What is biomass torrefaction?

- Smooth thermal decomposition in default of air
  - Between drying and pyrolysis
  - $T = 200-300^\circ C$
  - Solid residence time = 10 min to several hours
  - Atmospheric pressure

Biomass $C_6H_9O_4$ + moisture~20%

Volatile matter:
- Gas (CO, CO$_2$)
- Condensable species (H$_2$O, acids...)

Torrefied biomass $C_6H_8O_3$ + moisture~3%

Properties get more coal-like
- H/C and O/C decrease
- Hydrophobic nature
- Energy densification
- Better grindability and flowability

$>70\text{w\%}$
What is biomass torrefaction?

Biorefinery approach

Burnt or removed as waste

Source of Green chemicals

Biomass $C_6H_9O_4 + \text{moisture} \approx 20\%$

Torrefied biomass $C_{n}H_{m}O_{p}$

> 70w%

Volatile matter:
- Gas (CO, CO$_2$)
- Condensable species (H$_2$O, acids...)

Energy carrier
- Fuel suitable for gasification, combustion

Objective and working plan

Objective:
To develop a model of biomass torrefaction able to predict both solid and volatile matter versus operating conditions and biomass composition.

Approach: summative contribution of the main biomass constituents

$\Delta m_{\text{biomass}} = \Delta m_{\text{cellulose}} \cdot \%_{\text{cellulose}} + \Delta m_{\text{lignin}} \cdot \%_{\text{lignin}} + \Delta m_{\text{hemicellulose}} \cdot \%_{\text{hemicellulose}}$

Working plan:
- Lab-scale experiments:
  - Thermogravimetric analysis
  - Torrefaction unit TORNAD
- Kinetic modelling
5. Conclusion
4. Modelling
3. Experimental results
2. Materials and method
1. Introduction

Biomass: beech

- Drying at 105°C
- Milling <200 µm

**Extractives (3.0%)**
- Ash (0.6%)

**Lignin**
Extracted from beech

**Cellulose**
Avicel

43.3%
22.0%
31.1%

**Xylan**
Extracted from beech
(Representative of hemicellulose)

TGA: solid mass loss kinetics

- Study in chemical regime
- Error between replicates < 1%

**Setaram TG-DSC 111**
- Carrier gas N₂
- Electronic balance
- Alumina tubes
- Water
- Crucibles
- Water

<table>
<thead>
<tr>
<th>Temperature</th>
<th>720, 740, 760, 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas atmosphere</td>
<td>N₂</td>
</tr>
<tr>
<td>Gas flowrate</td>
<td>30 ml min⁻¹</td>
</tr>
<tr>
<td>Sample mass</td>
<td>4 mg</td>
</tr>
</tbody>
</table>

21st European Biomass Conference, Copenhagen – June, 7th 2013
**TORNADE: volatile matter production**

Study in chemical regime

Mass balance: 99 - 104%

<table>
<thead>
<tr>
<th>Temperature</th>
<th>220; 250; 280; 300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas atmosphere</td>
<td>N₂</td>
</tr>
<tr>
<td>Gas flowrate</td>
<td>1 NL.min⁻¹</td>
</tr>
<tr>
<td>Sample mass</td>
<td>100-200 mg</td>
</tr>
</tbody>
</table>

**Kinetics of solid mass loss**

- **Lignin**: smooth and continuous mass loss
- **Xylan**: fast and (very) sharp mass loss
- **Cellulose:**
  - T ≤ 250°C: nearly no mass loss
  - T ≥ 280°C: slow mass loss then the highest rate
Gas and condensable species yields

- Main species: H₂O, formaldehyde, acetic acid, CO₂
- Other species: CO, formic acid, methanol, furfural

Beech

- Each species not produced by all constituents
- Formic acid only produced by xylan torrefaction
- Acetic acid not produced by cellulose/lignin/xylan
- Comes from acetyl groups of hemicellulose
- Removed during extraction of xylan
Description with additive law?

- Correct at $T \leq 250^\circ\text{C}$
- Not correct at $T \geq 280^\circ\text{C}$

Interactions between beech constituents from $280^\circ\text{C}$?

Mix of beech constituents

Interactions from $280^\circ\text{C}$ between:
- Cellulose and Lignin
- Cellulose and Xylan

- Discrepancies linked with cellulose decomposition
- Decrease of the mix reaction rate
Interactions origin? One hypothesis

- Degradation of Xylan and Lignin:
  Production of numerous radicals \( R_{\text{xylan}}^* \) and/or of volatile matter
- Depolymerization of Cellulose

\[ \text{Cellulose} + R_{\text{xylan}}^* \rightarrow \text{Xylan} + \text{Lignin} \]

\[ \text{Xylan} + R_{\text{Lignin}}^* \rightarrow \text{Lignin} \]

- Ramification of Cellulose by \( R_{\text{xylan}}^* \) and/or \( R_{\text{Lignin}}^* \)

\[ \text{Cellulose with interactions} \]

\[ \text{Cellulose} \]

\[ \text{Lignin} \]

\[ \text{Xylan} \]

- Increase of Cellulose decomposition rate

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Kinetic model of biomass torrefaction

Biomass composition

- Cellulose
- Lignin
- Hemicellulose
  - Xylan
  - Acetyl groups

5. Conclusion

3. Experimental results

2. Materials and method

1. Introduction

4. Modelling

Constituents sub-models

- Model of Di Blasi (1997)
  - 2 steps
  - 2 parallel reactions
  - First-order kinetics
  - Arrhenius law
  - \( k_i = \alpha_i \exp \left(-\frac{E_a}{RT}\right) \)

- Yield of volatile species
  - \( \alpha_{ij} = \frac{\alpha_{ij}}{\alpha_{i2}} \)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Volatile Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>( \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{formaldehyde, furfural} )</td>
</tr>
<tr>
<td>Lignin</td>
<td>( \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{formaldehyde, furfural, methanol} )</td>
</tr>
<tr>
<td>Xylan</td>
<td>( \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{formaldehyde, methanol, formic acid} )</td>
</tr>
<tr>
<td>Acetyl groups</td>
<td>( \text{Acetic acid} )</td>
</tr>
</tbody>
</table>

- Determination of the parameters
  - Least-squares minimization method

Kinetic model of biomass torrefaction

Biomass composition

Cellulose

Lignin

Hemicellulose

Empirical factor $t_0$

Additivity

Torrefied solid

$CO, CO_2, H_2O, acetic acid, formaldehyde, formic acid, furfural, methanol$

5. Conclusion

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4. Modelling

Satisfactory results:
- Prediction of solid yield with a difference < 3%
- Estimation of 8 volatile species yields with differences < 40%
Conclusion

How to model torrefaction vs $T$, residence time and biomass composition?

- Sum of the main biomass constituents:
  - Correct when $T \leq 250^\circ C$
  - Interactions between cellulose and other compounds when $T \geq 280^\circ C$
    - Empirical factor on cellulose decomposition rate

- Satisfactory prediction of:
  - Solid mass loss
  - The 8 main volatile species yields: $H_2O$, formaldehyde, acetic acid, $CO_2$, CO, formic acid, methanol, furfural
    - Not produced by all constituents

What’s next?

- Confirm the interactions origin
- Apply the model to other biomasses
- Extend the model to other volatile species of interest for chemical industry
Tak!
Merci de votre attention!
Thank you!

And Welcome in Grenoble!

If you have any questions or want more details, please contact:
capucine.dupont@cea.fr