The Ammonia Fiber Expansion (AFEX™) Process: Fundamental Insights, Commercialization & Developing Sustainable Biofuel Systems

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DOE Bioenergy Research Centers

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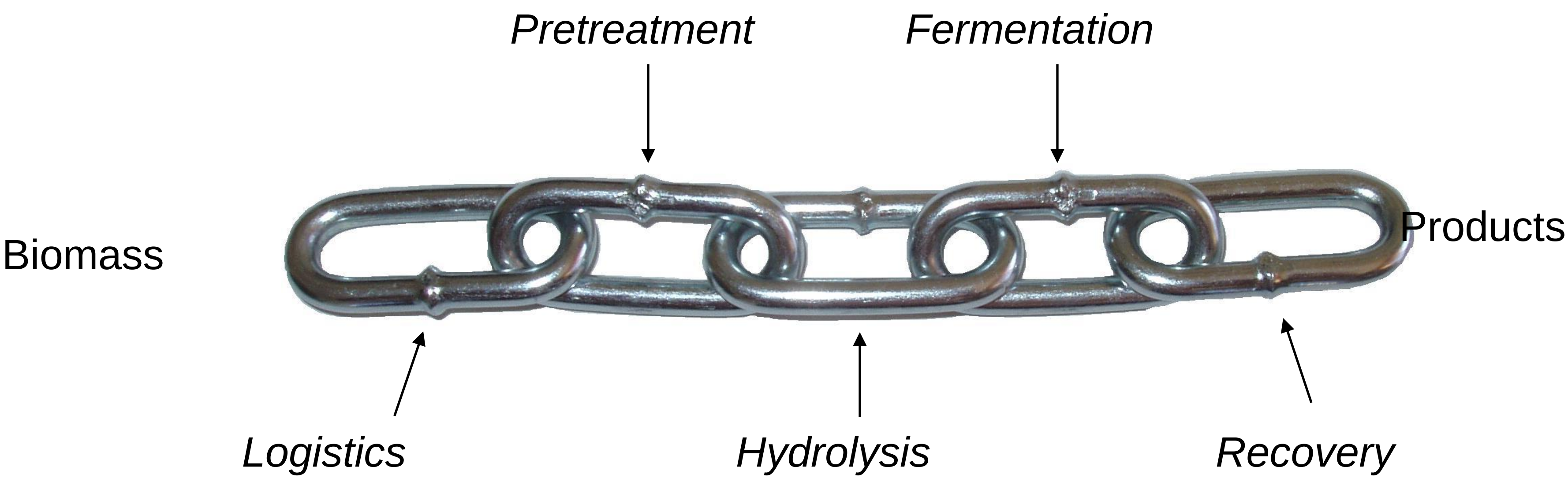
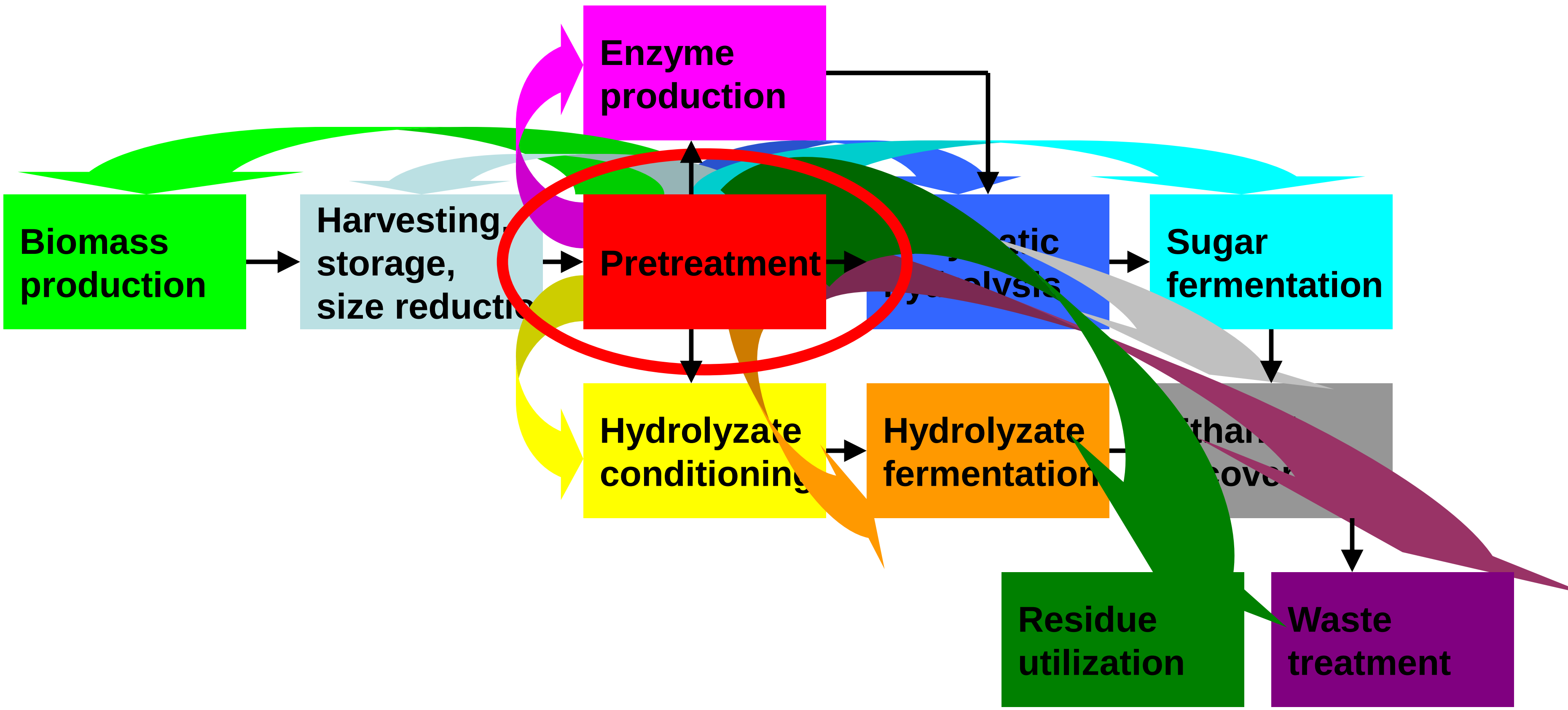
Biomass Processing Chain



Central Role and Pervasive Impact of Pretreatment for Biological Processing

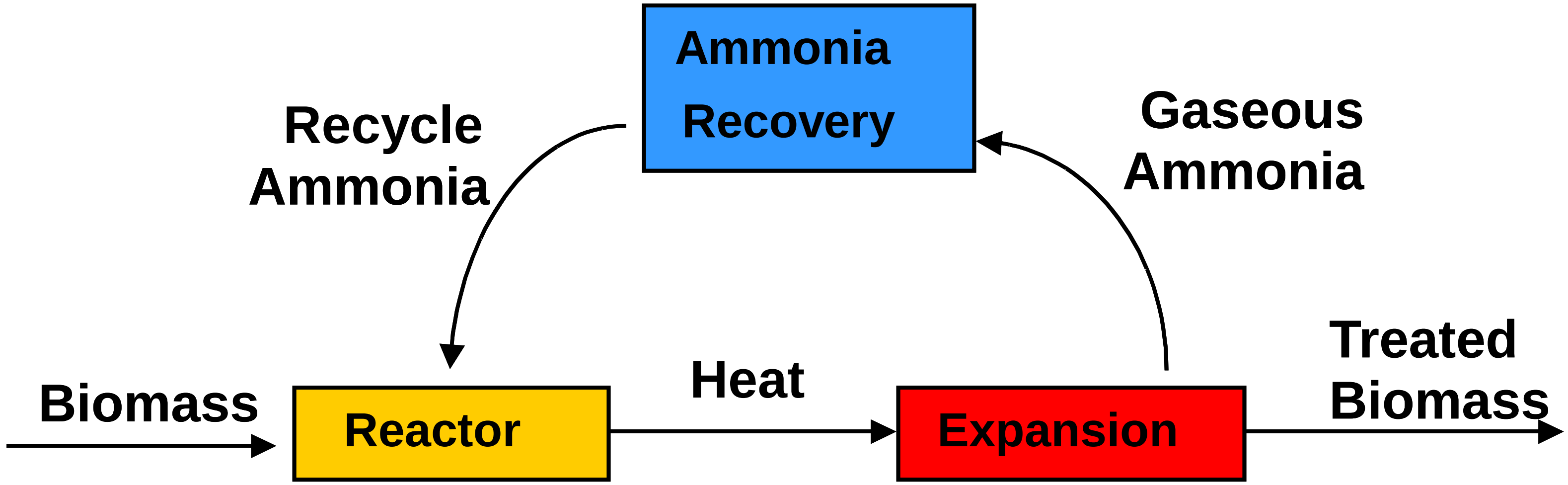


Yang and Wyman, 2008

Importance of Pretreatment- Dr. Charlie Wyman (mostly)

- Although significant, feedstock costs are low relative to petroleum: $60/dry ton ~ $20/bbl oil
- 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*
  - <u>Low yields</u> without pretreatment drive up all other costs more than amount saved
  - Conversely, enhancing yields via improved pretreatment would reduce all other unit costs
- *We need to reduce **overall** pretreatment costs to be competitive with petroleum fuels—and **we need low cost processes generally***
- Also reduce the “hidden” costs of pretreatment
  - Inhibitors produced, difficult to control wastes generated, **loss of intrinsic nutrients in biomass**, **water used**?
  - How does pretreatment fit (or not) with biomass logistics?

Conventional AFEX™ Process Overview



AFEX™ process description and properties

- hot, concentrated (~15M) ammonia:water mix, short reaction time
- rapid pressure release ends treatment, cools system
- little biomass degradation, high yields, residual ammonia value
- no separate liquid phase ("dry to dry")—very high solids loadings possible
- no loss of nutrients in wash stream
- Typical process conditions
    - Pressure 20-30 atm, Temperature 70-140 C, Holding time ~15 minutes
    - Ammonia: dry biomass loading (0.3 -2.0 to 1) (w/w)
    - Water: dry biomass content (0.2 – 2.5 to 1) (w/w)

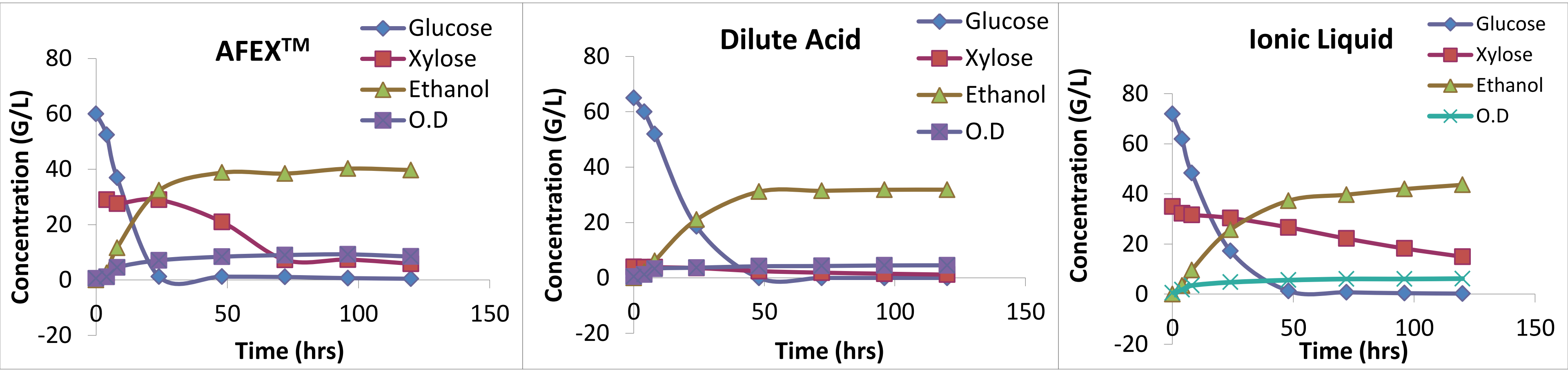
•*AFEX is a trademark of MBI International*

Water Used & Solids Solubilized for Several Pretreatments

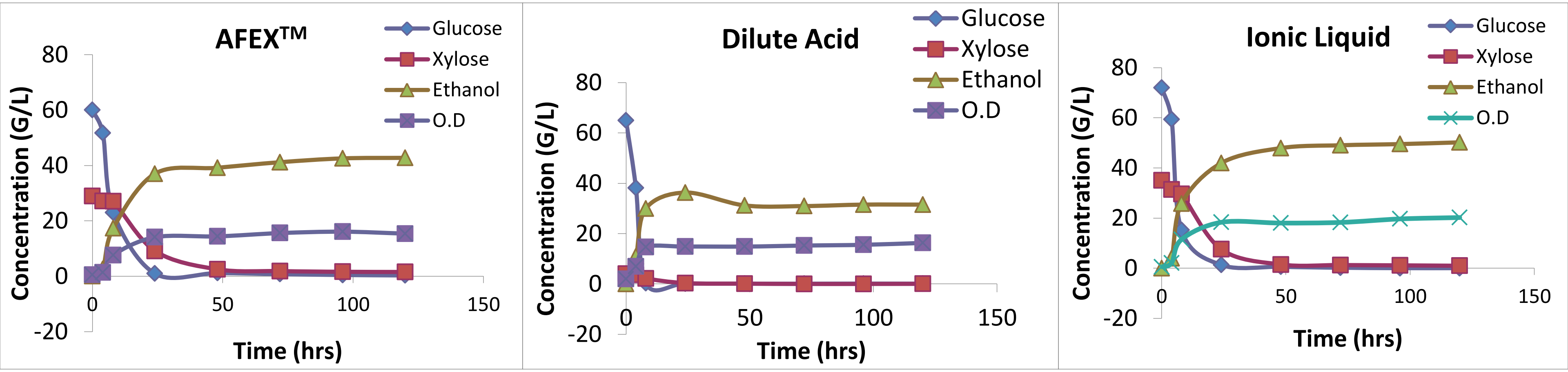
Pretreatment	Water:Solids Ratio	Typical % Solids Solubilized
Dilute acid	>5	~45
Ionic liquids	>30	~45
Controlled pH	6.2	~40
AFEX	0.6	~10
ARP	>5	~40
Lime	>5	~25

