Fast Pyrolysis of Biomass Under Gasification Conditions: Influence of Particle Size, Reactor Temperature and Gas Phase Reactions

Li CHEN ¹, Capucine DUPONT ¹, Sylvain SALVADOR ², Guillaume BOISSONNET ¹, Daniel SCHWEICH ³

1. Commissariat à l’Énergie Atomique (CEA), France
2. École des Mines d’Albi-Carmaux, France
3. École Supérieure Chimie Physique et Électronique de Lyon, France

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BtL Process: Biomass (lignocellulosic) → Liquid

One key step: Gasification

Biomass (wood, straw…)

Introduction

Comparison

Conclusions
The gasification

**Fast pyrolysis of biomass**

- Chemical Reactions
- Heat/Mass transfer phenomena

**Under FB gasification conditions**

(800 – 950 °C)

Controlled by chemical reactions

(Particles < 100 µm)

Thermal regime

(Particles > 10 mm)
Research on fast pyrolysis

**Objectives:**
To better understand at particle scale the pyrolysis behaviour of biomass (100 µm – 10 mm) under the typical heating conditions in industrial Fluidised Bed gasifiers:
- 1 bar
- High temperature (800°C < T < 1000°C)
- High heat flux (> 10^5 W.m⁻²)

**Plan of experiments (laboratory scale)**

- **Drop Tube Reactor (DTR)**
  (Sample # 350 µm – 800 µm)
- **Horizontal Tubular Reactor (HTR)**
  (Sample # 800 µm – 6 mm)

Comparison DTR/HTR
Sample # 800 µm
Drop Tube Reactor

(350 µm – 800 µm)
Facility description

**Biomass**
- Beechwood $C_6H_{8.8}O_4$ (moisture 7 wt.%)  
  - $N_2$ velocity (m/s) 0.35  
  - Particle size ($\mu$m) 350, 500, 700, 800  
  - Temperature (°C) 800; 950  
  - Pressure (bar) 1  
  - Reaction zone length (m) 0.3, 0.5, 0.7, 0.9  
  - Estimated solid residence time (s)  
    - ~ 0.6 – 2 # 350 µm  
    - ~ 0.3 – 1 # 800 µm

**Sampling probe**
- Gas analyzers: $H_2$, $CH_4$, $CO$, $CO_2$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_3H_8$, $C_6H_6$, $H_2O$

**Solid settling box**
- Gas analyzers: $H_2$, $CH_4$, $CO$, $CO_2$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_3H_8$, $C_6H_6$, $H_2O$

**Solid analysis**
- Ash content → Tracer method
Total gas evolution

- **Total Gas Yield (%wt. of biomass)**
  - 800 °C
  - 950 °C

- **Final gas yields:**
  - ~ 80 wt.% of biomass

- **Final char yields:**
  - < 10 wt.% of biomass

- **Uncertainty:** 5 %wt. of biomass

- **Dp** → solid devolatilization rate
- **T** → solid devolatilization rate

- **T = 950°C & Dp = 800 µm**, devolatilization finished at **L = 0.9 m** (τ_{solid} ~ 1 s).
The influence of temperature on the gas components yields is illustrated in the chart. When the temperature increases from 800 °C to 950 °C, the yields of \( \text{H}_2 \), \( \text{C}_2 \) species, and \( \text{C}_6\text{H}_6 \) seem to change mainly due to enhanced cracking reactions. The yields are as follows:

- \( \text{H}_2 \): from 1.7 to 1.7 wt.%,
- \( \text{C}_2\text{H}_2 \): from 1.6 to 3.1 wt.%,
- \( \text{C}_6\text{H}_6 \): from 1.5 to 2.2 wt.%,
- \( \text{C}_2\text{H}_4 \): from 5.4 to 3.6 wt.%,
- \( \text{C}_2\text{H}_6 \): from 0.7 to 0 wt.%,
- \( \text{CO} \): 48 wt.%,
- \( \text{CO}_2 \): 11 wt.%,
- \( \text{CH}_4 \): 5.5 wt.%

