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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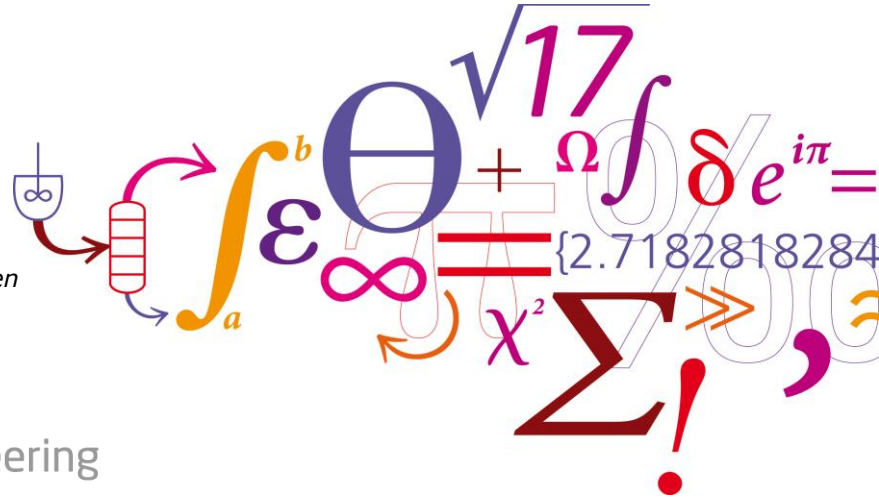
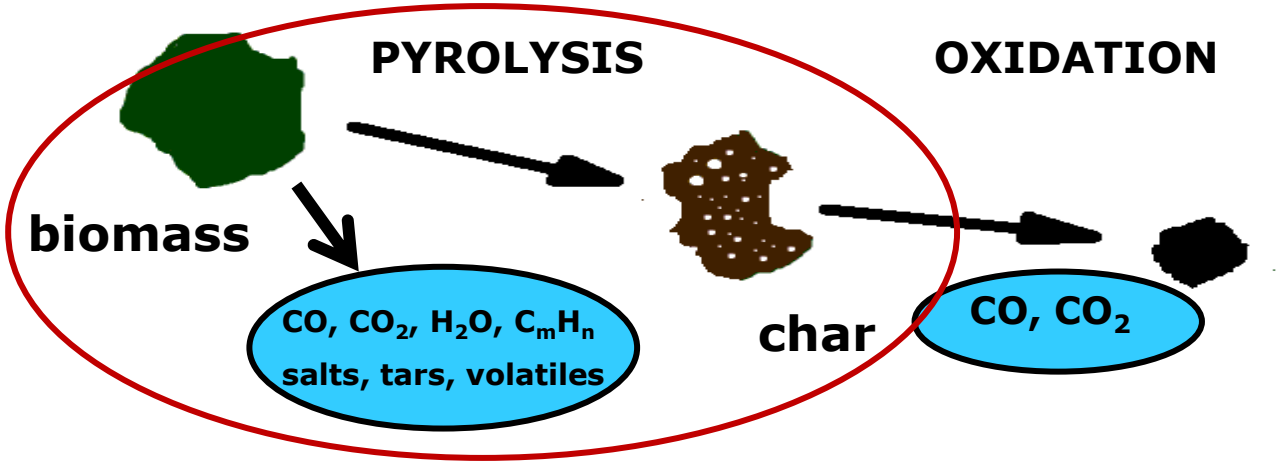


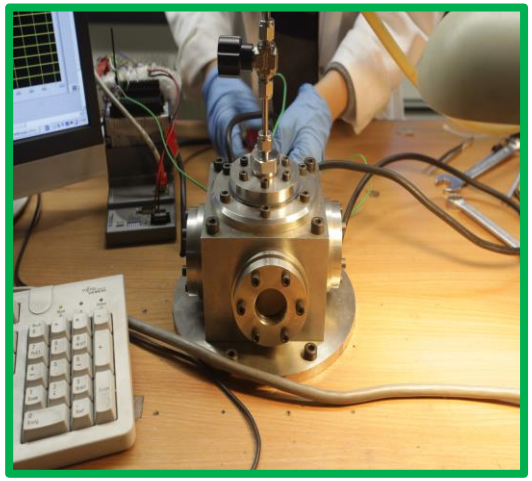
DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

