Extraction of spruce hemicelluloses

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Hemicellulose molecule
Extraction

H₂O, T

10 kDa <

Liquid and solid hemicelluloses

Medium and short chained hemicelluloses

< 10 kDa

Hydrolysis

Further processing

Emulsifiers, Films etc.

Platform chemicals

Oxidation
Hydrogenation
Fermentation
Esterification
Aqueous reforming

Sugar acids, Sugar alcohols, Lubricants, Fuels etc.
Background

- Protonation of glycosidic bonds
Starting material

Non-extracted chips, 1.25 – 2 mm
Non-extracted cubic blocks, 10 mm
Reactor system

- Cascade reactor
- Flexible 5 point sampling of liquid and solid phases
- Accurate control and measurement of temperature, pressure, and flow rate
Batch reactor versus cascade reactor

Traditional batch digester

Cascade reactor

The chips do not differentiate between reactor type
Liquid samples, 170°C, 0-60 min

- The viscosity of the extract increasing
- The color becomes brown
Solid samples, 170°C, 0-60 min

0 min  5 min  10 min

15 min  20 min  60 min
Experimental results

The influence of temperature and chip size on the overall extraction rate

Concentration of hemicellulose as a function of time (10 mm cubic blocks).

Liquid phase concentration as a function of time with different chip sizes.
The behaviour of pH during extraction

1.25 – 2.00 mm wood chips

10 mm cubic wood blocks
Influence of chip size on pH

The behavior of the pH during the reaction at four different temperatures:

- **120°C**
- **130°C**
- **160°C**
- **170°C**

The pH with 1,25 – 2 mm chips (open symbols) and 10 mm cubic blocks (solid symbols).

The pH with 1,25 – 2 mm chips (open symbols) and 10 mm cubic blocks (solid symbols).
The diffusion of the acetyl groups is clearly faster than for the hemicelluloses i.e. higher $\text{cH}_3\text{O}^+$ is obtained at the same conversion for the larger chips.
Modelling

\[ rate = k_I \cdot c_{\text{solid}}^{n_1} \cdot (H^+)^{n_2} \]

\[ k_I = k_{0I} \cdot e^{-\frac{E_{aI}}{RT}} \]

\[ T = \frac{1}{T} - \frac{1}{T_{\text{mean}}} \]

\[ T_{\text{mean}} = 150^\circ C \]

<table>
<thead>
<tr>
<th></th>
<th>1,25 - 2,00 mm chips</th>
<th>10 mm cubic blocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) [kJ / mol]</td>
<td>122</td>
<td>120</td>
</tr>
<tr>
<td>Estimated parameters</td>
<td>0,3</td>
<td>0,2</td>
</tr>
<tr>
<td>( k_{0I} ) ([L^{(n_1+n_2)-1} / (g^{(n_1+n_2)-1} \cdot \text{min})])</td>
<td>(9,57 \cdot 10^{-3})</td>
<td>(5,55 \cdot 10^{-3})</td>
</tr>
<tr>
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</tbody>
</table>

The model of the complicated system can be simplified significantly.
Sensitivity analysis and parameter correlations ($E_a$ and $k_{0l}$)

1,25 – 2,00 mm chips

10 mm cubic blocks
Modelling results

Fit of the model to experimental data (liquid-phase hemicellulose concentrations \( c \)) for the smaller chip size (1.25–2 mm).

Fit of the model to experimental data (liquid-phase hemicellulose concentrations \( c \)) for the larger chip size (10 × 10 mm).
So what did we learn from modelling exercise?

- Extraction and hydrolysis rate very temperature sensitive
- The chip size influences the overall extraction rate and the molar mass of the obtained hemicelluloses
- The extraction rate is not significantly influenced by pH
- The mathematical model for the complex system could be simplified significantly
- A good fit of the model to the experimental data was achieved

Rissanen, Grénman, Xu, Willför, Murzin, Salmi, ChemSusChem 2014, accepted, DOI 10.1002/cssc.201402282R1
Rissanen, Grénman, Xu, Willför, Murzin, Salmi, Cellulose Chemistry and Technology, submitted after revision
Molar mass of extracted hemicelluloses

Molecular weight as a function of time for different temperatures and chip sizes

Molar mass of extracted hemicelluloses
Molecular weight as a function of conversion for different temperatures and chip sizes
Percentage of sugars in the extract, 120–170°C

- Mannose, $R^2 = 0.95$
- Xylose, $R^2 = 0.97$
- Glucose, $R^2 = 0.98$
- Arabinose, $R^2 = 0.89$
- Galactose, $R^2 = 0.92$
Conclusions

• Industrial applications need long chained hemicelluloses and monomers

• The extraction kinetics is crucial in order to tailor the product as well as the production

• The overall extraction is influenced by several interlinked phenomena

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Rissanen, Grénman, Xu, Willför, Murzin, Salmi, Cellulose Chemistry and Technology, submitted after revision
Conclusion –
The influence of the extraction parameters is complex and interlinked

Temperature
Detachment of compounds

Solid-liquid ratio
Concentration in liquid phase

Chip size
pH

Hydrolysis
Morphology

Internal diffusion
Overall kinetics of extraction

Solid-liquid ratio

Chip size

Hydrolysis

Internal diffusion

Temperature

Detachment of compounds

Concentration in liquid phase

pH

Morphology