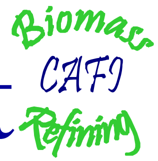
Sugar Yields from Corn Stover at 15 FPU/g Glucan

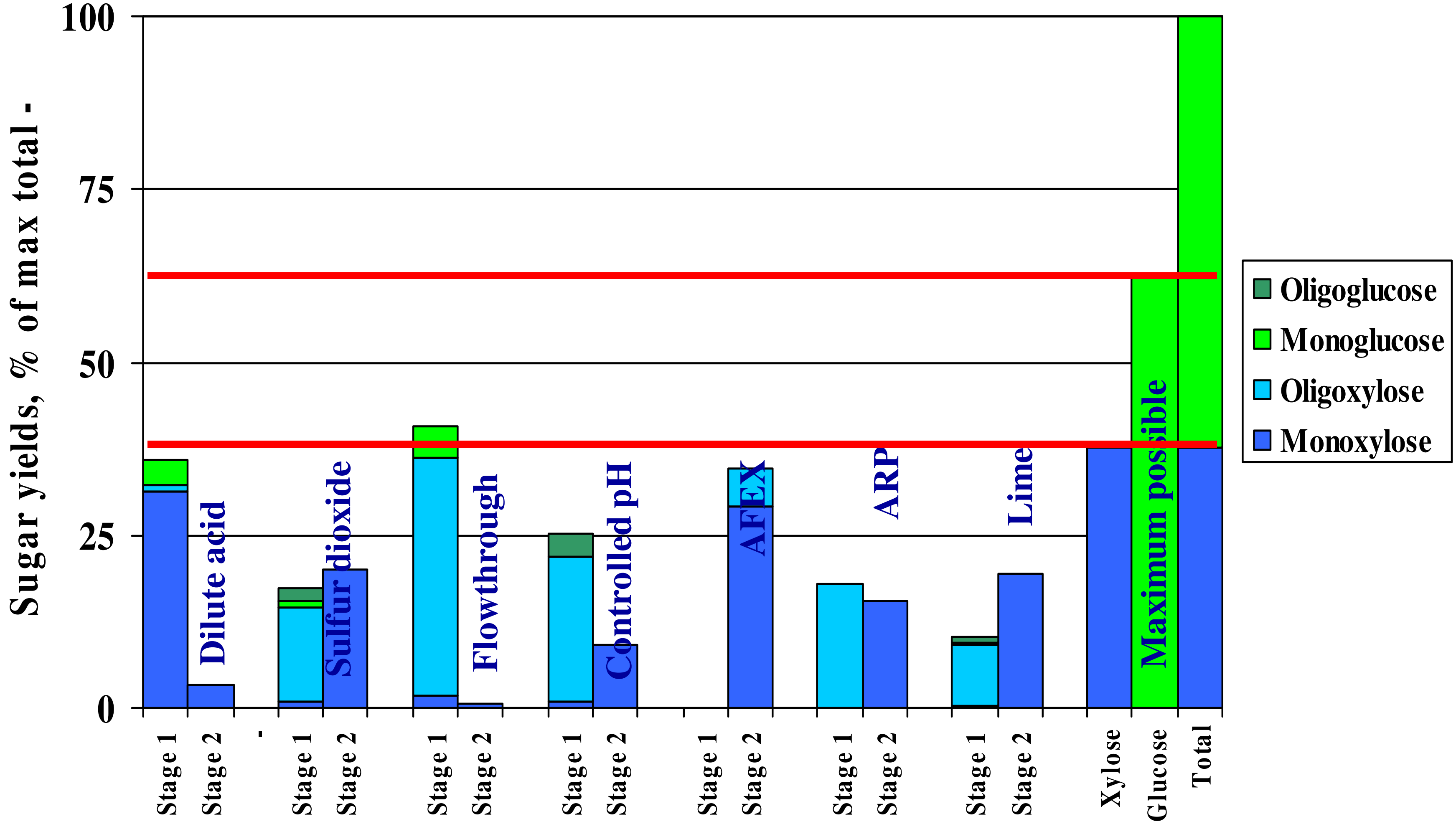


Sugar Yields from Corn Stover at 15 FPU/g Glucan

