Towards Biomass Sugars Purification

Wood Sugar Monomers: A Case Study

Conference Montreal – 18/6/13
Dan Cooper, Sales Area Manager
Frederic Schab, R&D Project Manager, PhD
Novasep Group Today

300 M€ turnover
1200 people, 200 in R&D
13 sites

Over 650 customers served worldwide
Over 100 R&D projects per year
Over 100 different active molecules produced per year
Over 2,000 purification systems installed worldwide
Industrial Biotech at Novasep

**Food Ingredients**
- Sucrose
- Starch and derivatives
- Milk

**Functional Ingredients**
- Polyphenols
- Anthocyanes
- Oligosaccharides
- HI Sweeteners

**Bio-Industries**
- Bio Based Chemicals
- Organic Acids
- Aminoacids
- Antibiotics
- Vitamins
Pure Chemicals from Complex Mixtures

Chemical Catalysis

Enzymatic Catalysis

Novasep Purification Technologies

- Feed material
- Side products
- Salts
- Proteins
- Biomass

Further valorization

Bio-Based Chemical

Cellulosic sugars

- Fermentation Broth
A Methodology from Lab to Commercial

Screening studies
Process Design & Optimization
Pilot studies

Supply of Equipment with Process Guaranteed

In-house Process Simulation
Process Integration With Upstream & Side Stream
Demo batch production
Cost-efficient Processes for Production Plants

Marketed products prices typically \(< 2\text{\(\varepsilon\)/kg}

From \(20 \text{ – } 250 \text{ kT/year}\)

Molasses desugarization plant
Biomass sugars
One Idea: Thousands Pathways

**Biomass sources**
- Wheat straw
- Hardwood - Softwood
- Paper pulp residues
- Corn stover
- Cane bagasse
- Etc.

**Hydrolysis routes**
- Acid
- Caustic
- Enzymatic
- Steam explosion
- Organosolv
- Ionic liquid
- Etc.

**Target products**
- Ethanol
- Fermentation substrates
- Alditols / glycols
- Oligosaccharides
- Polymers...
- Etc.

Multiple:
- Sugar profiles
- Impurities profiles
- Pathways

Need for process flexibility and robustness to meet the target
# Post-Hydrolysis Impurities

<table>
<thead>
<tr>
<th>Biomass Source</th>
<th>Paper pulp lignosulfonates</th>
<th>Wheat straw</th>
<th>Wheat straw</th>
<th>Wheat straw</th>
<th>Hardwood</th>
<th>Wood</th>
<th>Cane bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis type</td>
<td>Bisulfite (MgHSO3)2</td>
<td>Organosolv</td>
<td>Acid</td>
<td>Enzymatic</td>
<td>Enzymatic</td>
<td>Acid</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>pH</td>
<td>4</td>
<td>1.6</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>0 - 2</td>
<td></td>
</tr>
<tr>
<td>Monomer Sugar % / DS</td>
<td>54</td>
<td>28</td>
<td>73.4</td>
<td>77</td>
<td>72</td>
<td>56</td>
<td>5</td>
</tr>
<tr>
<td>Polymers / Oligomers % / DS</td>
<td>10.1</td>
<td>26</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>2.5 - 20</td>
<td>0.5</td>
</tr>
<tr>
<td>Ashes % / DS</td>
<td>19.2</td>
<td>16.4</td>
<td>11.4</td>
<td>3</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suspended solids % / DS</td>
<td>5.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5 - 10</td>
<td></td>
</tr>
<tr>
<td>HMF Furfural g/L</td>
<td>0.23</td>
<td>0.06</td>
<td>0.05</td>
<td></td>
<td>0.3 - 3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific impurities % / DS</td>
<td>8.4 g/L SO4</td>
<td></td>
<td></td>
<td></td>
<td>9.7 g/L acetate + SO4</td>
<td>60 % ZnCl2</td>
<td></td>
</tr>
</tbody>
</table>
Case Study

- Production of Pure Monomers
  From Softwood Sugars
# Acid hydrolysate composition

- **Source:** acid hydrolysate from softwood hemicellulose

- **Main component:**
  - Sugar monomers valorizable as a substrate for further transformation

- **Impurities of different nature**

## Post-hydrolysis Impurities

<table>
<thead>
<tr>
<th>Impurities</th>
<th>% / DS</th>
<th>% / Dry Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry substance</strong></td>
<td>%</td>
<td>8.8</td>
</tr>
<tr>
<td><strong>Monomers sugars</strong></td>
<td>% / DS</td>
<td>56</td>
</tr>
<tr>
<td>C6 (Mannose, Glucose...)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C5 (Xylose, Arabinose...)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Polymers sugars</strong></td>
<td>% / DS</td>
<td>21</td>
</tr>
<tr>
<td><strong>Ashes</strong></td>
<td>% / DS</td>
<td>11</td>
</tr>
<tr>
<td>Acetate, Sulphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Suspended materials</strong></td>
<td>% / DS</td>
<td>9</td>
</tr>
<tr>
<td><strong>HMF + furfural</strong></td>
<td>g/L</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Target:
- Sugar Monomers > 99.5 %
- Polymers < 0.5 % / DS
- Ashes < 0.1 %/DS
The Purification Challenge

What you think you will get!

What you actually get!
How to design a **cost-effective** and **low effluents** purification process to produce pure sugar monomers?

