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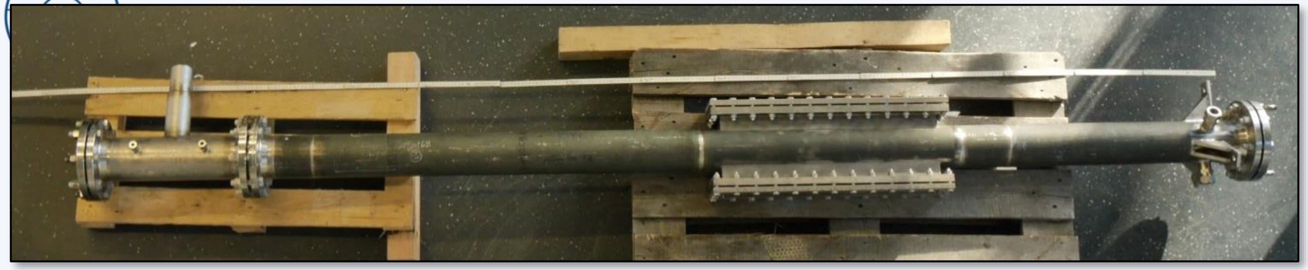
Drop Tube Reactor (Diameter: 0.1 m; Length: 4 m)



9th International Freiberg Conference
Berlin, Germany

Investigation of Biomass Gasification with non-thermal Plasma

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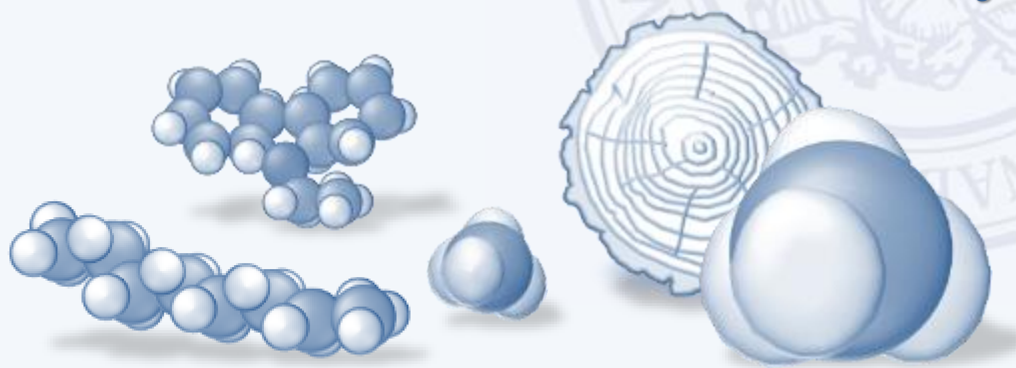

PLASMAGAS

Agenda

1. Motivation

2. Materials and Methods

3. Results & discussion

4. Summary

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Motivation

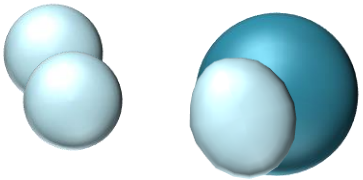
Motivation

Plasma-assisted biomass gasification with water steam

CH_xO_y
(biomass, e.g. wood)

H_2O —Plasma generation with excess electricity→ $H_2O + H + OH + O + e^-$
(radicals) (electrons with high T)

—gasification→ $CO + H_2 + CH_4$ + CO_2, H_2O, etc.



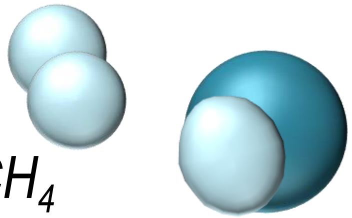
e.g.

$$CH_2 + O \rightarrow CO + H_2$$
$$CO + OH \rightarrow CO_2 + H$$

Conventional (thermochemical) biomass gasification with water steam

$$CH_xO_y + H_2O \xrightarrow{\text{gasification}} CO + H_2 + CH_4$$

(biomass) + CO_2, H_2O, etc.



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Motivation

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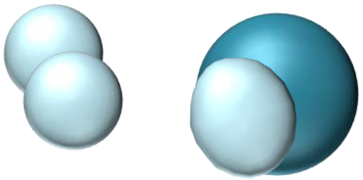

e.g.

$CH_2 + O \rightarrow CO + H_2$

$CO + OH \rightarrow CO_2 + H$

Thermal plasma:

- Thermal equilibrium reached
- Electrons, protons, radicals and molecules heated to high temperature

Non-thermal plasma:

- no thermal equilibrium
- Only electrons heated to high temperature
- Gas molecules heated merely by e.g. 10 – 100 K

Advantages of non-thermal plasma-assisted gasification process:

- Extremely high (local) electron temperature and the presence of radicals lead to better reaction kinetics
- Less energy demand for the generation of non-thermal plasma, since only electrons are heated to high energy level
- Storage of excess electricity from renewable sources (e.g. PV & Wind turbines) in the form of synthetic gases
- Treatment of waste (MSW, RDF) and "difficult" feedstock possible

Hypothesis to be experimentally validated !

