

Biomass Pretreatment: What do we really know?

Bradley A. Saville, Ph.D., P.Eng

University of Toronto

Department of Chemical Engineering and
Applied Chemistry

Pretreatment: Role and History

- Initiated > 100 years ago for P&P
 - Initially acid pretreatment, followed by steaming and steam explosion (1920s – Masonite steam gun)
 - Pretreatment of cotton with alkaline agents (Mercerization)
 - Continuous steam explosion (1970s)
 - Organosolv (1970s)
 - Ammonia pretreatment (1970s)

Desirable Pretreatment Features

- Results in a high recovery of all carbohydrates, with a minimum of degradation products
- Low capital and operating cost
- Produces a highly digestible solids fraction amenable to enzyme hydrolysis
- Minimizes the need for pre- or post-processing, either due to mechanical size reduction or downstream detoxification
- Operates at a sufficiently high solids loading to avoid dilution of sugars and ethanol
- Able to process a wide variety of feedstocks
- **Trade-offs required!**

Pretreatment “Benchmarks”

- Most of what we “know” about pretreatment comes from small scale batch tests
- Often reported as a severity factor:
 - $\text{Log}(R_o) = \log [t^* \exp((T - T_{ref})/14.75)]$
 - Assumes linear kinetics for xylan hydrolysis from aspen, isothermal operation, and no exogenous catalysts
 - Used widely, **and often used incorrectly**
- More General/Accurate Measure:

$$R_o = \int_0^t \exp\left(\frac{1}{\omega_o} \left(1 - \frac{T_{ref}}{T}\right)\right) t^{n-1} dt$$

Challenges with Scale-up

- The rate of chemical reaction (e.g., xylan hydrolysis) is controlled by heat and mass transfer.
 - HT and diffusion more critical at large scale, and for larger (or less porous) fibers/chips
 - Gases more efficient than liquids
 - But HT, MT, chip size aren't in "severity factors"
- Realistic version accounts for MT, porosity, etc.:

$$R_o = \frac{\text{Pretreatment time}}{\text{Diffusion time}} e^{\left(\frac{(T-100)}{14.7}\right)} 10^{-pH}$$

Key Factors

- ▣ Lignin type and structure
- ▣ Lignin removal
- ▣ DP of cellulose and hemicellulose
- ▣ Type of hemicellulose
 - ▣ Acetylation; presence of glucuronic acids, galacturonic acids
- ▣ Surface area
- ▣ Cellulose crystallinity
- ▣ Cellulose activation/reactivity