Separate monomers & polymers by size exclusion chromatography

- **Oligomers** (excluded)
- **Sugar monomers** (retained)

Hydrolysate - Cationic resin beads
The Scale-Up Challenge

How to switch from the **bench** to the integrated and optimized **industrial unit**?

Support the scale-up procedure with a robust methodology integrating the optimization of each unit operation.
### Novasep’s Solutions to Overcome Challenges

<table>
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<th>Obstacle to specifications</th>
<th>Related issue</th>
<th>Our technical solutions</th>
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<td><strong>Solids</strong></td>
<td>Resin clogging ➔ Pressure drop increase</td>
<td>Ceramic filtration</td>
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<td><strong>Ionic load</strong></td>
<td>Divalent cations ➔ Resin conversion decreases efficiency</td>
<td>Demineralization</td>
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<tr>
<td>Chloride</td>
<td>Chloride constraint ➔ Stainless steel compatibility</td>
<td></td>
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<tr>
<td><strong>HMF</strong></td>
<td>Fermentation &amp; reaction inhibitor ➔ Lower the product quality</td>
<td>Removal by adsorption</td>
</tr>
<tr>
<td><strong>Furfural</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Low dry substance content</strong></td>
<td>➔ Increase size and cost equipment</td>
<td>Concentration by evaporation</td>
</tr>
<tr>
<td><strong>Polymers</strong></td>
<td>➔ Main impurity to remove</td>
<td>Chromatographic separation</td>
</tr>
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</table>
Possible Purification Pathway

Each step helps in reaching target specifications.

The industrial design and technologies are adjusted to local area constraints.
Step 1 – Filtration and Clarification

Removal of > 99.5% of solids
> 99% yield

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Hydrolysate

Ultrafiltration

Filtrate

Before – After UF
Novasep Solutions for Filtration

- **Ceramic membranes**
  - Kerasep™ Modules
  - Large range of geometries and cut-offs
  - 99 membranes per modules at industrial scale
  - Compact, sanitary design
## Step 2 – Demineralization

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### Removal of >99.5% ashes, by various process routes:
- Combination of ED/IEX (reduces chemicals use by 10-fold)
- Chromatography
Novasep’s Electrodialysis and IEX Solutions

- Electrodialysis
  - High desalting efficiency
  - No chemicals consumption
  - Electricity-driven technology

- Ion exchange IEX
  - High desalting efficiency
  - Chemicals consumption (limited by the combination with ED)
  - Cyclic behaviour operated in columns
### Step 3 – Adsorption

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<tr>
<td>Furfural</td>
<td></td>
<td></td>
</tr>
</tbody>
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**Example of carbon Norit™**

**Reduction of the HMF and Furfural content**
Step 4 – Concentration by Evaporation

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<th>Related issue</th>
<th>Our technical solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low dry substance content</td>
<td>Increase size and cost equipment</td>
<td>Concentration by evaporation</td>
</tr>
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</table>

Concentration from 7% to 50 %DS
>99.9 % yield
Novasep Strategies to optimize the evaporation efficiency

- Multiple effects units
- Thermal vapor compression
- Mechanical Vapor Recompression

Novasep solutions for evaporation

- Plate evaporator
- Falling film evaporators
- Forced circulation evaporators
Separate two components using difference of affinity with a solid adsorbent phase
Two fractions are recovered

Raffinate (low affinity) = polymer sugars
Extract (high affinity) = monomer sugars
From Batch to Continuous Chromatography

- **Principle of Moving Bed**: Simulation of a counter current flux to separate more easily the different fractions

- **Simulated Moving Bed = continuous chromatography (SSMB)**
  - SSMB = Sequential simulated moving bed
  - Several cells in series: Simulation of a counter current flux by switching injection and recovering points
  - Discontinuous injection and recovery of extracts and raffinate
From Batch to Continuous Chromatography

High purity fractions
Low water usage
Very low chemicals consumption

Preparing to collect Red Blue, Inject feed and eluent
Inside SSMB Process

98% polymers reduction
> 97% monomers yield
Meeting the Challenge: A Full Process Line

Final purity > 99.5 % monomers purity easily adjustable

Chosen technologies depend on local conditions.
Possibility to separate C5 and C6 sugars with an additional separation step.
### Cash cost Study

#### Sugar Recovery OPEX

<table>
<thead>
<tr>
<th>Category</th>
<th>Costs ($) / ton monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrolysis</strong></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>20</td>
</tr>
<tr>
<td>Acid</td>
<td></td>
</tr>
<tr>
<td><strong>Chemicals</strong></td>
<td></td>
</tr>
<tr>
<td>Resin regeneration</td>
<td>18</td>
</tr>
<tr>
<td>UF cleaning</td>
<td></td>
</tr>
<tr>
<td><strong>Utilities</strong></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>62</td>
</tr>
<tr>
<td>Steam</td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td></td>
</tr>
<tr>
<td><strong>Consumables</strong></td>
<td></td>
</tr>
<tr>
<td>Membranes</td>
<td>70</td>
</tr>
<tr>
<td>Resins</td>
<td></td>
</tr>
<tr>
<td><strong>Cash cost</strong></td>
<td>170</td>
</tr>
</tbody>
</table>

Costs depend on area conditions (here: USA basis)
Thank you for your attention!

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Frederic.Schab@novasep.com (R&D Project Manager, PhD)