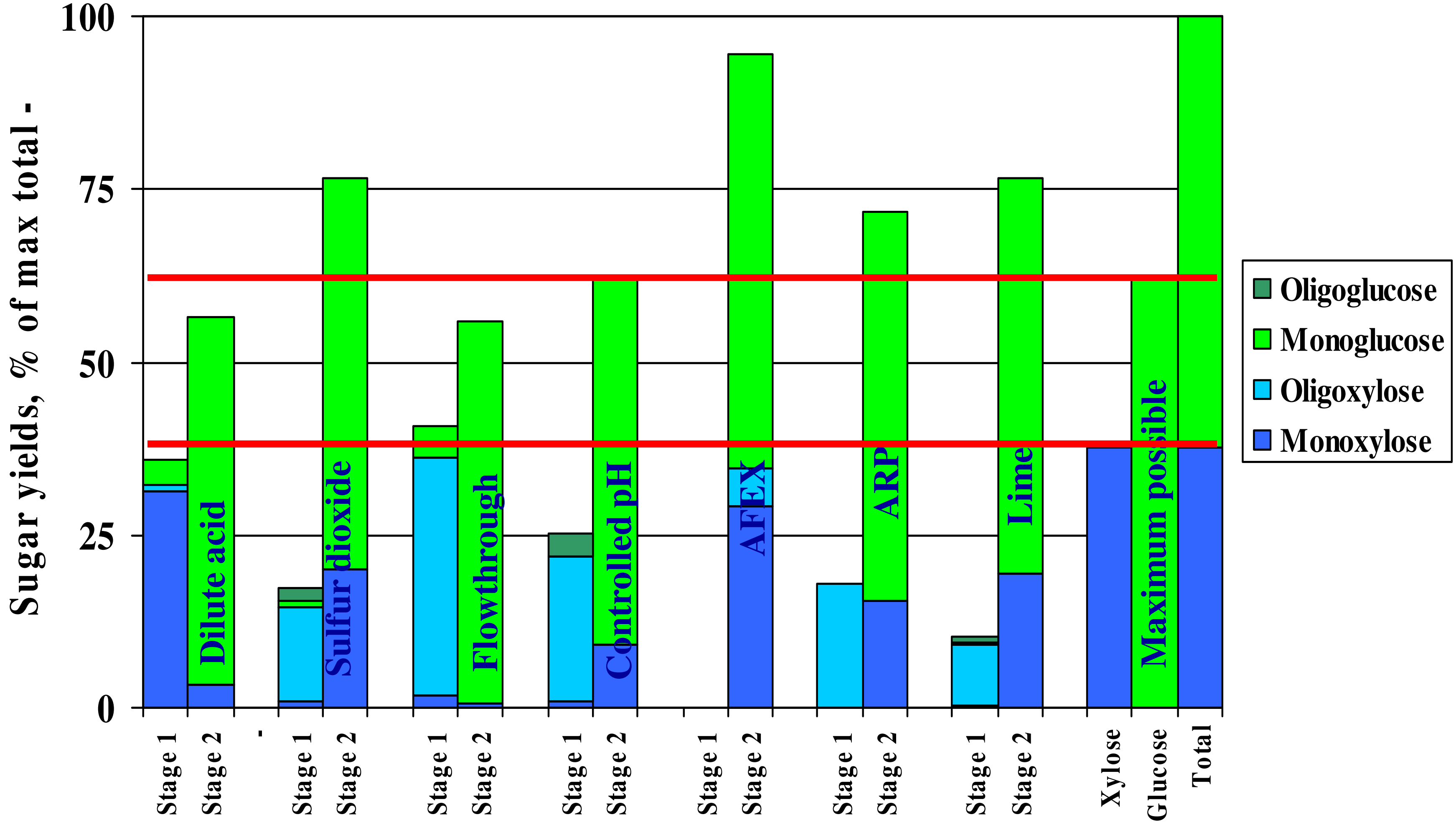


Sugar Yields from Corn Stover at 15 FPU/g Glucan

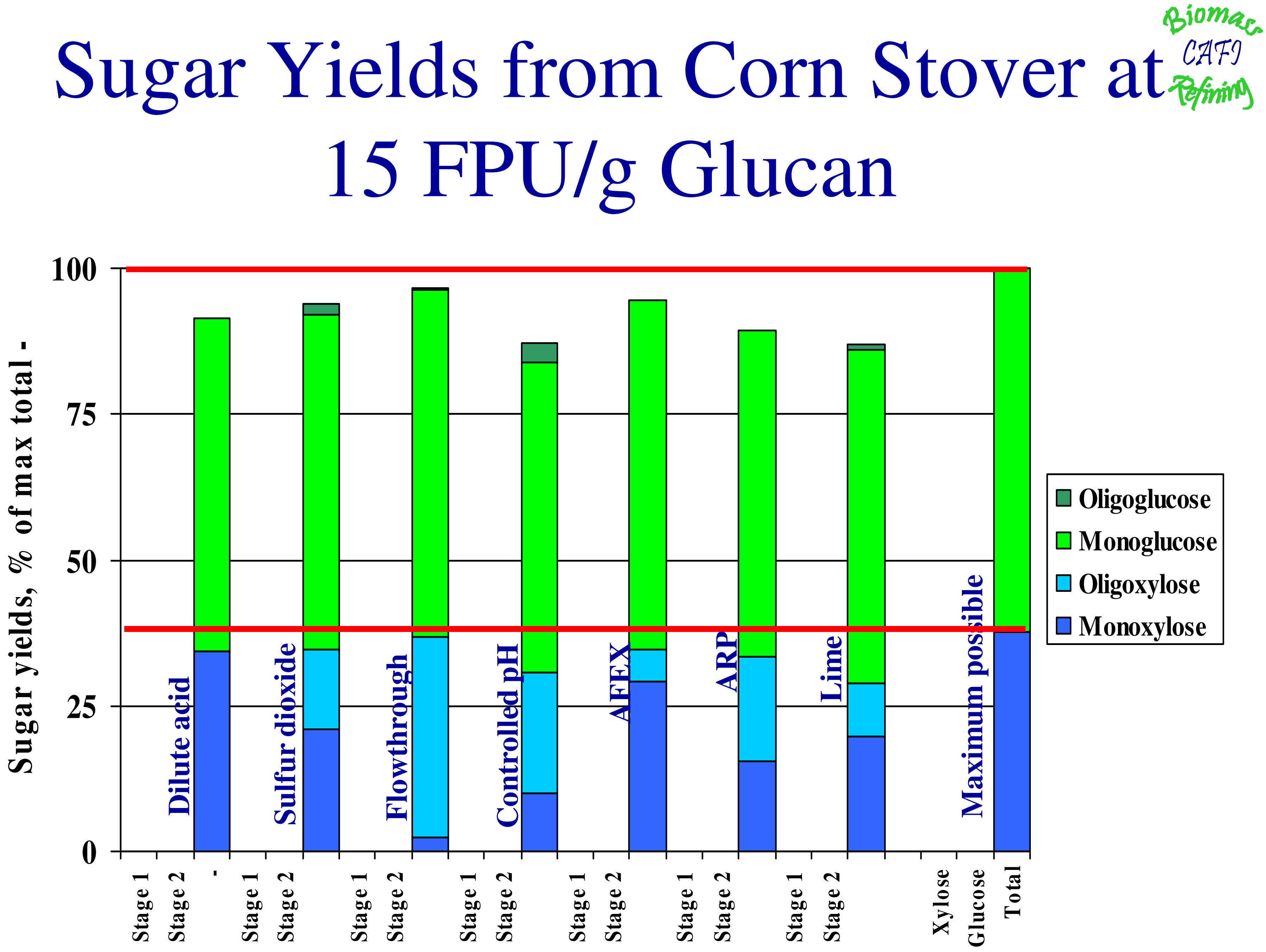




Sugar Yields from Corn Stover at 15 FPU/g Glucan



Sugar Yields from Corn Stover at 15 FPU/g Glucan



Process Considerations

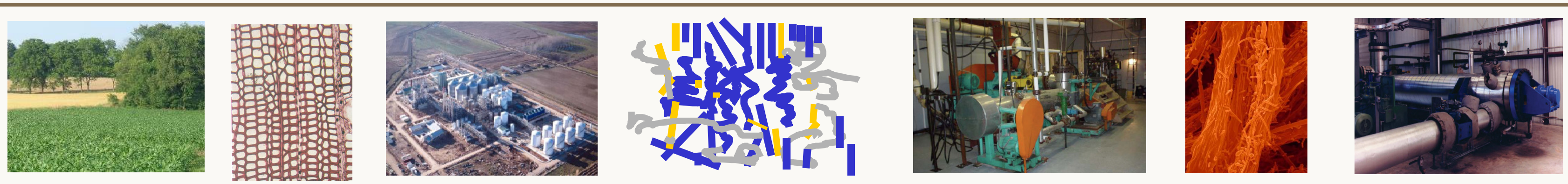
1. Process Integration – how pretreatment streams integrated into production process