PT Affects Fiber Size

High Severity vs. Low Severity Treatment

**Higher Severity
(Fine Fiber)**

**Lower Severity
(Coarse Fiber)**



Effect of Steam PT on Surface Area and Enzyme Accessibility

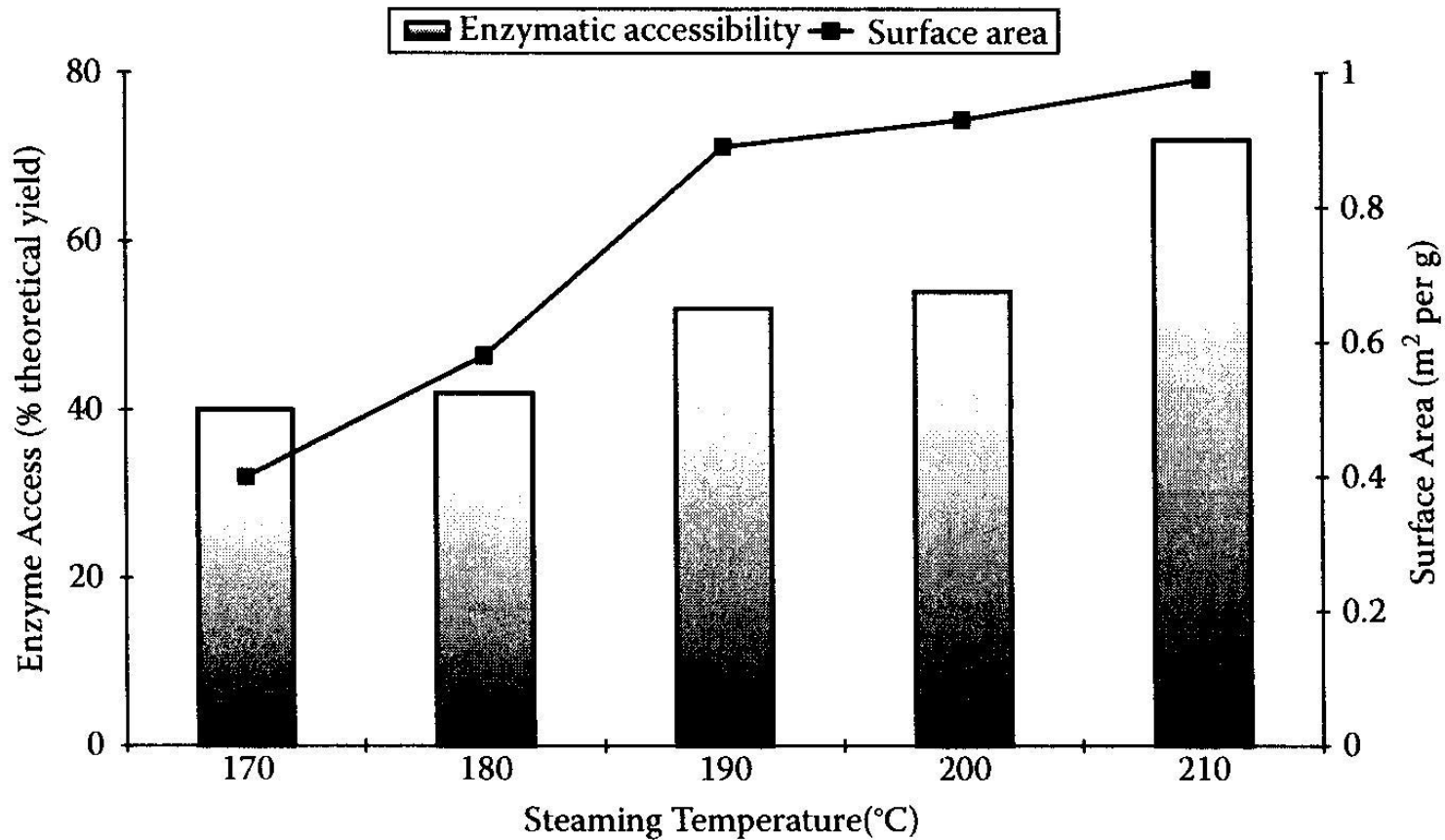


FIGURE 2.4 Efficacy of steaming pretreatments with birch wood. (Data from Puls et al.²³)

Cellulose Activation: Definition

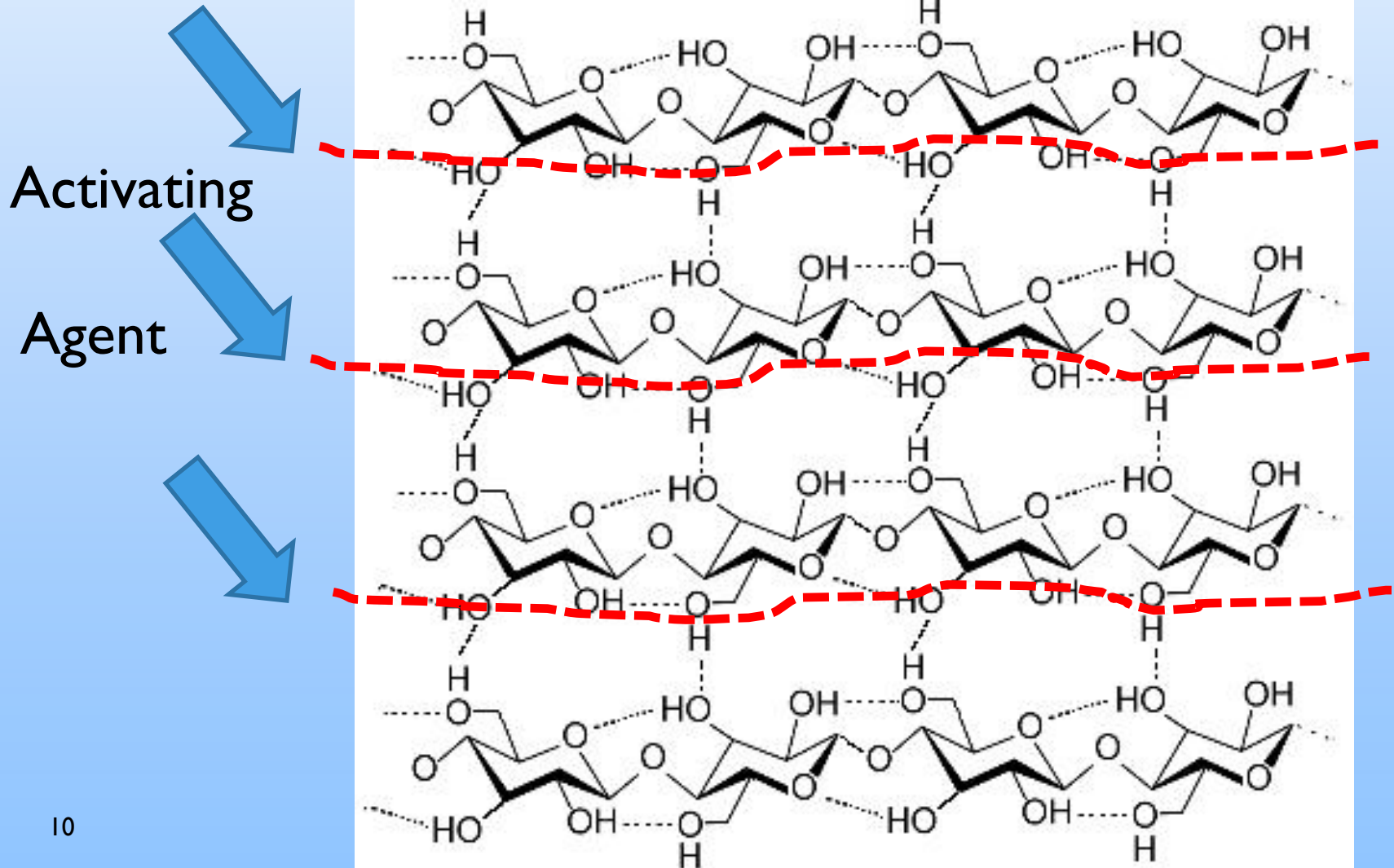
Objective

To increase the accessibility to cellulose supramolecular structure

Means

Inter and intramolecular penetration of activating agents that disrupt the strong water mediated H-bonds of the natural cellulose