Fermentation – Without/with Nutrient Supplementation

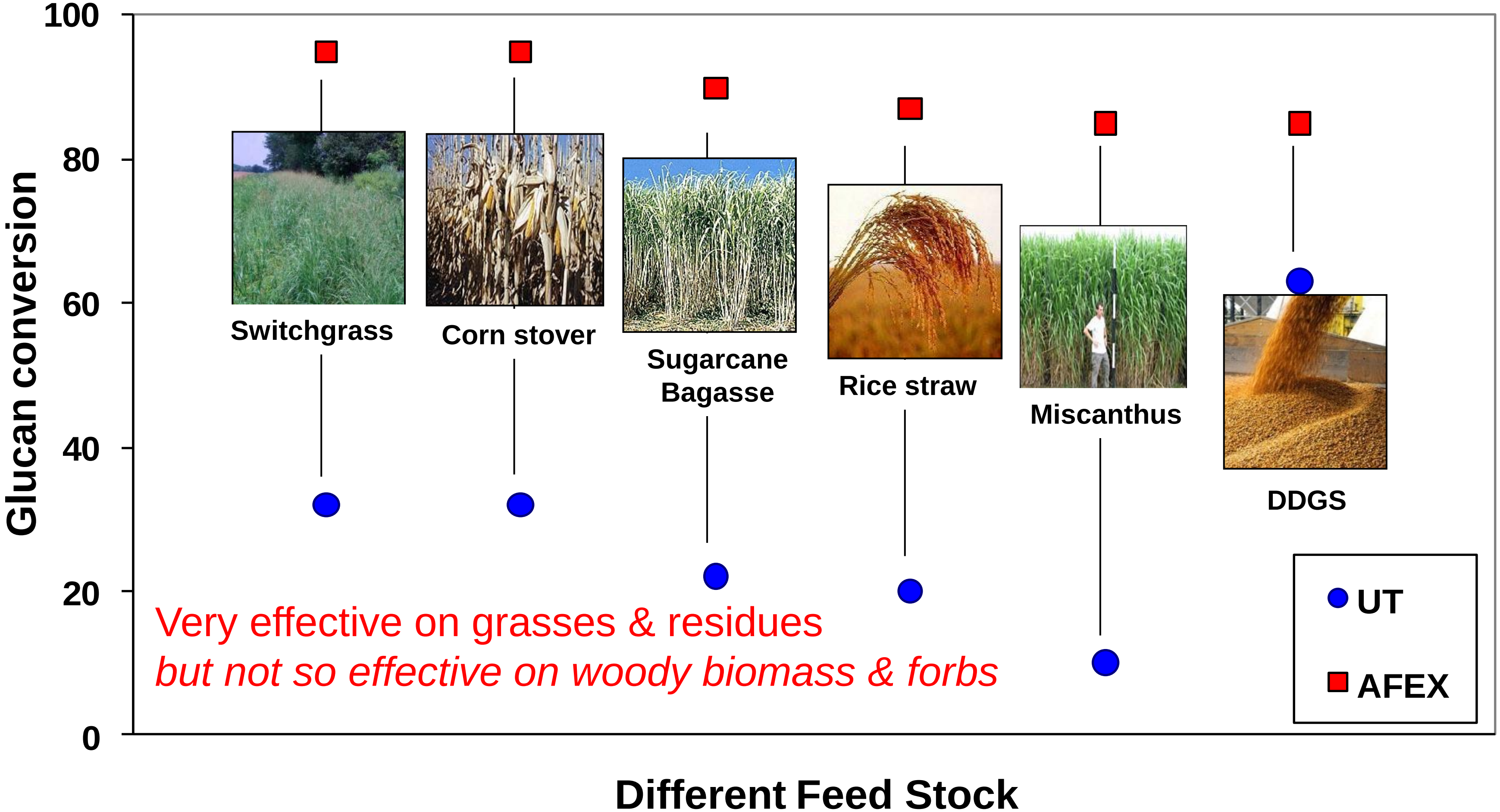
Without Nutrition



With Nutrition

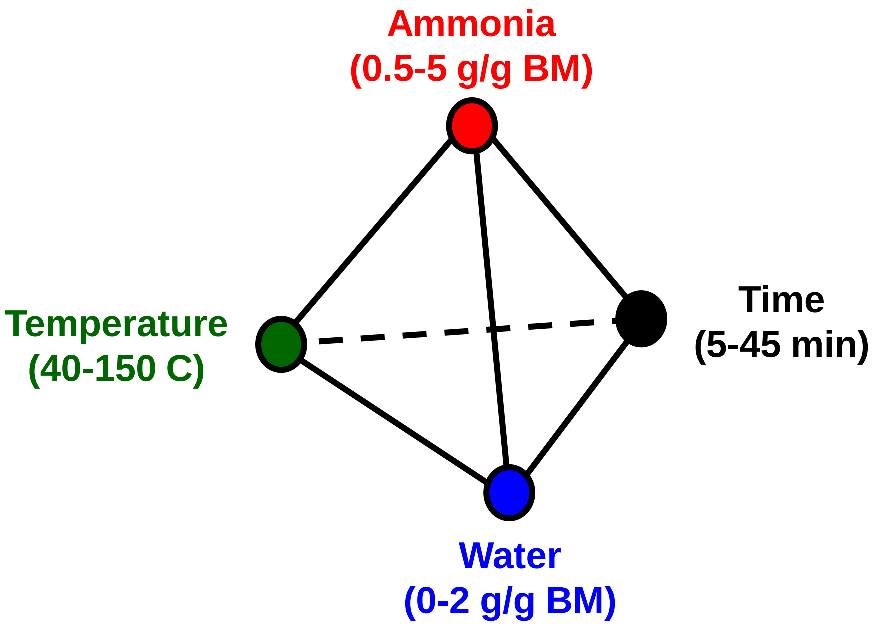


Biomass Conversion for Different Feedstocks Before and After AFEX™ Pretreatment

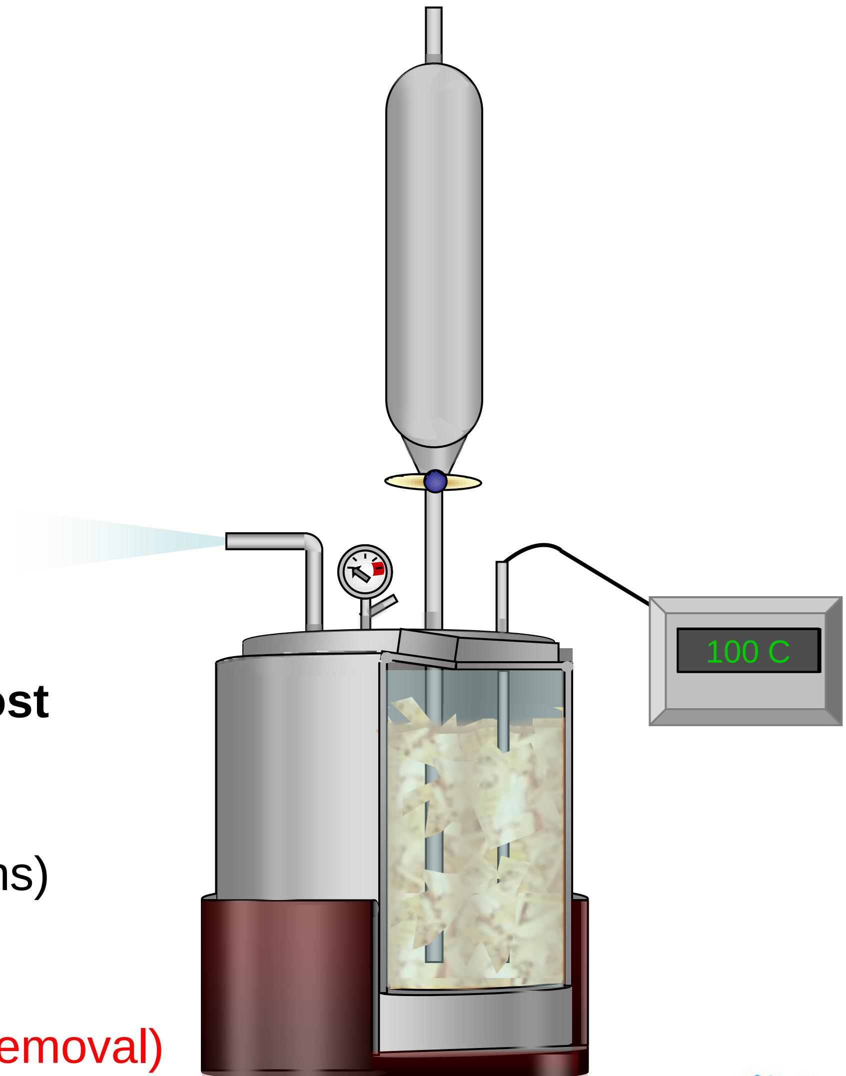


Enzymatic hydrolysis: 25 mg of Cellulase and 2.5 mg of xylanase/g of glucan, 50 °C, for 168h. About 70% xylan conversion achieved for most feedstocks.

Parameter Space (thru IP) of the AFEX Process



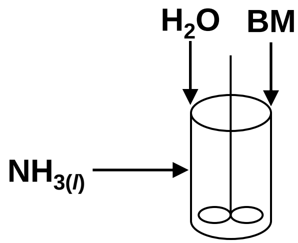
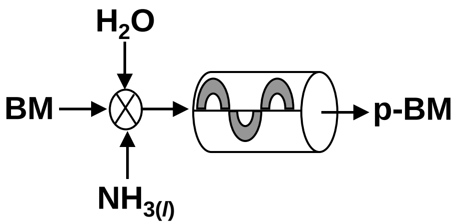
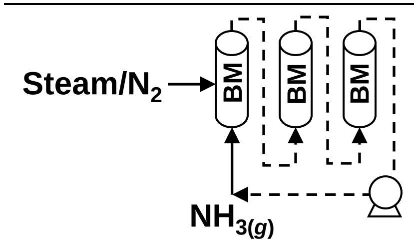
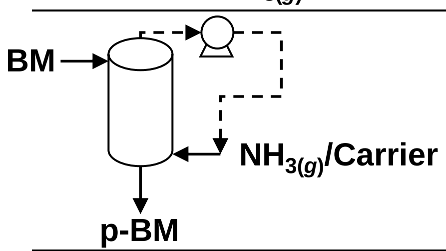
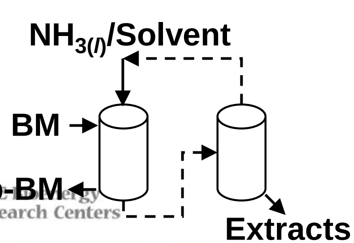
Ammonia Fiber Expansion



Comparison of AFEX with other Pretreatments:

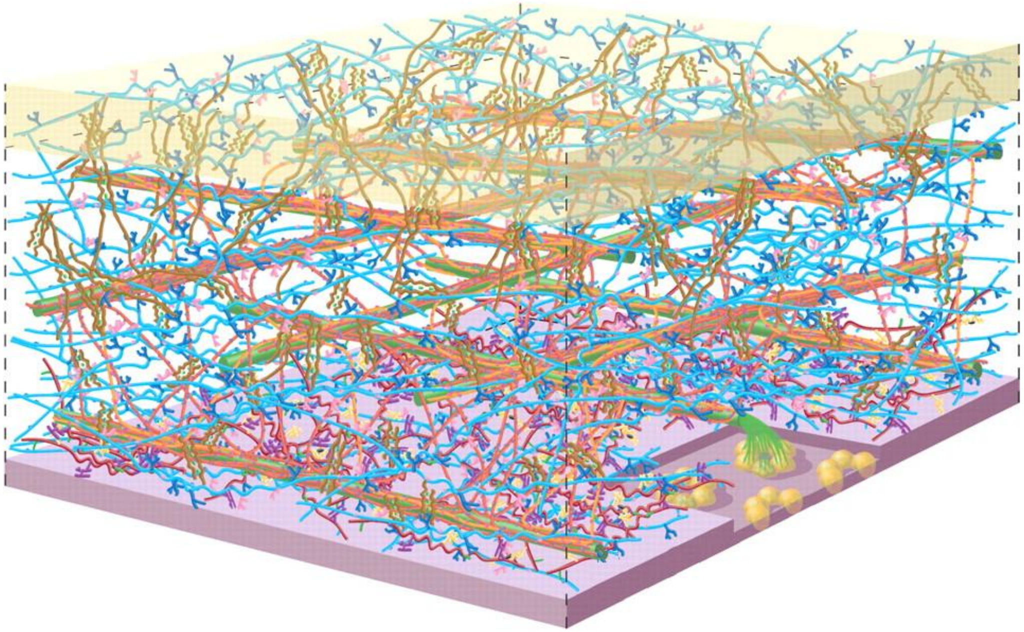
- High Catalyst Recovery (>98%)— **also the most costly AFEX process step**
- Minimal Water Usage (3-20 fold lower)
- Minimal Biological Inhibitors Formed (e.g. furans)
- Multiple Products (e.g. animal feed)
- Potential for Distributed Processing
- Further Improvements,e.g. cellulose III, lignin removal)

Different Ways of Carrying out the AFEX process

Pretreatment	Ammonia Recovery	AFEX classification
	$NH_{3(g)}$ & H_2O removed under hood after pretreatment with no recovery attempted	Batch AFEX: Lab scale Lower ammonia loadings "conventional" Water tolerant
	$NH_{3(l)}$ & H_2O recovery using flash tank, dryers and condensers	Plug flow AFEX
	$NH_{3(g)}$ recovery using steam/N_2 stripping and moist biomass	Packed bed AFEX: Very Low Cost Design Lower ammonia loadings "conventional" Water tolerant
	$NH_{3(g)}$ separation from biomass using cyclones Optional carrier gas includes steam, N_2	Fluidized gaseous AFEX
	$NH_{3(l)}$ is reused multiple cycles in liquid state Optional solvent includes water, acetone	Extractive AFEX- High Ammonia- Low Water tolerance

Part 1

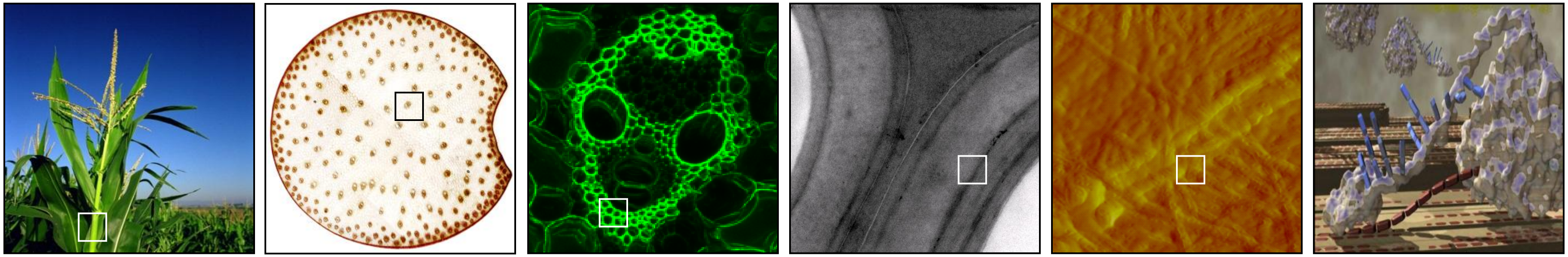
Overcoming Cell Wall Accessibility



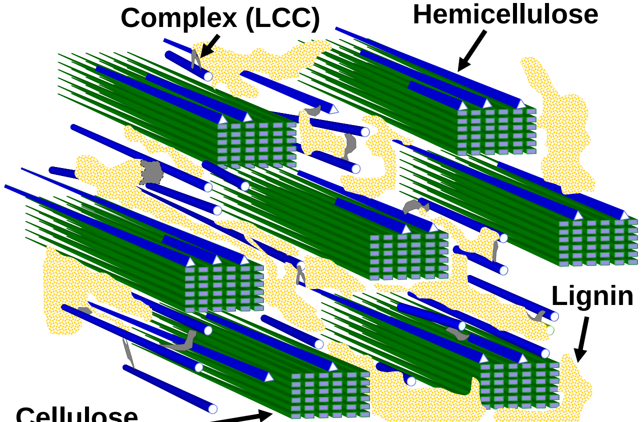
Somerville et al. 2004. Science 306 (5705):2206

Plant cell wall recalcitrance is a multi-scale issue

10^0 meters → 10^{-9} meters



Lignocellulosic Corn Plant*	Corn Stem Cross-section*	Vascular Bundle	Cell Walls	Cellulose Microfibrils	Cellulase acting on glucan chains*
• species heterogeneity • environmental effects • low bulk density • harvest time	• tissue heterogeneity • mass transport issue • milling issues • waxy rind	• cell heterogeneity • cell density	• lamellar organization • wall heterogeneity • wall thickness • pit density	• xylan cross-linking • LCC sheathing • lignification	• heterogeneous catalysis • crystalline cellulose I_β • nonproductive binding • enzyme denaturation • low mol wt. inhibitors



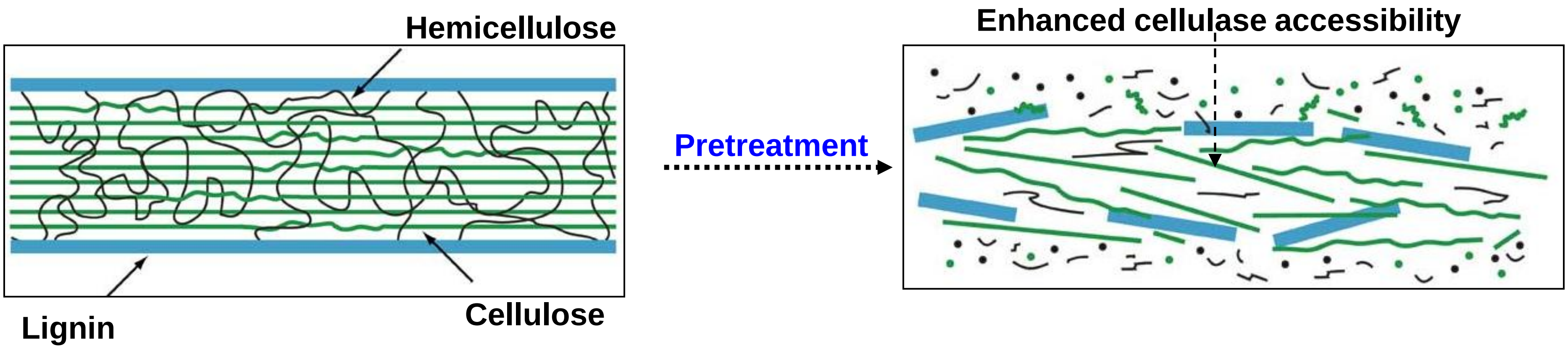
Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984

Barriers to plant cell wall deconstruction:

- Lignin – Accessibility, Binding, Inhibitors
- Hemicellulose – Accessibility, LCC, Diversity
- Cellulose – Crystallinity

Increasing enzyme accessibility to embedded polysaccharides is a major bottleneck that needs to be overcome…

Chemical Pretreatments Overcome Recalcitrance Differently

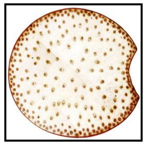


Pretreatment Catalyst	**Cellulose Crystallinity**	**% Cell Wall Solubilization**	**Inhibitors Produced**	**Overall digestibility**
Dilute Acid (BESC)	+	+++	+++	+++
Conventional AFEX* (GLBRC)	**-**	**-**	**+**	**+++**
Ionic Liquids (JBEI)	+++	++	++	+++

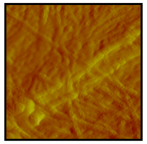
*AFEX (Ammonia Fiber Expansion)

Multi-faceted Characterization of AFEX

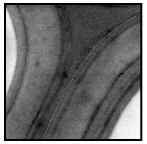
1. **Visualizing gross cell wall morphology**
   - Scanning Electron Microscopy
   - Confocal Fluorescence Microscopy



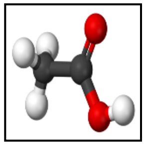
2. **Outer cell wall surface topography**
   - Atomic Force Microscopy
   - Transmission Electron Microscopy



3. **Ultra-structural modifications within cell walls**
   - 3D-Electron-Tomography
   - Immunolabeling
   - Raman Spectroscopy