2. Yield (outlined above) -> gallons of ethanol per ton biomass

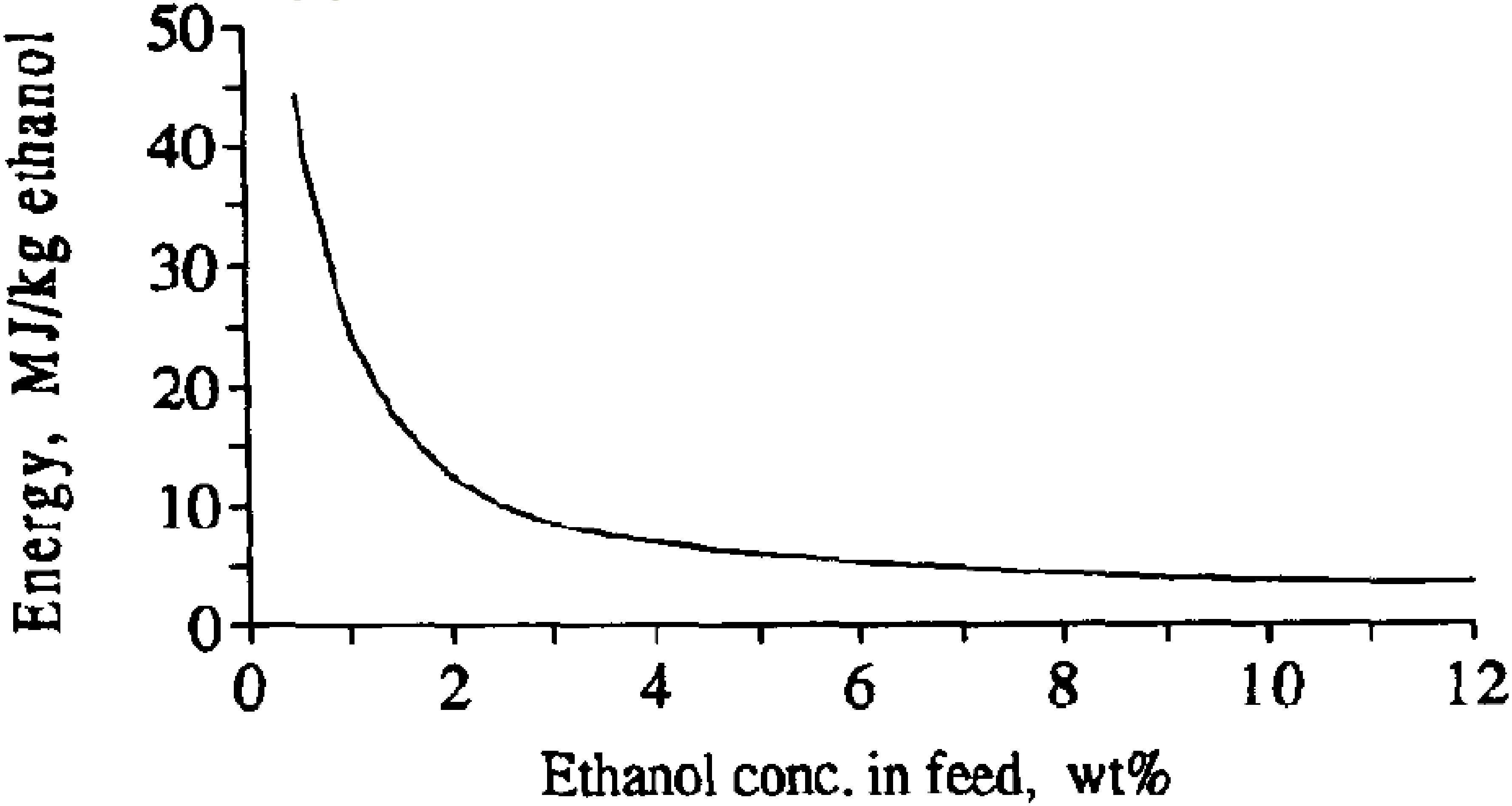
3. Energy -> $ per gallon of ethanol

Higher yield is better

Lower cost is better

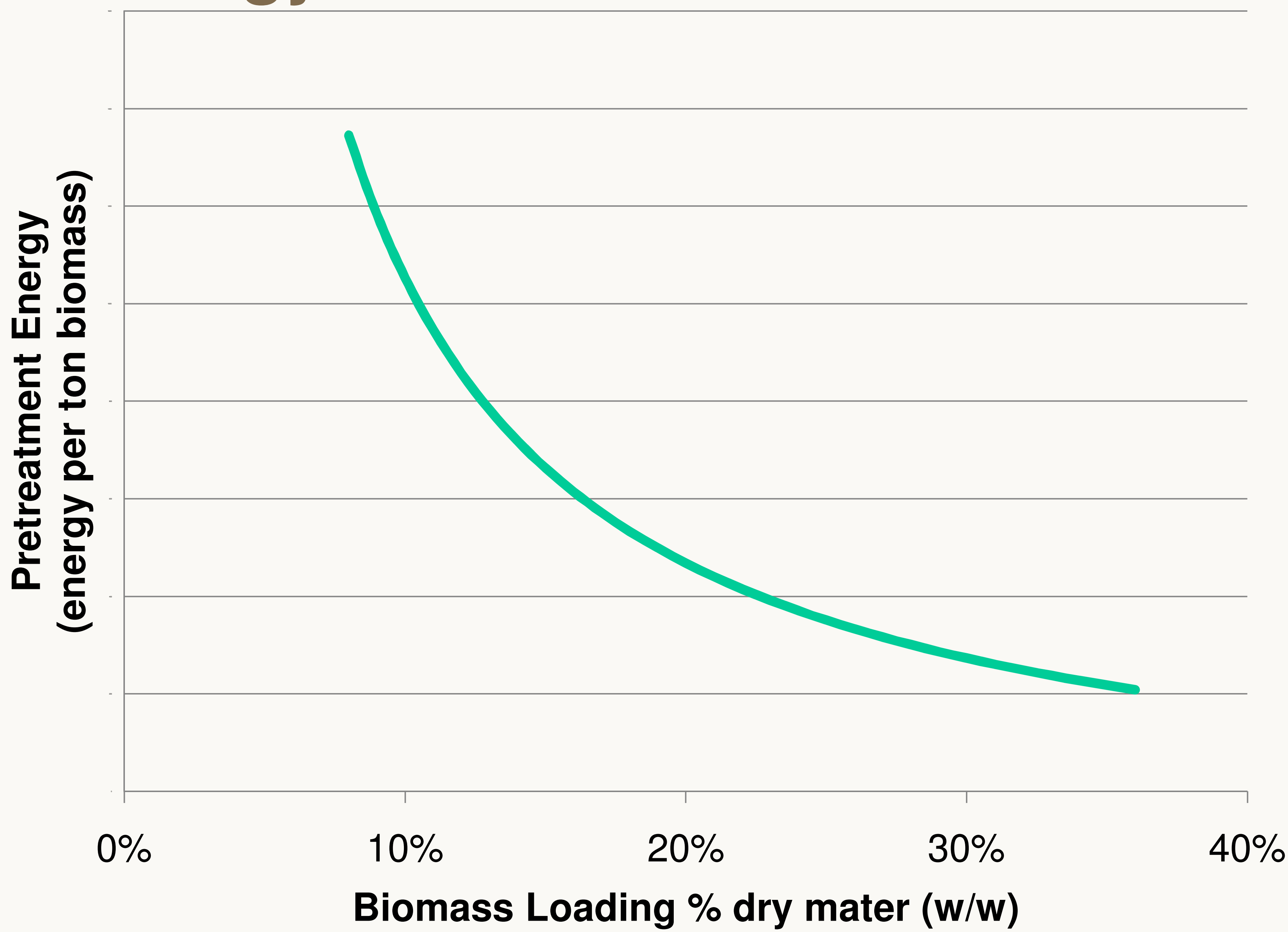


Energy for Distillation



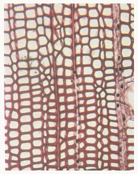
Galbe, M., Sassner, P., Wingren, A., Zacchi, G. (2007). Process engineering economics of bioethanol production. Biofuels. Berlin, Springer-Verlag Berlin. **108:** 303-327.

