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

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BtL Process: Biomass (lignocellulosic) → Liquid

One key step: Gasification

Biomass (wood, straw…)

Collection → Pretreatment → Gasification → Syngas (H₂, CO) → Post-treatment → Synthesis

Fischer-Tropsch Diesel

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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)

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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

Beechwood (0.5 g/min) Carrier gas (N₂)

Isothermal reaction zone

Biomass Beechwood C₆H₈O₄ (moisture 7 wt.%)

| Biomass | Beechwood C₆H₈O₄ (moisture 7 wt.%)
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>N₂ velocity (m/s)</td>
<td>0.35</td>
</tr>
<tr>
<td>Particle size (µm)</td>
<td>350, 500, 700, 800</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>800; 950</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1</td>
</tr>
<tr>
<td>Reaction zone length (m)</td>
<td>0.3, 0.5, 0.7, 0.9</td>
</tr>
</tbody>
</table>

Estimated solid residence time (s)

- ~ 0.6 – 2 # 350 µm
- ~ 0.3 – 1 # 800 µm

Solid analysis
Ash content → Tracer method

Gas analysis
H₂, CH₄, CO, CO₂, C₂H₂, C₂H₄, C₂H₆, C₃H₈, C₆H₆, H₂O

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Total gas evolution

- Final gas yields: ~ 80 wt.% of biomass
- Final char yields: < 10 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).
When $T$ increases ($800 \rightarrow 950 ^\circ C$),

- $H_2$ increases from 1 to 1.7 wt.%
- $C_2H_2$ increases from 1.6 to 3.1 wt.%
- $C_6H_6$ increases from 1.5 to 2.2 wt.%

- $C_2H_4$ decreases from 5.4 to 3.6 wt.%
- $C_2H_6$ decreases from 0.7 to 0 wt.%

- $CO$ increases to 48 wt.%
- $CO_2$ remains constant at 11 wt.%
- $CH_4$ remains constant at 5.5 wt.%

The increase of temperature ($800 \rightarrow 950 ^\circ C$) seems to change mainly the yields of $H_2$, $C_2$ species, and $C_6H_6$ 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 (N₂) preheating (double envelop)

Beechwood (0.5—1g)

- Biomass: Beechwood C₆H₈.8O₄ (Oven Dried)
- Sample mass (g): 0.5 – 1
- Particle size: 800 µm, 2 mm, 6 mm
- Temperature (°C): 800, 950
- Gas residence time (s): 1, 3.5, 10
- Solid residence time (s): 180

Solid analysis

- Mass measurement

Gas analysis

- H₂, CH₄, CO, CO₂, C₂H₂, C₂H₄, C₂H₆, H₂O

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Influence of Dp on the gas components yields

When Dp $\uparrow$ (800 µm $\rightarrow$ 6 mm),
- Total gas yield $\downarrow$ (10 wt.%)
- Char yield $\uparrow$ (3 wt.%)
- CO $\downarrow$ (~ 8 wt.%)

Under operating conditions in HTR
- Slight influence of particle size (800 µm $\rightarrow$ 6 mm) on the final products yields.
Influence of gas phase reactions

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

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

Increasing gas residence time seems to change the yields of $\text{H}_2$ and $\text{C}_2$ 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</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Total dry gas</strong></td>
<td><strong>73</strong></td>
<td><strong>75</strong></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:
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