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

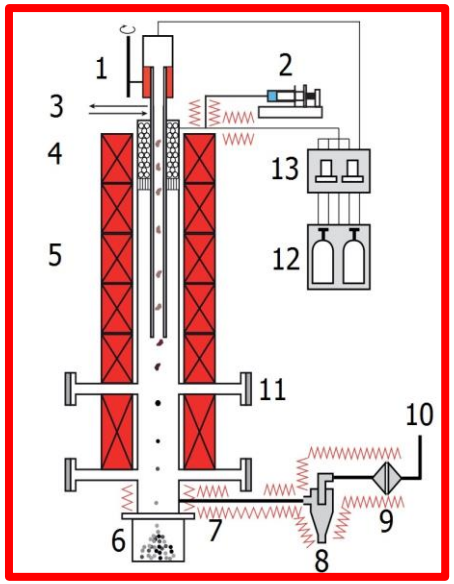


Experimental setup



Wire mesh reactor

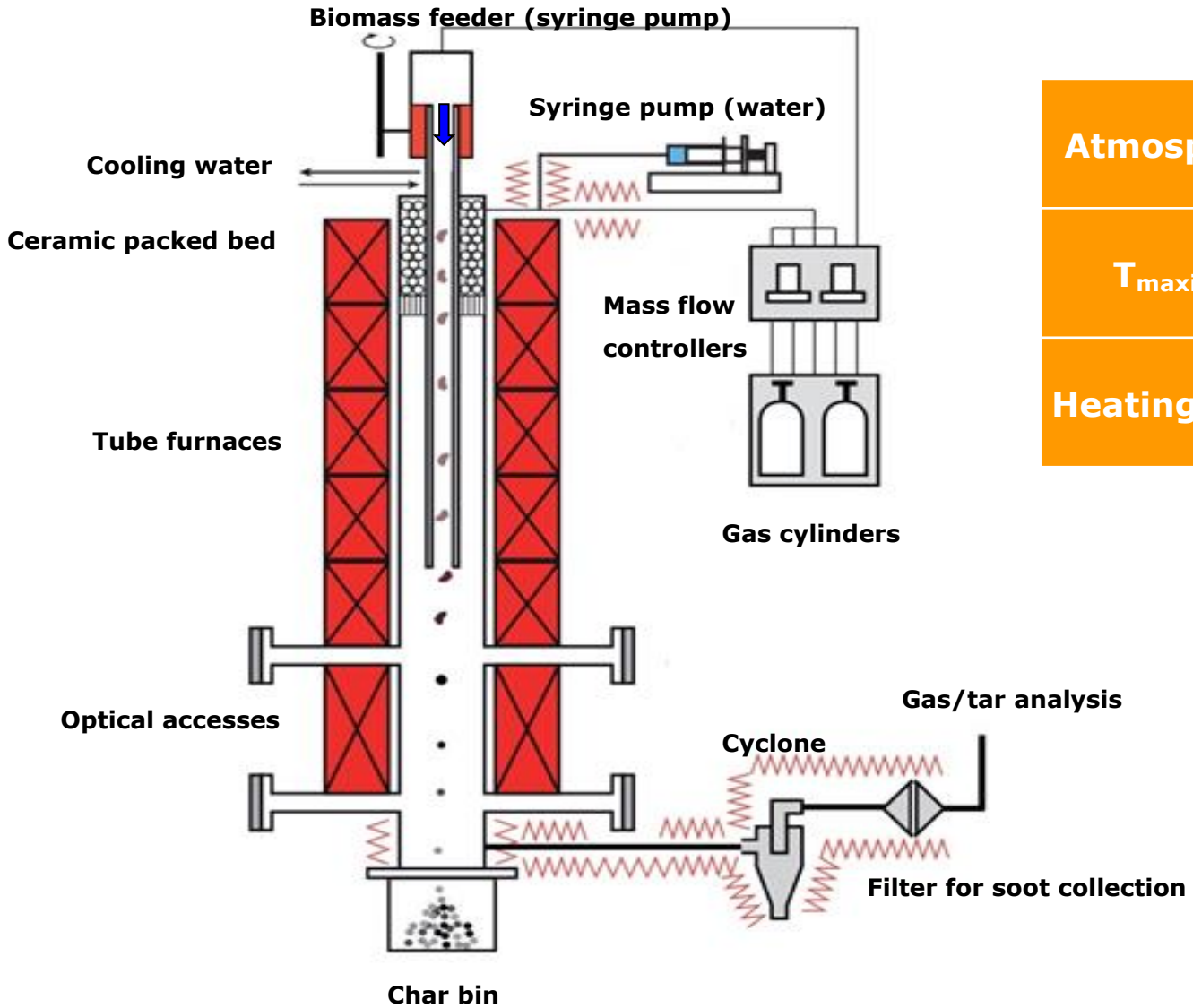
Single particle reactor



Drop tube reactor

Operational parameter	Wire mesh reactor	Single particle reactor	Drop tube reactor
Max. Temperature [°C]	1650	1500	1500
Heating rate [°C/s]	≤ 5000	≤ 200	≤ ≈ 10^4
Particle size range [mm]	≤0.65	≥ 3	≤ 1