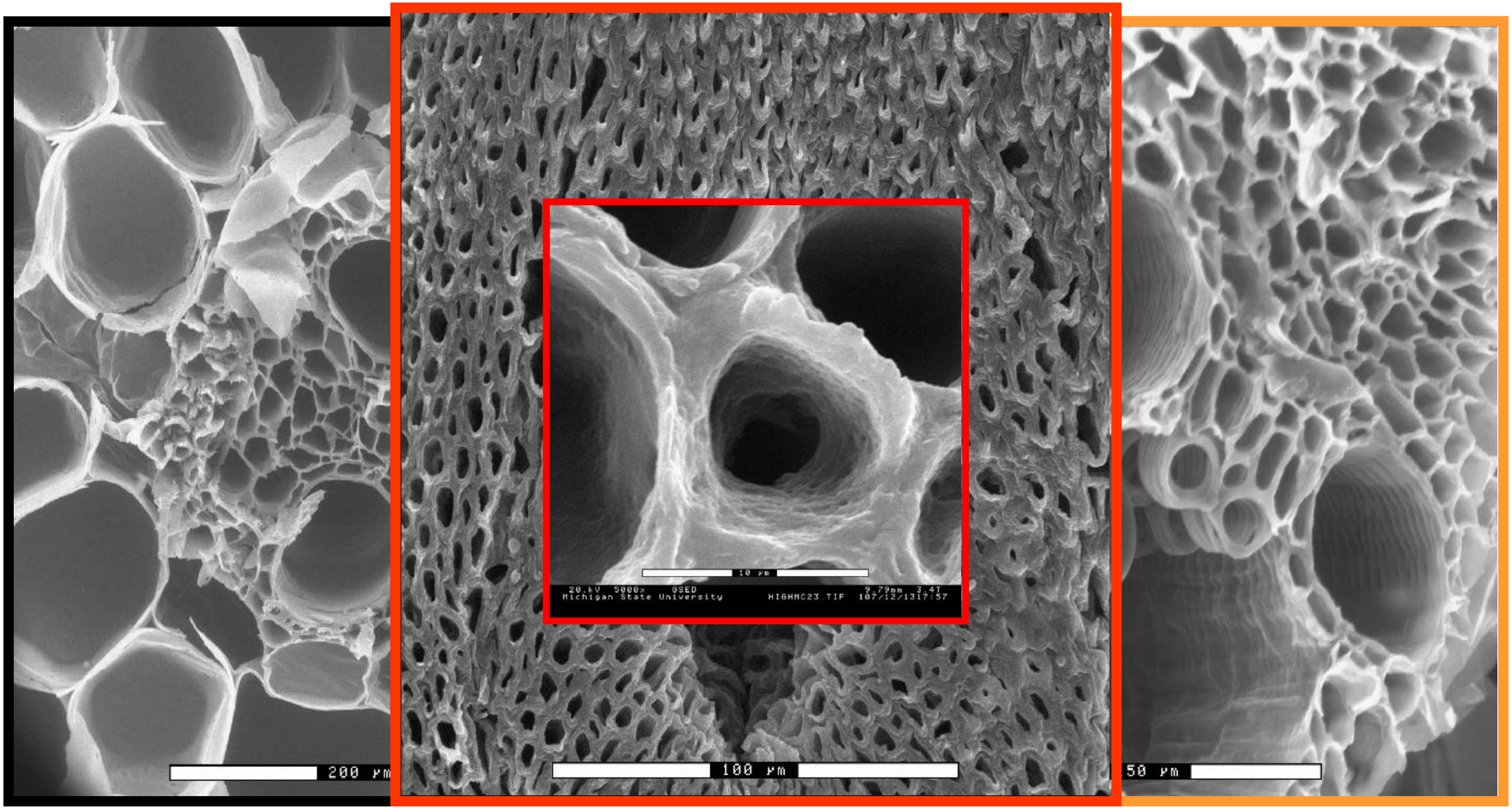
4. **Cell wall decomposition products analysis**
   - X-ray Photoelectron Spectroscopy
   - Mass Spectrometry
   - Nuclear Magnetic Resonance



Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984

Impact of Liquid Loading on Cell Wall Disruption

Untreated Corn Stover **Regular AFEX Corn Stover**

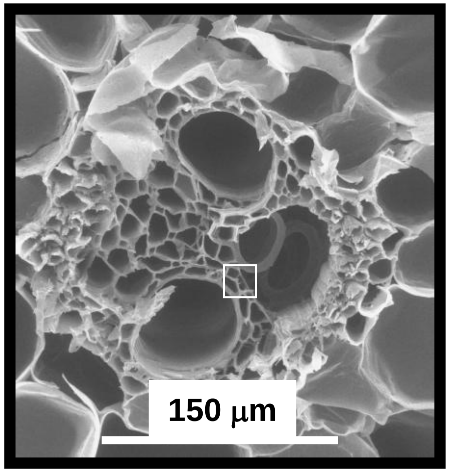


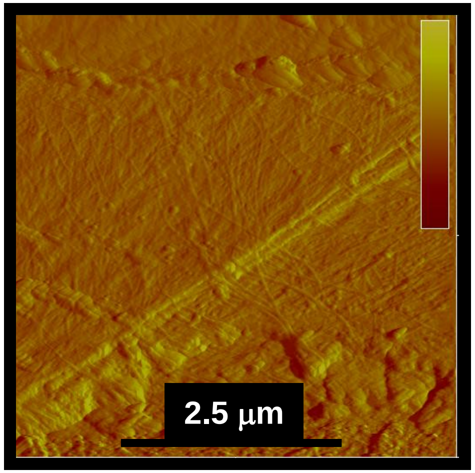
AFEX (High NH_3/H_2O) Corn Stover

Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984

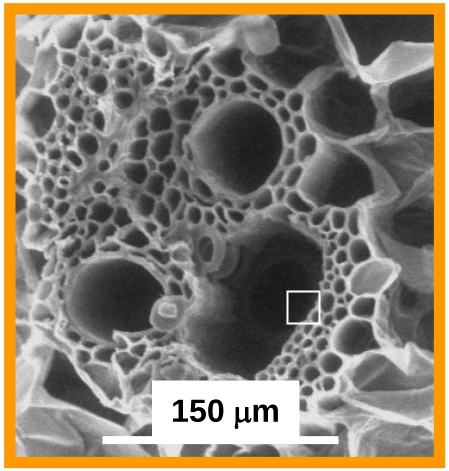
Nano-sized Deposits on Outer Wall Surfaces after AFEX

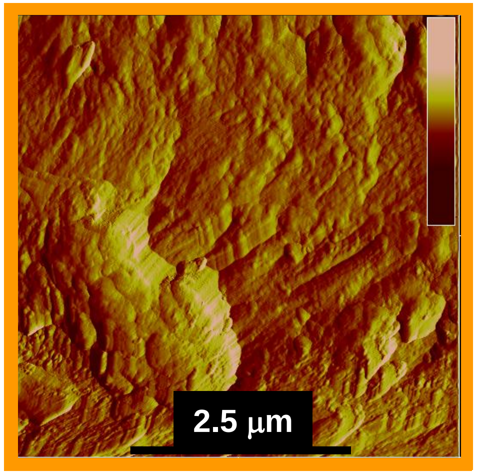
Untreated

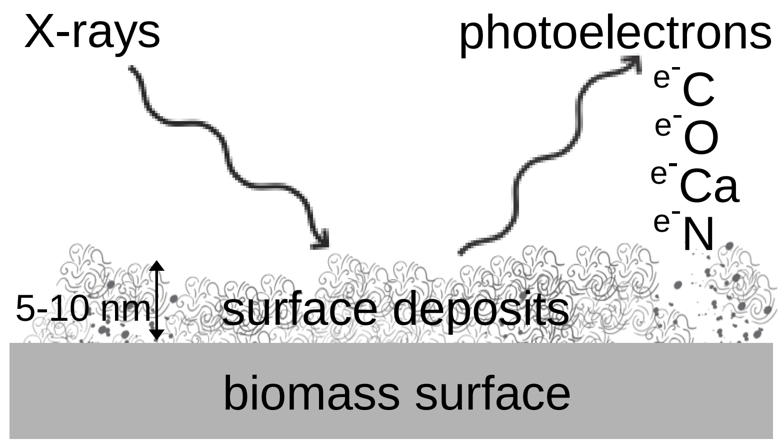




AFEX treated







	Untreated	AFEX
% C1 carbon	56%	64%
O/C ratio	0.37	0.31
% Calcium	n.d.	0.4%
% Nitrogen	1.7%	2.8%

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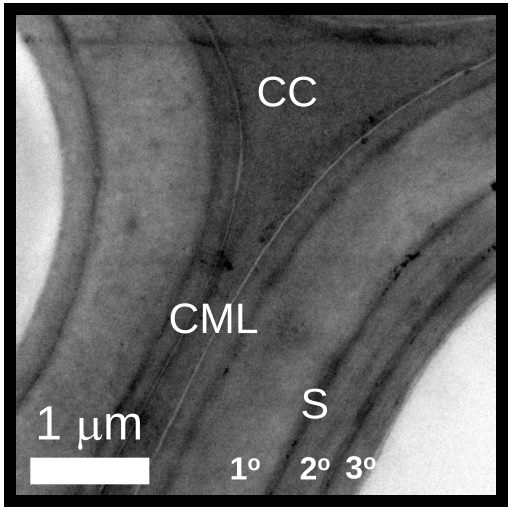
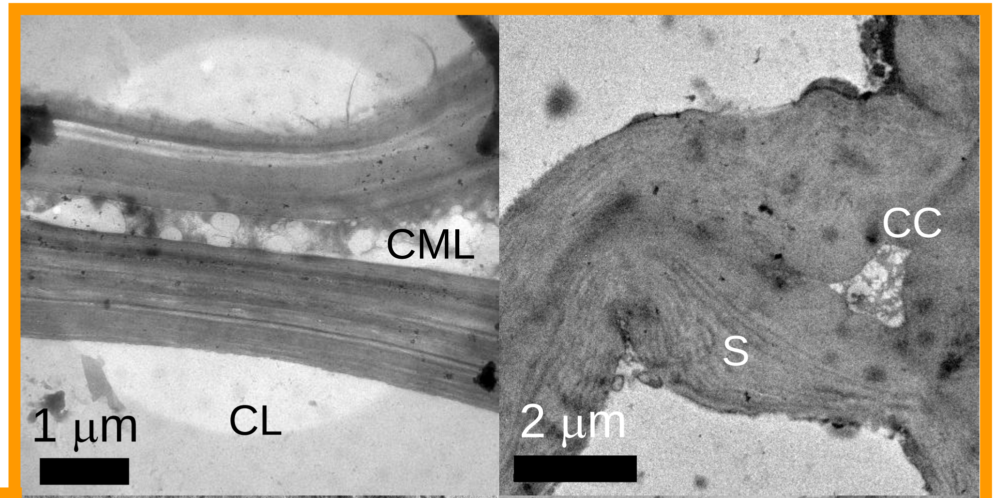
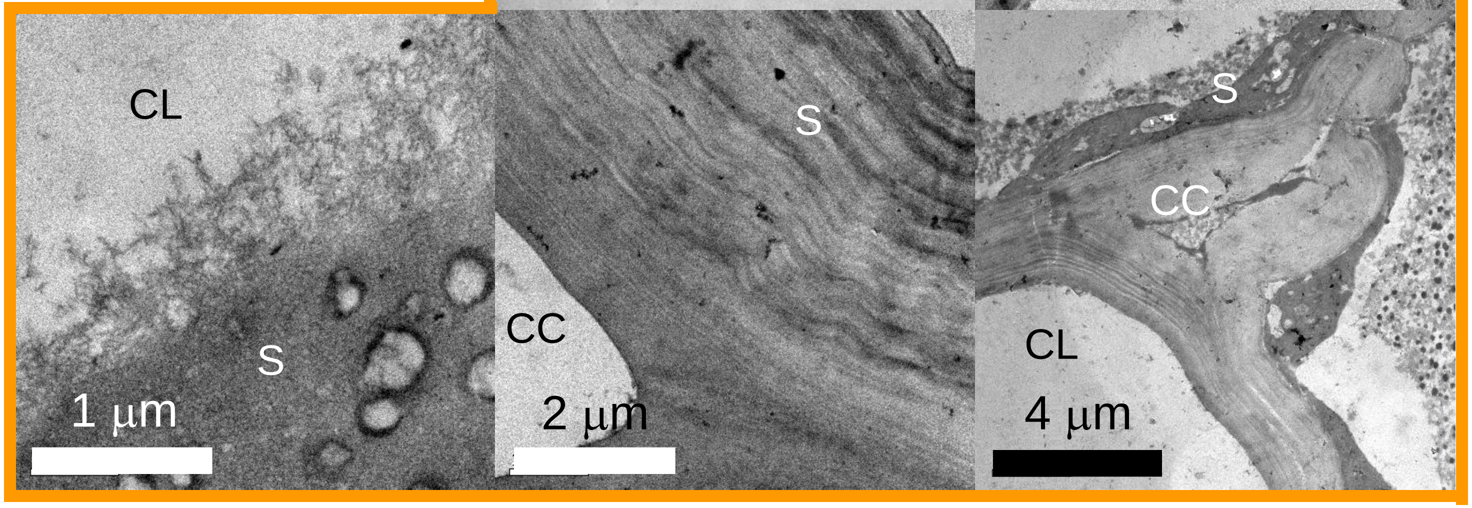
Inner Wall Architecture Reveals Complex Changes after AFEX