Cellulose Activation: Illustration



Cellulose Activation: Methods

- Agent-mediated

 - Ammonia > NaOH > Steam > Hot water

- Solvent-mediated

- Heat-mediated

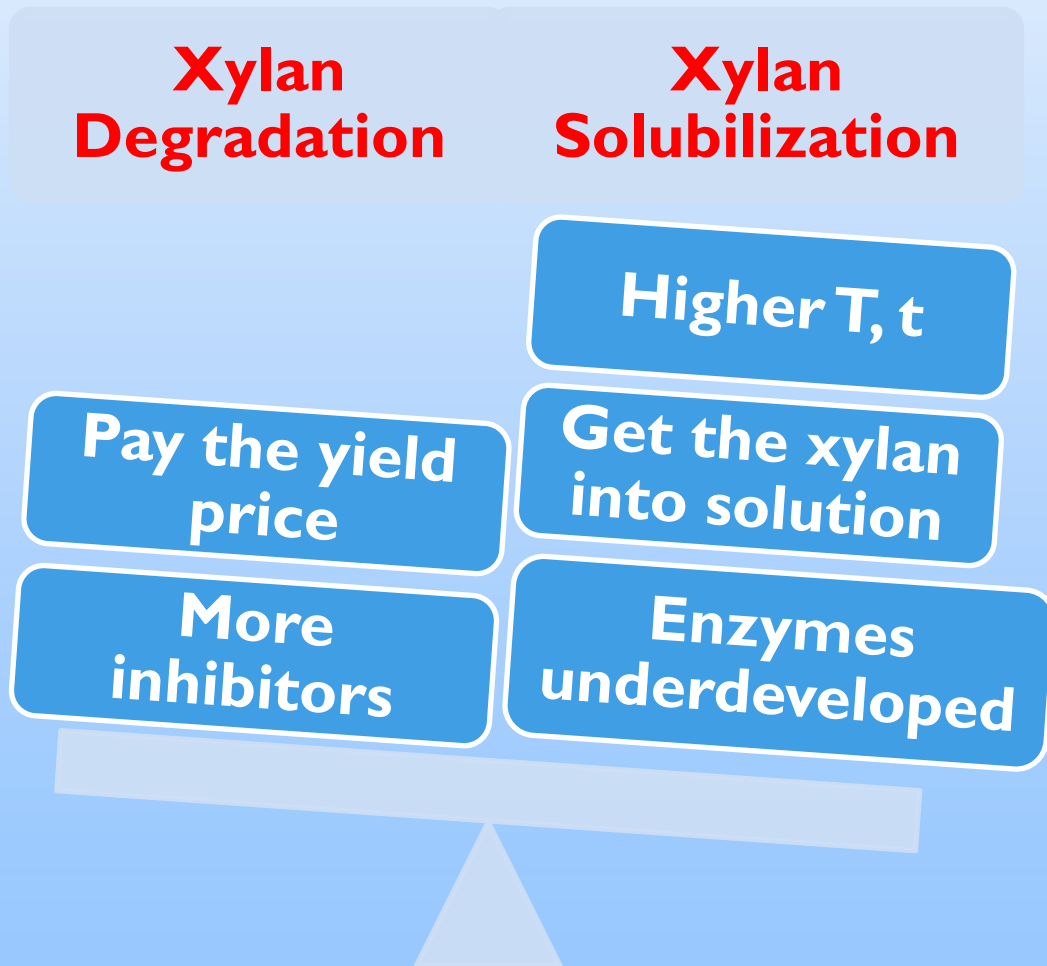
- Radiation-mediated

- Mechanically-mediated

PT Effects on Hemicellulose

- Goal of PT is to sufficiently disrupt hemicellulose and H bonds to facilitate cellulose hydrolysis
- Original goal was to create soluble xylose and oligos
 - May be useful if goal is immediate isolation/recovery of xylose
 - Usually requires very severe pretreatment conditions or long retention times
 - Degrades sugars into inhibitors (furfural, HMF, etc.)
 - More degradation under acidic conditions
- **Conditions needed to ensure cellulose activation are often too severe to avoid xylan/xylose degradation**
 - Option: separate PT stages focused on xylan, then cellulose