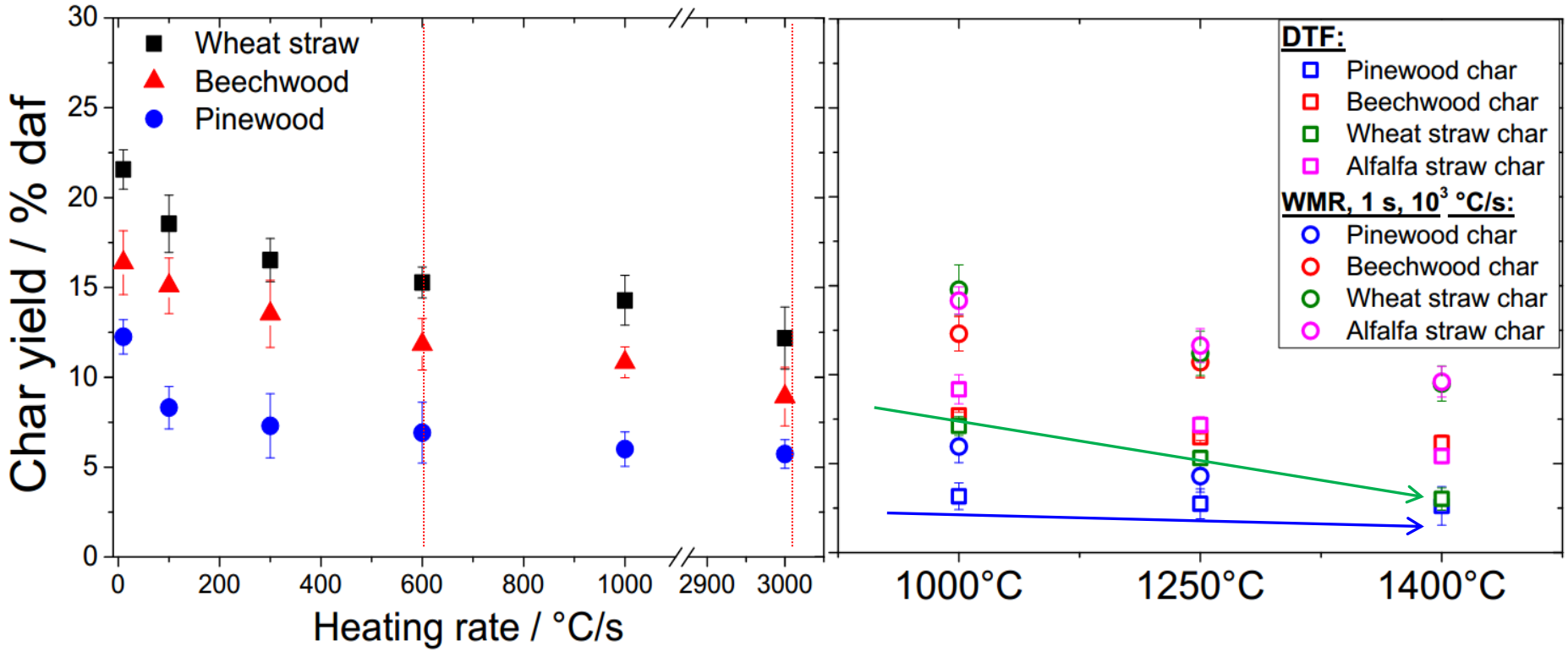
Luleå University Drop-Tube Furnace



Atmosphere	N_2, O_2, H_2, CO_2, H_2O, Ar, CO
$T_{maximal}$	1500°C
Heating rates	up to 10^4°C/s

Char yield comparison

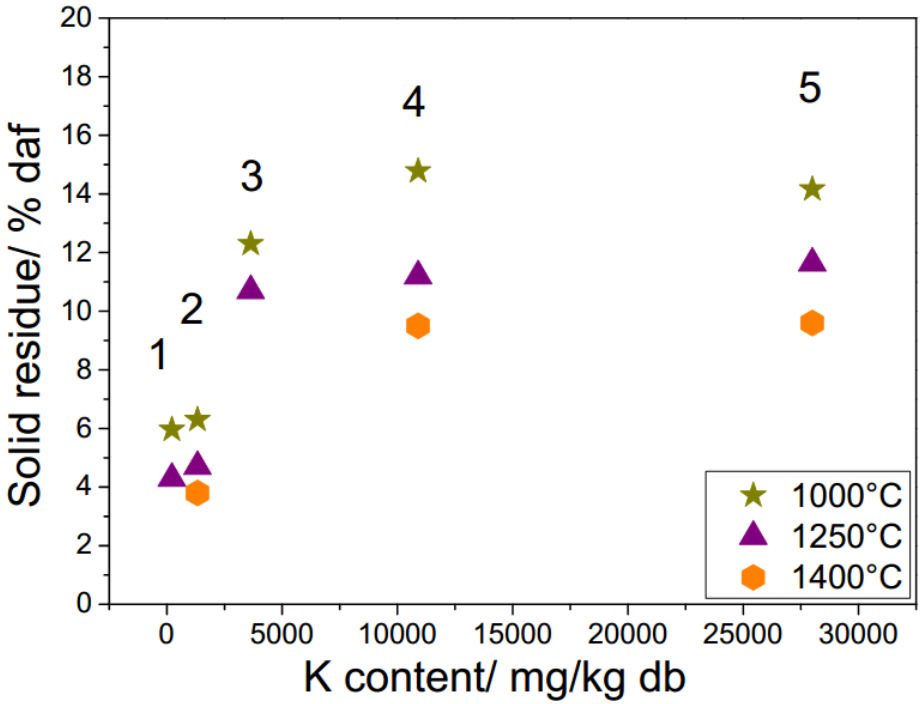
WMR (1000°C, 1 s holding time, 0.2mm) DTF (≈10^4°C/s) and WMR (10^3°C/s, 1 s, 0.2mm)



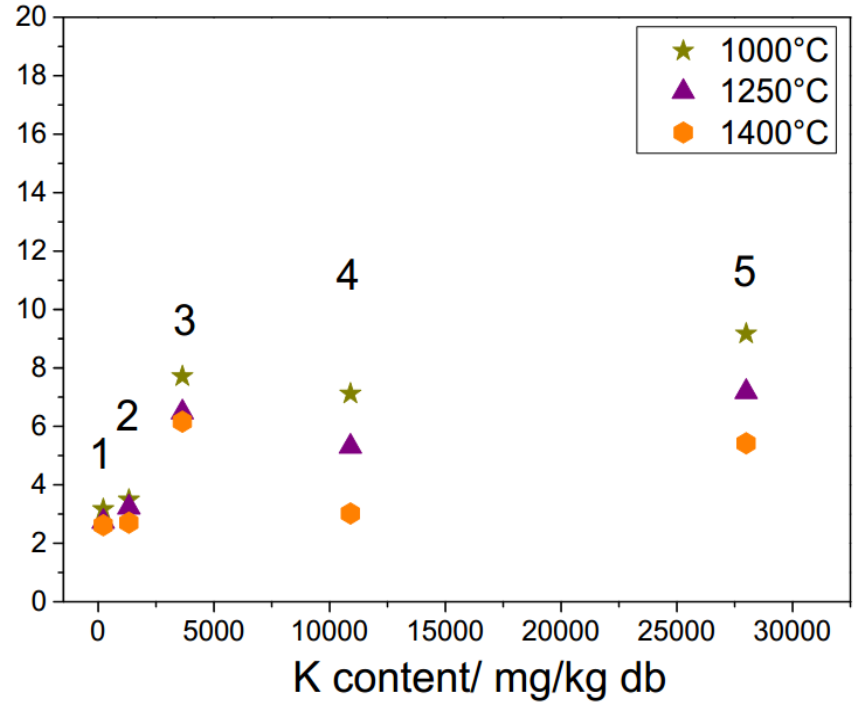
- (Graph 1) Char yields of wood and herbaceous biomass in the WMR decreased with the increasing temperature
- (Graph 1) At heating rates (> 600°C/s), the char yield is nearly constant, except wheat straw
- (Graph 2) DTF heating rates led to the char yield decrease
- (Graph 2) At final temperatures (> 1000°C) in the DTF, only wheat straw char showed 3.5% points decrease