Untreated



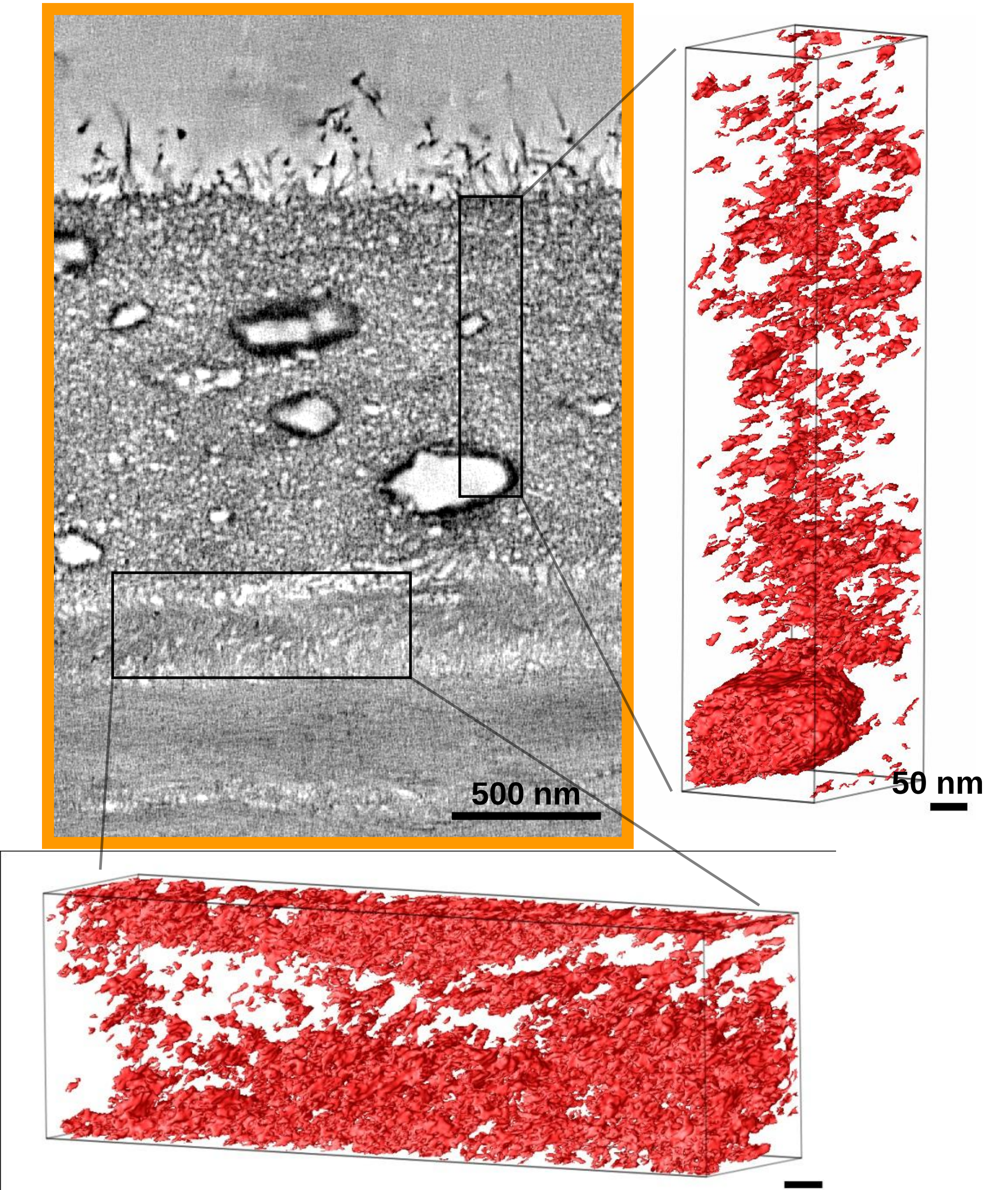
AFEX treated





Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984

Modeling Porous Regions via 3D-Tomography

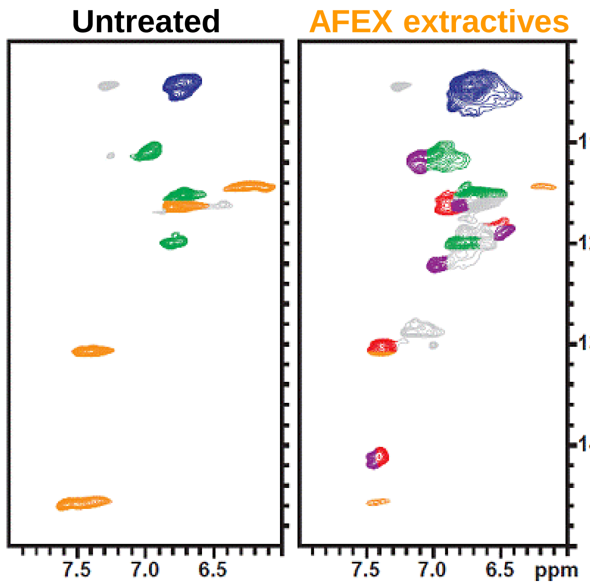


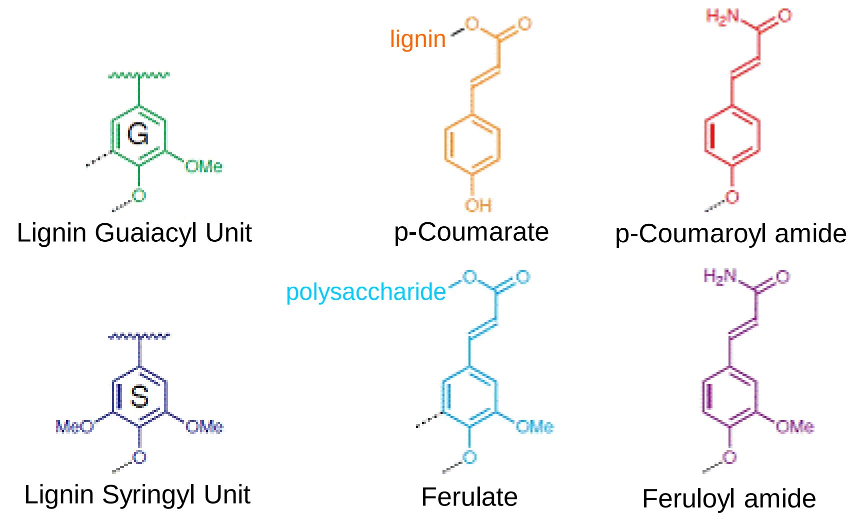
Tomogram Movie

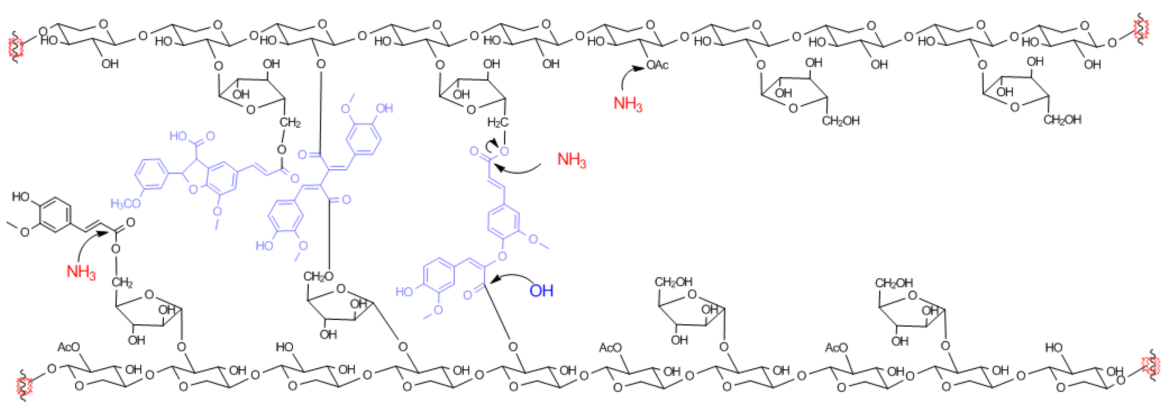
Wall porosity after AFEX ~ 5-50 m^2/gm

Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984

Analyzing AFEX Cell Wall Extractives



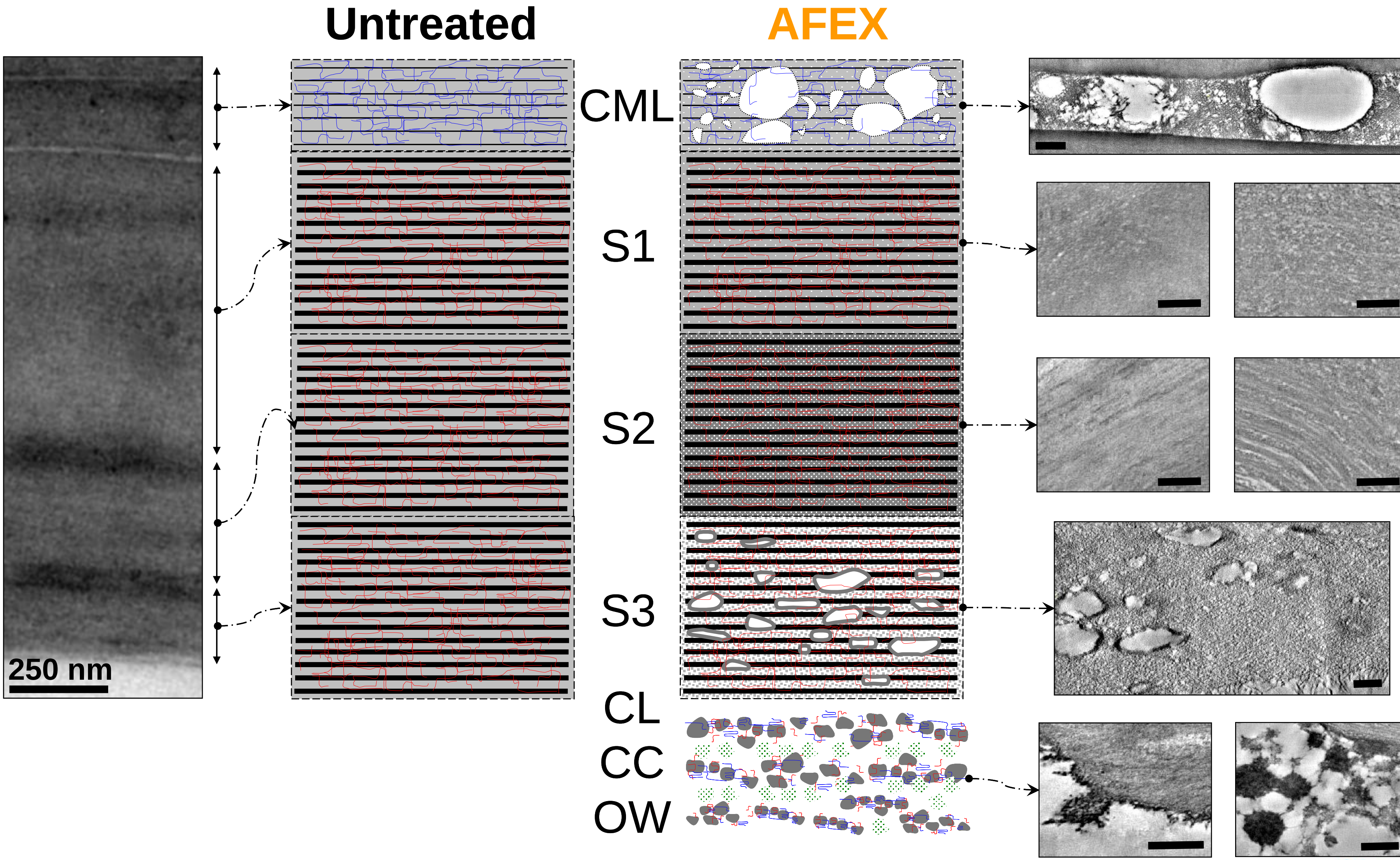




- Organic acids (10 mg/g BM)
- Amides (40 mg/g BM)
- Furans (0.5 mg/g BM)
- Sugar Oligomers (80 mg/g BM)
- Lignin Derivatives (2 mg/g BM)
- Minerals (20 mg/g BM)

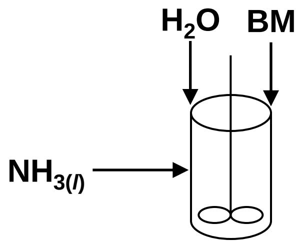
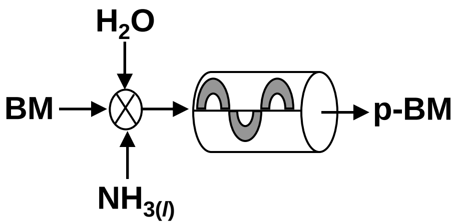
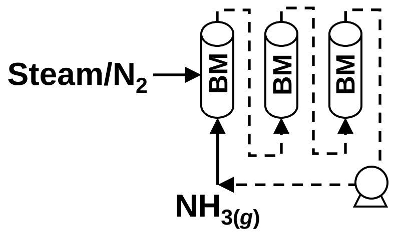
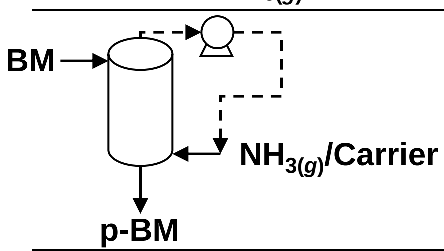
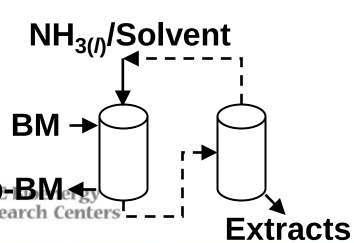
Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984
Chundawat et al. 2010. Biores Tech 101:8429

Effect of AFEX-treatment on Plant Cell Walls



Chundawat et al. 2011, Energy & Environ Sci, 4(3): 973-984

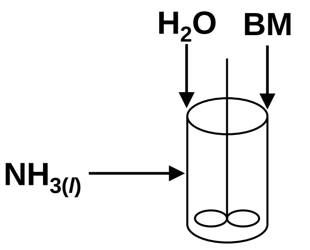
Different Ways of Carrying out the AFEX process

Pretreatment	Ammonia Recovery	AFEX classification
	$NH_{3(g)}$ & H_2O removed under hood after pretreatment with no recovery attempted	Batch AFEX: Lab scale Lower ammonia loadings "conventional" Water tolerant
	$NH_{3(l)}$ & H_2O recovery using flash tank, dryers and condensers	Plug flow AFEX
	$NH_{3(g)}$ recovery using steam/N_2 stripping and moist biomass	Packed bed AFEX: Very Low Cost Design Lower ammonia loadings "conventional" Water tolerant
	$NH_{3(g)}$ separation from biomass using cyclones Optional carrier gas includes steam, N_2	Fluidized gaseous AFEX
	$NH_{3(l)}$ is reused multiple cycles in liquid state Optional solvent includes water, acetone	Extractive AFEX- High Ammonia- Low Water required

Extractive vs. Conventional AFEX™

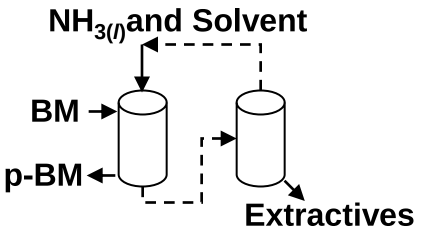
AFEX™ is a trademark of MBI International

- Conventional AFEX™
  - Dry-to-dry process (ammonia gas recyled)
  - Ammonolysis/hydrolysis reaction chemistry drives structural modification that enhances enzyme accessibility
  - Minimal formation of furans, but some inhibition seen due to residual lignin and other decomposition products
  - No cellulose III produced & no lignin extracted
  - **But "good enough" already for grasses and residues**



Conventional AFEX

- Extractive AFEX™
  - Novel ammonia-organic solvent combinations
  - Selective removal of lignin and other extractives
  - Cellulose modification to cellulose III
  - Improved enzymatic digestibility and fermentability
  - Compatible with conventional AFEX peformed in Regional Biomass Processing Depots (RBPDs)



Extractive AFEX

Extractive AFEX patent application: Chundawat, Sousa, Cheh, Balan, Dale (PCT/US2011/033079)

Part 2

Overcoming Cellulose Crystallinity
& Removing Lignin with Extractive AFEX

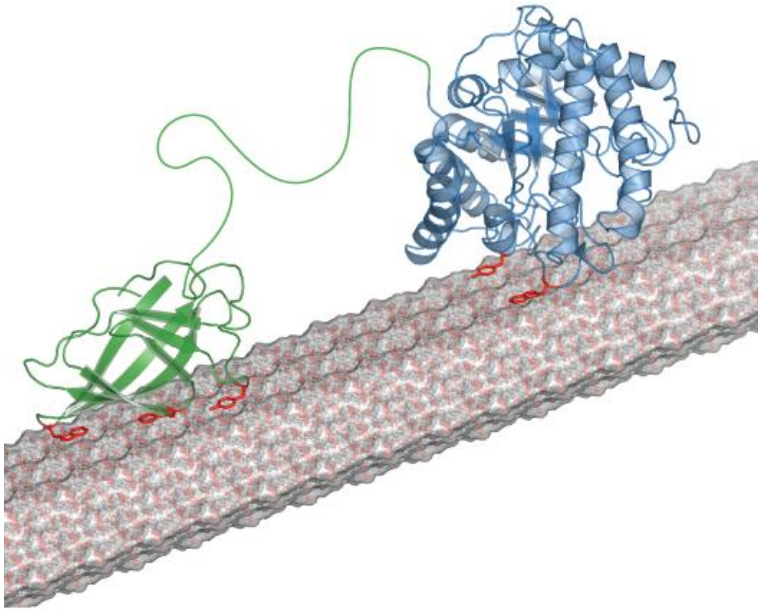
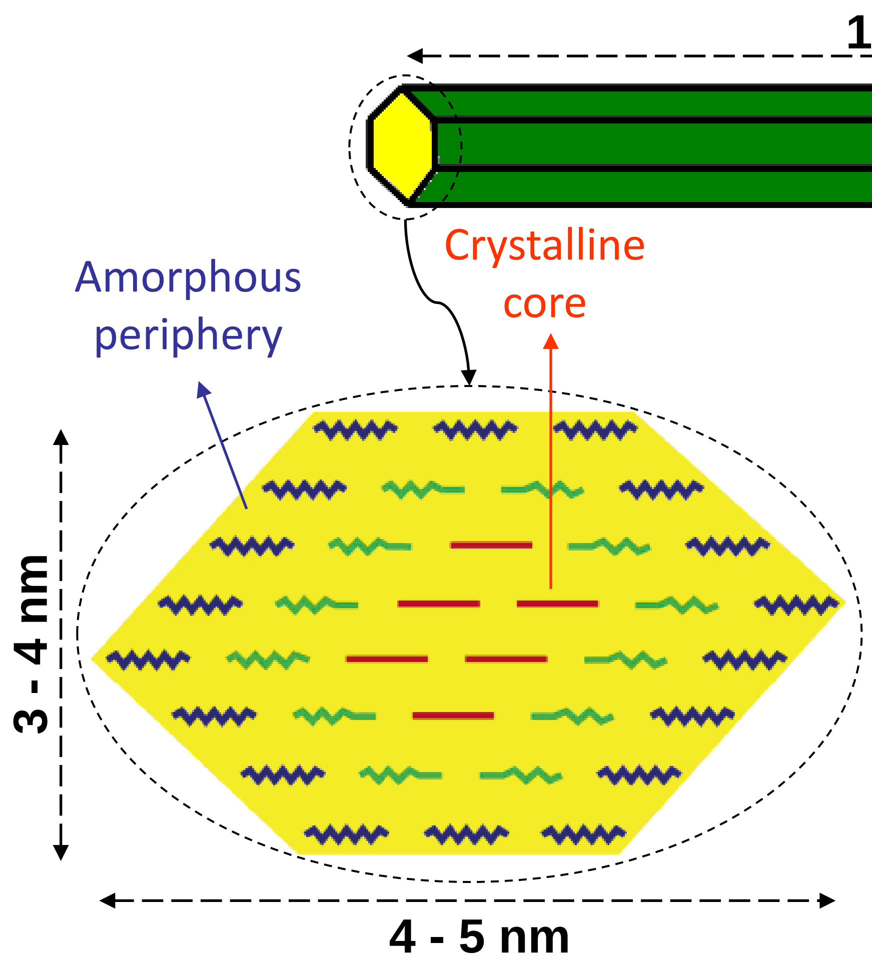
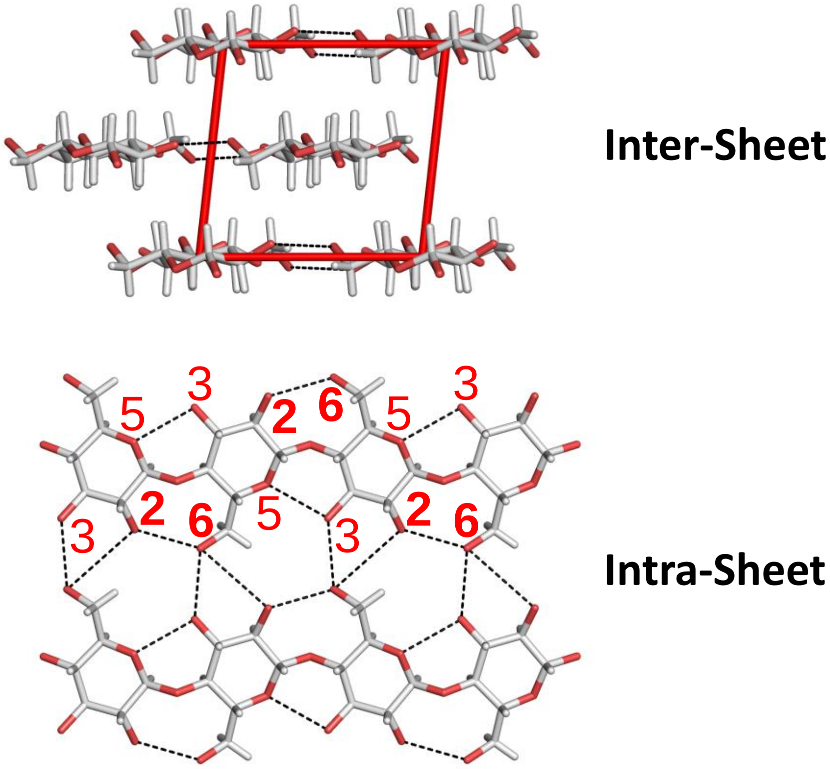


Image courtesy Chris Bianchetti

Plant derived cellulose is *para*-Crystalline

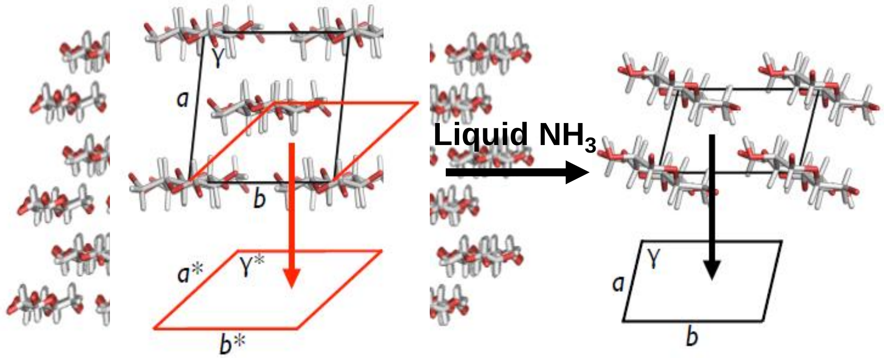




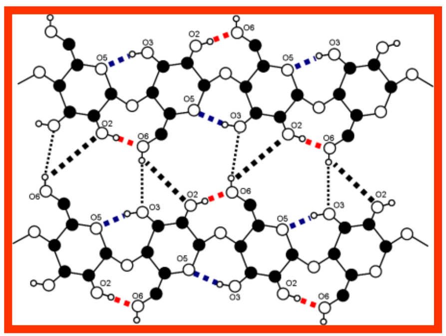
Chundawat et al., 2011, J Am Chem Soc, 133, 11163
Ding et al., 2006, J Agric Food Chem, 54, 597

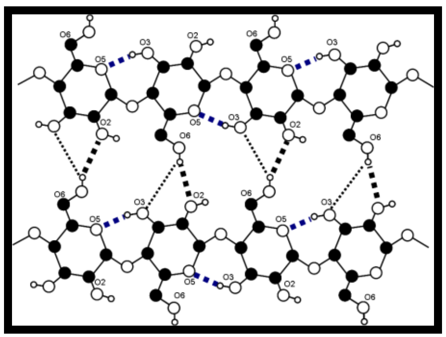
U.S. DEPARTMENT OF ENERGY DOE Bioenergy Research Centers www.glbrc.org GREAT LAKES BIOENERGY RESEARCH CENTER