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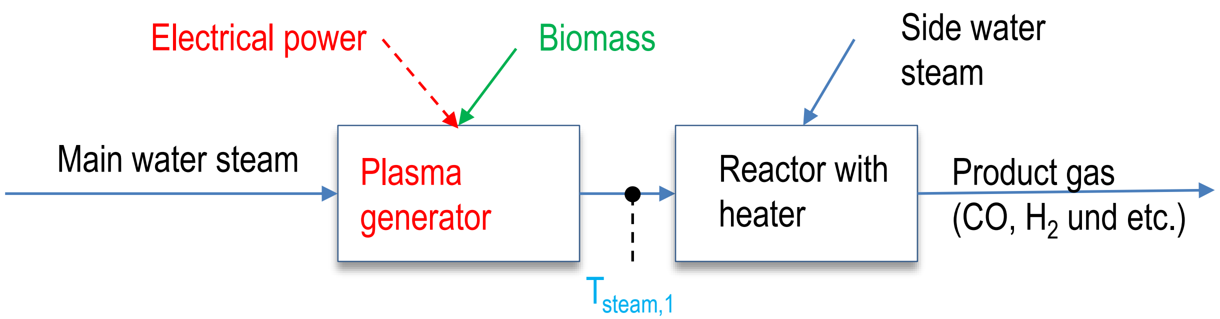
Influence of plasma to be investigated by ***Comparison of plasma-assisted to thermal gasification at similar conditions***

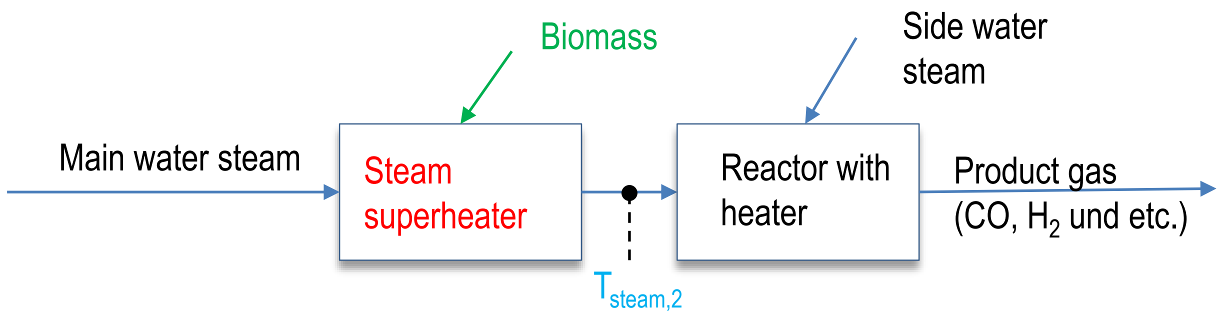
Comparison between plasma gasification and reference thermal gasification through:

- Temperature of water steam is kept similar $T_{steam,1} = T_{steam,2}$;
- biomass particles fall through plasma area;
- other parameters (e.g. fuel dosage, steam flow rates) are kept similar

- Case 1- plasma gasification: the working medium “main water steam” is simultaneously the plasma agent, which is heated by the electrical power .

