Biomass Pretreatment: What do we really know?

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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!
Most of what we “know” about pretreatment comes from small scale batch tests

Often reported as a severity factor:

\[ \log(R_o) = \log \left[ t \times \exp \left( \frac{(T - T_{\text{ref}})}{14.75} \right) \right] \]

Assumes linear kinetics for xylan hydrolysis from aspen, isothermal operation, and no exogenous catalysts

Used widely, and often used incorrectly

More General/Accurate Measure:

\[ R_o = \int_0^t \exp \left( \frac{1}{\omega_o} \left( 1 - \frac{T_{\text{ref}}}{T} \right) \right) t^{\gamma-1} dt \]
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.:

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

Activating Agent
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

Xylan Degradation
- Pay the yield price
- More inhibitors

Xylan Solubilization
- Higher $T, t$
- Get the xylan into solution
- Enzymes underdeveloped
Pretreatment: Modern Age

Xylan Preservation
- Minimize degradation
- Less inhibitors
- Lower T, t

Xylan Hydrolysis
- Hydrolysis can handle xylans
- Enzymes well developed
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?
<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Enzyme Use</th>
<th>Chemical Use</th>
<th>Inhibitors</th>
<th>PT Materials/equipment costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute Acid</td>
<td>Low to moderate</td>
<td>High</td>
<td>high</td>
<td>High</td>
</tr>
<tr>
<td>Ammonia</td>
<td>moderate</td>
<td>moderate to high</td>
<td>low</td>
<td>moderate to high</td>
</tr>
<tr>
<td>Autohydrolysis (steam explosion)</td>
<td>Low to moderate</td>
<td>Nil</td>
<td>low to moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Steam Explosion with SO₂</td>
<td>Low to moderate</td>
<td>High</td>
<td>moderate to high</td>
<td>moderate to high</td>
</tr>
<tr>
<td>Solvent Extraction</td>
<td>low to moderate</td>
<td>High</td>
<td>moderate</td>
<td>low to moderate</td>
</tr>
<tr>
<td>Hot Water</td>
<td>high</td>
<td>Nil</td>
<td>low</td>
<td>low to moderate</td>
</tr>
</tbody>
</table>
PT affects slurry viscosity: Normal Severity SE

Viscosity Reduction
Under Standard Pretreatment Severity

Cocktail A
Cocktail F

Mixer Torque

Hydrolysis Time, h

00:00 02:10 03:00 03:50 04:40 05:30 06:20 07:10 08:00 08:50 09:40 10:30 11:20 12:10 13:00 13:50 14:40 15:30 16:20 17:10 18:00 18:50 19:40 20:30 21:20 22:10 23:00
PT affects slurry viscosity: Low Severity SE

Viscosity Reduction Under Low Pretreatment Severity

Mixer Torque

Hydrolysis Time, h

Cocktail A
Cocktail F
PT Impact on Overall Process
Electricity Use

<table>
<thead>
<tr>
<th>Process</th>
<th>kWh/USG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute acid</td>
<td>2.0</td>
</tr>
<tr>
<td>Hot water</td>
<td>2.5</td>
</tr>
<tr>
<td>AFEX</td>
<td>2.7</td>
</tr>
<tr>
<td>ARP</td>
<td>2.0</td>
</tr>
<tr>
<td>Lime</td>
<td>2.5</td>
</tr>
<tr>
<td>Steam Explosion</td>
<td>1.0</td>
</tr>
</tbody>
</table>
PT Impact on Overall Process Thermal Energy Demand

Effect of Pretreatment Technology on Thermal Energy Demand for Cellulosic Ethanol

<table>
<thead>
<tr>
<th>Technology</th>
<th>BTU/USG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute acid</td>
<td></td>
</tr>
<tr>
<td>Hot water</td>
<td>140,000</td>
</tr>
<tr>
<td>AFEX</td>
<td>110,000</td>
</tr>
<tr>
<td>ARP</td>
<td>100,000</td>
</tr>
<tr>
<td>Lime</td>
<td>90,000</td>
</tr>
<tr>
<td>Steam Explosion</td>
<td>40,000</td>
</tr>
</tbody>
</table>
PT affects Process Economics

![Graph showing the impact of feedstock price on average annual ROI for different Ag Residue processes. The graph illustrates how different processes are affected by changes in feedstock price, with Ag Residue Steam explosion showing the most significant decrease in ROI as feedstock price increases.]
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
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
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.
Log($R_o$) = log [t*exp((T – $T_{ref}$)/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
\[ R_o = \int_0^t \exp\left(\frac{1}{\omega_o} \left(1 - \frac{T_{\text{ref}}}{T}\right)\right) dt \]

- \( \omega_o = \) characteristic reaction parameter
  - \( = RT_{\text{ref}}/E_A = \omega/T \)
  - 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!)
- $\omega = 14.75$ 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 $\omega$ from 14.75 to 11 increases $R_\omega$ ten-fold, and $\log(R_\omega)$ by 1
- MUST adapt $\omega$ to pretreatment process and feedstock
Versions thus far assume biomass is homogeneous (really!)

Account for this with a heterogeneity parameter, $\gamma$, based upon the shape/distribution of the activation energy curves for the heterogeneous feedstock

$$\gamma = 1$$ for a homogeneous system

$\gamma$ 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

\[
R_o = \frac{\text{Pretreatment time}}{\text{Diffusion time}} \cdot e^{\frac{(T-100)}{14.7}} \cdot 10^{-pH}
\]
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

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

- Hendriks and Zeeman, 2009, Bioresource Technol vol 100, 10-18
- Hosseini and Shah, 2009, Bioresource Technol, 100, 2621-2628
- B.A. Saville, in Plant Biomass Conversion, Ch 9; (Hood, Nelson, Powell (eds)