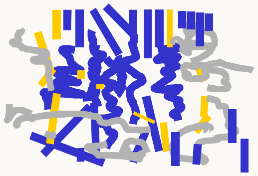
Energy for Pretreatment

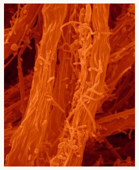


Practical Fuel Ethanol Production

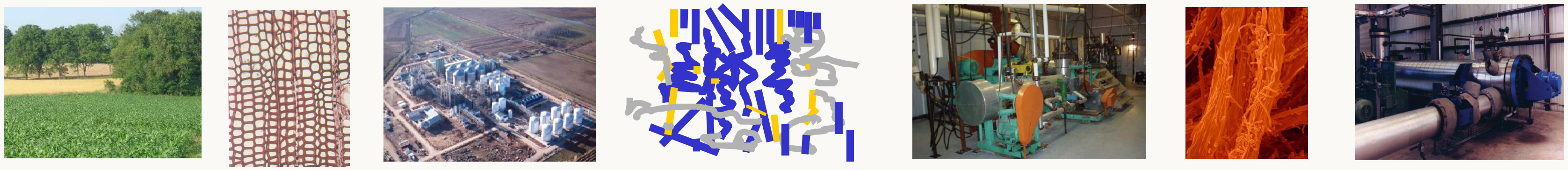
- At least 6% (w/v) ethanol
- Means: 13% (w/v) sugars (90% yield)
- Requires: 30 – 40% (w/v) feedstock in water
  - (300 – 400 g/L)






Pretreated DG – Effect of Solids Loading



Pretreated DG – Effect of Enzymatic Hydrolysis (1.5 hrs)

Liquefaction by enzyme hydrolysis

No additional liquid added


Corn
Fiber
After 4 days of enzyme
treatment
(20 FPU/gram dry fiber)

Pretreated Corn Fiber

160°C, 20 min.

After 1 day of enzyme treatment

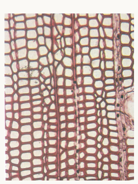
(20 FPU/gram dry fiber)

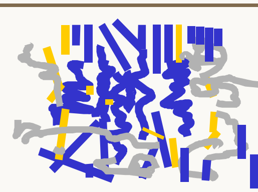
Sugar Yields: 24 hr Hydrolysis with Cellulase

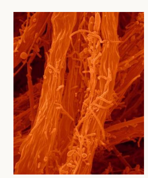
24 Hours of Hydrolysis by 15 FPU/g glucan in DG Cellulase + 40 IU/g glucan β-glucosidase

Sugar (g/L)	15% Solids	20% Solids	30% Solids
Glucose (g/L)	26.0	32.8	42.2
(% yield)	68%	71%	73%
Xylose (g/L)	4.5	5.8	2.8
(% yield)	19%	19%	19%

% yield includes polysaccharides from both DG and stillage

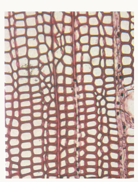



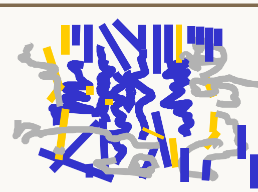


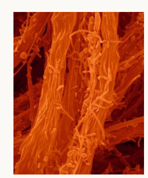



Viscosity

- Must be able to move (pump) slurry between unit operations
- Must be able to effectively mix slurry during processing (especially hydrolysis and fermentation)
- Energy for pumping and mixing should be minimized