The increase of temperature (800 °C to 950 °C) seems to change mainly the yields of \( \text{H}_2 \), \( \text{C}_2 \) species, and \( \text{C}_6\text{H}_6 \) by enhancing the cracking reactions.
Influence of Dp on the gas components yields

Under operating conditions in DTR

Negligible influence of particle size (350 µm → 800 µm) on the final gas components yields
Drop Tube Reactor (350 µm – 800 µm)

(Limitation of solid residence time by the reactor configuration)

larger particles

Horizontal Tubular Reactor (800 µm – 6 mm)
Facility description

Carrier gas (N\textsubscript{2})

preheating (double envelop)

Gas bag

Quartz tube, $\phi = 55$ mm

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Beechwood $C\text{\textsubscript{6}}H\text{\textsubscript{8.8}}O\text{\textsubscript{4}}$ (Oven Dried)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample mass (g)</td>
<td>0.5 – 1</td>
</tr>
<tr>
<td>Particle size</td>
<td>800 $\mu$m, 2 mm, 6 mm</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>800, 950</td>
</tr>
<tr>
<td>Gas residence time (s)</td>
<td>1, 3.5, 10</td>
</tr>
<tr>
<td>Solid residence time (s)</td>
<td>180</td>
</tr>
</tbody>
</table>

Solid analysis

Mass measurement

Gas analysis

$H\text{\textsubscript{2}}$, $CH\text{\textsubscript{4}}$, $CO$, $CO\text{\textsubscript{2}}$, $C\text{\textsubscript{2}}H\text{\textsubscript{2}}$, $C\text{\textsubscript{2}}H\text{\textsubscript{4}}$, $C\text{\textsubscript{2}}H\text{\textsubscript{6}}$, $H\text{\textsubscript{2}}O$
Influence of Dp on the gas components yields

When Dp (800 µm → 6 mm),

- Total gas yield ↓ (10 wt.%)
- Char yield ↑ (3 wt.%)
- CO ↓ (~ 8 wt.%)

Under operating conditions in HTR

Slight influence of particle size (800 µm → 6 mm) on the final products yields.
Influence of gas phase reactions

When $\tau_{\text{gas}}$ (1 $\rightarrow$ 10 s),

- $\text{H}_2$ $\uparrow$ (1.2 $\rightarrow$ 1.8 wt.%)
- $\text{C}_2\text{H}_4$ $\downarrow$ (3.5 $\rightarrow$ 1.2 wt.%)
- $\text{C}_2\text{H}_2$ $\downarrow$ (1.4 $\rightarrow$ 0.8 wt.%)
- CO, CO$_2$, CH$_4$ $\rightarrow$ (< 10% in relative)

Increasing gas residence time seems to change the yields of H$_2$ and C$_2$ species by favouring the cracking reactions of hydrocarbons.
Comparison DTR/HTR (Dp # 800 µm)

SAME T (950 °C), and gas residence time (~3.5 s)
ATTENTION: different reactor configuration and solid residence time

<table>
<thead>
<tr>
<th>Mass yield (wt.% of dry biomass)</th>
<th>DTR</th>
<th>HTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>CO</td>
<td>48.4</td>
<td>45.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>10.1</td>
<td>14.8</td>
</tr>
<tr>
<td>CH₄</td>
<td>5.7</td>
<td>9.1</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.7</td>
<td>2.7</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>3.1</td>
<td>1.0</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total dry gas</td>
<td>73</td>
<td>75</td>
</tr>
</tbody>
</table>

Results obtained in 2 reactors are comparable.
Conclusions

- Beech wood $\rightarrow$ char ($\sim 10$ wt.%) + gas ($\sim 80$ wt.%) + tar
  \[(\text{CO}, \text{H}_2, \text{CO}_2, \text{CH}_4, \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{C}_6\text{H}_6)\]

- Particle size (350µm – 6 mm) changes the solid devolatilization rate, but has no/slight influence on the final product yields.

- Increasing temperature increases solid devolatilization rate and favours gas phase cracking reactions.

- Gas phase reactions change mainly the yields of $\text{H}_2$ and $\text{C}_2$ species.
Obrigada

Thank you

Merci

谢谢

If you have any questions, please contact:
li.chen@cea.fr
capucine.dupont@cea.fr