Chair of Energy Systems
TUM School of Engineering and Design
Technical University of Munich

# Enabling waste-to-X pathways:

# A comprehensive analysis of the entrained-flow gasification kinetics of biogenic residues under industrial conditions

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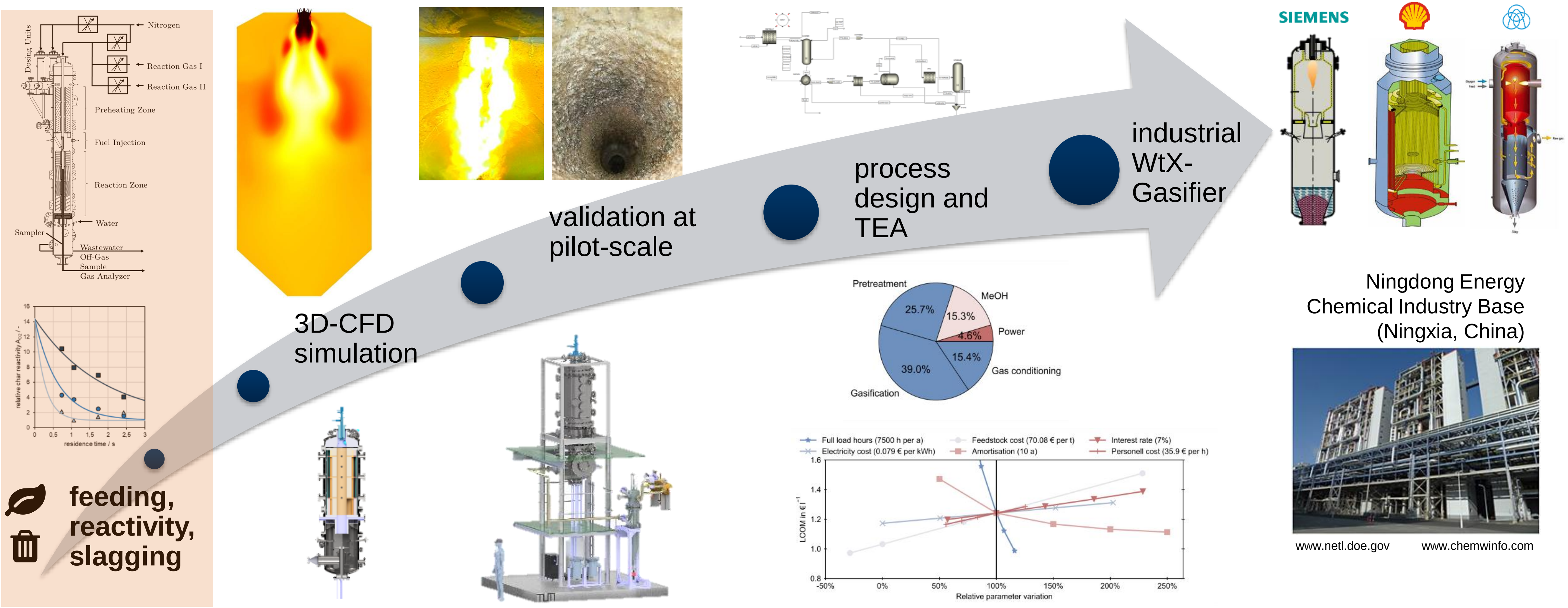
WACKER Chemical Site Gendorf, Bavaria, Germany

# Innovation roadmap of pulverized waste in entrained-flow gasification to commercial scale and market readiness

from reactivity studies to process design to *first-of-its-kind*



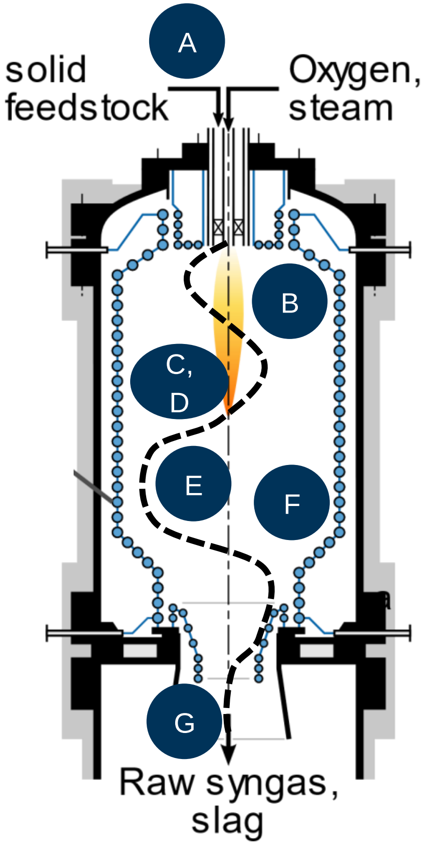
# Depicting the industrial gasifier performance prior to up-scaling