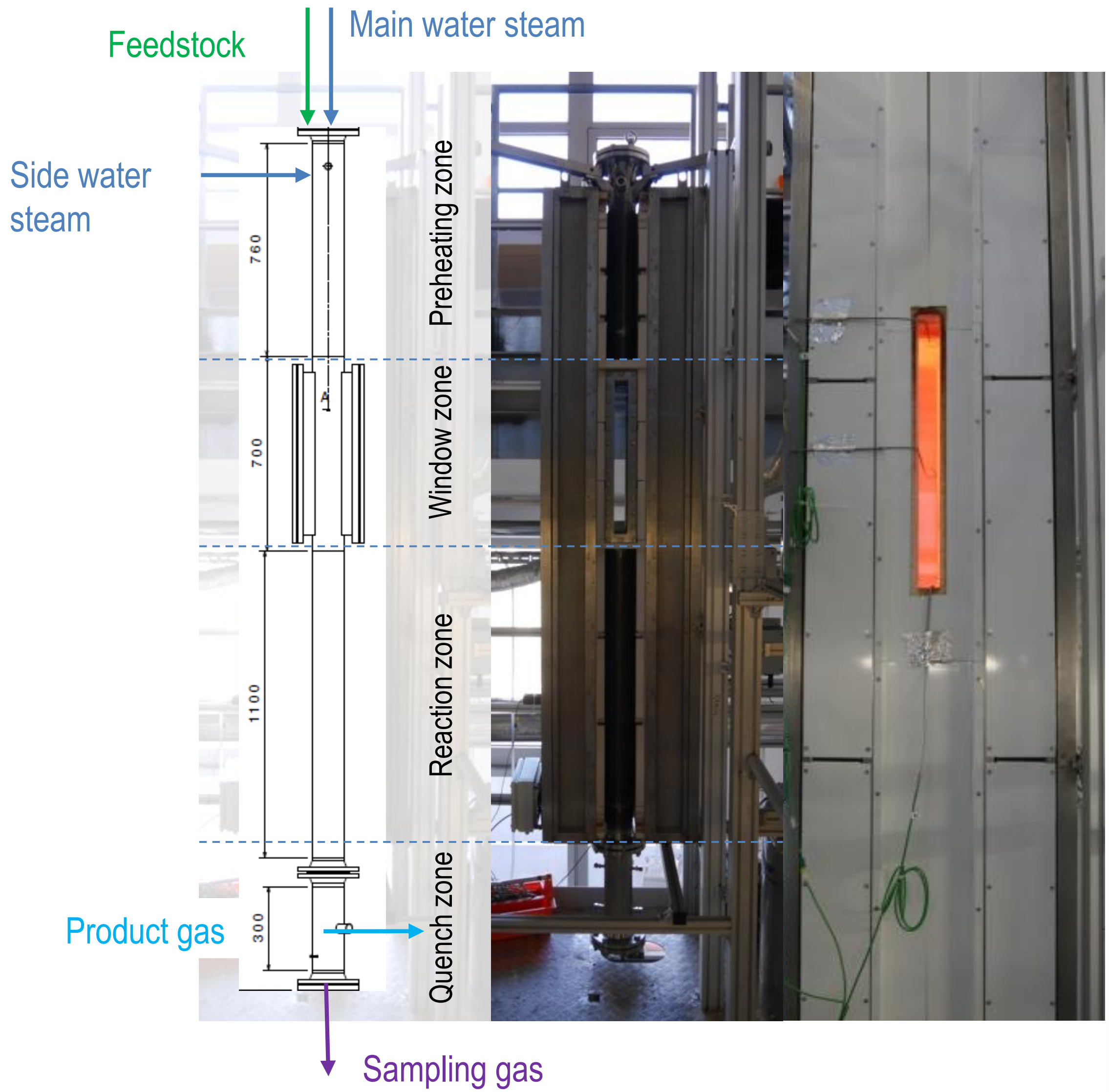


- Case 2 - thermal gasification: the working medium “main water steam” is heated by an external steam superheater.

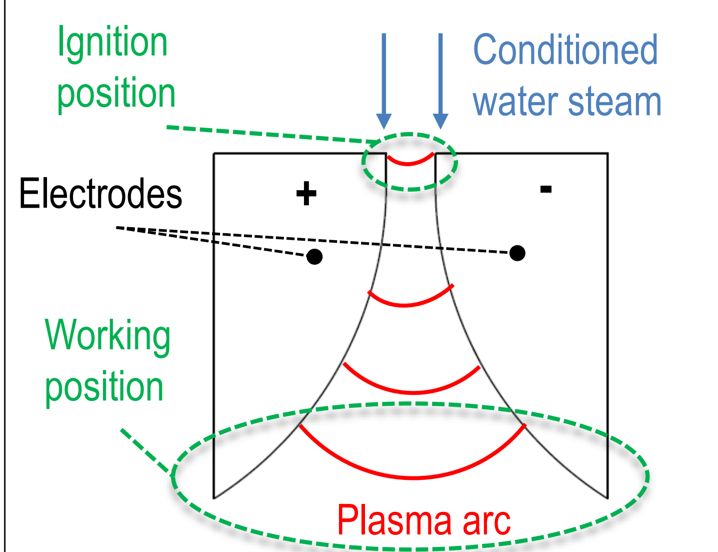


Experimental methods and conditions

- Drop tube reactor (西施装置 Xishi – reactor)



- Plasma generator *: Gliding arc
- Material of electrodes: Steel (no. 1.4841,
- no cooling necessary)
- El. Power of Plasma: ca. 1 kW
- Max. Voltage: 10 kV
- Frequency: 90 – 100 kHz in operation
- Current amplitude: 0.4 – 0.7 A in operation



* Corporation with Siemens AG (doi: 10.3390/en11051302)

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Experimental methods and conditions

Motivation
M&M
Results
Summary

General specifications	• Reactor temperature: 700 – 950 °C^{wall} • atm. Pressure
Plasma generator	• Plasma agent: conditioned water steam • el. power: max. 1 kW
Fuel	• Mass flow: 0.2 kg/h (Thermal output: ca. 1 kW) • Wood powder with variation of particle size • Charcoal powder with variation of particle size
Gasification agent	• Main water steam: 6 kg/h (plasma stabilization) • Side water steam: 2 kg/h (adjustment of S/C-ratio)
Optical measurement	• Gas temperature after visible plasma channel measured by Raman Spectroscopy * done by project partner, LTT-FAU
Reactor	• Diameter: ca. 0.1 m • Length: ca. 4 m

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Experimental methods and conditions

- The gas composition of **product gas(syngas),** considering the following one-step global reaction, is measured in gas chromatography & gas analyzer.

$$\mathrm{CH_xO_y + H_2O \rightarrow H_2 + CO + CH_4 + CO_2}$$

- Calculation of **Carbon conversion** from the gaseous products:

$$CC\ \% = \frac{C_{CH4} + C_{CO} + C_{CO2}}{C_{fuel}}$$

- Determination of **volatile content** before/after tests**:** Standard **DIN EN ISO 18123**

- **Reaction kinetics** is calculated by by data-fitting in Arrhenius Diagram (1. reaction order assumed: n=1):

$$r = \frac{d\xi^*}{dt} = \frac{1}{m}\frac{dm}{dt} \qquad \frac{dm}{dt} = -k \cdot m(t)^n \qquad k = A \cdot e^{-\frac{E_A}{RT}}$$