Pretreatment: Stone Age



Pretreatment: Modern Age

**Xylan
Preservation**

**Xylan
Hydrolysis**

**Minimize
degradation**

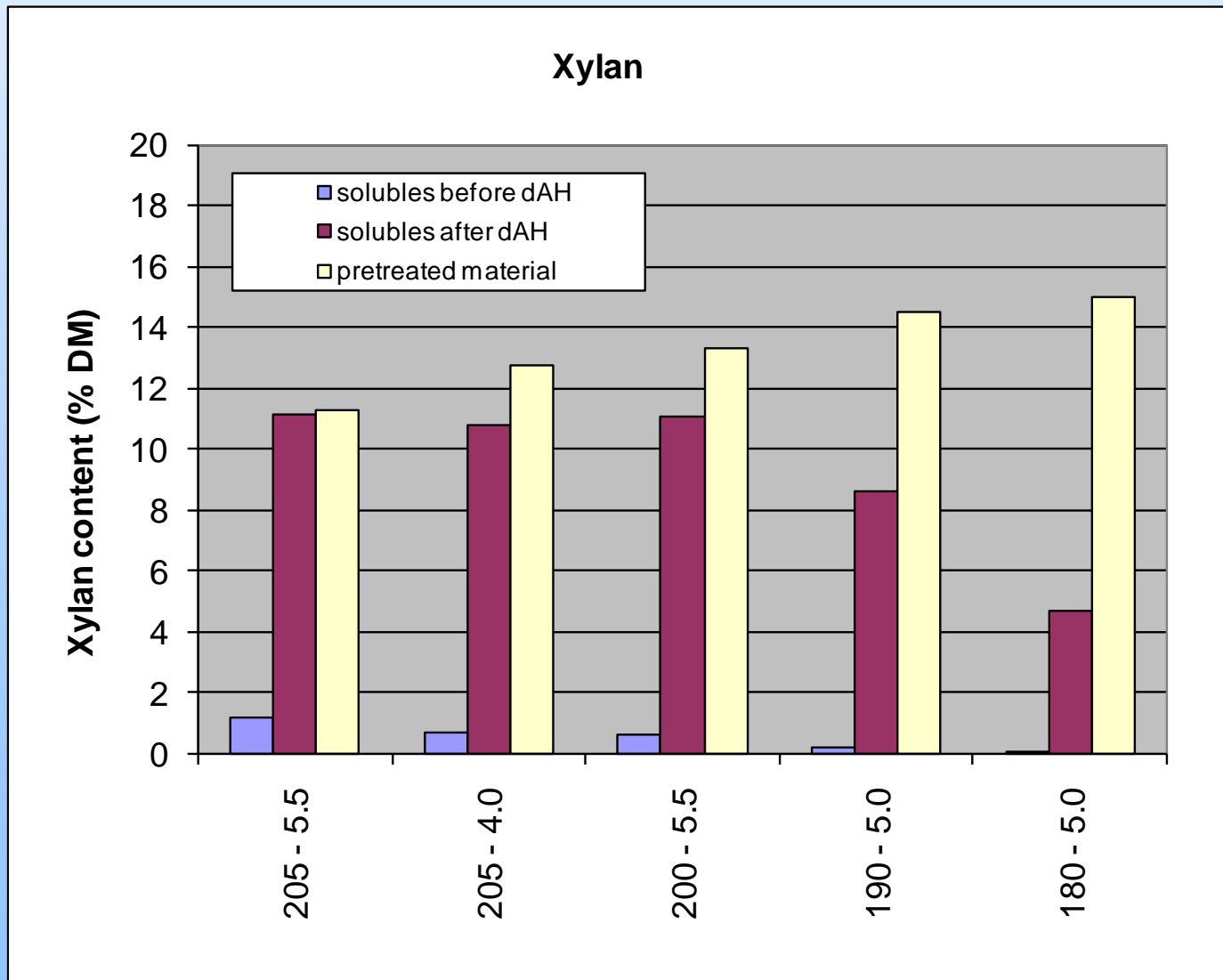
**Less
inhibitors**

Lower T, t

**Hydrolysis
can handle
xylans**

**Enzymes
well
developed**

PT Effects on C5 Solubilization



PT Performance

- Pretreatment performance is linked to all other downstream steps
 - Cannot be measured in isolation
 - Need to consider trade-offs in PT vs. trade-offs in hydrolysis and fermentation to identify a “global” optimum
 - PT impacts process in ways that cannot be analyzed by composition or enzyme hydrolysis, e.g., slurry viscosity and process hydraulic load

PT Effects on Overall Process

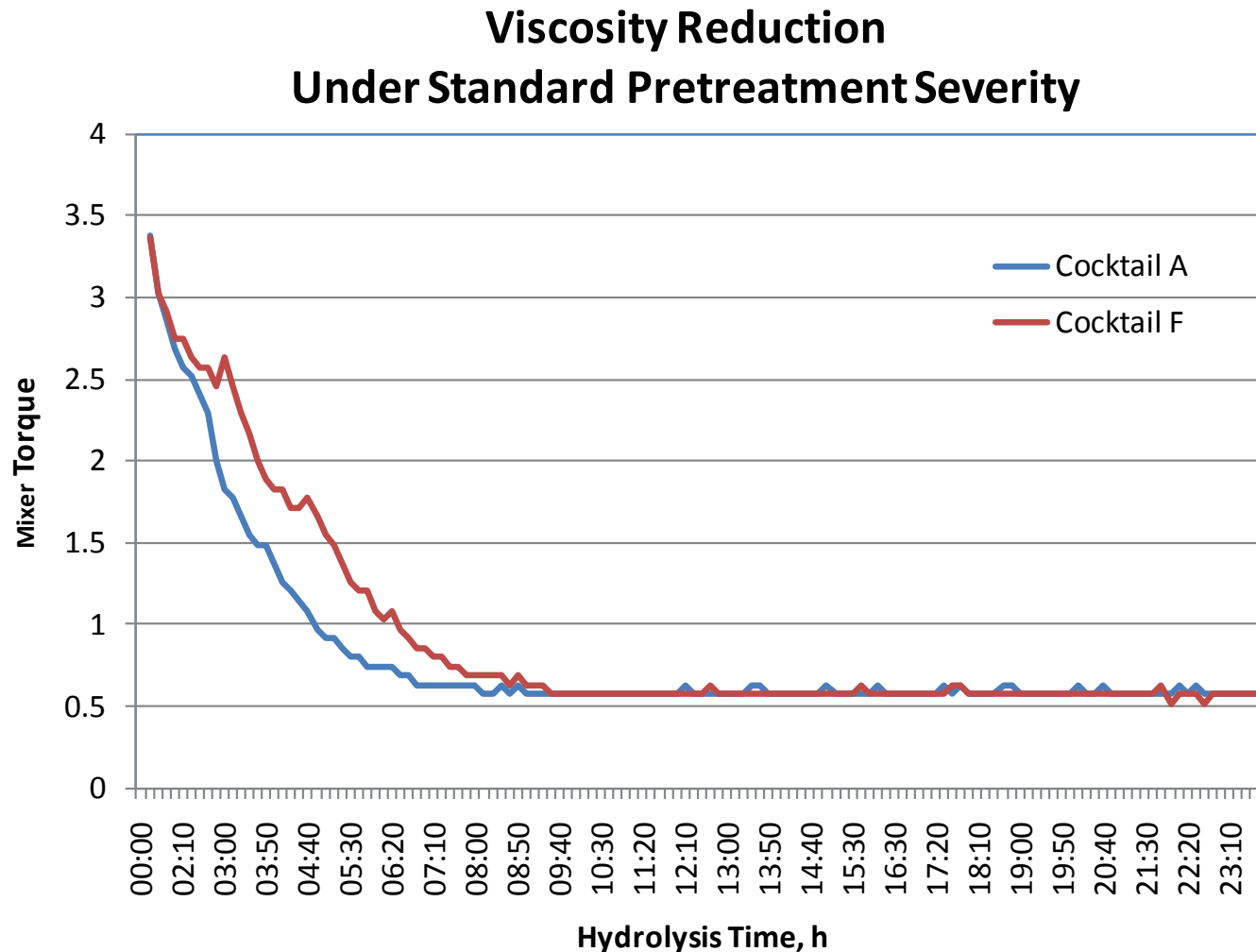


What are the Key Metrics?