# (1) comprehensive conversion assessment

setting the scene for the entrained-flow gasifier´s KPIs

**Objectives and Goals:**
- Identification of most suitable waste feedstock for industrial up-scaling
- determination of model parameters via comprehensive experimental procedure

| KPIs | |
|---|---|
| conversion | % |
| specific oxygen uptake | $Nm^3/kg_{fuel}$ |
| steam/fuel-ratio | $kg_{H2O}/kg_{Fuel}$ |
| cold gas efficiency | % |
| gas composition | Vol.-% |
| specific syngas yield | $Nm^3/kg_{fuel}$ |




Safronov D. et al. (2017), Fuel Processing Technology 161:62–75

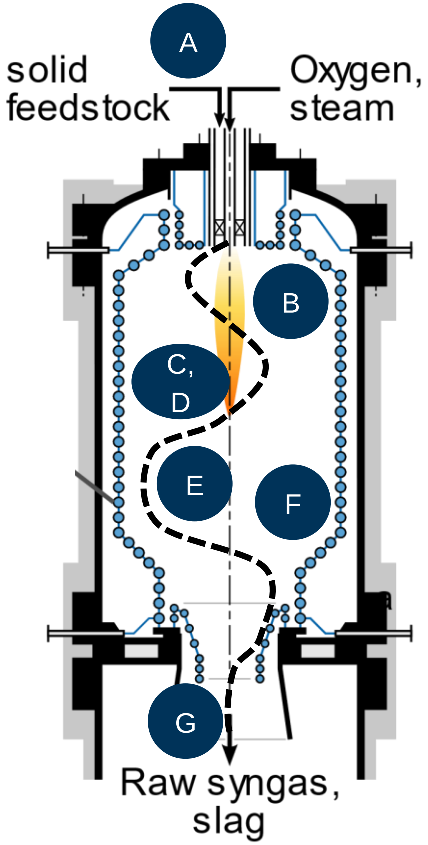
**feedstock assessment**
fuel analysis, dosing, reacitivty / kinetics, slagging

- A feedstock characterization
- B devolatilization kinetics
- C char sampling
- D char structure & model verification
- E char reactivity development & thermal annealing
- F surface reaction kinetics
- G slag viscosity behavior

# Depicting the industrial gasifier performance prior to up-scaling

# (2) Experimental concept, model selection and utilization

individual investigation of kinetic phenomena and aggregation in a cohesive CFD model

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pulverized biogenic residues and RDF fuels (A)

pressurized high-temperature entrained-flow reactor

pressurized wire-mesh reactor

gasification

pyrolysis

representative chars derived under industrial conditions (C)

solid state characterization

atm. TGA

pressurized TGA

surface area modelling (D)

thermal deactivation (E)

power Law LH approach (F)

single-first order reaction (B)

**CFD modelling: gasifier design and engineering**

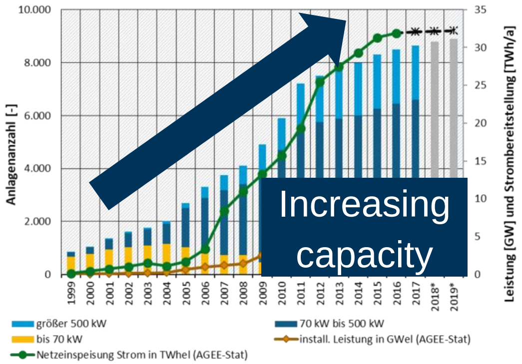

**Session 10-5:** CFD modeling of allothermal plasma-assisted entrained flow gasification (Sebastian Wilhelm, TU Munich)

# Biogas plants for bio-methan production are steadily increasing in Germany: residues show major potential for gasification

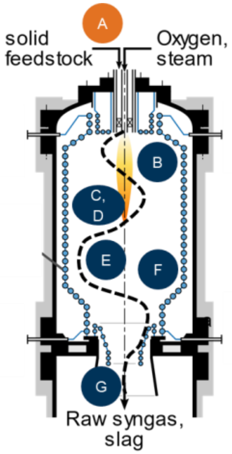
A

feedstock challenges: particle size, feeding, mineral matter: Is thermal pre-treatment necessary?