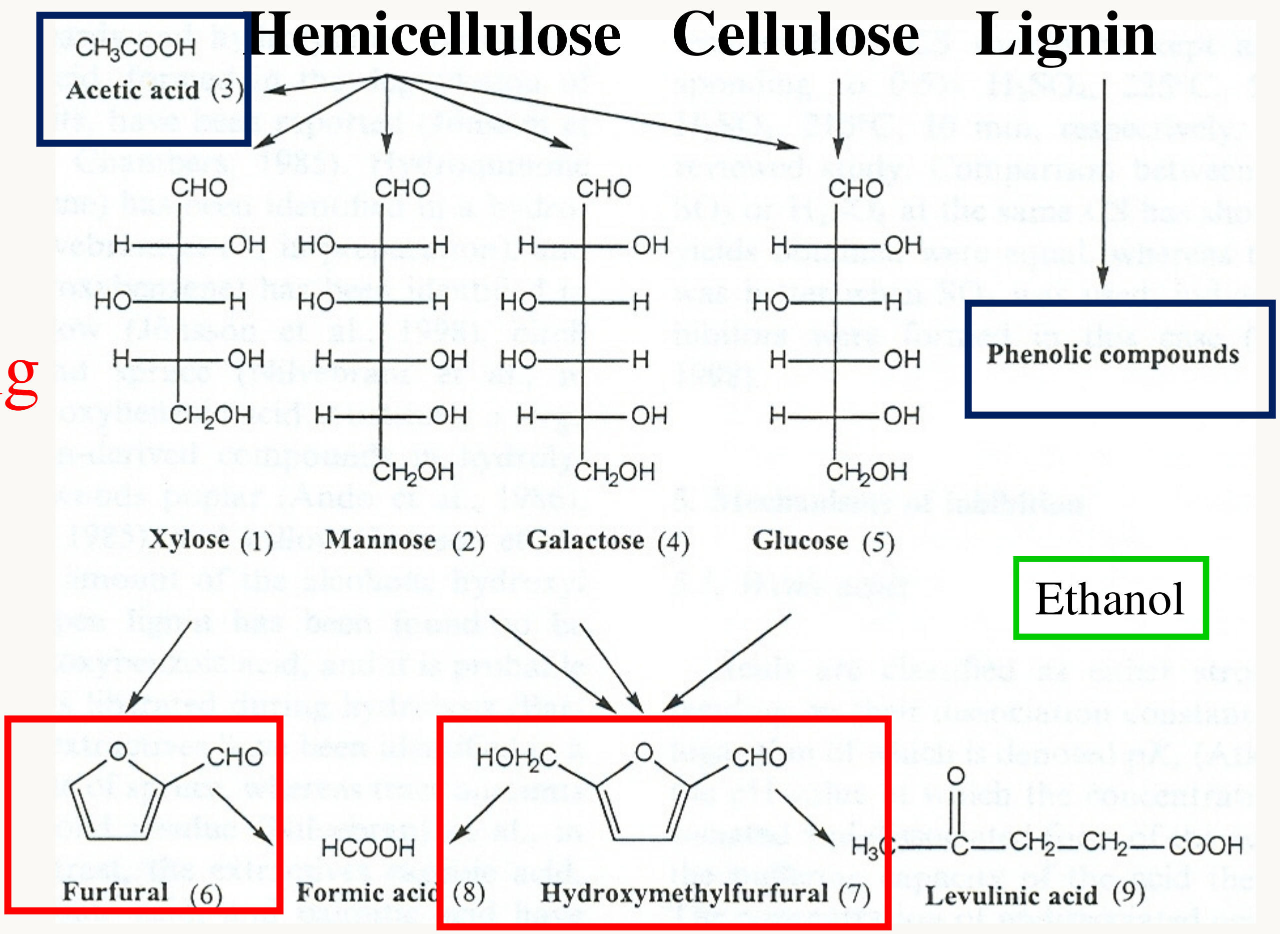








Sources of Inhibitors to Biocatalyts

Biomass
Pre-processing
Fermentation



Adapted from
Palmqvist *et al*. Bioresource Technology 74:25-33 (2000)