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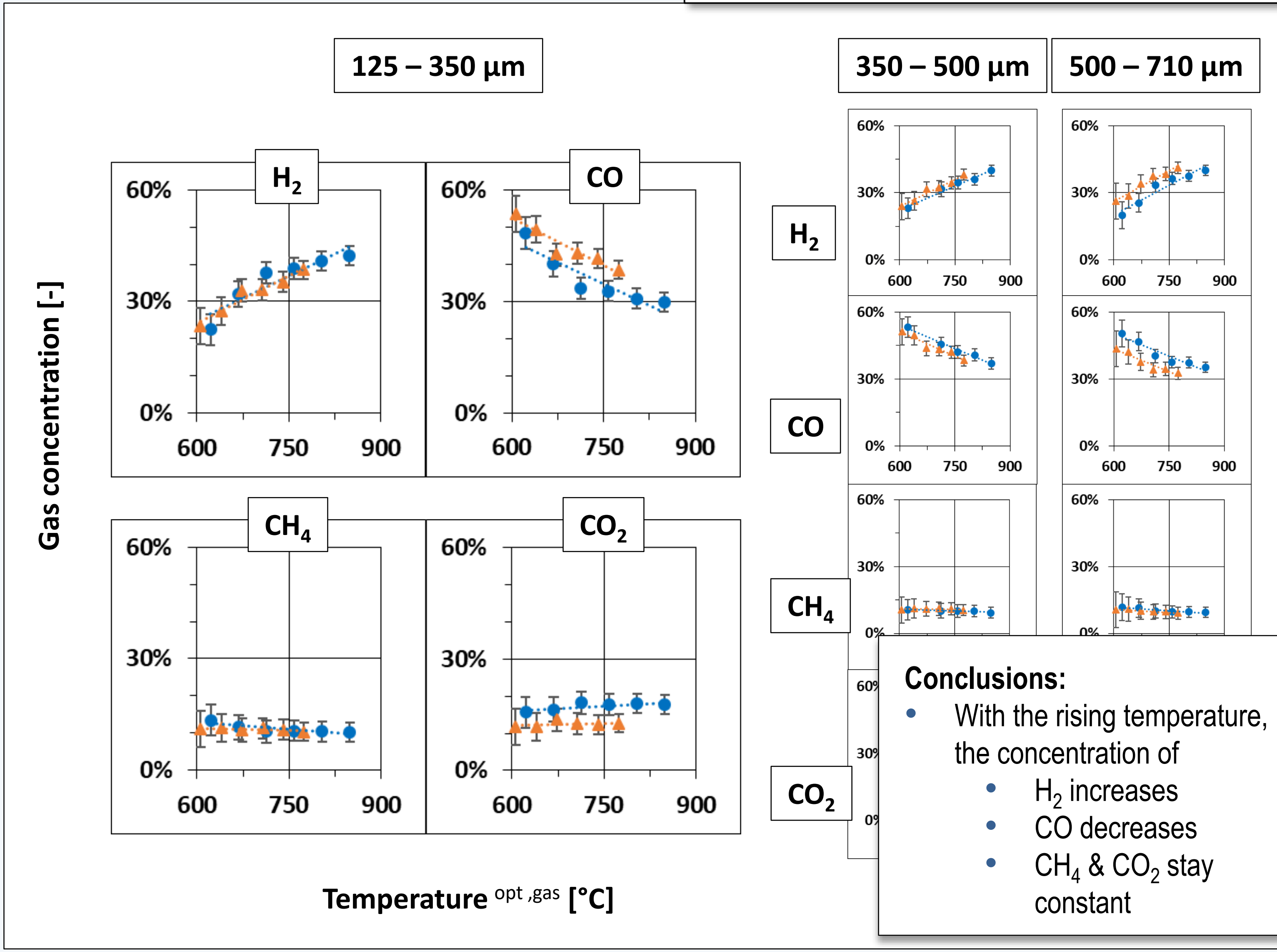
Results – wood powder

- Syngas composition dry-basis

One-step global gasification reaction:

$$CH_xO_y + H_2O \rightarrow H_2 + CO + CH_4 + CO_2$$



Syngas composition of ***plasma*** *and* ***thermal*** *gasification with trend lines and systematic errors at dry-basis*

Conclusions:

- With the rising temperature, the concentration of
  - H_2 increases
  - CO decreases
  - CH_4 & CO_2 stay constant