pulverized solid digestate




www.dbfz.de www.biogas.org

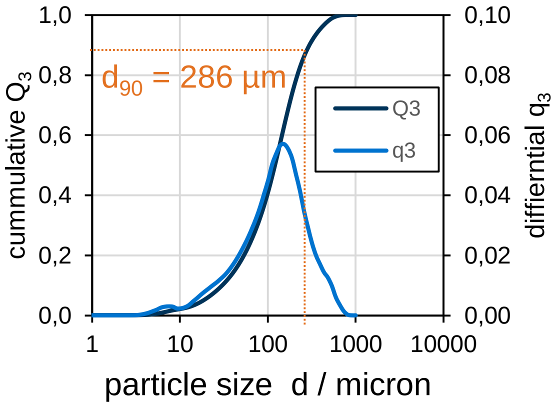


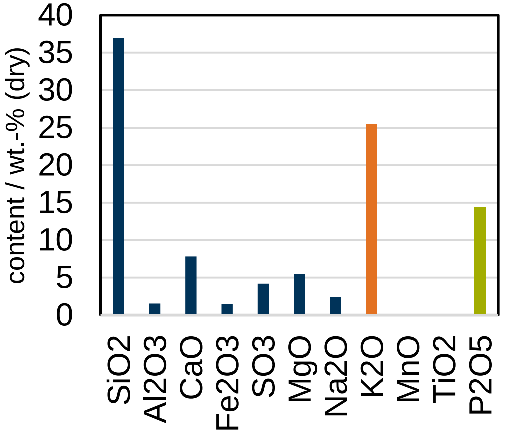

**Feedstock challenges**

- heterogeneous nature
- particle size–dosing–relationship
- milling technique (e.g. hammer mill, …)

| Proximate Analysis | / wt.-% |
|---|---|
| water (ar) | 10,2 |
| volatiles | 50,7 |
| fixed carbon (by difference) | 15,4 |
| ash (815 °C) | 23,7 |

| Ultimate Analysis | / wt.-% (daf) |
|---|---|
| C | 56,7 |
| H | 7,3 |
| O | 32,1 |
| N | 3,6 |
| S | 0,3 |

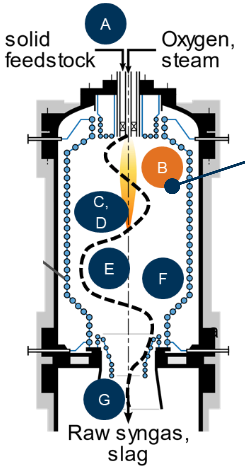


# Devolatilization kinetics under entrained-flow conditions wire-mesh reactor: parameter study (T, p, t)

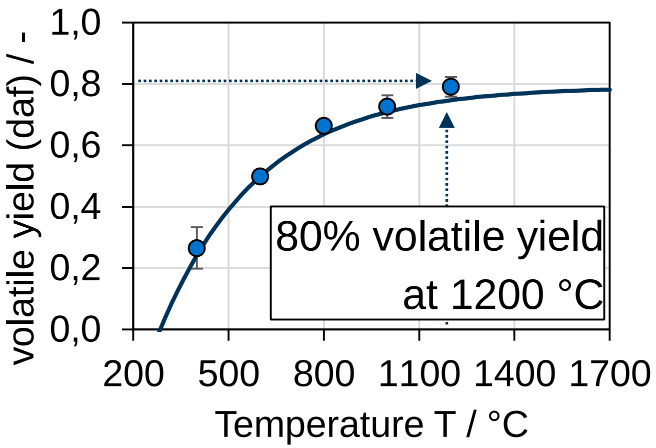
B

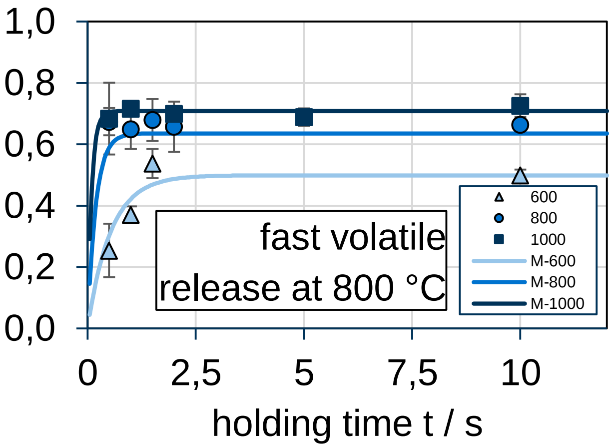
fast devolatilization within 250ms with 80% fuel conversion under high-temperature conditions