Alkali effect on char yield

WMR, 1000°C/s, 1 s holding time



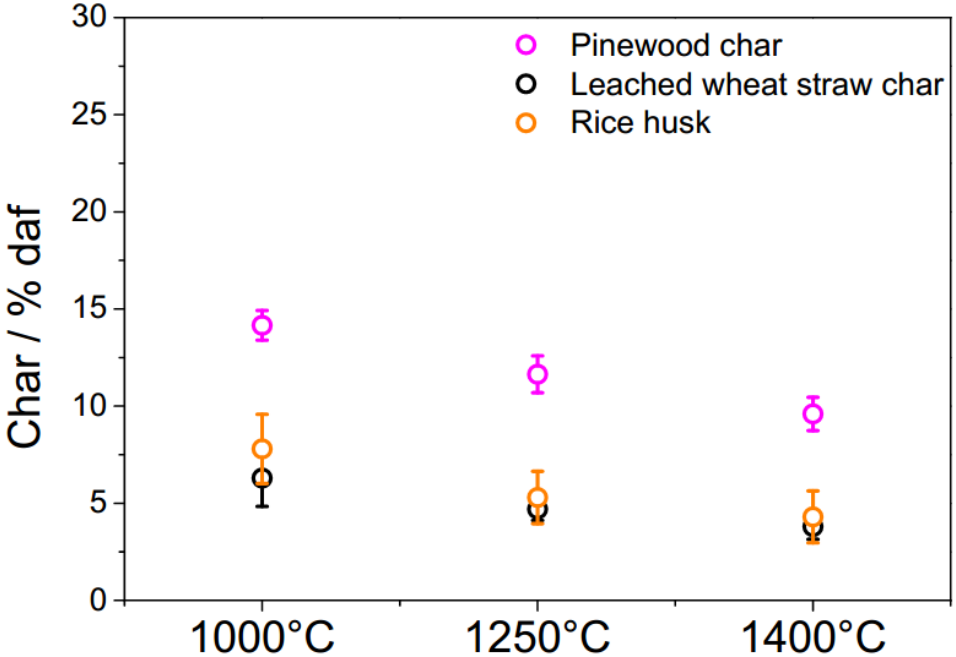
DTF, ≈10^4°C/s, 1 s residence time



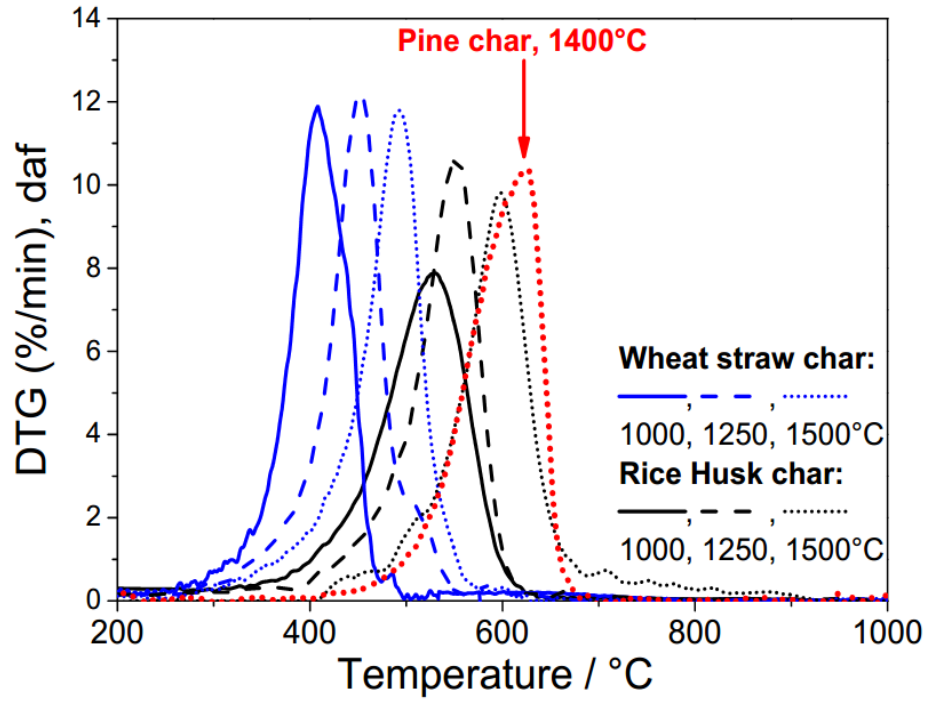
- Graphes 1 and 2 show char yield (daf) of pinewood (1), leached wheat straw (2), beechwood (3), wheat straw (4) and alfalfa straw (5) over the potassium content in original biomass
- Potassium compared to all other ash elements in the fuels had the highest influence on the char yield (daf)
- At intermediate 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

