Study on gas release during torrefaction of woody biomass and its constituents

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The process: from biomass to fuel

1. Introduction
2. Additive law
3. Mass balance
4. Gas and condensables formation
5. Conclusion

~200 µm “spherical” particles required for injection in entrained flow gasifier

- Technically difficult and expensive

Thermal pretreatment: torrefaction
- Enhances grindability

- inert atmosphere
- 250-300°C
- atmospheric pressure

Biomass → Collection → Pretreatment → Gasification → Post-treatment → Synthesis

Drying → Milling

Syngas (H₂, CO)

Liquid fuel (Diesel Fischer-Tropsch, methanol/DME)
Torrefaction issues

1. Introduction
2. Additive law
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**Solid mass loss**
- Process: How to keep mass loss as low as possible?
- Fundamental: How does the biomass polymer decompose?

**Gas and condensables formation**
- How to deal with harmful gas and condensables?

TORREFACTION MODELLING
Objective and working plan

**Objective:** To develop a model able to describe kinetics of

**Approach:** sum of decomposition of the biomass main constituents

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

**First step:** *Experiments* in TGA-FTIR and lab-scale device

1. To check additive law
2. To close mass balance with released gas and condensables
3. To study the gas and condensables formation
TGA facility

TGA (Setaram 92)

Gas analyzer: FTIR (Perkin-Elmer System 2000)

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flowrate</td>
<td>30 mL.min⁻¹</td>
</tr>
<tr>
<td>Pressure</td>
<td>atmospheric</td>
</tr>
<tr>
<td>Temperature</td>
<td>250;280;300 °C</td>
</tr>
</tbody>
</table>

- Beech
- Lignin (extracted from beech)
- Cellulose
- Xylan (85% hemicellulose)

Study in chemical regime

Error between replicates < 1%
Results at 250°C

- Lignin: smooth and continuous mass loss
- Xylan: significant mass loss
- Cellulose: nearly no mass loss
- Additive law: OK
Results at 280°C

- Lignin: smooth and continuous mass loss
- Xylan: fast and sharp mass loss
- Cellulose: slow but significant mass loss
- Additive law: OK except for long duration (>2500 s)

Mass balance

Additive law
Results at 300°C

- Lignin: smooth and continuous mass loss
- Xylan: fast and very sharp mass loss
- Cellulose: slow but the highest mass loss after long duration
- Additive law: not valid
2. Additive law

Synthesis of the results

Additive law:
- Valid at 250°C and 280°C for typical process duration
- Not valid at 300°C

Slower decomposition of cellulose in beech
Long duration test at 300°C

- Additive law valid for very long durations (3h)
  - OK for prediction of “final” solid yield
- Confirmation: gap due to slower decomposition of cellulose in beech
  - Interaction between constituents?
  - Structure of cellulose?
The lab-scale device ALIGATOR

Study in chemical regime

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<tr>
<td>Temperature</td>
<td>280°C</td>
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<tr>
<td>Biomass</td>
<td>beech</td>
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<tr>
<td>Sample mass</td>
<td>1.5 g</td>
</tr>
</tbody>
</table>

T (°C)

280

1h

5°C.min⁻¹

20

10 min

0
Global mass balance

Torrefaction of beech
(280°C, 1h)

- Main products: H₂O, CO₂, acetic acid
- Significant yields of other species

**Pie Chart**

- H₂O
- CO₂
- CO
- Acetic acid
- Formic acid
- Formaldehyde
- Furfural
- Methanol
- Solid

**Bar Chart**

- Mass produced (mg/mg raw biomass)
- H₂O
- CO₂
- CO
- Acetic acid
- Formic acid
- Formaldehyde
- Furfural
- Methanol

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**TGA-FTIR device**

- **TGA** (Setaram 92)
- **Gas analyzer** : FTIR (Perkin-Elmer System 2000)

**Graph:**
- Reaction temperature ($T$) vs. time ($t$) graph with:
  - Initial temperature: 20°C
  - Final temperature: 230°C
  - Heating rate: 20°C min$^{-1}$
  - Reaction time: 60 min

**Absorption Spectra:**
- **FTIR Spectrum**
  - Torrefaction of beech (300°C, 900s)

**Table:**

<table>
<thead>
<tr>
<th>$t$ (min)</th>
<th>$T$ (°C)</th>
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</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>60</td>
<td>230</td>
</tr>
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</table>

**Notes:**
- **Beech**
- **Lignin (extracted from beech)**
- **Cellulose**
Beech: Gas species mean value vs temperature

Increase of temperature   ➔   Increase of each gas yield
**Beech: CO$_2$ and formic acid vs time**

- **Increase of temperature** ➡ **Increase of each gas yield**
- **For both products: peak of concentration at the same time for all temperatures**
- **Long duration time:**
  - CO$_2$ still released
  - No more formation of formic acid
Beech, lignin and cellulose: comparison at 300°C

**CO₂ and CO produced both by lignin and cellulose**

**Formaldehyde and methanol not produced by cellulose**

**Acetic and formic acids neither produced by lignin nor cellulose**

Produced by hemicellulose
Conclusion and outlook

What's next?

1. TGA-FTIR experiments on hemicellulose
2. Calibration of TGA-FTIR for quantification
3. Model development
Thank you very much! Merci de votre attention!

If you have any questions or want more details, please contact:

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