Wet (ensiled) storage

- Low pH for long term storage
- Reduced dry matter losses
- Platform for biological pretreatment
- But – increased organic acids…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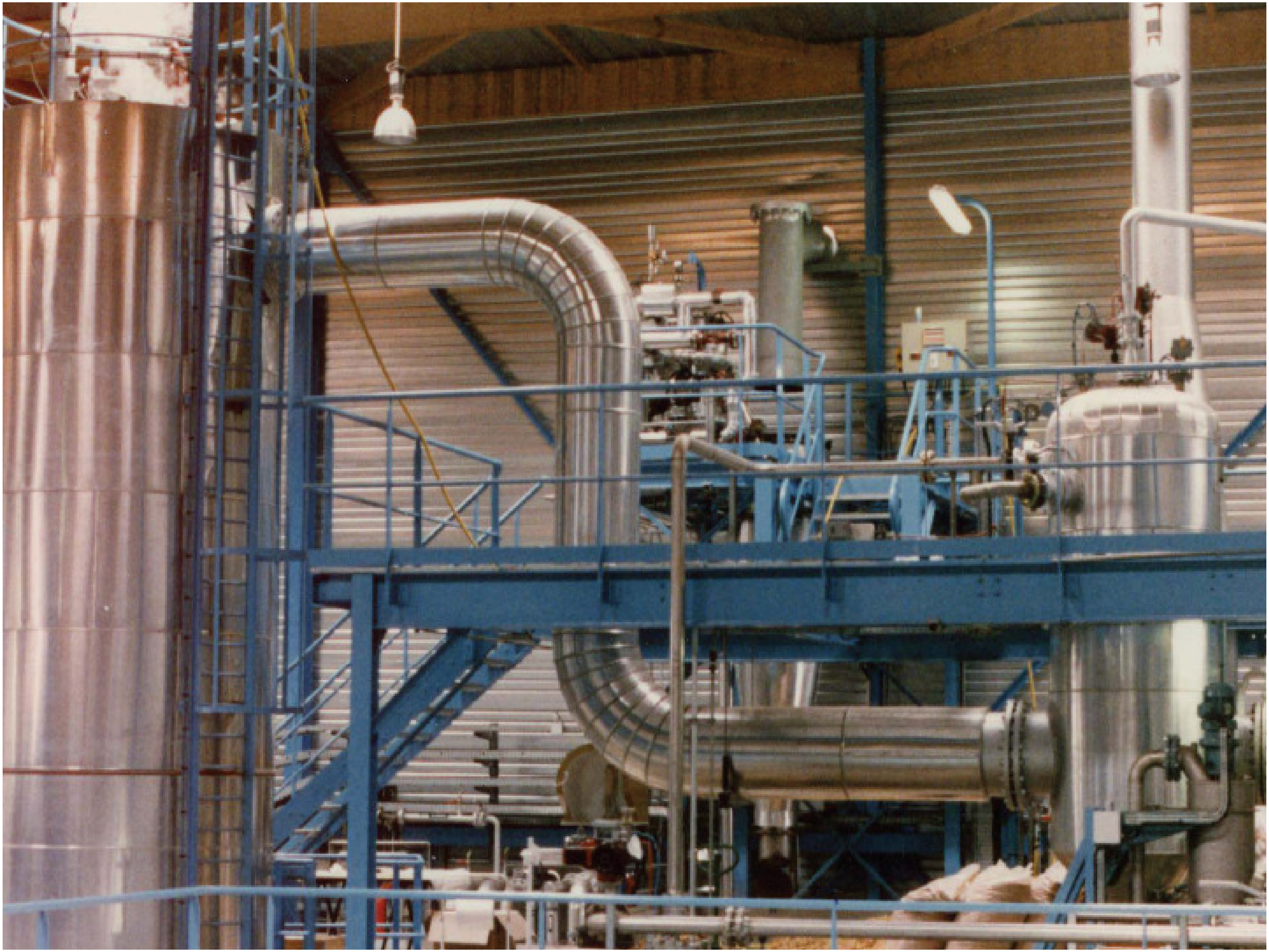
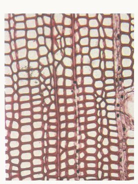
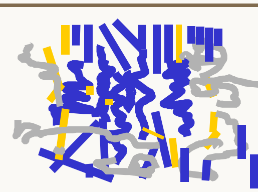
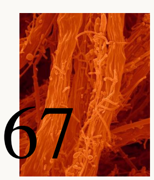


Pretreatment Needs

- Liquid hot water-like technology
- Limited chemical use
- Reduced milling: Use chips not sawdust
- Low cost materials of construction
- High hemicellulose yields
- High yields of glucose from cellulose
- Robust performance with multiple feedstocks

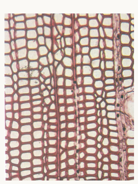



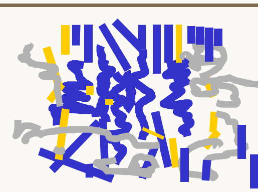


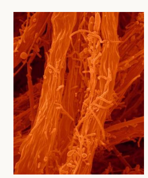



Conclusions

- Pretreatment keystone technology for biological route to biofuels
- Pretreatment enhances rate and yield of sugar release from lignocellulosic biomass
- Pretreatment is thermochemical process that fractionates and/or alters physiochemical structure of biomass
- Pretreatment technologies employ wide array of solvents/catalysts
- Process integration key to evaluating pretreatment technology for commercial application






Questions