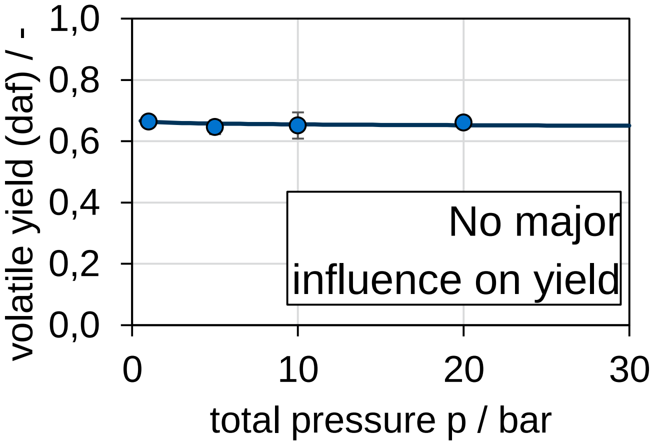


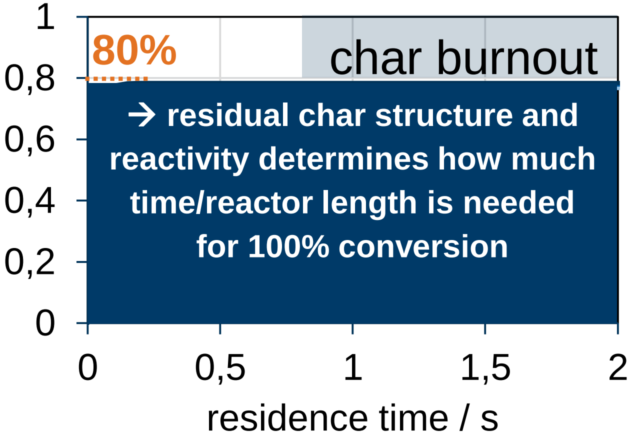

- primary pyrolysis
- high $N_2$-dilution of pyrolysis volatiles
- single layer fuel in mesh
- $dT/dt$ = 1000-5000 K $s^{-1}$

| model parameter | value |
|---|---|
| v / - | 0,0032 |
| ρ / - | 255,35 |
| $A_V$ / $s^{-1}$ | 463,17 |
| $E_A$ / kJ $mol^{-1}$ | 40,03 |



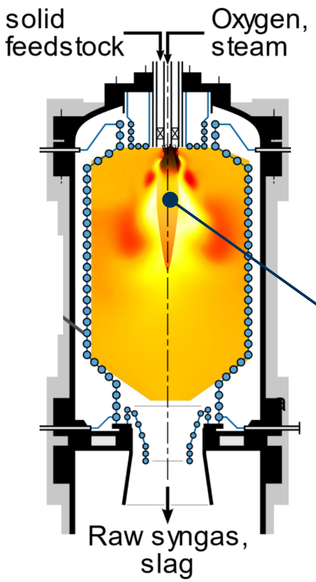



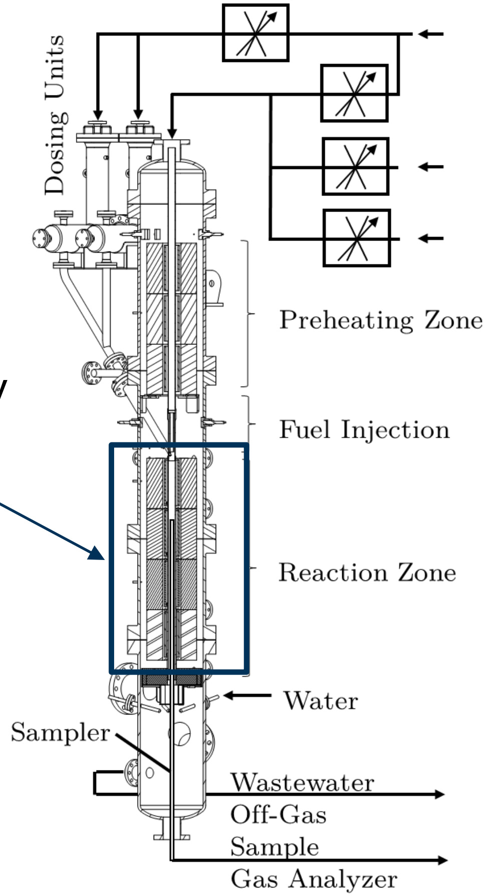
# Representative char production near industrial conditions: pressurized high-temperature entrained-flow reactor (PiTER)

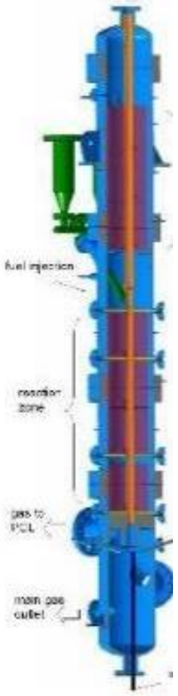
C

physical and chemical char characterization allows the verification of kinetic sub models at microscopic level

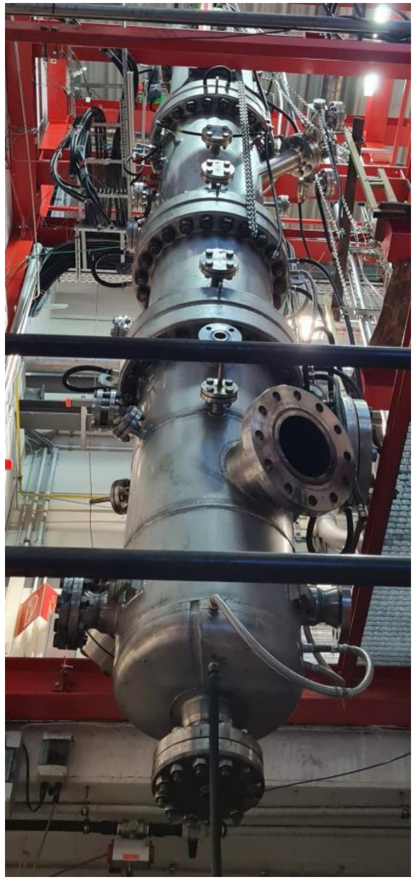



particle thermal history can be replicated!



