Oligosaccharide Hydrolysis in Plug Flow Reactor using Strong Acid Catalyst

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Joan Goetz, Composition Analysis
Winnie Chen, Comments
Outline

• Goal
• Strong Acid Cation Exchanger
• Effect of Resin Crosslinking and Particle Size
• Economic Evaluation
• Conclusions
Motivation

Fuel Ethanol

• Annual U.S. ethanol production capacity from corn will reach 4 billion gallons in 2005 (RFA, 2005)\(^1\)

• Lignocellulosics are potential source of ethanol

• Estimated production cost from cellulose to be from $1.15 to $1.43/ gal (Wooley et al, 1999)\(^2\)

• Enzyme cost contributes 20-30 ¢/ gal to the production cost of ethanol (Williams and Bryan, 2005)\(^3\)

2. Wooley, R; Ruth, M.; Glassner, D; Sheehan, J. Biotechnology Progress, Vol. 15, pp. 794-803, 1999
Goal of Research

- Solid acid catalysts for saccharification of oligosaccharides
- Study mechanisms of solid acid catalysis
- Reduce cost of saccharification to 10¢/gal
Pretreatment Forms Oligosaccharides

Corn Fiber → Pretreatment

Water → Pretreatment

Liquid with Dissolved Oligosaccharides (Glucan, Xylan) → Solids

Pretreatment → Corn Fiber
Pretreatment of Corn Fiber

Pressure cooking in water

- Solubilize hemicellulose and glucans
  (Weil et al, 1998)$^1$

- Minimize monosaccharide formation and loss of sugar due to further degradation
  (Weil et al, 1997)$^2$

## Composition of Corn Fiber

<table>
<thead>
<tr>
<th>Component</th>
<th>% of dry weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucan (Cellulose)</td>
<td>14.3</td>
</tr>
<tr>
<td>Glucan (Starch)</td>
<td>23.7</td>
</tr>
<tr>
<td>Xylan/Galactan</td>
<td>16.8</td>
</tr>
<tr>
<td>Arabinan</td>
<td>10.8</td>
</tr>
<tr>
<td>Protein</td>
<td>11.8</td>
</tr>
<tr>
<td>Lignin</td>
<td>8.4</td>
</tr>
<tr>
<td>Acetyl</td>
<td>NA</td>
</tr>
<tr>
<td>Ash</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Composition of Liquid from Corn Fiber Pretreated at 160 ºC, 20 min

9.6 g of Corn Fiber + 24.1 ml of DI water
- 16% Solids in Liquid (160 g/L)
Stainless steel tube reactor
- total vol. : 35 ml

<table>
<thead>
<tr>
<th>Dissolved in de-ionized water (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligosaccharides (Glucan, Xylan, Arabinan)</td>
</tr>
<tr>
<td>Monosaccharides</td>
</tr>
<tr>
<td>Proteins</td>
</tr>
<tr>
<td>HMF, Furfural</td>
</tr>
</tbody>
</table>
Liquid Clean-up

- Proteins and minerals in pretreated liquid deactivate acid groups of catalyst
- Precondition of corn Fiber pretreated liquid to remove proteins and minerals

Liquid from Pretreated Corn Fiber

Protein In : 4.9 ± 0.8 g/L

2%, A35, Room Temp.

Preconditioning

Protein Out : 0 g/L
This Work: Fixed Bed Catalysis for Monosaccharide Formation

Cleaned-up Liquid with Dissolved Glucan Xylan Arabinan

Strong Cation Exchange Resin

Glucose Xylose Arabinose
Catalyst

**Gel Type**
10-20 Å (Dorfner, 1972)
4-10 % Crosslinked

**Macroreticular Type**
200-250 Å
A35

Dorfner, K., Ion exchangers: properties and applications, Ann Arbor Science, 1972, p. 34
Liquid from Pretreated Corn Fiber before and after Hydrolysis (Catalyst: Dowex 50WX2)

HPLC chromatogram using HPX-87H column

Retention Time (min)

1. Oligosaccharides (DP >2)
2. Cellobiose
3. Xylobiose
4. Glucose
5. Xylose
6. Arabinose

Before Hydrolysis
After Hydrolysis
### Strong Acid Cation Exchangers Screened as Possible Catalysts

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Moisture Content (%)</th>
<th>Ion Exchange Capacity (meq / g dry resin)</th>
<th>Acid Density (M) (25 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A35</td>
<td>Macro-Reticular</td>
<td>52</td>
<td>5.12</td>
</tr>
<tr>
<td>50WX2</td>
<td>Gel (2% cross linking)</td>
<td>82</td>
<td>6.4</td>
</tr>
<tr>
<td>SK104</td>
<td>Gel (4% cross linking)</td>
<td>71</td>
<td>5.0</td>
</tr>
<tr>
<td>SK110</td>
<td>Gel (10% cross linking)</td>
<td>48</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Effect of Resin Cross Linking and Resin Type
Maltooligosaccharide Hydrolysis,
(2 g/L, MW=800, at 130 °C, R_p =1.05 mm )