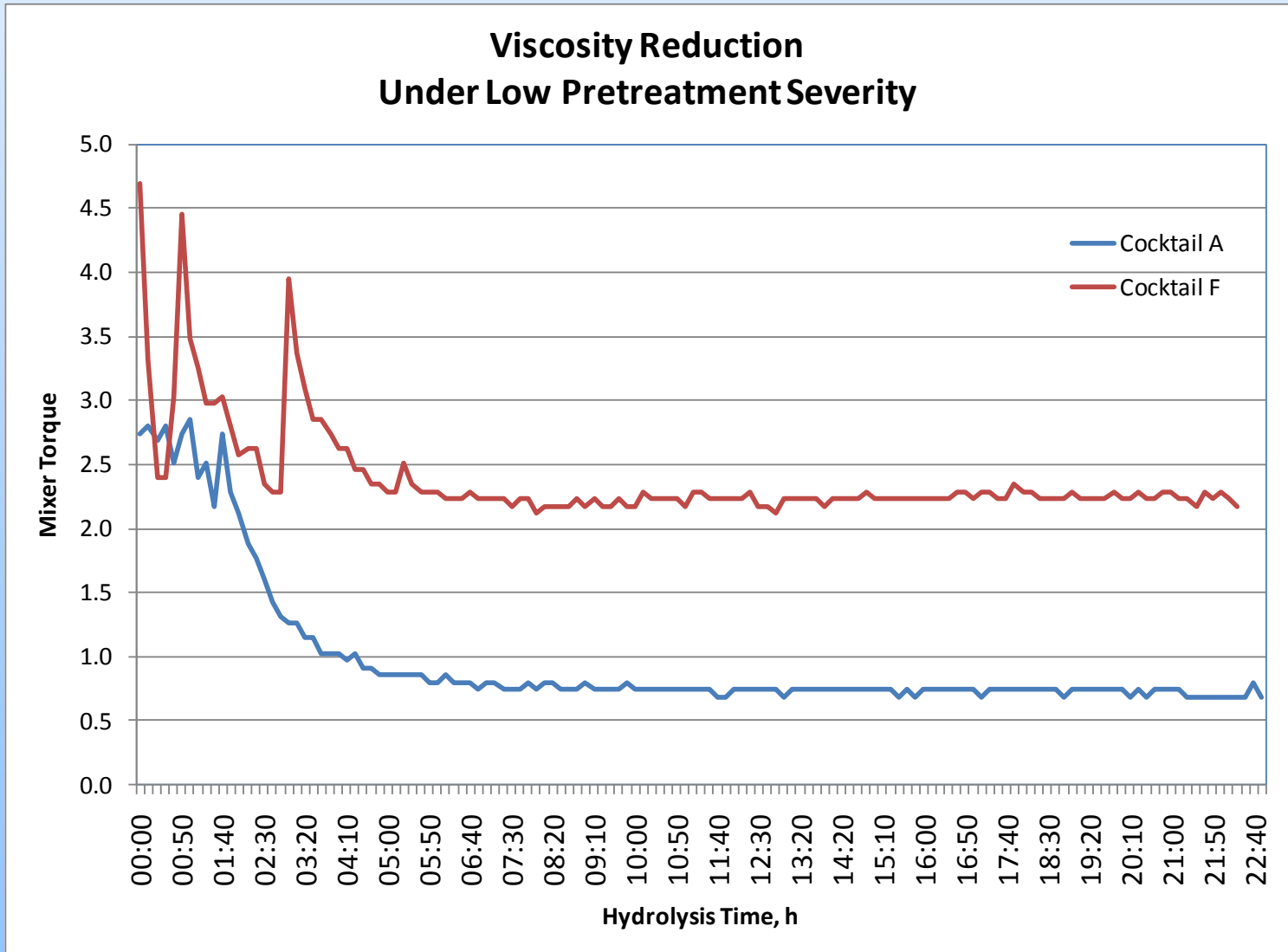
PT Trade-offs: No Free Lunch

Pretreatment	Enzyme Use	Chemical Use	Inhibitors	PT Materials/equipment costs
Dilute Acid	Low to moderate	High	high	High
Ammonia	moderate	moderate to high	low	moderate to high
Autohydrolysis (steam explosion)	Low to moderate	Nil	low to moderate	Moderate
Steam Explosion with SO ₂	Low to moderate	High	moderate to high	moderate to high
Solvent Extraction	low to moderate	High	moderate	low to moderate
Hot Water	high	Nil	low	low to moderate