PiTER: 7,2m



- height-adjustable char sampling lance is inserted in reaction zone for char sampling
- online gas-analysis via sampling lance

PiTER is used for char production under various conditions:

T = 1200, 1400, 1600 °C

p = 10 bar

t = 0,4-2,4s

**Focus of today:**

Influence of gasifier conditions on:

D physical & chemical structure

E char reactivity

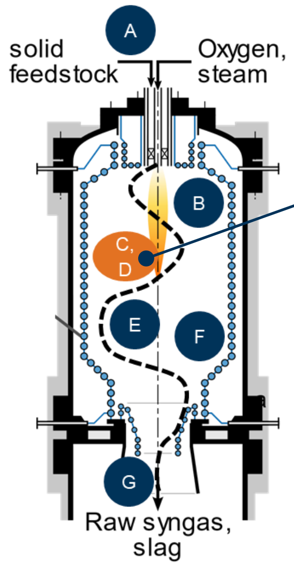
F reaction kinetics

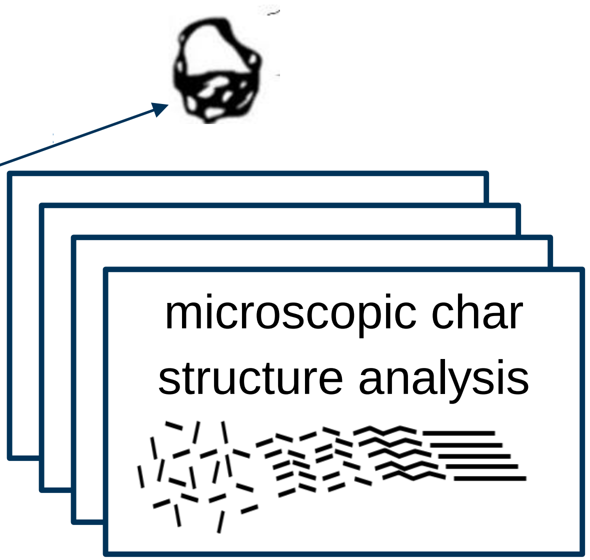
# Char structure analysis: surface area & graphitization

# $CO_2$-Physisorption, FT-IR, XRD, Raman spectroscopy, SEM-EDS

D

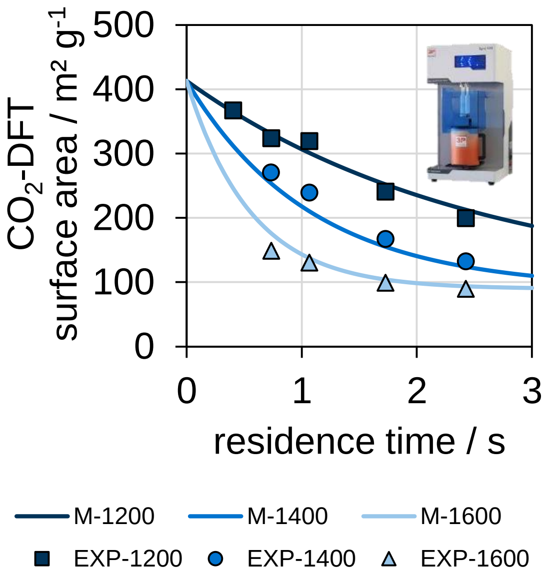
Physical and chemical char characterization allows the verification of kinetic sub models at microscopic level



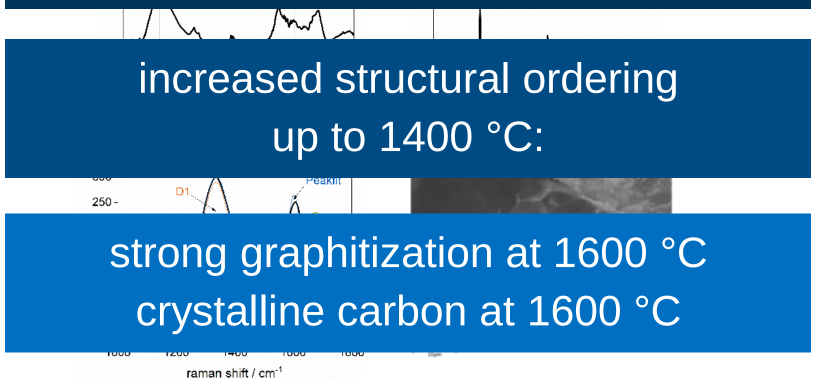

lower char surface area & increased graphitization correlates to lower reaction rates