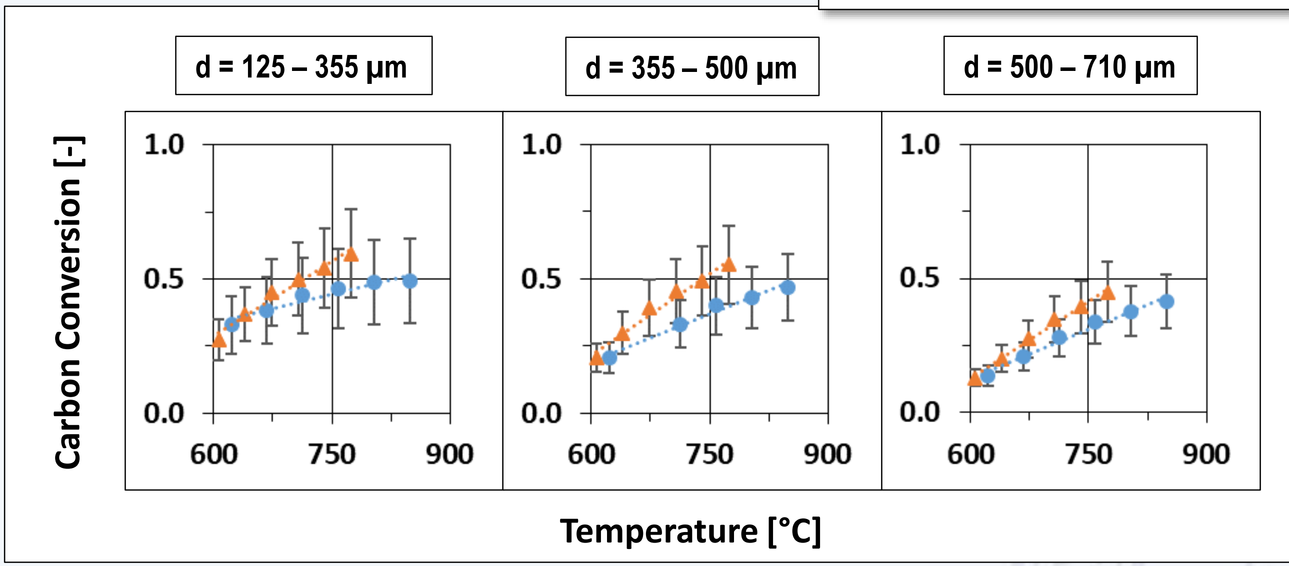
Results – wood powder

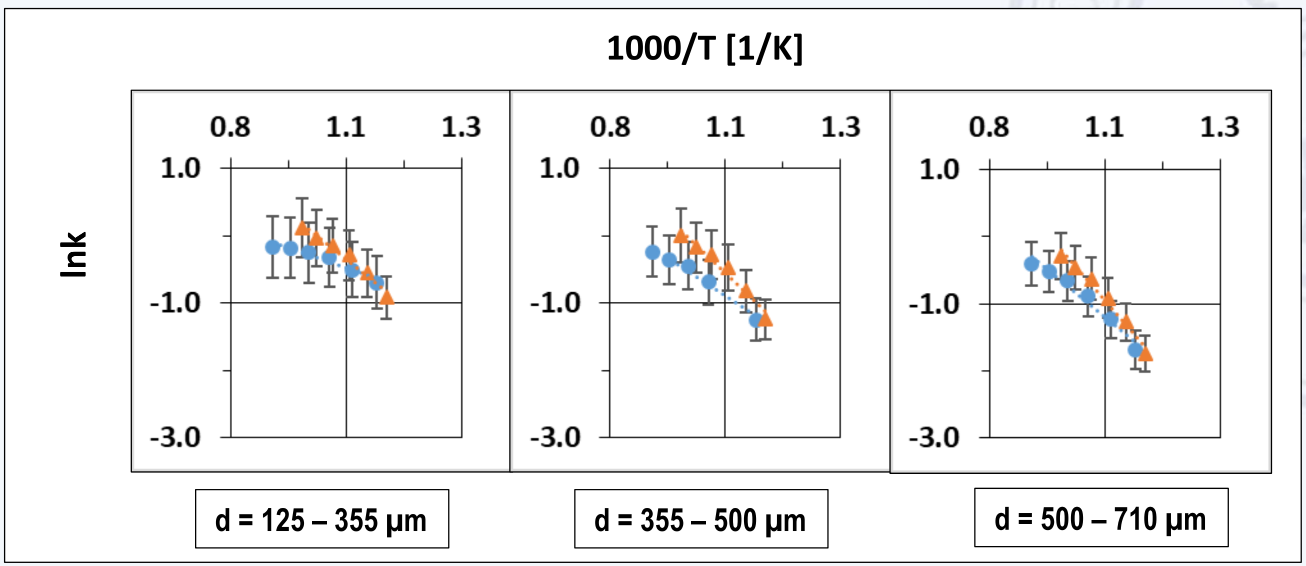
- Carbon conversion and reaction kinetics of wood gasification

Conclusions:

- With the rising temperature…
  - Carbon conversion increases from 13 to 60%
  - Reaction rate increases

Motivation
M&M
Results
Summary



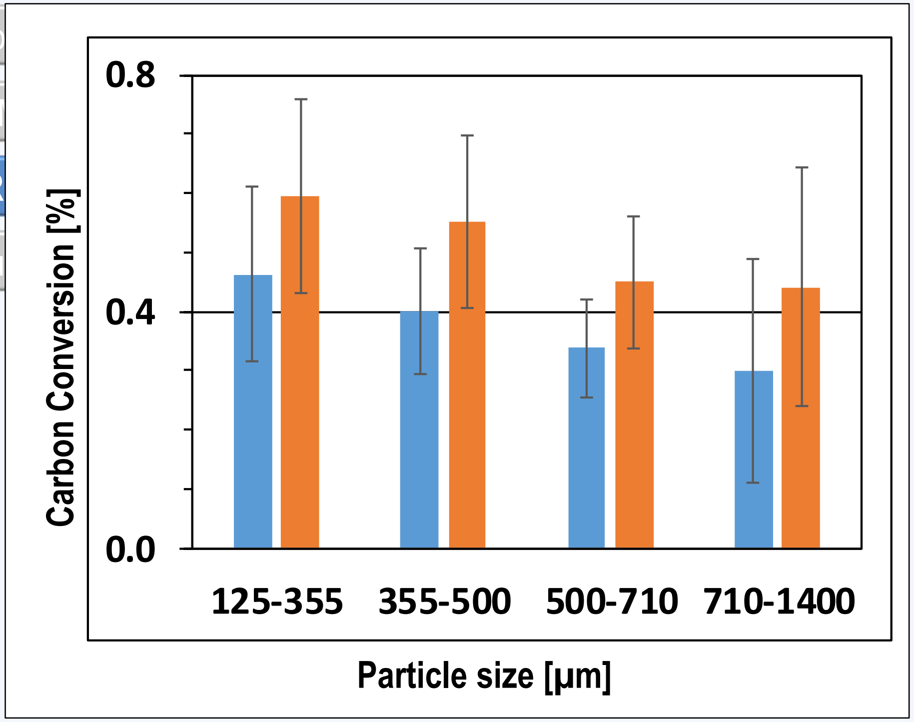


Carbon conversion and reaction rates of ***plasma*** *and* ***thermal*** *gasification with trend lines and systematic errors at dry-basis*

