OBJECTIVES

- Modelling & simulation
- Biomass hydrothermal fractionation (packed bed)
- Kinetic modelling & validation
- 3 different reactors: 3 L, 6 L & 40 L
- 3 biomasses: holm oak, catalpa and wheat straw
- Focused on hemicellulose (T around 180 ºC)
- Improvement of a preliminary approach (0.1 L)

INITIAL MODEL

**MECHANISM**
- Oligomers & sugars
  - 1st soluble (high Mw)
  - Last (low Mw)
- pH variations
- Deacetylation
- $H^+$ consumption (buffering effect)
- Two phases
- Mass transfer
- Porosity changes
- Lignin as an inert

**Assumptions:**
- Isothermal
- No diffusion
- Globalised solid profiles

**Reaction pathway**

**Dissolved biomass (Hemicellulose)**

**Biomass** (A)

**Water:** (C, A, Q)

**Terms**

- Reaction
- Mass transfer
- Extraction effect
- Convective flow
- Time dependence

**Mass balances**

**Liquid (A)**

\[
\frac{dC_A}{dt} = \frac{1}{\sigma} \left[ \frac{dC_C}{dt} - \frac{dC_Q}{dt} - \phi \cdot C_A \cdot k_h \cdot \left( C_A^* - C_A^h \right) \right] + r_p
\]

**Solid (B)**

\[
\frac{dC_B}{dt} = \frac{1}{\sigma} \left[ \frac{dC_C}{dt} - \frac{dC_Q}{dt} - \phi \cdot C_A \cdot k_h \cdot \left( C_A^* - C_A^h \right) \right] + \sum_{i=1}^n k_i \cdot \left( C_A^i - C_A^h_i \right)
\]

**Terms**

- Time dependence
- Convection flow
- Extraction effect
- Mass transfer
- Reaction

**Assumptions:**
- Isothermal
- No diffusion
- Globalised solid profiles
INITIAL MODEL

**MASS BALANCES**

Extraction effect

\[ \phi - \frac{dC_\phi}{dt} \]

\[ \phi = f(\text{biomass}) \]

\[ \phi = f(t, x) \]

Mass transfer

\[ C_{\phi} = \phi \cdot C_{\phi}(t) \]

\[ C_{\phi} = \frac{1}{2} \cdot \frac{d}{dx} C_{\phi}(x, t) \]

\[ C_{\phi} = \frac{1}{2} \cdot \frac{d}{dx} C_{\phi}(x, t) = f(t) \]

**INITIAL MODEL**

MODEL

PARAMETERS

SOLVER

SIMULATION

DATA

**INITIAL MODEL**

**MASS BALANCES**

Validation

RLB & QC

**INITIAL MODEL**

**MASS BALANCES**

Reaction → Autocatalytic kinetics

\[ r_j = \sum_{i=1}^{n_j} a_{ij} \cdot r_i \]

\[ r_j = k_i \cdot \left( C_{\phi}^0 \cdot (1 - a_{ij} \cdot x_j)^{n_i} \right) \]

**INITIAL MODEL**

PREVIOUS RESULTS

- Holm oak (powder)
- V: 100 ml
- T ∈ [180 °C, 200 °C]
- Q ∈ [5 ml/min, 40 ml/min]
- dp: 3 & 6 mm

**MODIFIED MODEL**

Model changes

- New mechanism
- Sugar degradation
- Soluble lignin
- Direct deacetylation
- Three kinds of hemicellulose
- Direct deacetylation (HC1)
- "Easy" to extract (HC2)
- Not able to be extracted (HC3)
- Two bases
  - Soluble (B1)
  - Insoluble (B2)
- Diffusive term in the LMB
### MODIFIED MODEL VALIDATION

**Wheat straw (WS)**
- Experimental
- $V$: 3 L
- $T$: 185, 200 & 215 $^\circ$C
- $Q$: 0.25 kg/min
- $M$: 900 g (pellets)
- Reactor output:
  - Sugar profile
  - Oligomer profile
  - pH profile
  - DP profile
  - Acetic acid profile
  - Dissolved lignin profile

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<table>
<thead>
<tr>
<th>$t$, min</th>
<th>0</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{DP}]$, g/m</td>
<td>100</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{SUG}]$, g/m</td>
<td>200</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

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**Dissolved biomass**

**Water**

(1, $t$, $Q$)

### MODIFIED MODEL VALIDATION

**Wheat straw (WS)**
- **Oligomers**

<table>
<thead>
<tr>
<th>$t$, min</th>
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<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{OLIG}]$, g/m</td>
<td>100</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{Acetic acid}]$, g/m</td>
<td>200</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>pH</td>
<td>10</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

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**Acetic acid**

---

**Soluble lignin**

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<th>0</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{SL}]$, g/m</td>
<td>100</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{Acetic acid}]$</td>
<td>200</td>
<td>1.5</td>
<td>2</td>
</tr>
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<td>pH</td>
<td>10</td>
<td>1</td>
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</table>

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**Reactor**

(1, $t$, $Q$)
PARAMETERS ANALYSIS

Analysis of the parameters
- Kinetics $K_i$
  - Simulated equilibrium constant $K_{eq}$
  - Kinetic rates similar
  - Reactions: 6, 7 and 8
- Autocatalytic coefficients $A_i$
  - Function of the temperature
- Liquid effective diffusivity (axial) $D_{eff}$
  - Function of the temperature
- Acetic acid stoichiometric coefficient $0.18 - 0.30$ g/g HC
- HC1(40%) & HC2 (60%) values
  - B1 (10%) and B2 (90%) values
- Oligomers length
- Acetyl content
- Bed porosity
  - Internal profiles: liquid and solid
  - Global mas balance error: 4.6 %

PARAMETERS ANALYSIS

Analysis of the parameters
- Proton reaction order $n_i$
  - Reactions: 6, 7 and 8
  
$K = \frac{\frac{d[H]}{dt}}{[H]} = A \cdot e^{[\beta \cdot (T - T_0)]}$
  
$K = A \cdot e^{[\beta \cdot (T - T_0)]}$
  
$K = \frac{[\beta \cdot (T - T_0)]}{R_{eq}}$

PARAMETERS ANALYSIS

Analysis of the parameters
- Kinetics $K_i$
  - Kinetic rates similar
  - Reactions: 1, 2, 5, 9 and 10
- Different kinetic rates
  - Reactions: 3, 4, 6, 7, 8 and 11
  - Similar order of magnitude
- Morphology (pellets vs powder)
  - Structural reasons
- Oligomers length
- Acetyl content

PARAMETERS ANALYSIS

Analysis of the parameters
- Kinetics $K_i$
  - Simulated equilibrium constant $K_{eq}$
  - Kinetic rates similar
  - 1, 2, 5, 9 and 10
- Different kinetic rates
  - 3, 4, 6, 7, 8 and 11
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- Bed porosity
  - Internal profiles: liquid and solid
  - Global mas balance error: 4.6 %
CONCLUSIONS

Conclusions
- Kinetic model validated
- 3 different tubular reactors used (3.0 L, 6.0 L and 40.0 L)
- 3 different biomass tested (HO, WS & CAT)
- Main sources of errors
  - Initial heating
  - Lab scale assumptions (like isothermal reactor)
  - pH simulation (reactions: 3, 4, 6, 7, 8 and 11)

Further work
- Energy balance
- Initial heating period
- Buffering effect
- Errors between 8-38 %

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