Kinetic behaviour of biomass mixtures during torrefaction and steam gasification

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The process: from biomass to fuel

Lignocellulosic biomass

Collection → Pretreatment → Gasification → Post-treatment → Synthesis

Feedstock / process interface

Syngas (H₂, CO)

• Liquid fuel (Diesel Fischer-Tropsch, MeOH)
• Gaseous fuel (SNG, H₂)

Suitability is crucial for industrialization
Feedstock/process suitability

- To improve feedstock/process suitability → two issues:

  - **Quantity**
    - Limited
    - Can vary along the year

  - **Quality**
    - Properties intrinsically variable
    - Can vary along the year

SOLUTION?
A solution: biomass blends

Biomass blends

Reactor design

Feedstock thermal behaviour

Nevertheless... so far:

- No characterization
- No modelling

of thermal behaviour of biomass blends
Phenomenology

Drying
50-100°C

Torrefaction
200-300°C

Steam gasification
800-1500°C

Biomass $C_6H_9O_4$ + moisture: 20%

Biomass $C_6H_9O_4$ + moisture: 0%

Torrefied biomass $C_6H_8O_3$

Pyrolysis

Char (mainly C)

Steam gasification

$H_2, CO$

Syngas

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

Limiting steps:
Kinetic study

Volatile matter:
- Gas (H$_2$, CO, CO$_2$, CH$_4$...)
- Condensable species (H$_2$O, tars)
Objective and working plan

Objective:
- study biomass blends kinetics during torrefaction and steam gasification of char
- check existence/lack of additive law

Working plan:
- Lab-scale experimentation → thermobalance
  - Torrefaction → non-reactive atmosphere
  - Steam gasification → reactive atmosphere
- Kinetic modelling
Torrefaction: experimental device

**CHEMICAL REGIME**

**Temperature program**

- **Mass (%)**
- **Temperature (°C)**
  - 105°C
  - 300°C
  - 3 hours

**Sample nature** | Beech/wheat straw blend
---|---
**Blend ratio** | 25/75, 50/50, 75/25
**Sample mass** | 5 mg
**Particle size** | <200µm
**Flow gas** | N₂

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Torrefaction: kinetic modelling

Comparison 50% beech-50% wheat straw model and experimental blend

\[ \Delta m_{\text{BLEND}} = \Delta m_{\text{BIOMASS 1}} \cdot \%_{\text{BIOMASS 1}} + \Delta m_{\text{BIOMASS 2}} \cdot \%_{\text{BIOMASS 2}} \]
Steam gasification: experimental device

### Slow pyrolysis

<table>
<thead>
<tr>
<th>Sample nature</th>
<th>Beech/ wheat straw blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend ratio</td>
<td>25/75, 50/50, 75/25</td>
</tr>
<tr>
<td>Temperature</td>
<td>450°C</td>
</tr>
<tr>
<td>Time</td>
<td>4h</td>
</tr>
<tr>
<td>Flow gas</td>
<td>( \text{N}_2 )</td>
</tr>
</tbody>
</table>
Steam gasification: experimental device

- **Sample mass**: 5 mg
- **Atmosphere**: H$_2$O
- **Temperature**: 800°C
- **P$_{H2O}$**: 0.2 bar
Steam gasification: experimental device

\[ \text{N}_2 \quad \text{H}_2\text{O} + \text{N}_2 \]

Time (s) vs. Mass (mg)

0 \quad 6000

800
Steam gasification: kinetic modelling

Average reaction rate 1-80%

\[ r_{1-80\%} = \frac{\int_{t_{X=0.01}}^{t_{X=0.80}} r(t) \, dt}{t_{X=0.80} - t_{X=0.01}} \]

ADDITIVE LAW \( \Rightarrow \) globally valid... ✓
Steam gasification: kinetic modelling

Comparison 25% beech-75% wheat straw model and experimental blend

...but in detail → ADDITIVE LAW
Steam gasification: kinetic modelling

Comparison 75% beech-25% wheat straw model and experimental blend

ADDITIVE LAW

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Steam gasification: kinetic modelling

Rate evolution
- At low conversions: Constant
- At high conversions: Moderate decrease

Wrong!

Agricultural biomass

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Steam gasification: kinetic modelling

Experimental curve is accelerated comparing to model

Synergetic effect linked to inorganic matter?

Parameter to be considered: \((K/Si)\)

\[
(K / Si)_{BLEND} = \frac{\%_{BEECH} \cdot K_{BEECH} + \%_{WHEATSTRAW} \cdot K_{WHEATSTRAW}}{\%_{BEECH} \cdot Si_{BEECH} + \%_{WHEATSTRAW} \cdot Si_{WHEATSTRAW}}
\]
Conclusions and outlook

Conclusions
- Torrefaction $\rightarrow$ ADDITIVE LAW
- Steam gasification $\rightarrow$ NO ADDITIVE LAW $\rightarrow$ $(K/Si)_{\text{BLEND}}$ to be considered

Outlook
- Model biomass blends behaviour $\rightarrow$ inorganic matter influence in steam gasification $\rightarrow$ parameters
- Other ratios
- Other types of biomass
We are in Grenoble!

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

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GRAZIE MILLE!!    THANK YOU!!
MERCI BEAUCOUP!!  MUCHAS GRACIAS!!