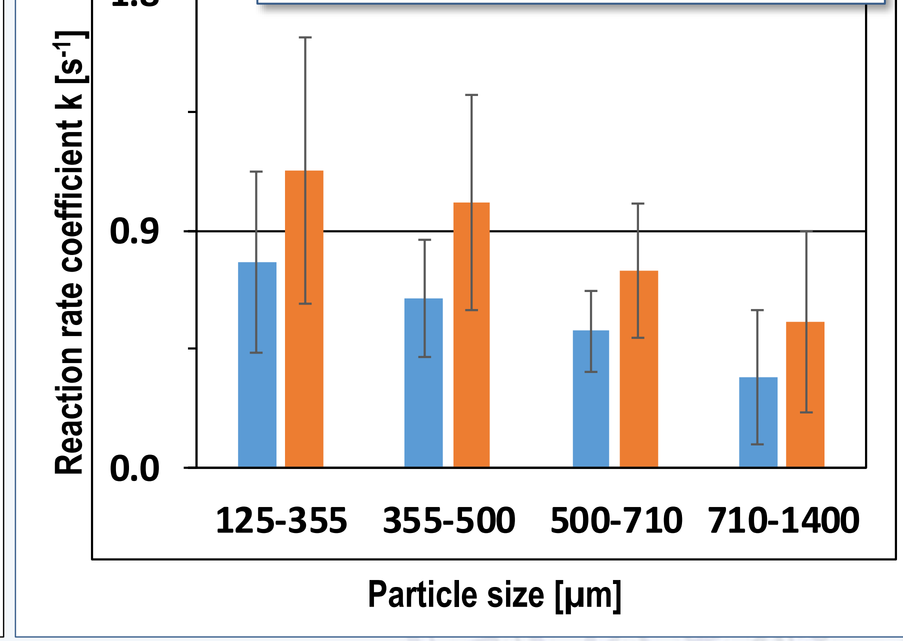
Results – wood powder

- Carbon conversion & Reaction kinetics*tar yield excluded

Conclusions:
- Increasing of carbon conversion and reaction rate coefficient by decreasing particle size (**reaction-rate-limited**)
- **Plasma promotes** both of conversion (**+22%**) and reaction kinetics (**+34%**)



***Carbon conversion** of plasma and thermal gasification with systematic errors at T = 760°C*opt,gas*



***Reaction rate** of plasma and thermal gasification with systematic errors at T = 760°C*opt,gas*

Calculation of Carbon Conversion from gaseous product:

$$CC\,\% = \frac{C_{CH4} + C_{CO} + C_{CO2}}{C_{fuel}}$$

Calculation of reaction rate coefficient k by data-fitting in Arrhenius Diagram (1. reaction order: n=1):

$$r = \frac{d\xi^*}{dt} = \frac{1}{m}\frac{dm}{dt} \qquad \frac{dm}{dt} = -k \cdot m(t)^n$$

$$k = A \cdot e^{-\frac{E_A}{RT}}$$

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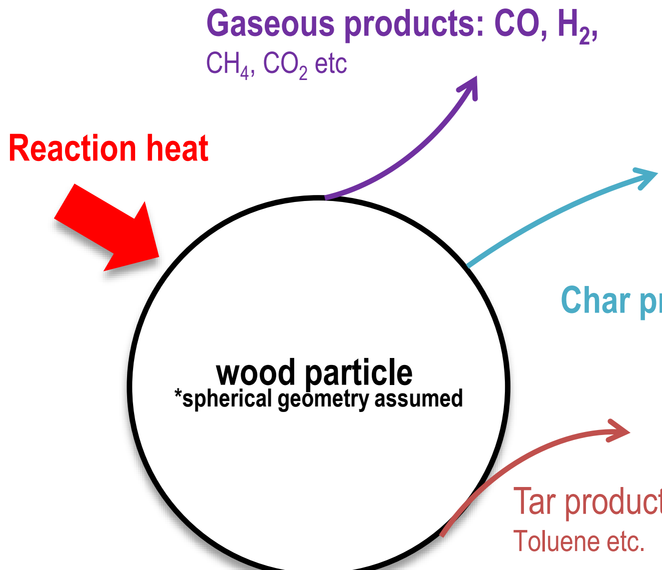
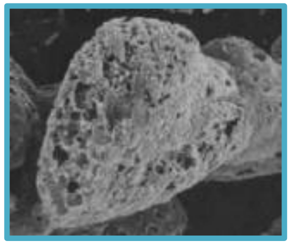
Results – wood powder