Char yield, WMR, 1000°C/s, 1 s holding time

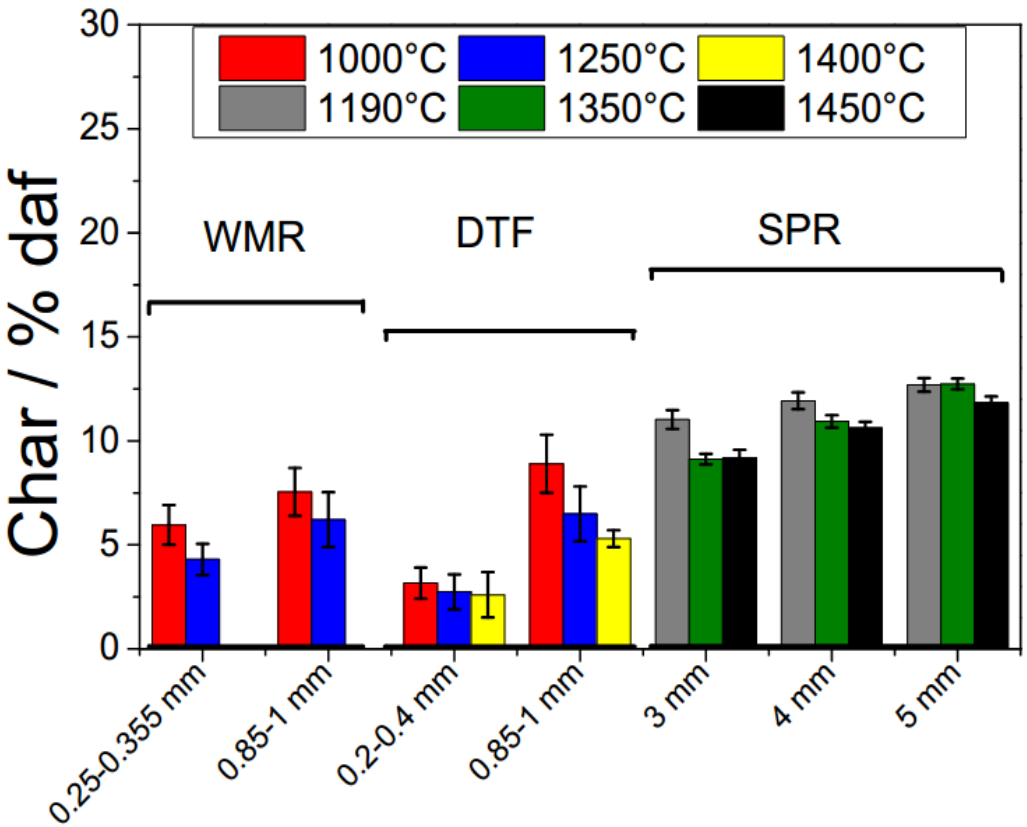


TGA, 5 vol.% O_2 + 95 vol. % N_2



- 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

Large particle effect on the char yield



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:

