Effect of Fast Pyrolysis Conditions on the Biomass Solid Residues at High Temperatures (1000-1400°C)

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Effect of Fast Pyrolysis Conditions on the Biomass Solid Residues at High Temperatures (1000-1400°C)

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Objectives

- Woody (pine, beech) and herbaceous biomass (alfalfa straw, wheat straw, rice husk)
- Pyrolysis of smaller and larger particle size (> 0.5 mm)
- Experimental investigations and modeling of char yield at fast heating rates ($10^2$-$10^4$°C/s) and at high temperatures (up to 1500°C)
- Potassium and silicon bearing compounds influence on the char yield, reactivity and morphology
### Experimental setup

Wire mesh reactor  Single particle reactor  Drop tube reactor

<table>
<thead>
<tr>
<th>Operational parameter</th>
<th>Wire mesh reactor</th>
<th>Single particle reactor</th>
<th>Drop tube reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Temperature [°C]</td>
<td>1650</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Heating rate [°C/s]</td>
<td>≤ 5000</td>
<td>≤ 200</td>
<td>≤ ≈ 10^4</td>
</tr>
<tr>
<td>Particle size range [mm]</td>
<td>≤0.65</td>
<td>≥ 3</td>
<td>≤ 1</td>
</tr>
</tbody>
</table>
Luleå University Drop-Tube Furnace

Atmosphere
- $N_2$, $O_2$, $H_2$, $CO_2$, $H_2O$, $Ar$, $CO$

$T_{\text{maximal}}$ 1500°C

Heating rates up to $10^4^\circ C/s$

- Biomass feeder (syringe pump)
- Syringe pump (water)
- Cooling water
- Ceramic packed bed
- Tube furnaces
- Mass flow controllers
- Gas cylinders
- Optical accesses
- Gas/tar analysis
- Cyclone
- Filter for soot collection
- Char bin

Tube furnaces

Ceramic packed bed

Cooling water

Biomass feeder (syringe pump)

Syringe pump (water)
Char yield comparison

WMR (1000°C, 1 s holding time, 0.2mm)  DTF (∼10⁴°C/s) and WMR (10³°C/s, 1 s, 0.2mm)

- (Graph 1) Char yields of wood and herbaceous biomass in the WMR decreased with the increasing temperature
- (Graph 1) At heating rates (> 600°C/s), the char yield is nearly constant, except wheat straw
- (Graph 2) DTF heating rates led to the char yield decrease
- (Graph 2) At final temperatures (> 1000°C) in the DTF, only wheat straw char showed 3.5% points decrease
Graphes 1 and 2 show char yield (daf) of pinewood (1), leached wheat straw (2), beechwood (3), wheat straw (4) and alfalfa straw (5) over the potassium content in original biomass.

- Potassium compared to all other ash elements in the fuels had the highest influence on the char yield (daf).
- At intermediate heating rates (WMR), potassium influenced the char yield significantly more than at high heating rates in the DTF.
Silicon oxides effect on char yield and reactivity

- Graph 1 shows that silica has no influence on the char yield compared to potassium.
- Graph 2 shows that the reactivities of pinewood and rice husk chars were similar in oxidation, indicating less influence of silica on the char reactivity.
- Graph 2 shows that the alkali rich wheat straw chars were 6, 18 and 50 times more reactive than wood and rice husk chars.
The larger pinewood particles (> 0.85 mm) required more than 1 s holding time for the complete conversion at intermediate and fast heating rates.

The influence of heating rate on the char yields was less pronounced for particle sizes from 0.85 to 4 mm obtained at temperatures > 1000°C/s.

**WMR:**
- Heating rate: 1000°C/s
- Holding time: 1 s
- Particle size: 0.25-0.355 mm, 0.85-1 mm

**DTF:**
- Heating rate: 10^4°C/s
- Residence time: 1 s
- Particle size: 0.2-0.4 mm, 0.85-1 mm

**SPR:**
- Heating rate: 200°C/s
- Particle size: 3-5 mm pine cubes
Char and soot yields in the drop tube reactor

- Both graphs compared char and soot yields of woody (Graph 1) and herbaceous biomass (Graph 2).
- Lignin content of leached wheat straw decreased from 25.6 to 15.6 wt.%
- Lignin has a stronger influence on the soot formation than potassium.
Soot morphology with TEM microscopy

Pinewood soot, 1250°C

Mean $d_p = 77.7$ nm  
$\sigma_g = 2.2$  
Min. $d_p = 27$ nm  
Max. $d_p = 263$ nm

Pinewood soot, 1400°C

Mean $d_p = 47.8$ nm  
$\sigma_g = 1.9$  
Min. $d_p = 8.9$ nm  
Max. $d_p = 174$ nm

Wheat straw soot, 1250°C

Mean $d_p = 42.6$ nm  
$\sigma_g = 1.9$  
Min. $d_p = 11.5$ nm  
Max. $d_p = 165.4$ nm

Wheat straw soot, 1400°C

Mean $d_p = 30.8$ nm  
$\sigma_g = 1.8$  
Min. $d_p = 10.3$ nm  
Max. $d_p = 102.1$ nm
Soot morphology with TEM microscopy

- Pinewood formed particles with the pre-dominating multi cores and located on a larger distance
- Beechwood formed a mixture of multi cores and single cores at 1250 and 1400°C
- Wheat straw soot particles were mostly with single cores
- TEM microcropy showed a more graphitic structure of beechwood and wheat straw soot particles
1D modeling of fast pyrolysis

Broido-Shafizadeh schema*

Original biomass $\rightarrow$ Metaplast $\rightarrow$ Volatiles $\rightarrow$ Char

Reaction equations*:

$r_i = k_i \cdot m_i$

$k_i = -k_{0,i} \cdot \exp\left(-\frac{E_{a,i}}{R \cdot T}\right)$

$E_{a,3} = E_{a,3}(\omega) = E_a \cdot (1 - (1 - C_1)) \cdot \left(1 - \exp\left(\frac{\omega}{C_2}\right)\right)$

Initial boundary conditions*:

$m_{BM}(0) = 1$

$m_{MP}(0) = m_{VM}(0) = m_{Char}(0) = 0$

$T_{particle}(0, r) = T_{amb}$

$C_1, C_2 = \text{constants}$

$\omega = \text{potassium content}$

*Broido et al., 1971, Bradbury et al. 1979 et al.
1D modeling of fast pyrolysis

Pinewood 0.2mm particles

Wheat straw 0.2 mm particles

Pinewood 1mm particles

Advantages:
- Internal thermal gradient
- Potassium effect on the char yield
- A simple 1D model
- Unique kinetic parameters

Improvement:
- No differences in the char yield of smaller and larger particles => secondary reactions
- Oversimplifications
Summary

- The heat treatment temperature and potassium content affected the char yield stronger than the heating rates and differences in the plant cell wall compounds between 600 and 3000°C/s.

- Potassium compared to all other ash elements in the fuels had the highest influence on the char yield.

- At intermediate heating rates (WMR), the catalytic effect of potassium was more pronounced than at high DTF heating rates.

- Low lignin content leads to the lower soot yields.

- The proposed kinetic model for the fast biomass pyrolysis is relatively simple and predicts reasonably the char yield of wood and herbaceous biomass particles < 10 mm.
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