- Evaluation

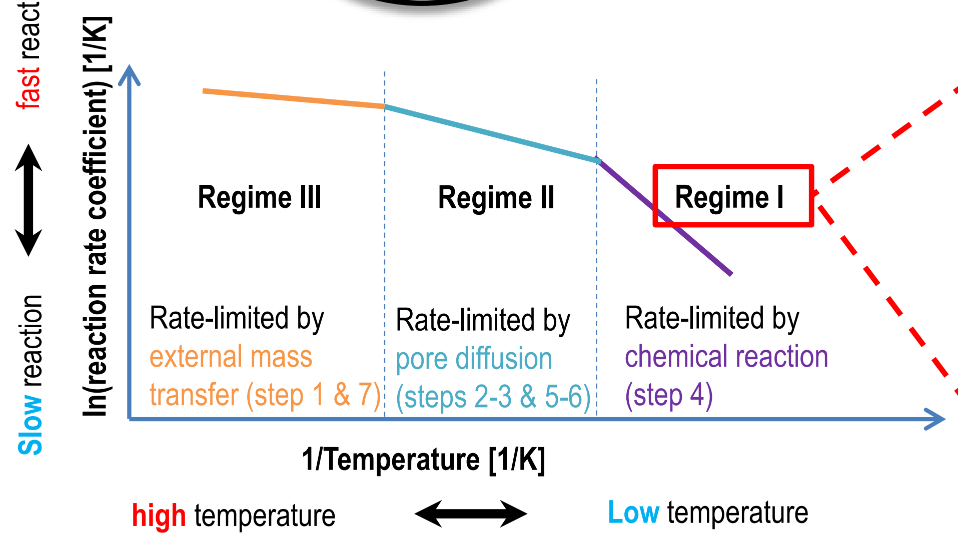


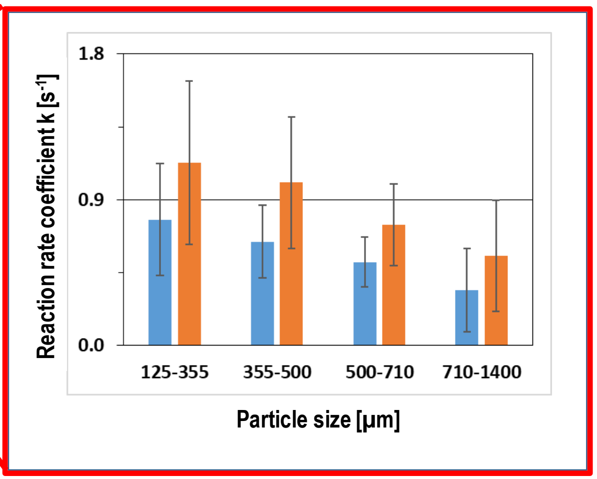
Source: (Liu, 2003)



Conclusions:

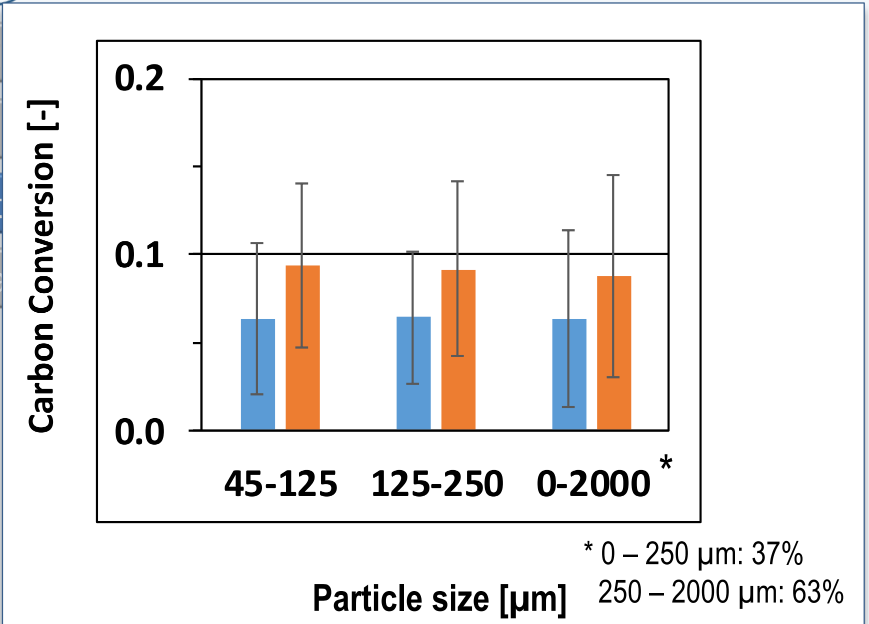
- Endothermal pyrolysis is a **reaction-rate-limited** process (Regime I) !
- **Plasma** influenced the pyrolysis by extremely <u>high heating rates</u> due to high local electron temperature and the presence of <u>radicals</u>.



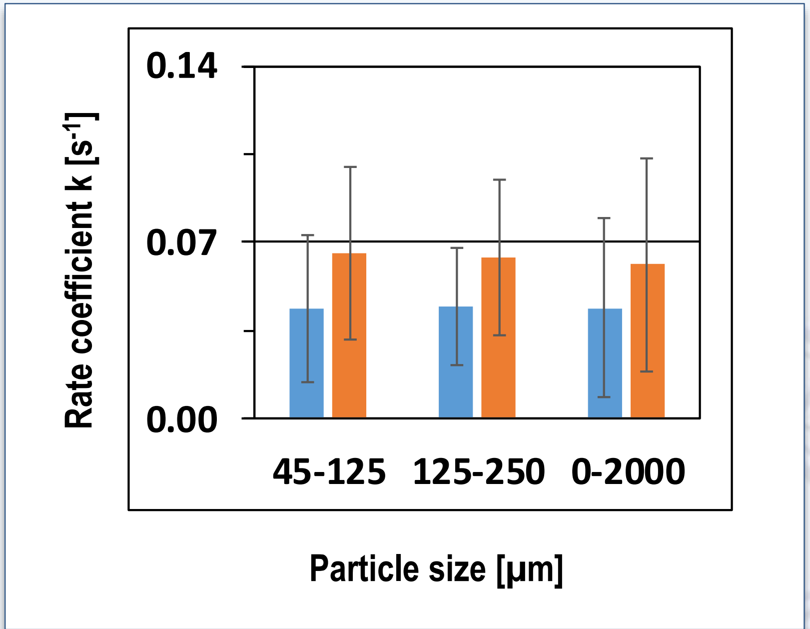


Results – charcoal powder

- Carbon conversion and reaction rate



***Carbon conversion** of plasma and thermal gasification with systematic errors at T = 670°C*opt,gas*



***Rate coefficient** of plasma and thermal gasification with systematic errors at T = 670°C*opt,gas*

Conclusions:

- Carbon conversion and reaction rate are **independent** of particle size (**diffusion-rate-limited**)
- Rate of reaction less slower than the rate in case of wood powder (factor ca. 0.1)
- **Plasma promotes** both of conversion (**+31%**) and reaction kinetics (**+30%**)

- **Method 1: Carbon Conversion = 5 – 18%** based on the product gas (CO, CO_2, CH_4)

$$CC\% = \frac{C_{CH4} + C_{CO} + C_{CO2}}{C_{fuel}}$$

- **Method 2: fuel conversion = 4.6 – 10.6%** based on the change of volatile content before/after tests

Both methods confirmed the results from each other !