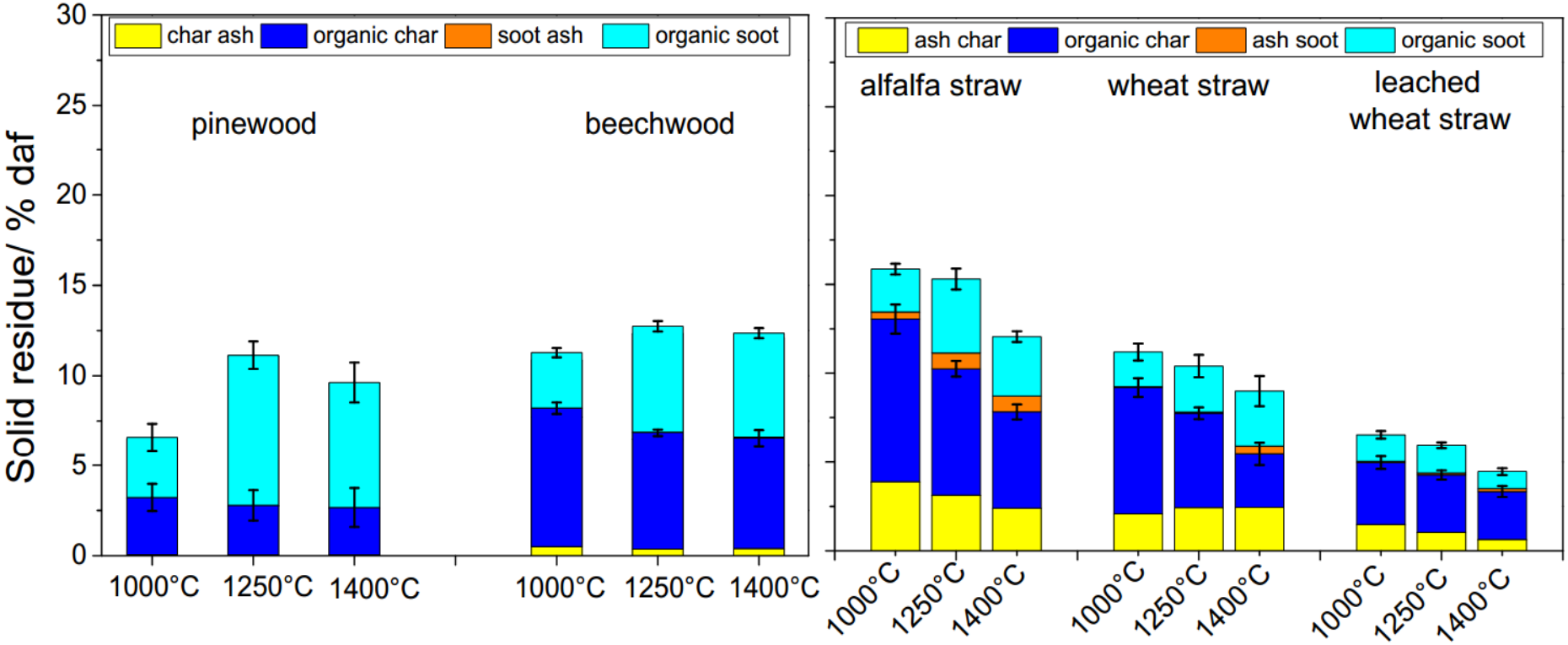
Heating rate: 200°C/s

Particle size: 3-5 mm pine cubes

- 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

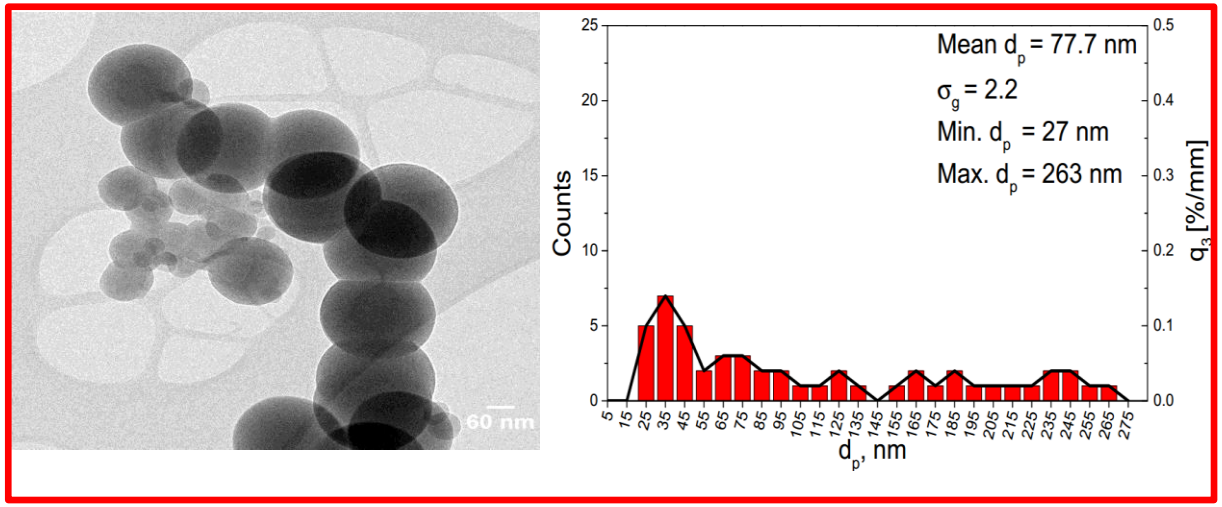
Char and soot yields in the drop tube reactor



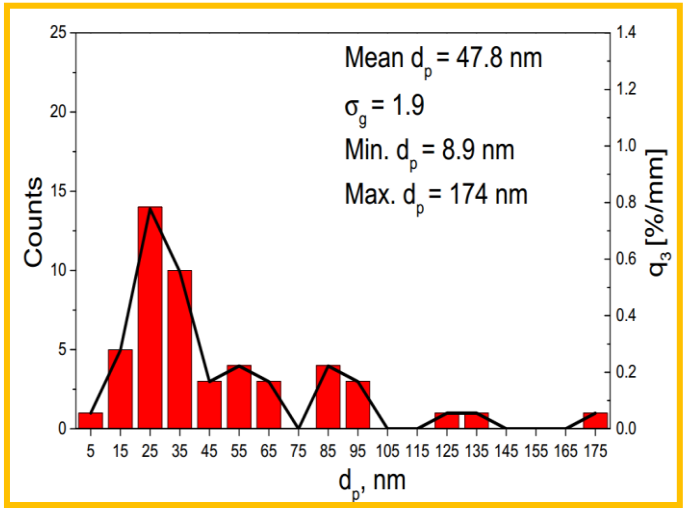
- Both graphes compared char and soot yields of woody (Graph 1) and herbaceous biomass (Graph 2)
- Lignin content of leached wheat straw decreased from 25.6 to 15.6 wt.%
- Lignin has a stronger influence on the soot formation than potassium