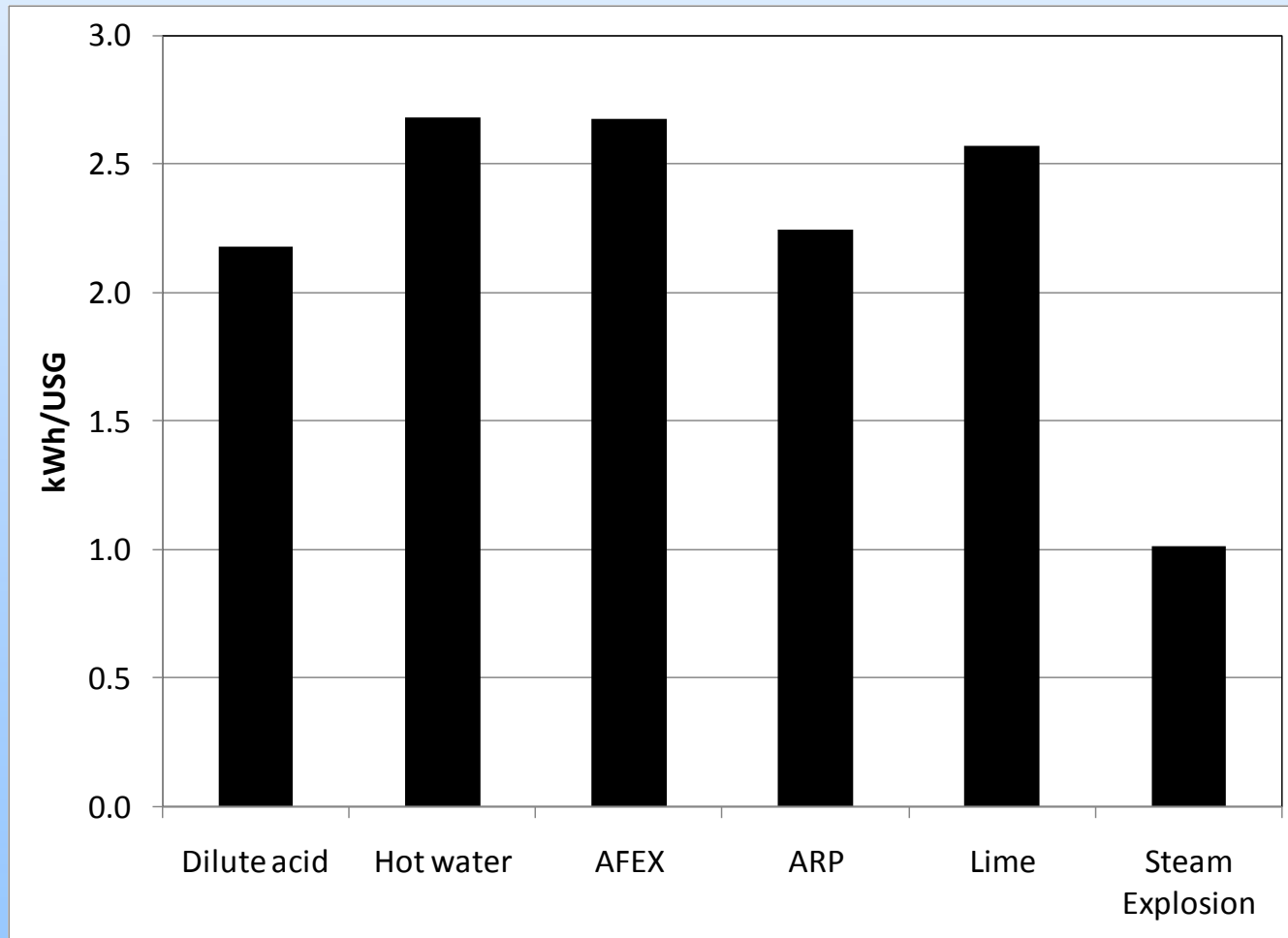
PT affects slurry viscosity: Normal Severity SE



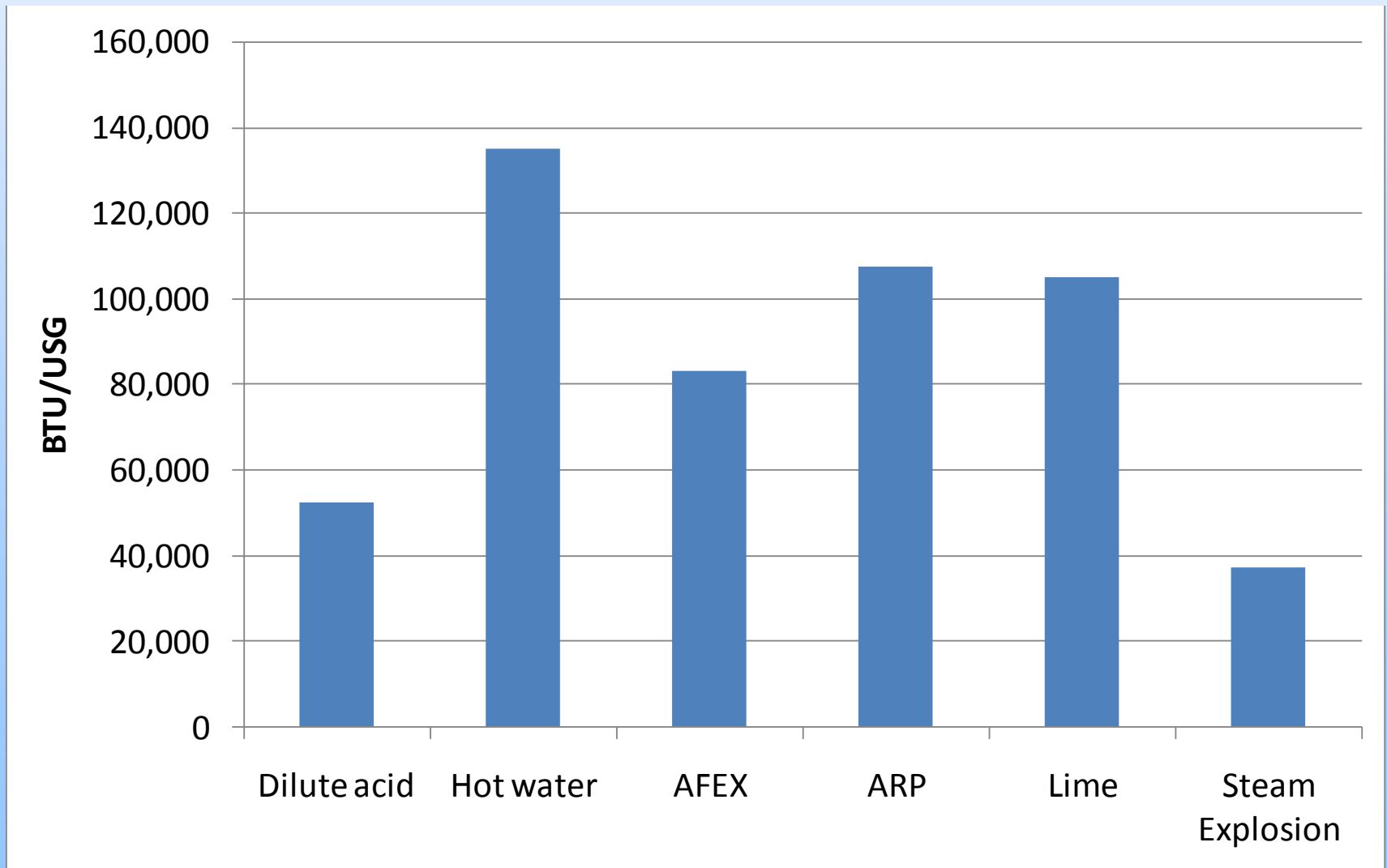
PT affects slurry viscosity: Low Severity SE