## physical structure




| model parameter | value |
|---|---|
| $S_{max}$ / m² g$^{-1}$ | 413,4 |
| $A_{min}$ / - | 0,22 |
| $k_0$ / s$^{-1}$ | 453,6 |
| $E_A$ / kJ mol$^{-1}$ | 86,2 |

## chemical structure




char structure always a mix of armorphous and graphene-like carbon

increased structural ordering up to 1400 °C:

strong graphitization at 1600 °C crystalline carbon at 1600 °C

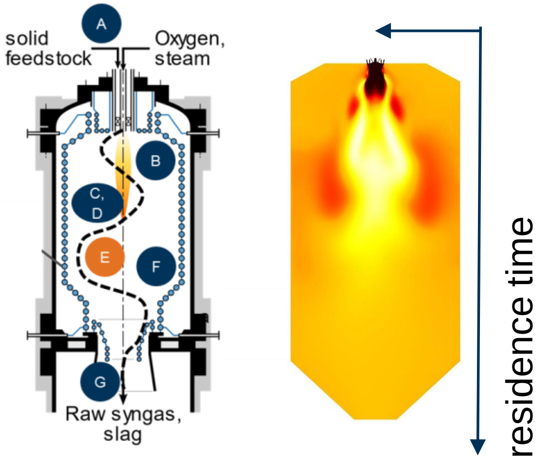
RWE KIT

FT-IR, XRD & Raman by Dr. P. Treu (KIT)
SEM-EDS by Dr. M. Dohrn (RWE)