Soot morphology with TEM microscopy

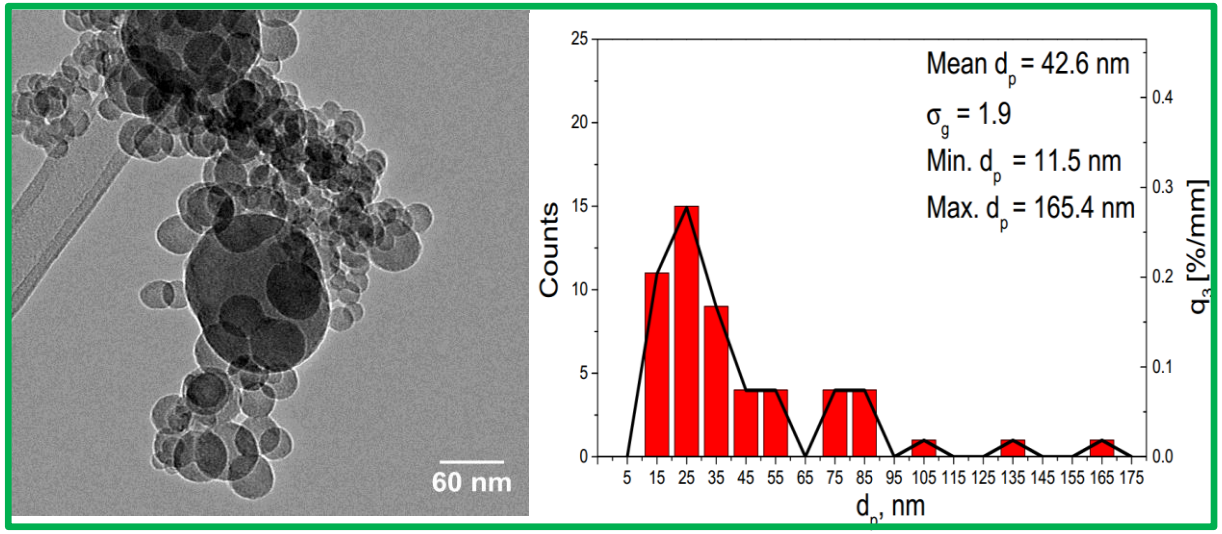
Pinewood soot, 1250°C



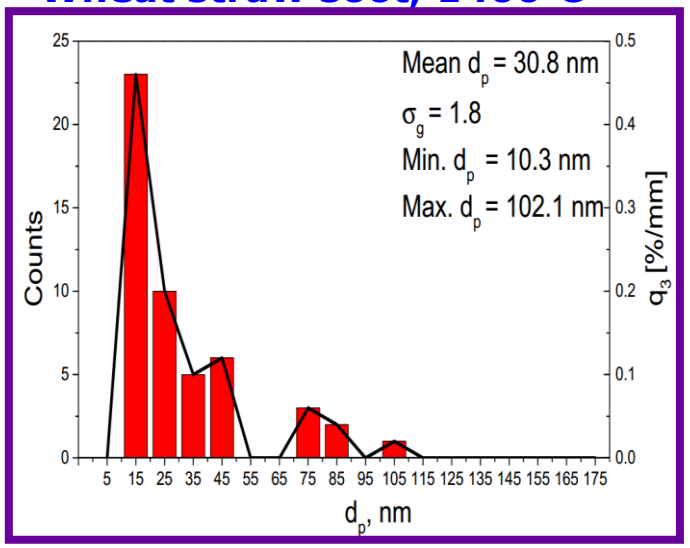
Pinewood soot, 1400°C



Wheat straw soot, 1250°C

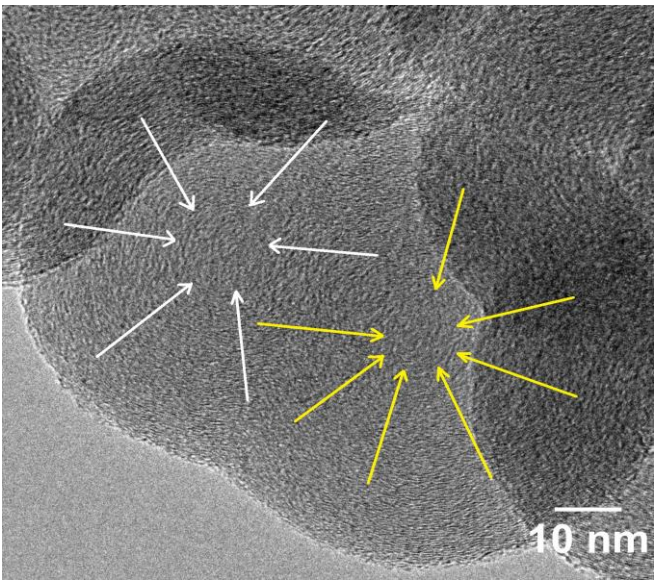


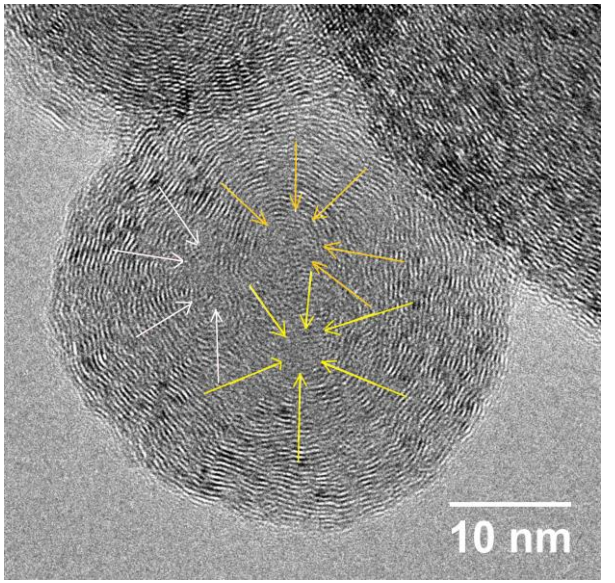
Wheat straw soot, 1400°C

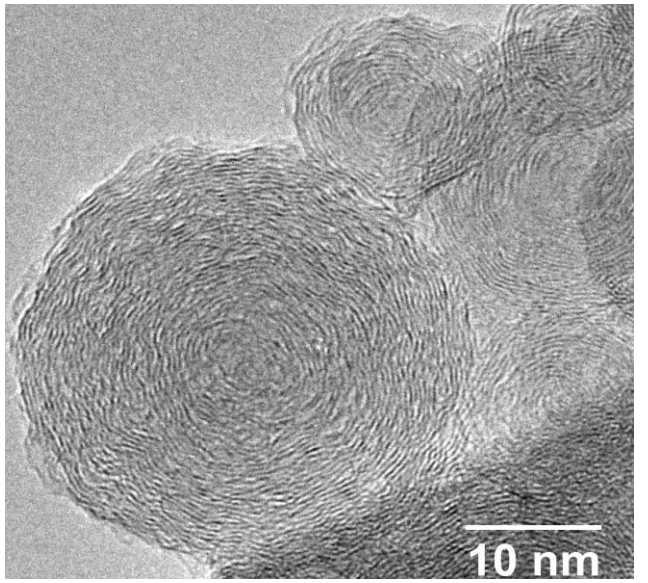


Soot morphology with TEM microscopy

Pinewood soot, 1250°C **Beechwood soot, 1400°C** **Wheat straw soot, 1250°C**



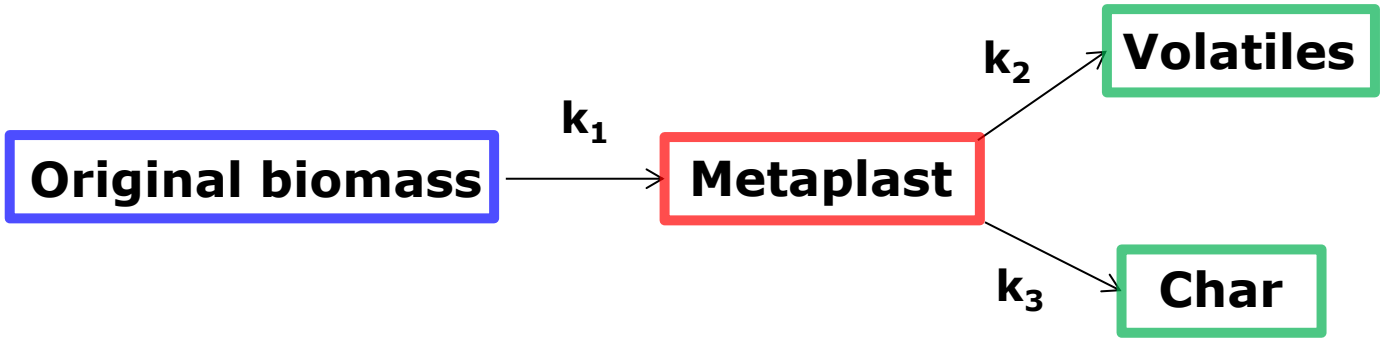




- Pinewood formed particles with the pre-dominating multi cores and located on a larger distance
- Beechwood formed a mixture of multi cores and single cores at 1250 and 1400°C
- Wheat straw soot particles were mostly with single cores
- TEM microcropy showed a more graphitic structure of beechwood and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