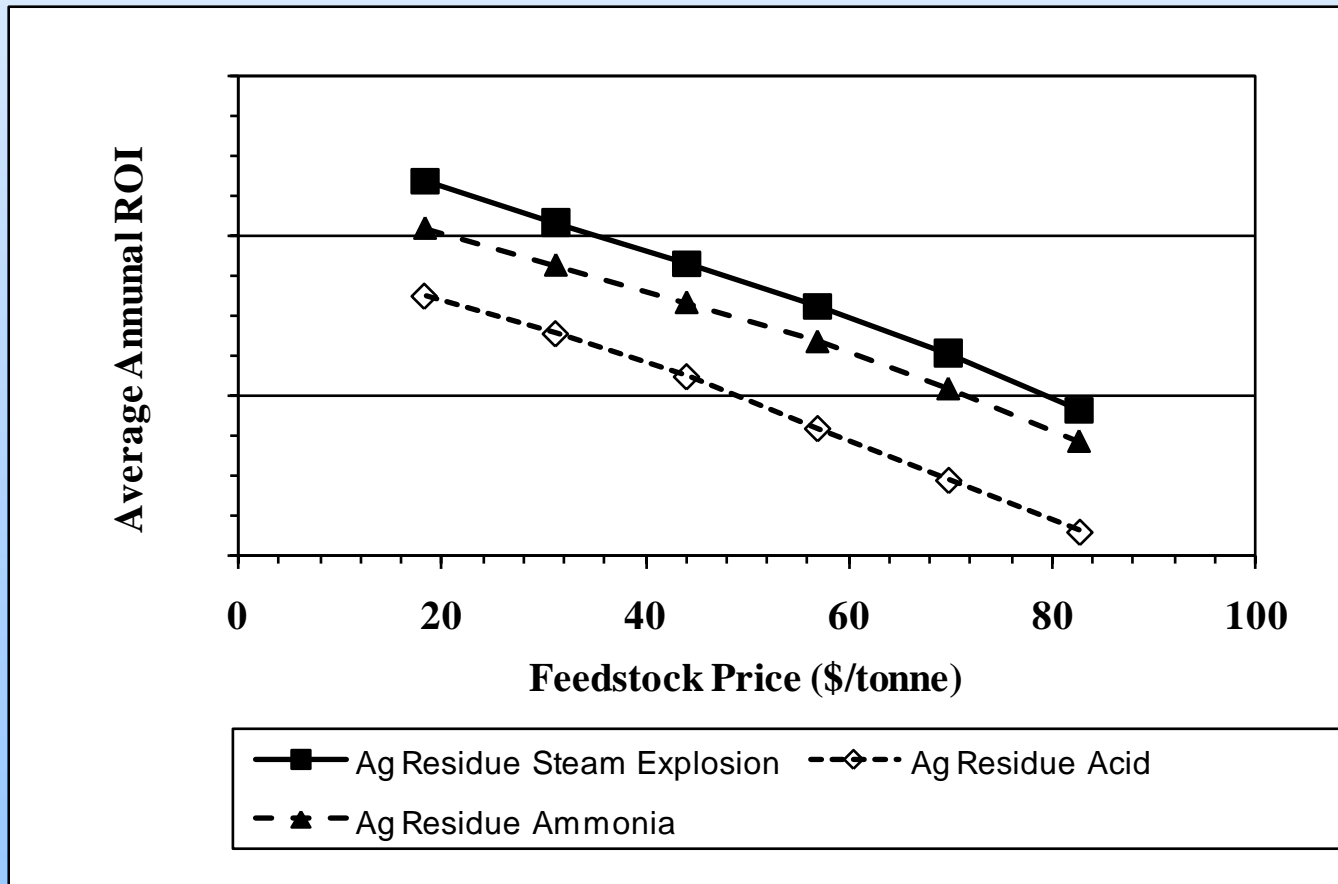
PT Impact on Overall Process Electricity Use