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Results – charcoal powder

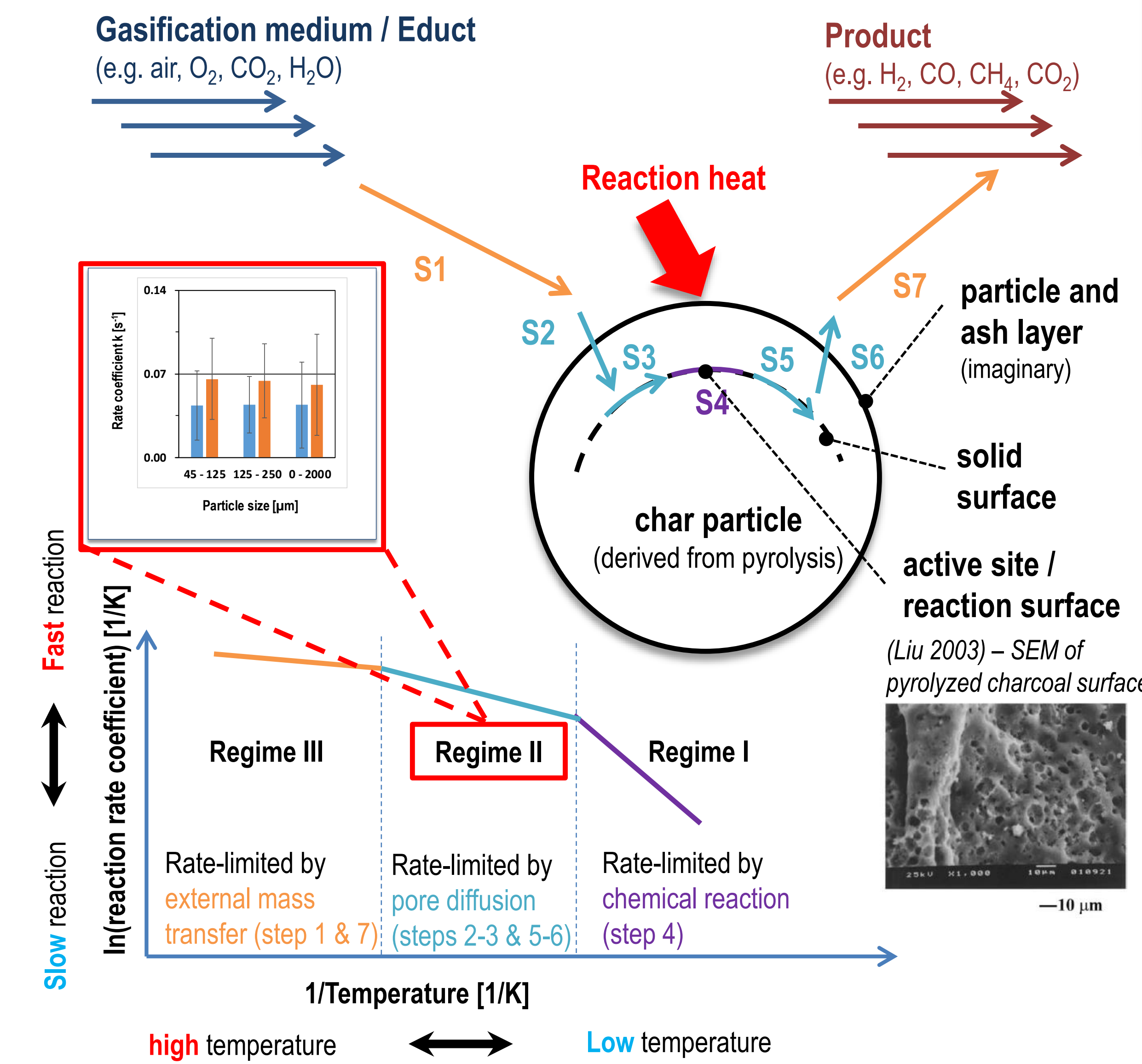
- Evaluation

Conclusions:

- Charcoal gasification is a **diffusion-rate-limited** process (Regime II) !
- **Plasma** influenced the process probably by the presence of radicals

Simplified process of (diffusion-)rate-limited char gasification

- Step 1: fluid flow and diffusion of gasification medium (bulk diffusion)
- Step 2: absorption of medium on solid surface
- Step 3: diffusion to active site (pore diffusion)
- Step 4: chemical reaction of adsorbed gasses and the solid ~ f(T)
- Step 5: diffusion from active site (pore diffusion)
- Step 6: desorption of product gases
- Step 7: fluid flow and diffusion back into the ambient gas (bulk diffusion)



(Liu 2003) – SEM of pyrolyzed charcoal surface

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Conclusion

Thank you for your attention!

- ✓ A drop tube reactor with non-thermal plasma generator has been designed, built, commissioned and optimized for experimental work
- ✓ Comparison between thermal and plasma gasification using wood and charcoal powder has been conducted and evaluated
  - ✓ **Wood powder** – Conversion and reaction kinetics depend significantly on particle diameter
    – **reaction-rate-limited** process!
    - ✓ Plasma promotion: +22% fuel conversion; +34% reaction kinetics
  - ✓ **Charcoal powder** –Conversion and reaction kinetics are independent on particle diameter
    – **diffusion-rate-limited** process!
    - ✓ Plasma promotion: +31% fuel conversion; +30% reaction kinetics

Outlook

- Plasma gasification of hydrocarbon (toluene, isopropanol etc.) is currently under investigation

Acknowledgement

This work has been supported by the Campus Future Energy Systems (Campus FES) under the grant „Biomassevergasung in nichtthermischen Plasmen".