High Ammonia Loadings Restructure Hydrogen Bonding Network



Cellulose I_β Cellulose III_I

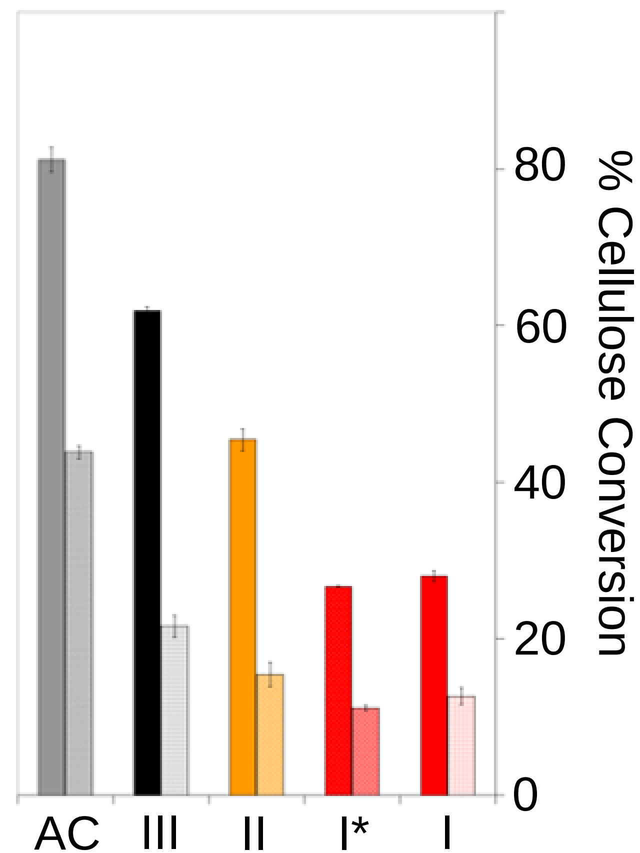




	Cellulose I_β	Cellulose III_I
Intra-chain	**O2-O6**, O3-O5	O3-O5
Intra-sheet	O6-O2, O6-O3	O6-O2, O6-O3
Inter-sheet	Weak C-H…O	O2-O6
$-CH_2OH$	TG (Trans)	GT (Gauche)

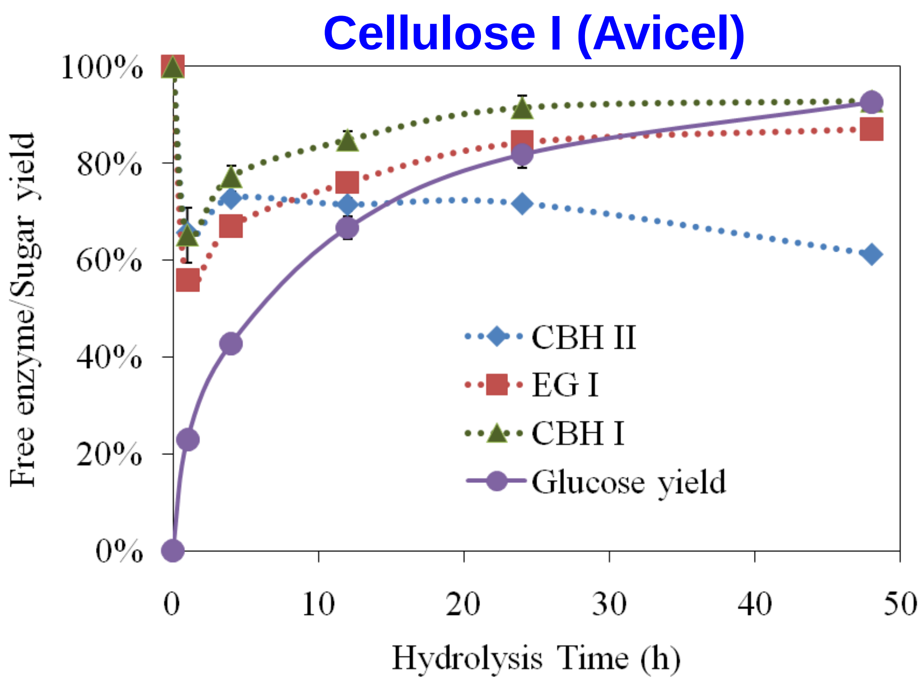
Wada, 2004, *Macromolecules*, 37, 8548-8555 Nishiyama et al., 2002, *JACS*, 124, 9074-9082

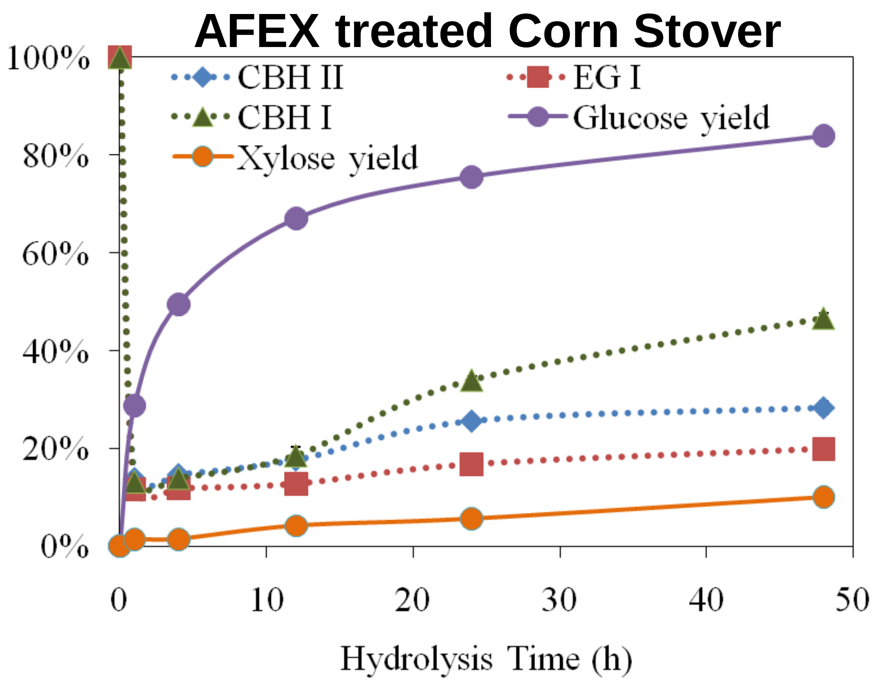
Glucan chain packing within different cellulose allomorphs influences hydrolysis rate



Chundawat et al., 2011, J Am Chem Soc, 133, 11163

Impact of lignin on non-productive cellulase binding

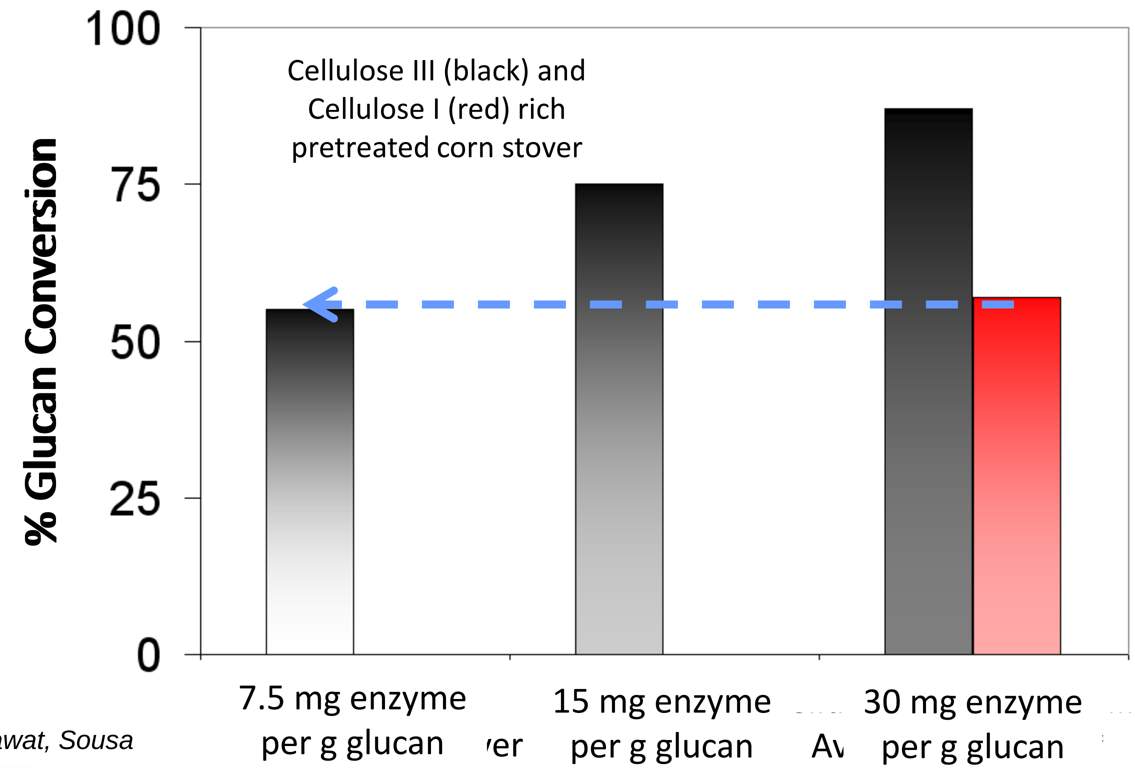




- Nearly all cellulases are recovered (except CBH II) after cellulose I hydrolysis (pure cellulose I) is complete
- CHB II is least stable member of complex
- Most cellulases are non-productively bound (to lignin?) for real pretreated lignocellulosic biomass (like AFEX-CS)

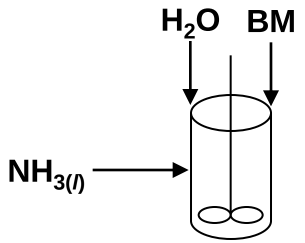
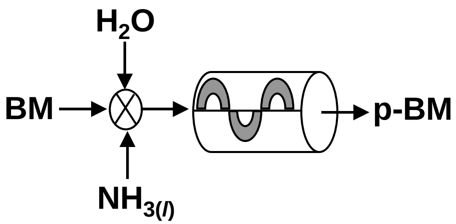
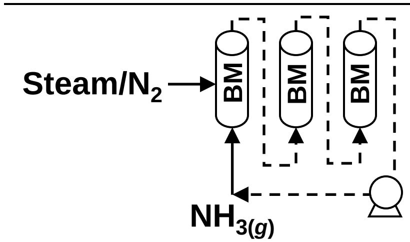
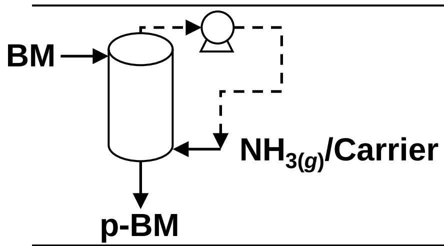
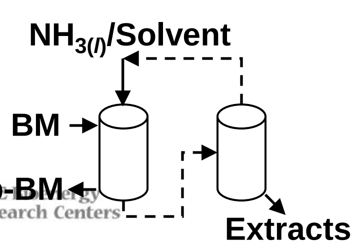
What's next?

- Cellulose III formation mechanism
- Engineering (finding?) better enzymes for cellulose III
- Integrating cellulose III formation with lignin removal



Unpublished data: Chundawat, Sousa

Different Ways of Carrying out the AFEX process

Pretreatment	Ammonia Recovery	AFEX classification
	$NH_{3(g)}$ & H_2O removed under hood after pretreatment with no recovery attempted	Batch AFEX: Lab scale Lower ammonia loadings “conventional” Water tolerant
	$NH_{3(l)}$ & H_2O recovery using flash tank, dryers and condensers	Plug flow AFEX
	$NH_{3(g)}$ recovery using steam/N_2 stripping and moist biomass	Packed bed AFEX: Very Low Cost Design Lower ammonia loadings “conventional” Water tolerant
	$NH_{3(g)}$ separation from biomass using cyclones Optional carrier gas includes steam, N_2	Fluidized gaseous AFEX
	$NH_{3(l)}$ is reused multiple cycles in liquid state Optional solvent includes water, acetone	Extractive AFEX- High Ammonia- Low Water tolerance

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De-Risking and Scale-Up of Bio-Based Technologies

Evolution of AFEX™ Equipment

Early Design

- Batch Reactor
- Up to 5 gallon capacity
- Suitable for bench scale research

↓

1st Gen AFEX™

- Modified version of continuous steam reactor
- Engineering design completed
- Use Pulp and Paper processing equipment-**costly**

↓

2nd Gen AFEX™

- Innovative reactor design for pumpable feedstocks
- Low capital cost
- Pilot scale operation
- Effective, but only for pumpable biomass

Evolution of AFEX™ Equipment: "Conventional AFEX"

Early Lab Design

↓

1st Gen AFEX™

↓

2nd Gen AFEX™

↓

3rd Gen AFEX™

December 2009

To move AFEX™ forward, we needed a 3rd Generation technology with:

- Lower capital cost than 1st Gen
- Greater feedstock flexibility than 2nd Gen

- *Innovative reactor design for non-pumpable feedstocks*
- *Very low capital cost*
- *New in 2010 – patent application filed*

AFEX™ 3 – Concept

Biomass Properties:

- High specific surface area
- High liquid absorption capacity
- Small, fairly uniform particles
- Readily packed into porous beds

Moist biomass is a very effective material for absorption of water-soluble vapors and gases, for example, *ammonia*

Bed of biomass at 44% moisture packed into a 4-inch OD tube using a vacuum blower

AFEX™ 3 – Ammonia In A Biomass Bed

- Absorption of NH_3 vapor by moist biomass is strongly exothermic
  - $\Delta H < -1{,}600$ kJ/kg, depending on pressure
  - Bed temperature > 90^{o}C attainable at pressure > 150 psig
  - Good AFEX™ conditions (temperature, NH_3 concentration) can be achieved in the bed without external heating, mechanical mixing, or any free liquid

- Desorption of NH_3 from moist biomass is strongly endothermic
  - Bed temperature may drop to < 10^{o}C for desorption at P < 10 psig
  - NH_3 can be completely stripped from bed using heated N_2/ steam at near-ambient pressure

AFEX™ 3 – Continuous Operation

Three-bed skid fabricated

Proof of concept:

- Demonstrated NH_3 absorption, desorption, & transfer from bed to bed
- Good pretreatment results – comparable to conventional AFEX™

U.S. DEPARTMENT OF ENERGY
DOE Bioenergy Research Centers
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AFEX™ 3 - Advantages

Summary:

- Feedstock versatile
    - No biomass feed pump needed
- Low capital cost
    - No plug screw feed, no plug screw discharge
    - No expensive dryer for NH_3 recovery
    - No distillation to purify ammonia
- Low operating cost
- Fits well with distributed biomass processing (perform size reduction/pretreatment/densification operations separate from central biorefinery)

Future AFEX™ Development Plans

- Scale up 3rd gen AFEX™ in pilot plant: 1 ton per day by the end of 2011
- De-risk downstream applications
  - Densification, Animal Feed, Chemicals
- Pretreat a variety of feedstock materials
- Find corporate partners
  - Equipment suppliers
  - System installers
  - End users
- License the technology

One of My Best Birthday Presents Ever

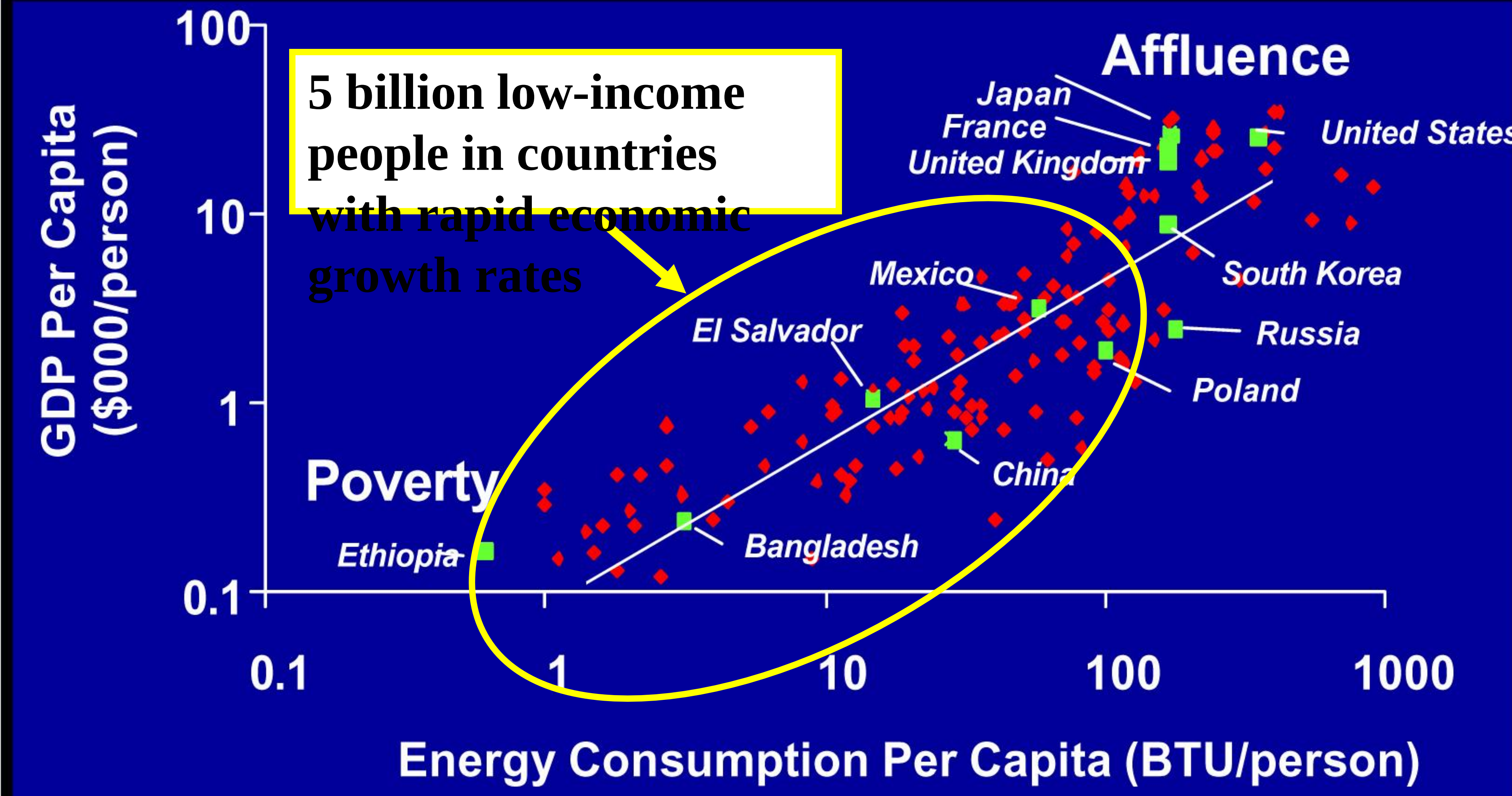
THE DEPARTMENT OF ENERGY
Office of Public Affairs

News Media Contact: (202) 586-4940
For Immediate Release: Friday, June 10, 2011

Department of Energy Announces up to $36 Million to Support the Development of Drop-In Biofuels and Bioproducts
Investments will help diversify America's sources of clean, renewable alternatives to fossil fuels

Michigan Biotechnology Institute (*up to $4.3 million, Lansing, Michigan*): The project will focus on improvements to a pretreatment process, which provides a stable, conversion-ready intermediate of consistent quality at a cost and in a format compatible with long-term storage and ease of transfer between multiple modes of transportation.