Glucose Yield (%) = 100 x [G] / [Oligo]_t=0

Space Time (g catalyst min/cm^3)
Effect of Resin Particle Size
Maltooligosaccharide Hydrolysis,
(SK104, $R_p = 1.05 \text{ mm or 0.55 mm, at 130 } ^\circ\text{C}$)

![Graph showing glucose yield vs. space time for 0.55 mm and 1.05 mm particle sizes.](image-url)
Kinetic Expressions

Oligosaccharides (P) \[ k_1 \rightarrow \text{Monomeric Sugars (G)} \]
\[ k_2 \rightarrow \text{Degradation Products (D)} \]

\[
k_1 = \eta_1 \cdot K_1 \cdot [H^+]^m \cdot \exp\left(\frac{-E_1}{RT}\right)
\]

\[
k_2 = \eta_2 \cdot K_2 \cdot [H^+]^n \cdot \exp\left(\frac{-E_2}{RT}\right)
\]

\[
\frac{k_1}{k_2} \uparrow \quad \text{Sugar Yield} \uparrow
\]

\[
\eta = \frac{\text{rate with diffusion resistance}}{\text{rate without diffusion resistance}} = \frac{3}{\phi} \left(1 - \frac{1}{\tanh \frac{1}{\phi}}\right)
\]

\[
\phi = R_i \sqrt{\frac{k_1}{D_{eff}}}
\]

\[ k= \text{Apparent rate constant, cm}^3/\text{g catalyst·min} \]
Factors affecting Sugar Yield

If pore diffusion resistance is important, to increase sugar yield,

\[ \frac{k_1}{k_2} \uparrow \eta_1 \uparrow \phi = R_i \sqrt{\frac{k_1}{D_{eff}}} \downarrow \]

\( R_i \) (Resin Particle Size) \downarrow

\( D_{eff} \) (Effective Diffusivity) \uparrow

= f (degree of cross-linking, pore size, pore tortuosity)

Less Diffusion Resistance
Dowex® 50WX2

- Size: 100-200 mesh (75-150 µm)

- Gel type strong cation exchange resin (2% Cross-Linked)

- Tested for hydrolysis of cellobiose and oligosaccharide from corn fiber pretreated liquid
Cellobiose Hydrolysis

50WX2 (2% Crosslinked Gel type) and A35 (Macroreticular)

\[
\begin{align*}
G-G & \quad k_1 \quad 2G \quad k_2 \quad HMF
\end{align*}
\]

- 50WX2 (150 °C, \( k_1/k_2 = 370 \))
- 50WX2 (130 °C, \( k_1/k_2 = 520 \))
- A35 (130 °C, \( k_1/k_2 = 51 \))
Hydrolysis of Pretreated Corn Fiber Liquid
(Preconditioned using 2% A35, 50WX2, 150 °C)

Space Time (g catalyst min/cm³)

Remaining Oligosaccharides
Fermentable Sugars, and Sugar Loss to Degradation Products (%)

Sugar Yield
Degradation Products
Remaining Oligosaccharides
Deactivation of Resins

- Desulfonation: Irreversible deactivation of resin through loss of sulfonic groups occurring at above 120°C

- Half life of 50WX2 at 150°C: 150 hrs

- Fouling: by irreversible adsorption of degradation products or unremoved proteins

First Estimate Incremental Cost of Catalyst per Gal of EtOH Produced from Glucose

- $10/ lb catalyst
- $5/ lb catalyst
- $2/ lb catalyst
- $1/ lb catalyst
Estimated Incremental Cost of Catalyst per Gal of EtOH Produced from Glucose

- Feed Concentration : 50 g/L
- Hydrolysis using 50WX2 at 150 °C, Space Time=0.85 g catalyst min/ cm³
  Conversion :90%
  Sugar Yield : 80%
- Assume all fermentable sugars present as glucose

<table>
<thead>
<tr>
<th></th>
<th>No deactivation</th>
<th>Deactivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose Produced after 150 hr (lb glucose/ lb catalyst)</td>
<td>970</td>
<td>700</td>
</tr>
<tr>
<td>Incremental Cost (¢/ gal Ethanol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>For $2/lb catalyst</td>
<td>3.0</td>
<td>4.1</td>
</tr>
<tr>
<td>For $5/lb catalyst</td>
<td>7.4</td>
<td>10.2</td>
</tr>
</tbody>
</table>
Conclusions

• Oligosaccharide hydrolysis is diffusion controlled.
• Sugar yield increases as % cross-linking and size of resin particle decrease (consistent with diffusion control).
• 90% conversion and 80% of sugar yield were achieved using 50WX2 resin at
  150 °C
  Space time = 0.85 g catalyst min/cm³.
• Improvements in catalyst life and selectivity are required.