# $O_2$/$CO_2$-char reactivity development & structural-relationship atmospheric TGA & Raman spectroscopy

E

## The influence of the particle thermal history on the char reactivity




isothermal experiments

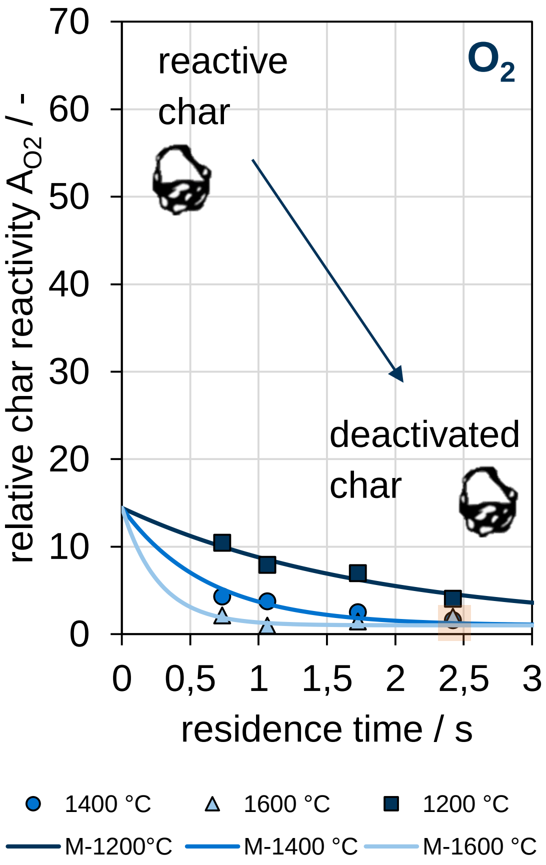
initial reaction rate at X = 5-20%

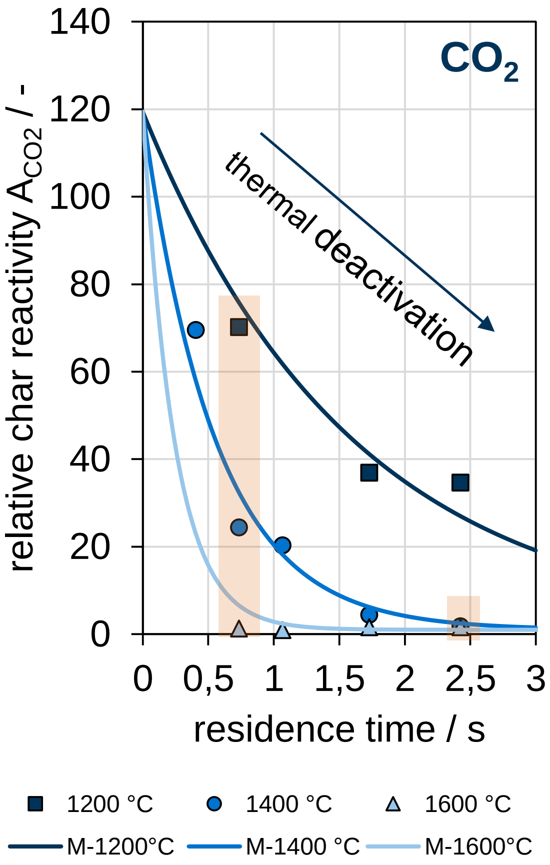
$p_{O2}$ = 100 mbar

$T_{isothermal}$ = 325 °C

$p_{CO2}$ = 500 mbar

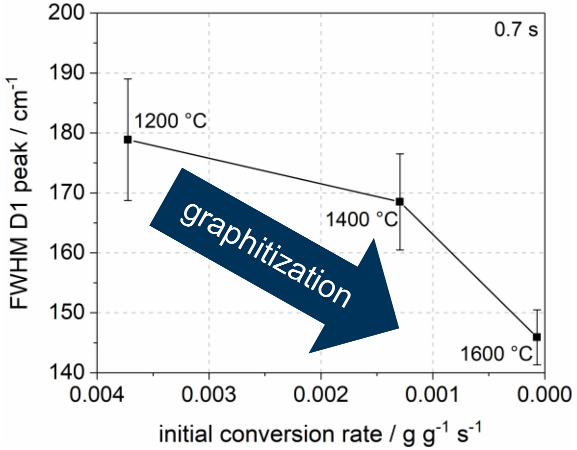
$T_{isothermal}$ = 750 °C




| model parameter | $O_2$ |
|---|---|
| $A_{max}$ / - | **14,5** |
| $F_0$ / $s^{-1}$ | 4366,2 |
| $E_A$ / kJ $mol^{-1}$ | 110,1 |

| model parameter | $CO_2$ |
|---|---|
| $A_{max}$ / - | **119,4** |
| $F_0$ / $s^{-1}$ | 4488,6 |
| $E_A$ / kJ $mol^{-1}$ | 108,8 |



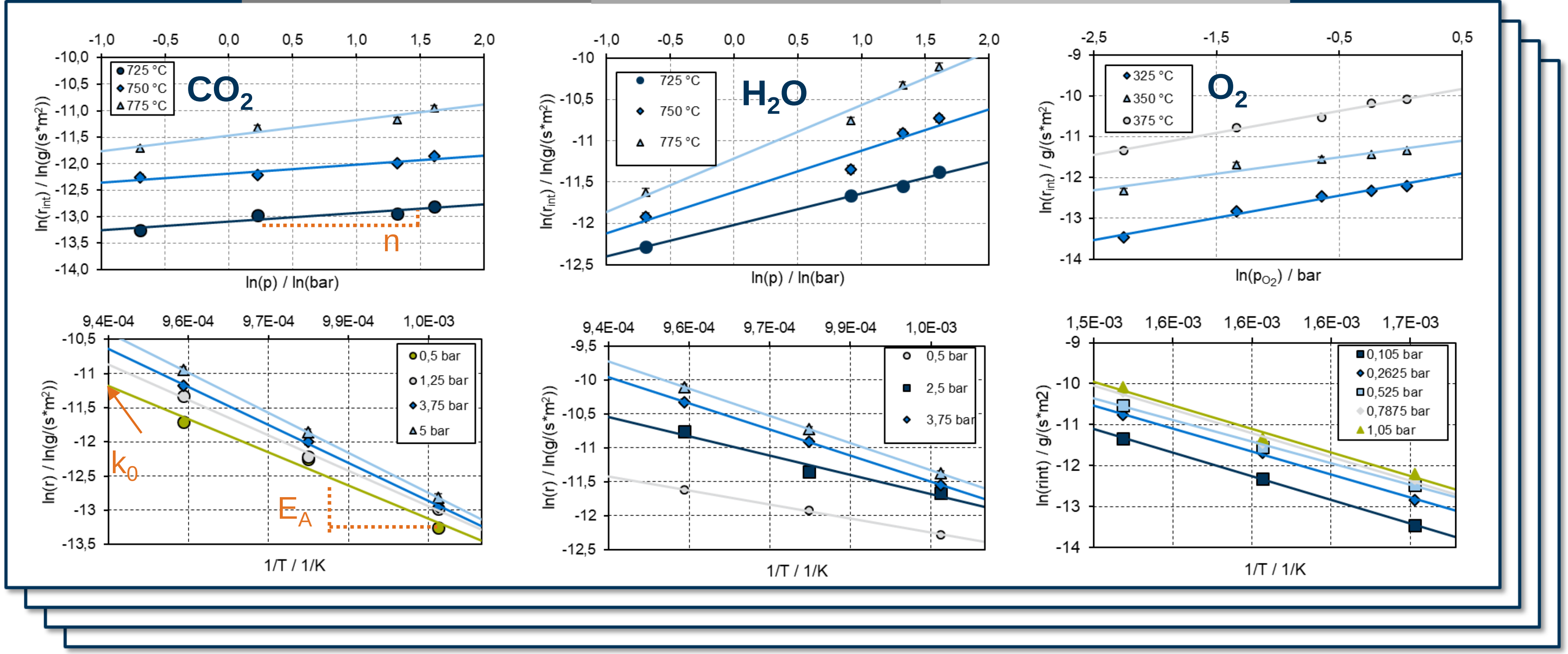
# Pressurized TGA: char gasification kinetics in chemically-controlled regime shows high intrinsic reactivity