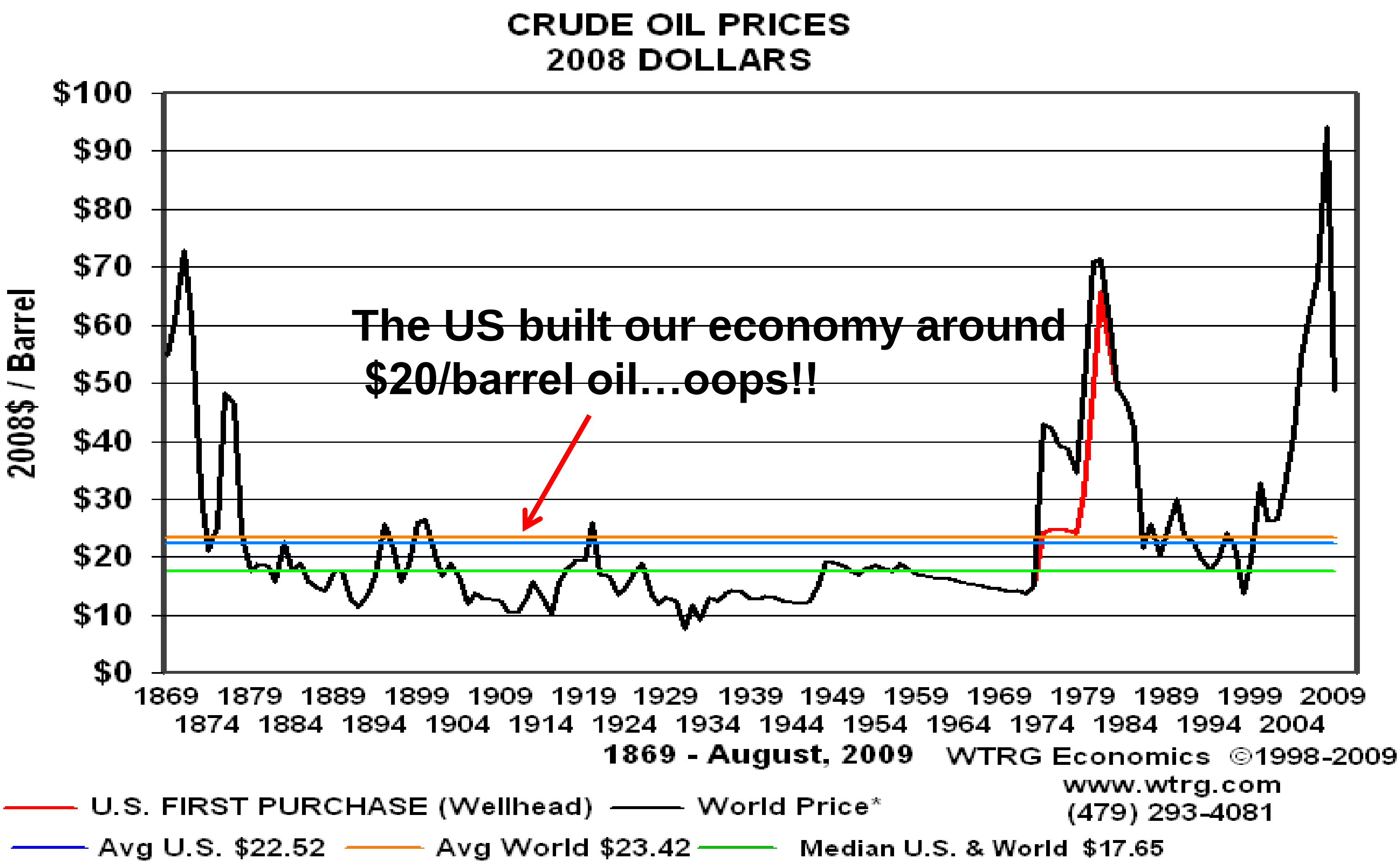
Energy Consumption and Income are Linked

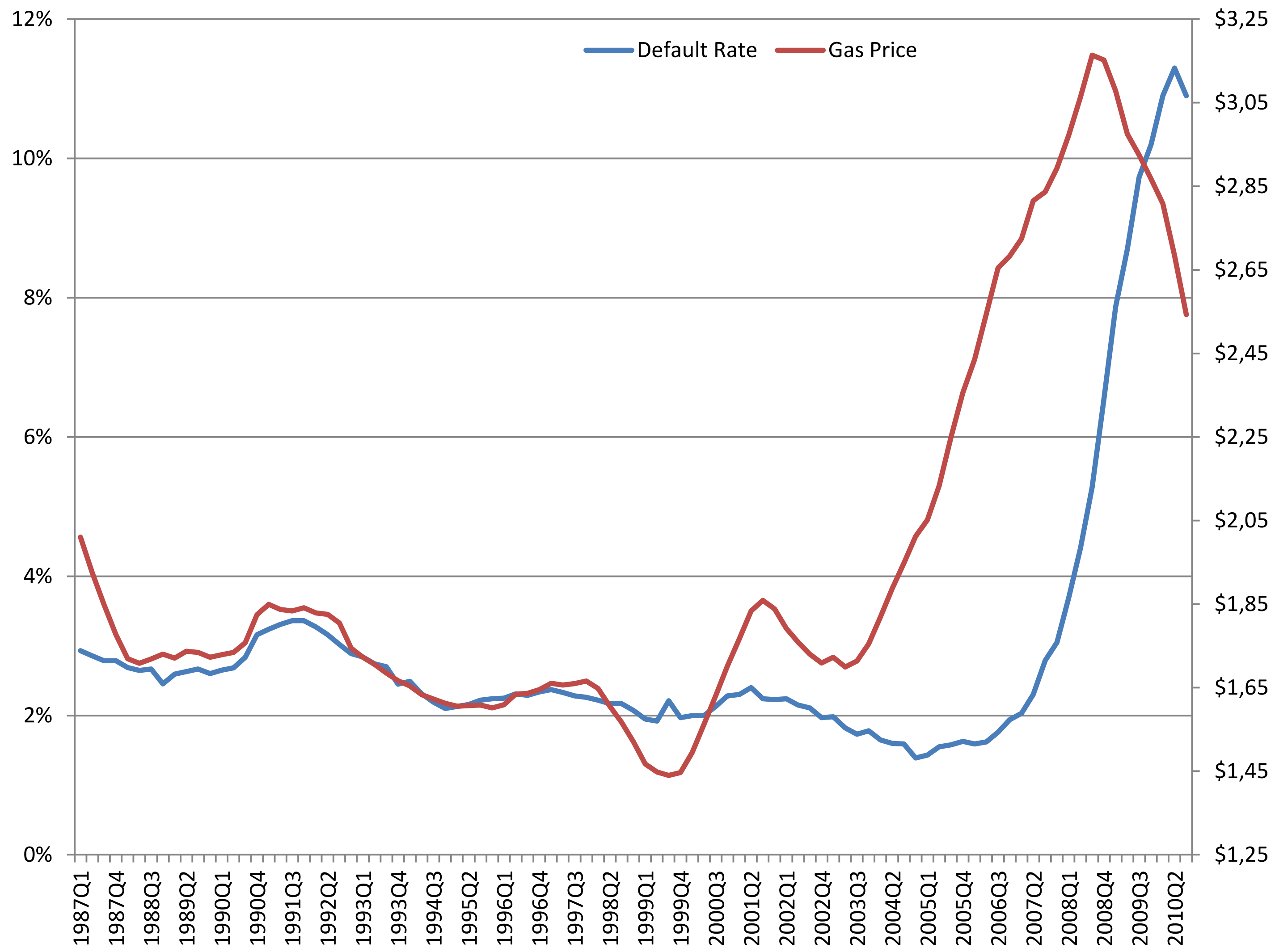


Source: Energy Information Administration, International EnergyAnnual 1998 Tables E1, B1, B2; Mike Grillot, 5/17/00
Gross Domestic Product per capita is for 1997 in 1990 dollars. Energy Consumption per capita is 1997.

38

1869-2009 CRUDE OIL PRICES



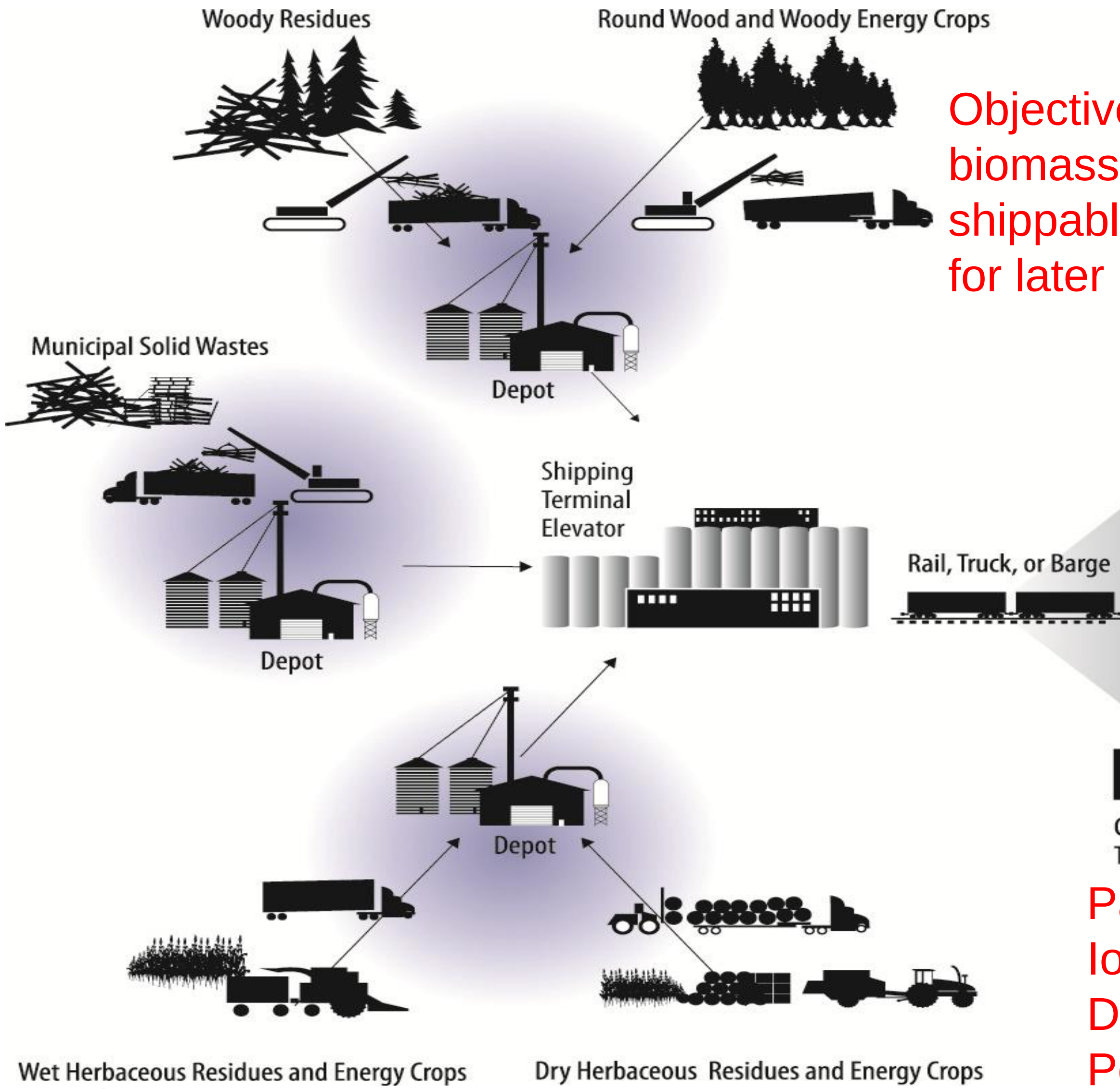


Delinquency rate on loans secured by real estate; All commercial banks (Seasonally adjusted) vs. Real Motor Gasoline Retail Price (adjusted for inflation) Data from Morgan Stanley—24 month moving averages 1987-2010 Courtesy Eyal Aronoff

Questions for a Cellulosic Biofuels Future

- Premise: *the cellulosic biofuels industry can and should grow rapidly in the coming decades. Why?*
  - We are at "peak oil": 2-4% per year declines from here on
  - Many are waking up to the energy=wealth equation
  - Conversion technology getting "good enough"
  - Feedstock cost & <u>supply</u> will become dominant issues
- Need to address the following questions:
  - How can scalable, reproducible supply chains develop?
  - How to commoditize cellulosic biomass—make it a tradable, fungible, more uniform product?
  - How to improve the environmental performance of biofuel systems?
  - Given a large biofuel demand, what are the implications for food/feed/fiber markets?
  - Can we coproduce fuels (& foods/feeds)?
  - How can farmers & local communities benefit?

Attacking Biomass Supply Challenges



Objective: convert regional, distinct biomass sources into dense, stable, shippable *intermediate commodities* for later upgrading at (bio)refineries

Partners:
Iowa State U.
DOE Idaho National Lab.
Pennsylvania State U.
Michigan State U.

Logistics of supplying a Biorefinery

	Stover Biorefinery	Corn grain refinery	RBPD
Capacity: gal/yr	100 million	100 million	N/A
Capacity: tons/day	3360	2850	100
Collection radius (mile)	39.5	21.8	6.8
Farms to contract with	2600	N/A	78
Transportation	1 truck every 4 min	1 truck every 11 min	10 trucks per day
Storage footprint	630 acres	37 acres	7.6 acres