1D modeling of fast pyrolysis

Broido-Shafizadeh schema*



Reaction equations*:

$$r_i = k_i \cdot m_i$$

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

$$E_{a,3} = E_{a,3}(\omega) = E_a \cdot \left(1 - (1 - C_1)\right) \cdot \left(1 - \exp\left(\frac{\omega}{C_2}\right)^2\right)$$

$$C_1, C_2 = constants$$

$$\omega = potassium\ content$$

Initial boundary conditions*:

$$m_{BM}(0) = 1$$

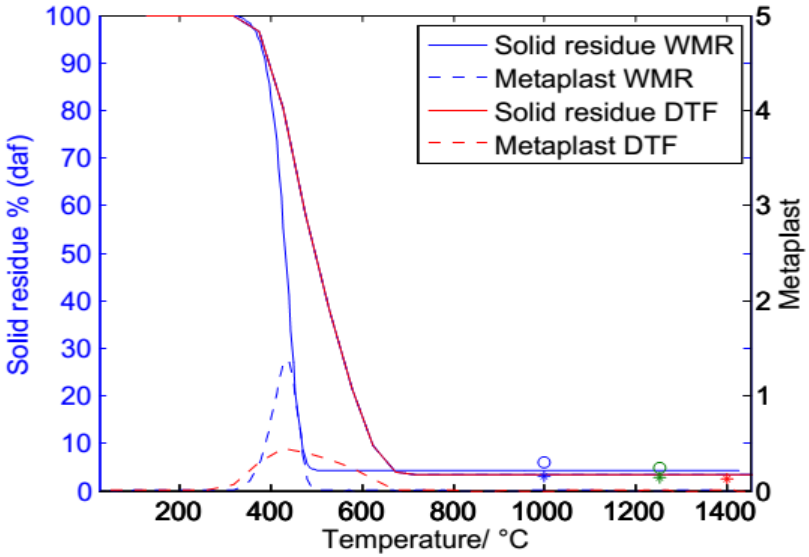
$$m_{MP}(0) = m_{VM}(0) = m_{Char}(0) = 0$$

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

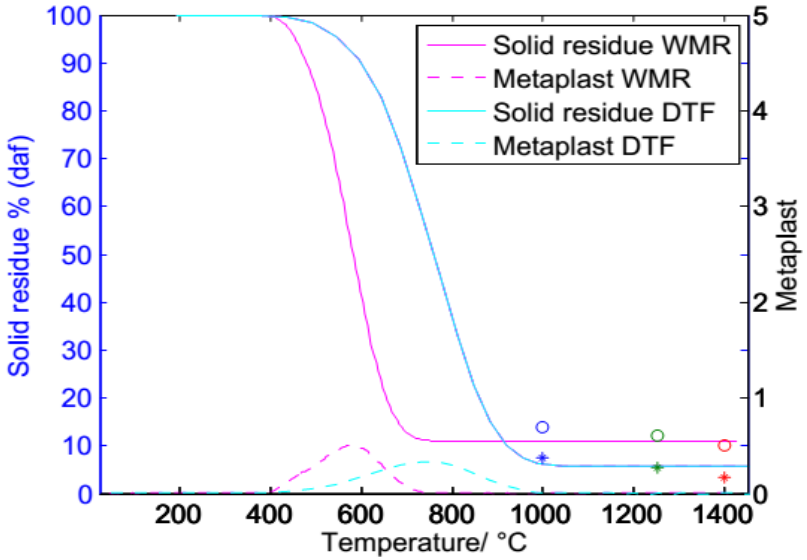
Broido et al., 1971, Bradbury et al. 1979 et al.

1D modeling of fast pyrolysis

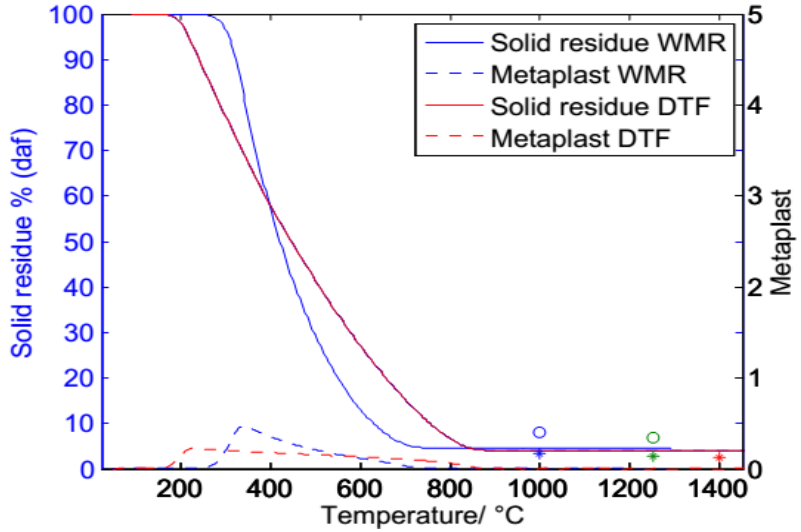
Pinewood 0.2mm particles



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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