PT Impact on Overall Process Thermal Energy Demand



PT affects Process Economics



Example: SE Poplar with Optimized Hydrolysis and Fermentation


- **Multistage hydrolysis:** 25 - 40% solids & ~72h retention time
 - **First stage:** 50 g/L glucose/xylose + ~ 50g/L soluble oligosaccharides
 - **Second stage:** 150 - 220 g/L sugars (~70% monomers)
- **Fermentation:**
 - Up to 8 wt% ethanol
 - Residual oligos converted to monomers
 - Properly managed, >95% glucose conversion in <30h

Summary

- Multitude of PT Options under development
 - Match to process/product/co-product objectives
- Still a lot to be learned
 - Not easy to translate lab results into pilot performance
- Need to use overall process metrics – consider downstream effects
 - Consider trade-offs between cost, chemical use, enzyme use, rate and yield
 - Avoid extra “clean-up” steps if possible

Implications for Pretreatment

- ▣ Scale and solids loading are critical
- ▣ Pre-treatment:
 - ▣ affects slurry viscosity
 - ▣ affects xylan solubilization and xylose degradation
 - ▣ affects yield
 - ▣ affects enzyme use and hydrolysis rate
 - ▣ affects ethanol titer
 - ▣ Affects **ECONOMICS!**



Thank You!
Questions?

What is a severity factor, really?

- Should be a means to account for heat transfer, mass transfer, diffusion, solubility and substrate reactivity – all factors that dictate the effectiveness of a pretreatment
- Simplified models exclude key parameters
- For example, chip size is not present in any of the severity factor equations, yet it is well known that larger chips require a “more severe” pretreatment than smaller chips

PT Severity Factor

- ▣ $\text{Log}(R_o) = \log [t \cdot \exp((T - T_{\text{ref}})/14.75)]$
- ▣ R_o = “reaction ordinate”
- ▣ 14.75 = constant based on reaction and species
- ▣ t = reaction time, min
- ▣ T = temperature
- ▣ T_{ref} = reference temperature (100C)
- ▣ Assumes linear reaction kinetics, isothermal operation, and no exogenous catalysts
- ▣ Used most often, **and often used incorrectly**

PT Severity Factor:V2

$$R_o = \int_0^t \exp\left(\frac{1}{\omega_o} \left(1 - \frac{T_{ref}}{T}\right)\right) dt$$

- ω_o = characteristic reaction parameter
 - $= RT_{ref}/E_A = \omega/T$
 - Activation energy (E_A) is depends on substrate, desired reaction, and presence of catalysts or solvents
- T can now vary with time – important for batch processes with heat-up and cool-down time (reactions continue!)

PT Severity Factor:V2

- $\omega = 14.75$ for hemicellulose solubilization from hardwoods
- $\omega = 10$ for lignin solubilization during acid-catalyzed organosolv PT of aspen
- $\omega = 11$ for xylan solubilization during acid-catalyzed organosolv PT of aspen
- Changing ω from 14.75 to 11 increases R_o ten-fold, and $\log(R_o)$ by 1
- **MUST adapt ω to pretreatment process and feedstock**

PT Severity Factor:V3

- ▣ Versions thus far assume biomass is homogeneous (really!)
- ▣ Account for this with a heterogeneity parameter, γ , based upon the shape/distribution of the activation energy curves for the heterogeneous feedstock

$$R_o = \int_0^t \exp\left(\frac{1}{\omega_o} \left(1 - \frac{T_{ref}}{T}\right)\right) t^{\gamma-1} dt$$

- ▣ $\gamma = 1$ for a homogeneous system
- ▣ γ depends on feedstock, reaction, presence of catalysts, etc.

Alternate view on pretreatment severity

- See Hosseni and Shah (cited earlier)
 - Considered time-dependent gradients, diffusional effects, reaction kinetics
 - Applies Fick's law, Re, Sc, Gr, and fundamental kinetics
 - Includes porosity of fiber
 - Suggested modified severity factor considering time constants for diffusion and pretreatment

$$R_o = \frac{\text{Pretreatment time}}{\text{Diffusion time}} e^{\left(\frac{(T-100)}{14.7}\right)} 10^{-pH}$$

Severity factors

- Proliferation of incorrectly developed severity factors makes it an unreliable means to compare pretreatment processes, feedstocks, the impact or value of catalysts or solvents

Effect of Pretreatment Severity on Xylan Degradation

Biomass	Glucan	Xylan	Xylan Degrad.	Ash	Lignin^a
Poplar wood chips	46.1%	18.3%		0.7%	29.5%
Pretreated Fibre (206/207°C, 8-9minutes)	48.9%	7.7%	58%	0.7%	35.0%
Pretreated Fibre (205°C, 8minutes)	49.3%	12.9%	30%	0.8%	34.0%
Pretreated Fibre (200°C, 8minutes)	48.7%	14.3%	22%	0.6%	31.1%
Pretreated Fibre (200°C, 7 minutes)	48.9%	12.2%	10%	0.7%	32.0%

Pretreatment: References

▣ References:

- ▣ L. da Costa Sousa et al., *Curr. Opin. Biotechnol.*, 2009, vol 20, 339-347
- ▣ Hendriks and Zeeman, 2009, *Bioresource Technol* vol 100, 10-18
- ▣ Hosseini and Shah, 2009, *Bioresource Technol*, 100, 2621-2628
- ▣ G. Hu et al., *Bioresources*, 2008, vol 3(1), 270-254.
- ▣ B.A. Saville, in *Plant Biomass Conversion*, Ch 9; (Hood, Nelson, Powell (eds)
- ▣ Yang and Wyman, *BioFPR*, 2008, vol 2, 26-40