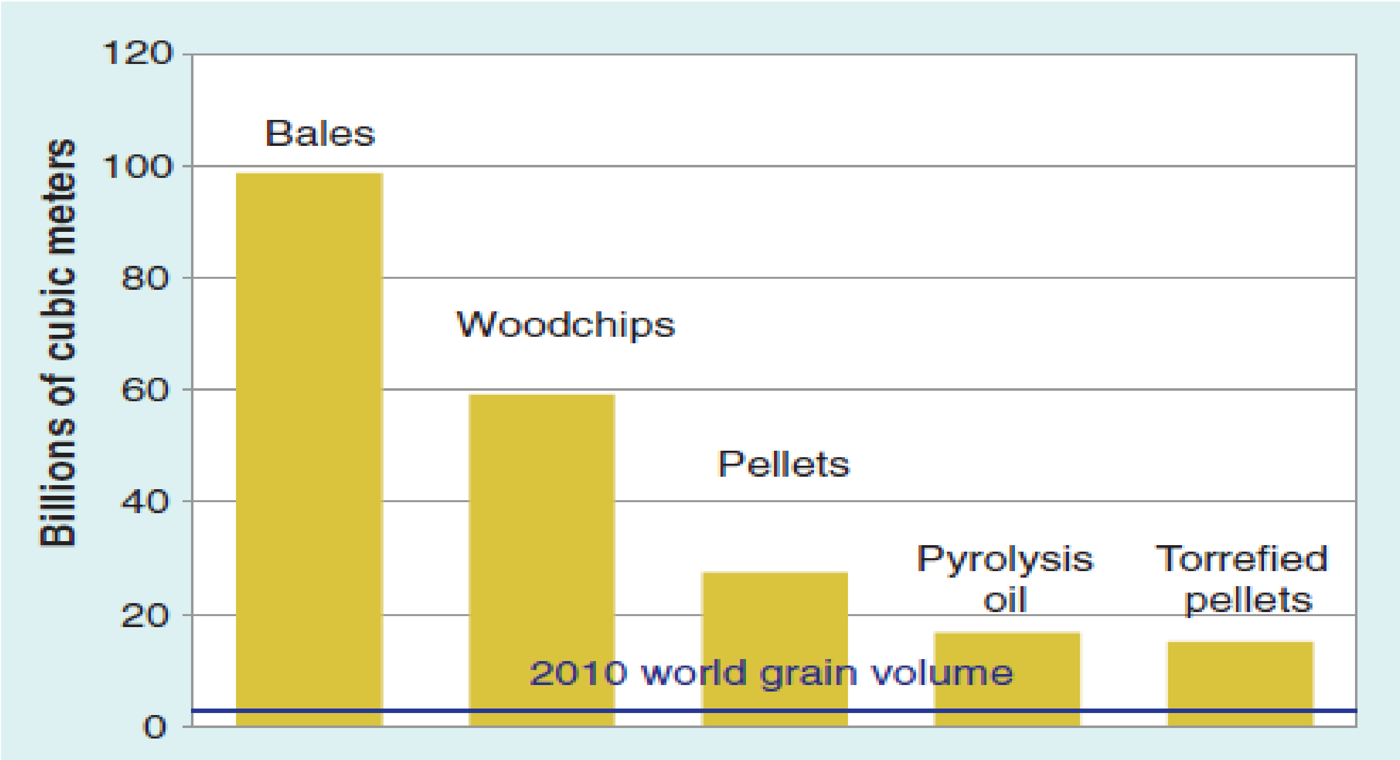


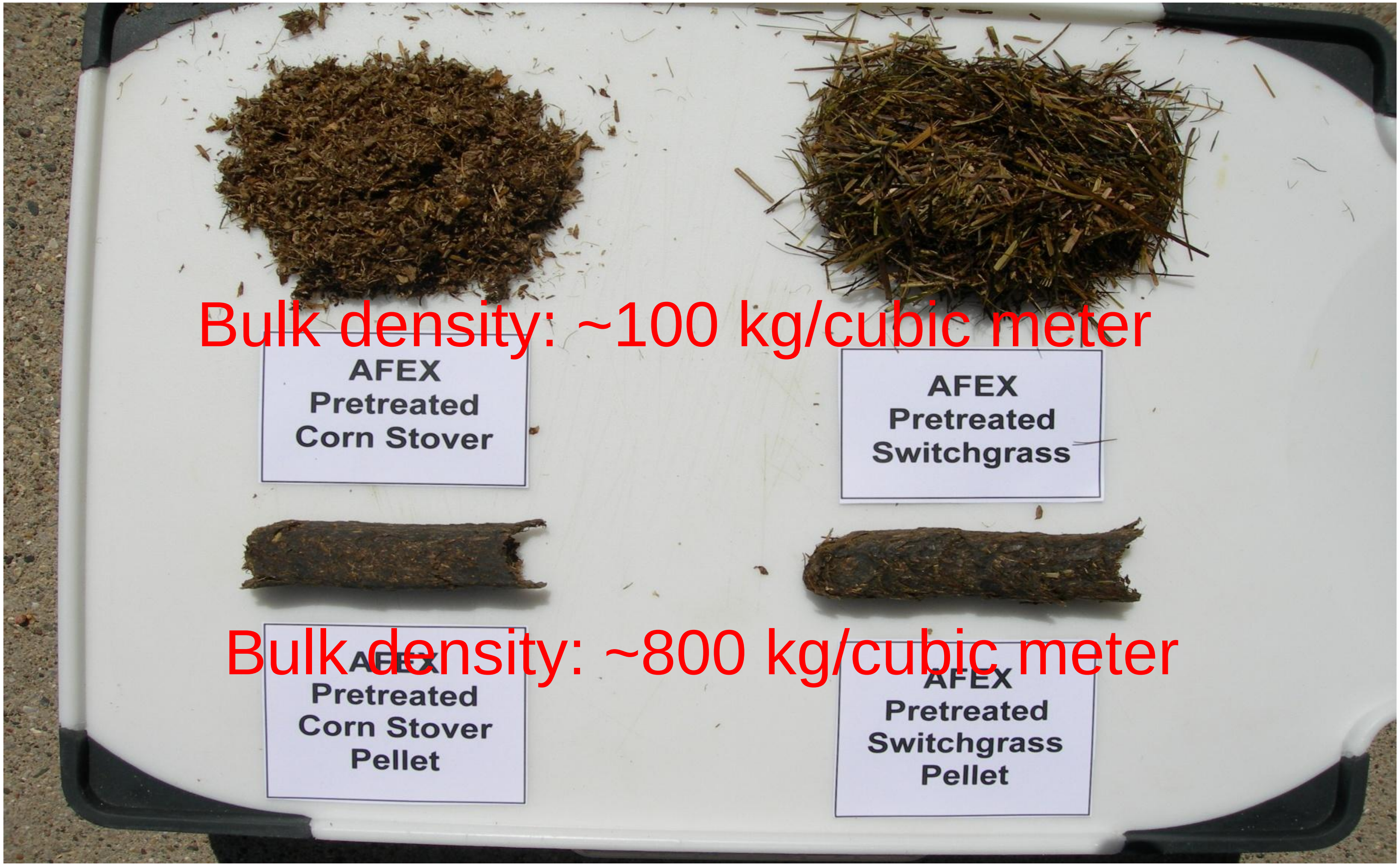
Fig. 1. Global biomass volumes required to achieve a 50% reduction in greenhouse gas emissions by 2050. A wide range of densification options are possible, but even the most effective will still require several times the biomass-handling capacity that the commodity grain system uses today.

Challenges in Scaling Up Biofuels Infrastructure
Tom L. Richard, *et al.*
Science **329**, 793 (2010);
DOI: 10.1126/science.1189139

Supply chain: What do we want?

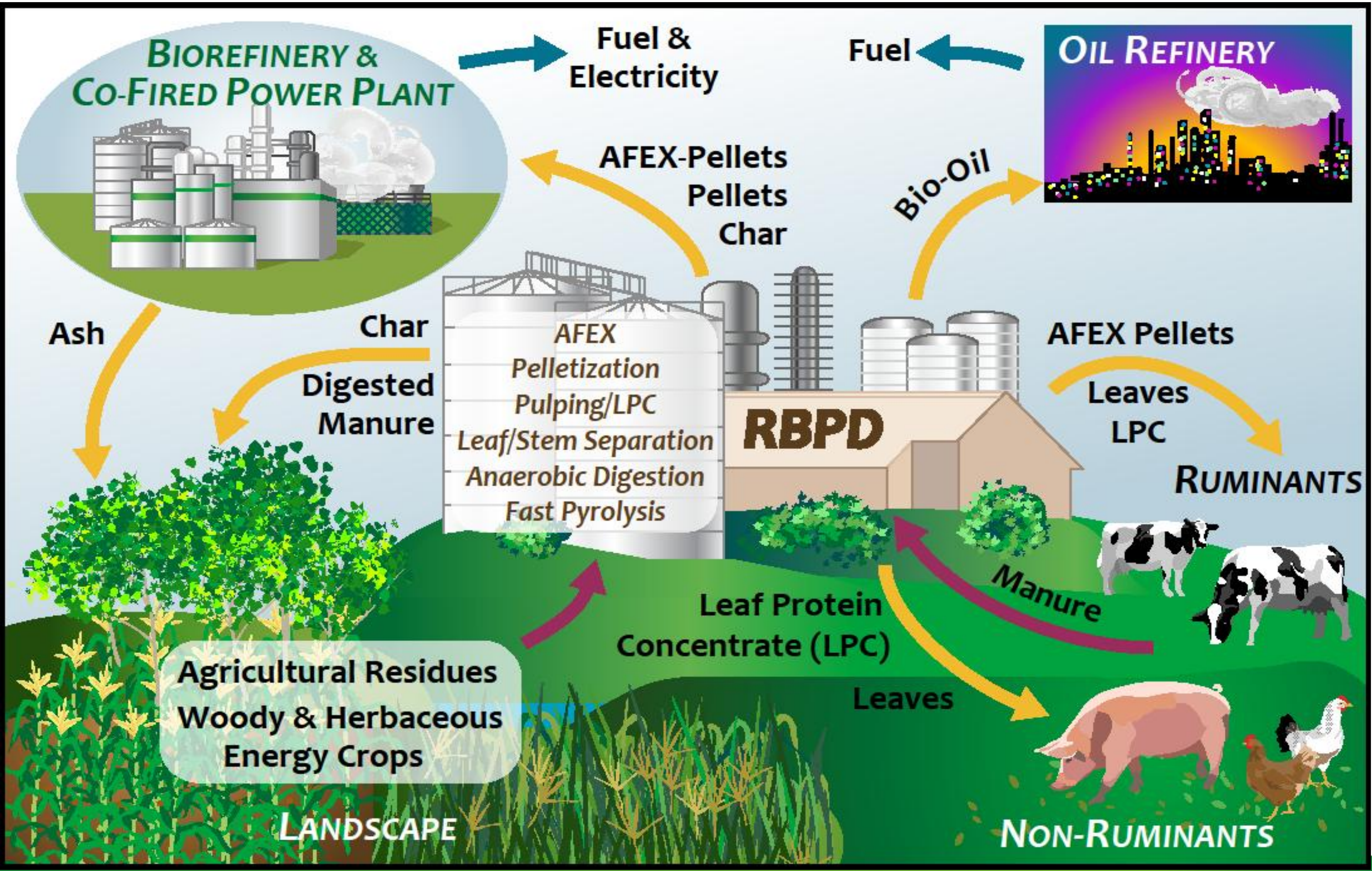
Desirable Cellulosic Feedstock Properties	Desirable Supply Chain Properties
• Low cost	• Low transportation cost
• Price stability	• Multiple markets available
• Consistent composition	• Uniform, consistent (commodity) feedstock
• Easily stored	• Provides local economic opportunities
• Dense or easily densified	• Satisfies local and global environmental criteria
• Not competitive with food crops	
• Potential for co-product generation	

AFEX™ Biomass Pellets: No Binder



Estimated cost to densify: $5-10/ton (per Federal Machine, Fargo, ND)

Regional Biomass Processing Depots: Serving Multiple Markets?



Benefits of Regional Biomass Processing Depots

- Advantages of RBPDs
  - Address biomass variability near point of production
  - Produce dense, stable, shippable *intermediate commodities* for biofuel producers ("biorefineries")
  - Reduce transaction costs: a few RBPDs vs 1000s of farmers
  - Reduce capital at risk by 1/3 (feedstock handling, pretreatment & storage)
  - Enable integration with low cost heat? (biomass cofired power)
  - Benefit rural communities through job creation & ownership
  - Address "food vs. fuel" and sustainability issues locally "all biomass is local"
- *But we have much to learn about RBPDs*

In Closing-Some Biofuel Perspectives

- Profound transition in how the world will be fueled & fed– *we cannot continue along our current pathways, we must change*
- Prof. Lee Lynd: "Business as usual is a fantasy, not a baseline"
- Seek large, complementary, beneficial changes: we need food (feed) and fuel and sustainability and rural development
- This will not happen by accident—we must design sustainable biofuel systems and then implement them
- *Stop "playing defense" by apologizing for or arbitrarily limiting biofuels —biofuels are an essential part of a sustainable future*
- If we want to continue as a rich society, we must figure out how to have moderately priced and abundant energy… or both rich and poor are going to be a lot poorer before too long
- Time to choose and move ahead—the transition will take decades

We are choosing for them: not just ourselves

***Muito obrigado*!**

What Can This Group Do to Help?

- Teach the facts
- Don't apologize for biofuels—cane and starch fuels are both much better than petroleum fuels
- But we must have cellulosics for really large scale biofuels
- We actually have lots of land
- We can integrate food and fuel production to their mutual benefit
- Biofuels are a huge opportunity for rural growth & good jobs & security
- There are "win-win-win-win" scenarios for food-biofuels-environment-rural development
- *We need to identify desirable scenarios and work to achieve them….*

Some Evaluation Criteria for Pretreatments

Minimum Criteria (?)

- Good sugar yield (~85% raw material potential)
- High (10%) sugar conc.
- Good hydrolysis rate (<2 day)
- Mass balance (~95% closed)
- Fermentation compatible sugars—minimal washing
- Good scalability
- Low water use (~3 gal/gal)
- Low enzyme use (2 mg/gm biomass?)
- Lignin value preserved?
- Low (no?) waste production

Other Key Criteria

- Distributed processing?
- Animal feed coproducts?
- Low energy requirements (<5% of biomass LHV)
- CAPEX costs (<$2/gal annual capacity?)
- Are nutrients conserved?
- Low chemical costs (ionic liquids???)
- Difficult process control?
- Moderate temp/pressure?
- Toxic/hazard conditions?
- Effective on all biomass?

Example #2: Designing Biomass Logistical Systems to Provide Economic Benefits for Rural Areas

- Large scale biofuels will require moving huge quantities of bulky, low density biomass—moving mostly "thin air"
- This is simply not tenable… therefore we must densify the energy content of the biomass close to where it is grown
- Provides opportunities for advancing rural economies by adding value to the biomass near the farm or forest
  - More jobs in rural areas
  - More wealth creation in rural areas
  - Produce energy products in rural areas
  - **A potential boon to Africa in particular!**
- <u>Requires low capital investment technologies</u>

Comparison of Three Pretreatment Processes

Method	Pretreatment						Post-Wash	
	Temp (° C)	Residence Time	Catalyst Type	Catalyst Loading[a]	Catalyst Re-cyclable?	Water Loading During Pretreat-ment[b]	Post-Wash Water Use[b]	Water Temp (° C)
AFEX™ (GLBRC)	140	15 mins	Anhydrous Ammonia	100Kg	Yes	60	N/R	NA
Dilute Acid (BESC)	160	20 mins	0.5% Sulfuric acid	5kg	No	895	3000	Room temp
Ionic Liquid (JBEI)	140	180 mins	Ionic Liquid (1-ethyl-3-methyl-imidazolium acetate)	900kg	Yes	N/R	3000	Room temp

[a]Catalyst Loading: kg/100 kg DBP
[b]Water Use: L/100 kg DBP
N/R – Not required, NA - Not Applicable

Basis: 100 kg dry untreated biomass

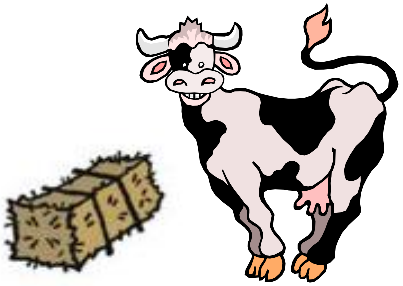
Ruminant Animals & Biorefineries:

Improve Cellulose Conversion for Biorefinery
= Improve Cellulose Digestibility for Cows

Stationary Cellulose Biorefinery

=

Mobile Cellulose Biorefinery
(a.k.a. Cow)



SSCF Bioreactor:

Biomass Input ~ 5,000 Dry Ton/Day
= 10 M Dry Lb/Day

Capacity ~ 45 M Gal Fermentor

Ruminant Bioreactor:

Biomass Input ~ 26 Lb/Day*

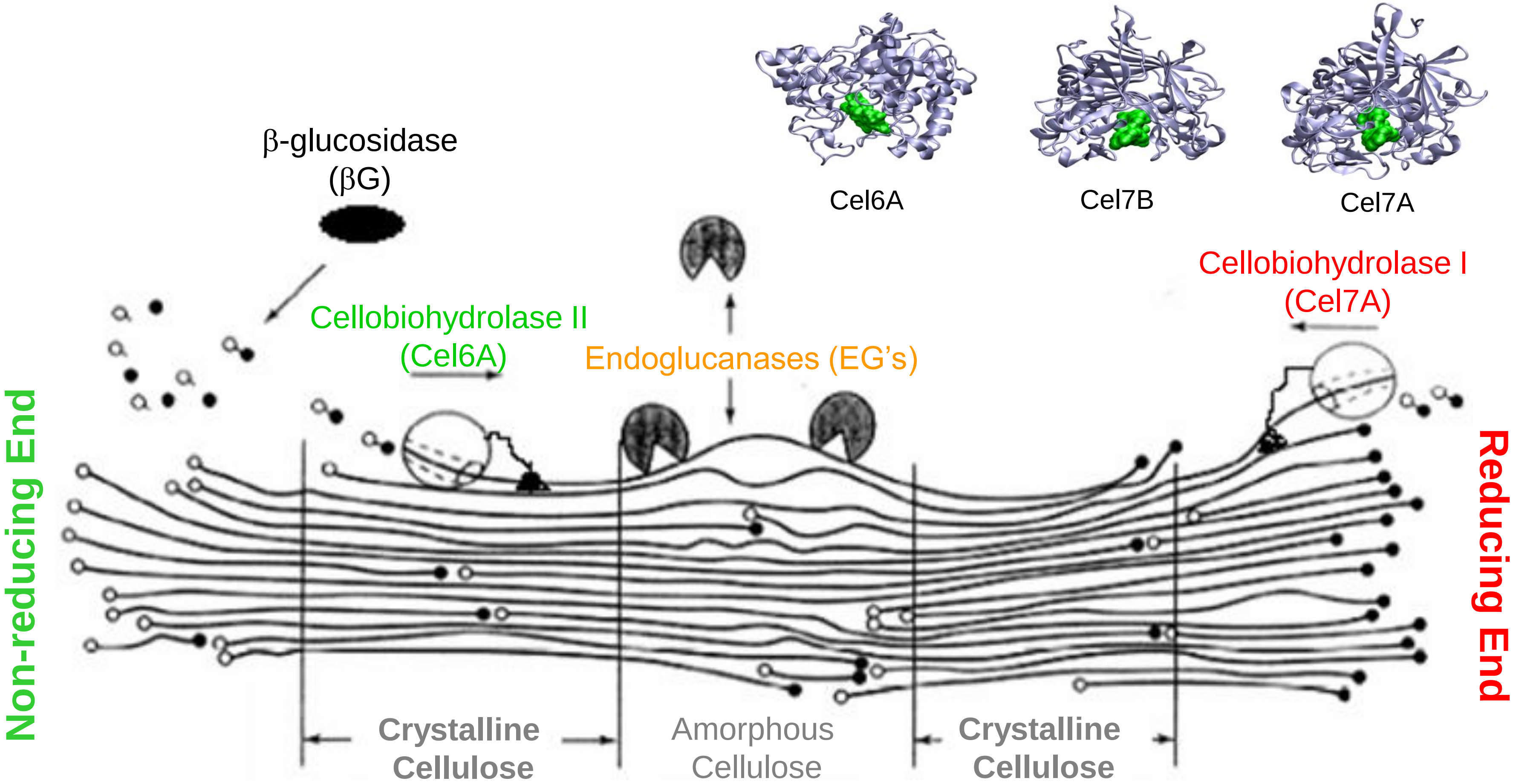
Capacity ~ 40 Gal Fermentor

Cow is 3x more efficient than industrial bioreactor

U.S. Livestock Consumption of Calories & Protein

ANIMAL CLASS	HERD SIZE (THOUSANDS)	TOTAL PROTEIN (MILLION KG/YR)	TOTAL ENERGY (TRILLION CAL/YR)
Dairy	**15,350**	**10,400**	**184.8**
Beef	**72,645**	**25,100**	**525.3**
Hogs	60,234	6,900	136.2
Sheep	10,006	461	10.6
Egg production	446,900	2,470	4.3
Broilers produced	8,542,000	9,540	150.3
Turkeys produced	269,500	1,760	28.6
Total consumed by U.S. livestock		**56,630**	**1,040.00**
Human requirements		**5,114**	**205**