F

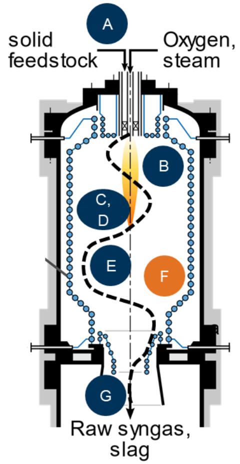
high-pressure tests allow Langmuir-Hinshelwood fitting on saturation, product inhibition & mixed atmospheres

**preliminary results**

| Power Law | Langmuir-Hinshelwood | Product Inhibition | Mixed Atmosphere |
|---|---|---|---|




| para-meter | $CO_2$ | $H_2O$ | $O_2$ |
|---|---|---|---|
| n / - | 0,28 | 0,49 | 0,54 |
| k0 / g $s^{-1}$ $m^{-2}$ $bar^n$ | $6{,}9\cdot10^9$ | $6{,}9\cdot10^6$ | $2{,}7\cdot10^6$ |
| $E_A$ / kJ $mol^{-1}$ | 286,2 | 191,2 | 133,1 |



# Summary: solid digestate shows promising reactivity and conversion behavior for up-scaling

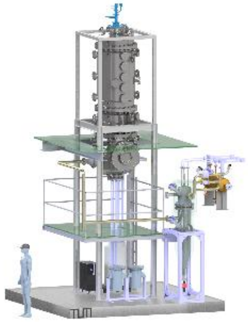
- reliable fuel dosing in pressurized entrained-flow reactor without thermal pre-treatment (vibrating units)
- devolatilization kinetics: **80% conversion after 250ms**
- char structure: **low surface area and strong graphitization at 1600 °C**
- thermal annealing: **especially relative $CO_2$-reactivity deteriorates strongly at 1600 °C**
- reaction kinetics: **highly reactive biomass char**

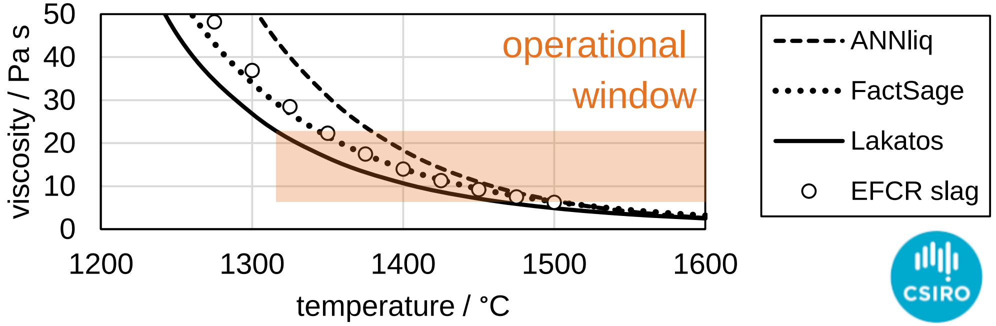
# Up-scaling to an 100 MW pressurized entrained-flow gasifier

Solid digestate ticks all boxes for up-scaling! What are the ideal operating conditions? → CFD simulation

## Tasks done

- reliable fuel dosing (dense-phase) in 100 kW pilot-scale gasifier
- reactivity assessment (this work)
- sufficient slagging behavior and viscosity

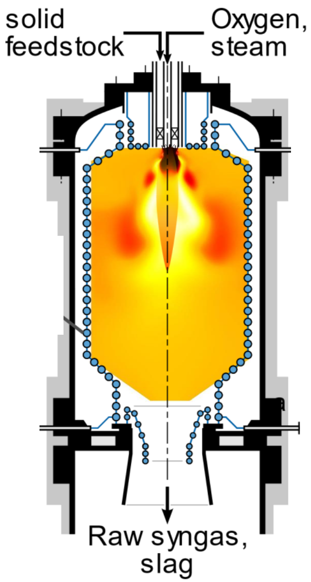





## Actions to be taken

3D-CFD simulation

- PiTER
- validation of 100 kW pilot-scale gasifier
- up-scaling to 100 MW




Validation at 100 MW

www.netl.doe.gov www.chemwinfo.com

# Q&A

Thank you!

VERENA

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