Trichoderma cellulases necessary to hydrolyze cellulose

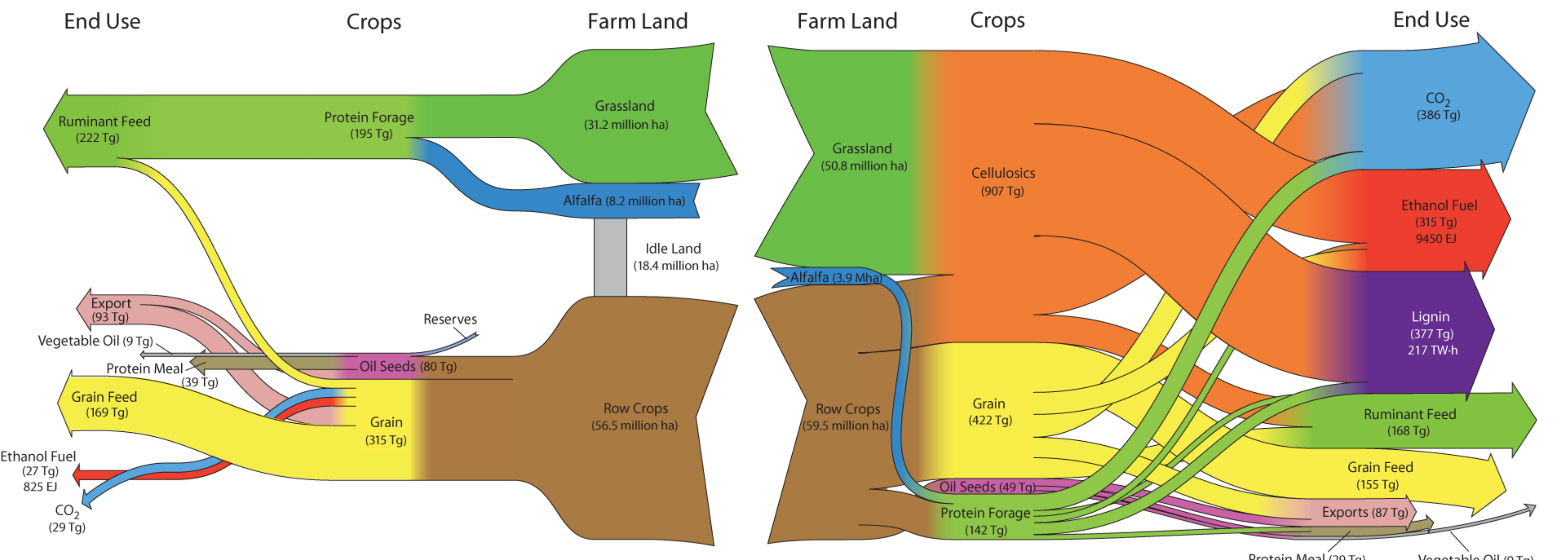


Exo-cellulases (CBH I, CBH II) and Endo-glucanases (EG I) contribute nearly 50-80% of the total protein (wt%) necessary to hydrolyze pretreated lignocellulosic biomass…

Chundawat S, Beckham G, et al. 2010, Annu Rev Chem Biomol Eng, Vol 2, 121-145

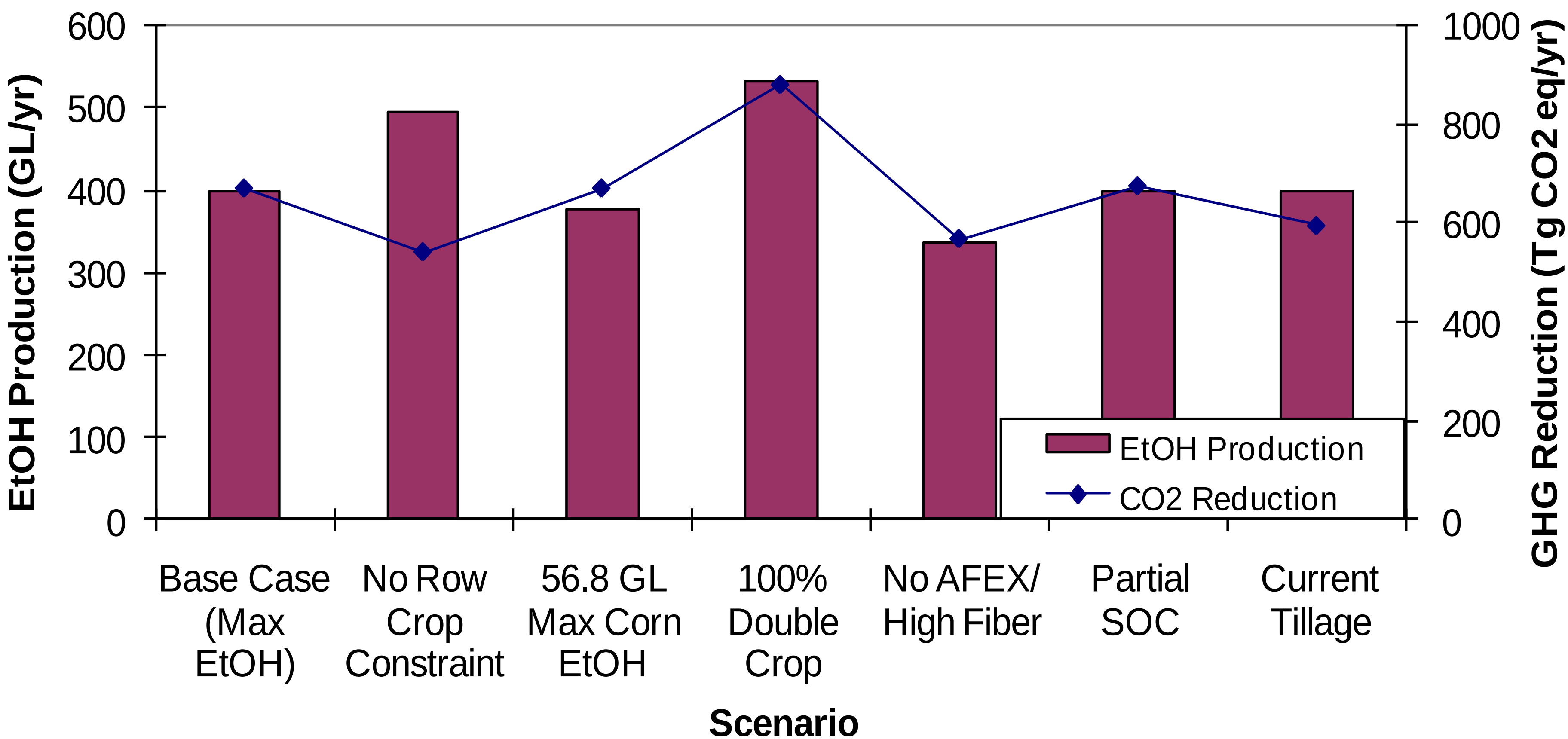
Actual vs Possible Land Use

- On the same land, total biomass production increases by 2.5 fold
  - Displaces 50% of US gasoline & 5% of US electricity
  - Reduces US GHGs by 10%
  - Food & feed production remain the same



Sensitivity Analysis

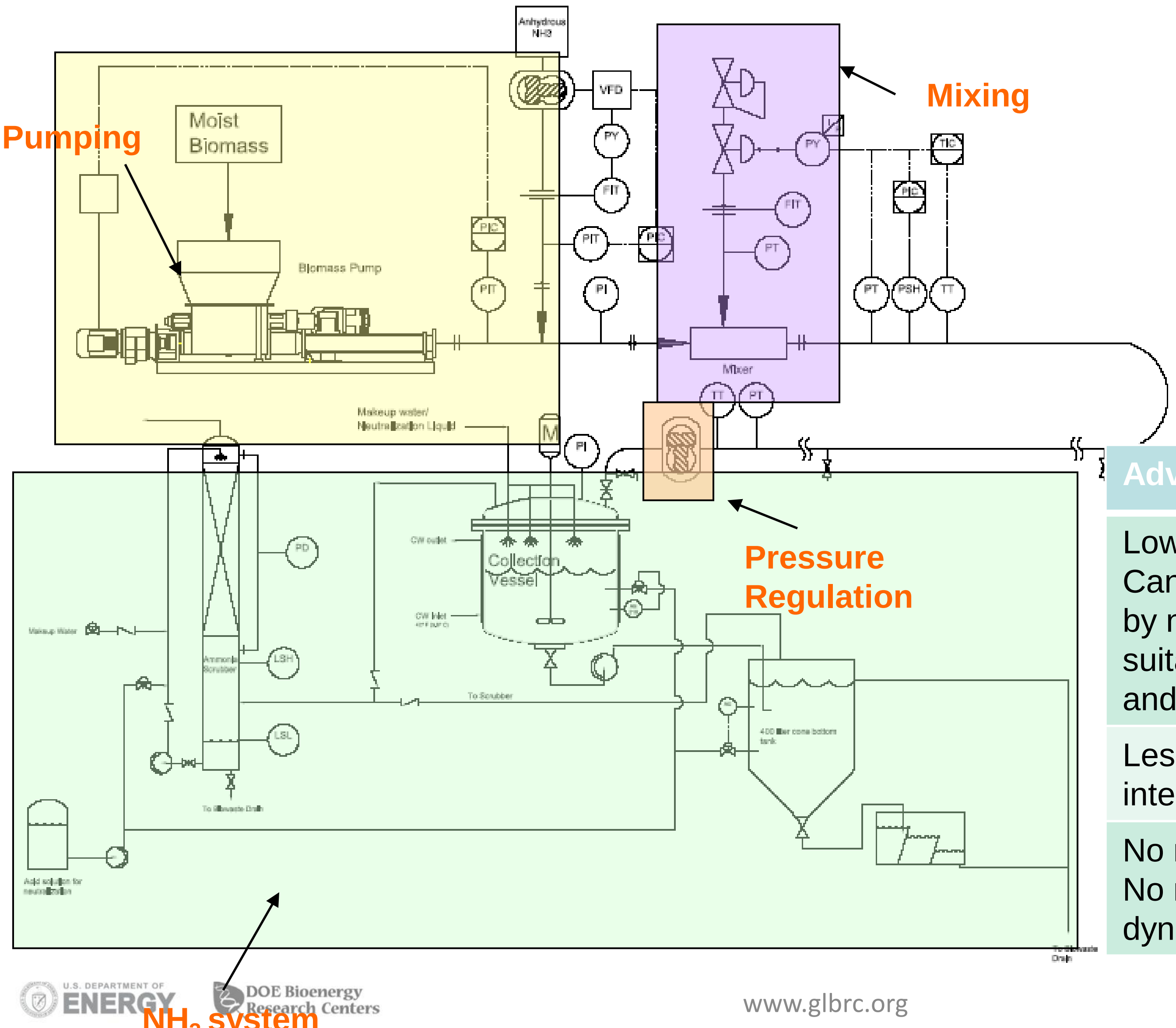
- High double-cropping desired



Demonstrated AFEX™ 2 at 300lb/hr capacity with DDGS

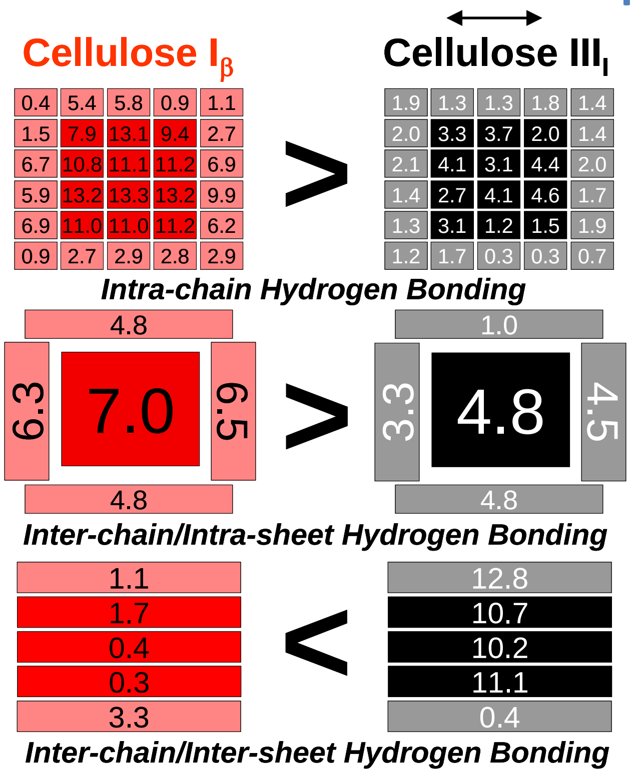
More than 250kg of AFEX™ treated DDGS was generated for an animal feeding trial

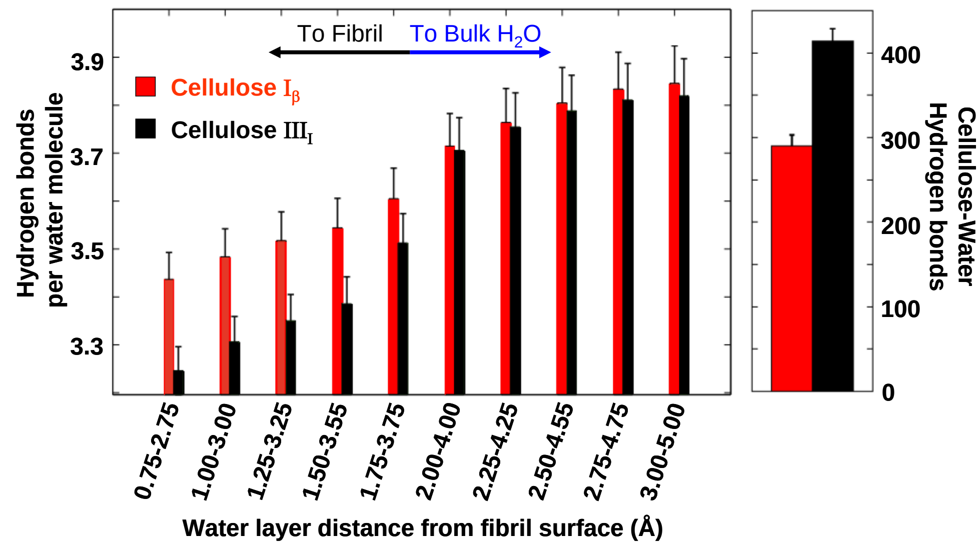
2nd Generation AFEX™ System Design

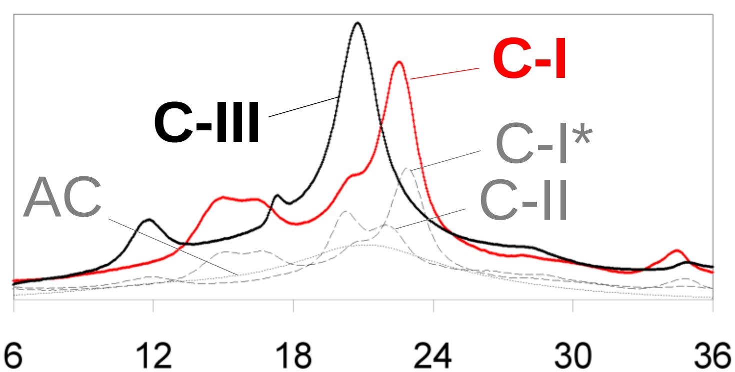


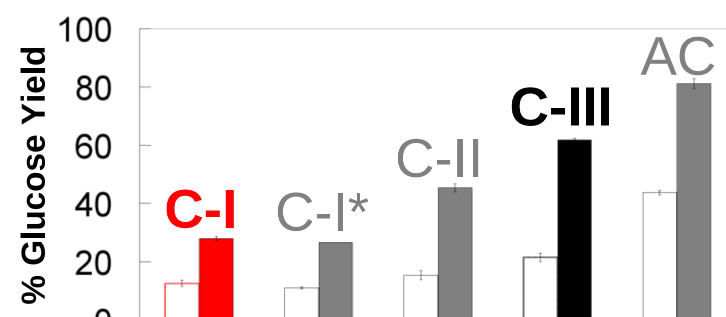
Advantage	Disadvantage
Low capital cost Can be scaled by number, suitable for small and large scale	Can only process pumpable biomass
Less energy intensive	
No moving parts. No need for dynamic seals.	

Cellulose III_I has *amorphous-like* features









- Increased glucan chain flexibility
- Increased hydration of crystal surface
- Increased enzymatic digestibility
- But, equivalent crystallinity to cellulose I

Chundawat et al., 2011, J Am Chem Soc, 133, 11163

“The Stone Age did not end for lack of stone, and the Oil Age will end long before the world runs out of oil.”

Sheikh Zaki Yamani
Former Saudi Arabia Oil Minister

Advantages of an AFEX™ Integrated Biorefinery

"Unique" Feature	Systems Benefit	Overall Outcomes
AFEX can be linked with upstream and downstream steps via stable intermediates	High level of overall process integration from biomass to ethanol	Performs favorably in terms of cost and reduced greenhouse gas emissions
AFEX-treated biomass can be stored and transported	Centralized and decentralized options for integrated biorefinery operation	Flexible deployment of commercial biorefineries in varied geographical areas
Properties of AFEX-treated biomass facilitate densification	Efficient storage and transportation between stages utilizing existing infrastructure	Improves supply-chain logistics
AFEX is effective on multiple agricultural feedstocks	Multiple feedstocks can be processed in a given integrated biorefinery	Mitigates vulnerability to supply chain disruption and facilitates year-round operation
AFEX treatment does not produce high levels of metabolic inhibitors	AFEX treated biomass is compatible with fermentation using diverse organisms	Speeds application to next generation organisms
AFEX treated biomass does not require neutralization, washing or conditioning	AFEX treated biomass can be used as feedstock for a variety of bio-based products	AFEX infrastructure can support both fuels and bio-based chemicals
AFEX-treated biomass can be better digested by ruminants	AFEX-treated biomass can be used as animal feed	Addresses food versus fuel tradeoff and land use issues; Reduces market vulnerability