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Full Length Article

In-situ investigation of single particle gasification in a defined gas flow applying TGA with optical measurements

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HIGHLIGHTS

- A reactor with optical ports and TGA suited for single particle gasification was developed.
- Inhomogeneous particles affect gasification kinetics.
- The surface temperature of single particles was measured during gasification.
- A relationship between particle surface temperature and reactivity was discovered.
- Quantitative gas analysis with in-situ Raman spectroscopy was performed.

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ABSTRACT

The newly developed HITECOM reactor provides the possibility of in-situ analysis of single particle reactions. It combines the capabilities of a magnetic suspension thermobalance with state of the art optical analysis. The surface temperature and carbon conversion of single particles are measured under well-defined flow conditions. The generated data enables the detailed validation of CFD single particle models. For this reactor, a special temperature resistant particle holder had to be constructed, which is able to fix various particles in direct flow during gasification. An in-situ Raman spectroscopy setup was established for quantitative gas analysis at pressures between 1 and 20 bar and temperatures up to 965 °C. Here, a pulsed Nd:YAG laser at 355 nm was used as excitation source. The Rayleigh/Raman scattering was measured perpendicular to the flow direction with a spectrograph and ICCD camera. From the recorded spectra the gas concentrations were calculated. Generally, the calculated concentrations of CO, CO_2 and N_2 match the reference values from the gas chromatograph.

In the present study, single coal particles of one Central German lignite and one hard coal were analyzed and monitored during gasification. The particle diameter ranged from 1 to 3 mm. Gasification experiments with CO_2 were carried out under isothermal conditions at 1 bar total pressure and temperatures of 800–1200 °C.

The experimental data were adjusted with models by data fitting. It was found that the Random Pore Model (RPM) matches the carbon conversion of the hard coal sample and the Shrinking Core Model (SCM) matches the carbon conversion of the lignite sample.

Further analysis revealed that inhomogeneous particles affect gasification kinetics. The differences in reactivity between several particles from the hard coal are significantly larger than for the lignite particles, which is in accordance to the results of the respective ultimate and proximate analyses.

Additionally, it was discovered that the difference between gas and particle temperature is negligible for low reactive feedstocks within the investigated temperature range ($\Delta T \leqslant 5$ K at 1070 °C, hard coal), whereas there was a significant difference for reactive particles ($\Delta T \leqslant 40$ K at 1070 °C, lignite).

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Nomenclature

AVG	average
d	diameter, mm, m
daf	dry and ash free
db	dry basis
DIN	German institute for standardization
DTF	Drop Tube Furnace
GC	gas chromatograph
h	heat transfer coefficient, W m^{-2} K^{-1}
$I_{Raman,i}$	Raman signal intensity
k	kinetic constant, s^{-1}
LIF	laser-induced fluorescence spectroscopy
m	mass, mg, g
MAX	maximum
MIN	minimum
n	number density
p	pressure, bar
R	ideal gas constant, 8.314 J mol^{-1} K^{-1}
r	reaction rate, s^{-1}
Re_p	Reynolds number based on particle diameter
RPM	random pore model
SCM	Shrinking Core Model
STD	standard deviation
t	time, s
T	temperature, °C, K
TC	thermocouple
TGA	thermal gravimetric analysis
u	slip velocity between gas and particle, m/s
X	conversion
Δ	delta, %
ν	kinematic viscosity, m^2/s
$\sigma_{Raman,i}$	Raman cross section
τ	normalized time
χ_i	mole fraction
Ψ	structural parameter

Subscripts

c	carbon
g	gas bulk phase
p	particle
s	surface
0.5	carbon conversion of 50%

1. Introduction

Solid carbonaceous materials conversion processes at high temperatures and high pressures are of great importance in providing of energy and recycling of chemicals. One example of high temperature conversion of materials is coal gasification [1]. Syngas produced from gasified solid carbonaceous materials plays an important role in the generation of electricity by fueling a combined cycle power plant [2]. Another application of syngas are the reduction processes in metallurgy [1].

To develop optimized gasifier designs, heterogeneous reaction kinetics at high pressures and temperatures are required. This kinetics are then used in the modeling of gasification processes to understand the behavior of a reactor when varying different input parameters [3]. Therefore, the combined experimental and theoretical modeling of these complex processes is the key to an effective strategy of technology development.

High temperature kinetics are measured in so-called drop tube furnaces (DTF) [4–7] and TGA [8–10], see Fig. 1. The drop tube furnace, see Fig. 1 – left is used for small sized particles that are dropped from the top of the tube. The wall of the tube is heated. Due to gravity, the chemically reacting particles settle down. From the gas composition and/or composition of the particles at the bottom of the tube, the conversion rate is determined. Disadvantages of a DTF are a limit of particle velocity corresponding to the terminal velocity and unknown species concentrations close to the reacting particles. That is why measurements are always coupled with modeling, e.g. see the works [11–13].

The second well established method for studying the kinetics of gasification reactions is Thermogravimetric analysis (TGA) [8,14,15]. Fig. 1 – right shows the principal scheme of a TGA. The main disadvantage of any TGA is the need for a sample holder which may affect the species transport to the sample at high temperatures. The kinetically controlled regime cannot always be assumed, where the concentration of reacting species does not change across the sample and reactor. The pore diffusion limitations can be reduced by grinding the particles to a smaller size and to use a single layer of particles inside the holder. However, the small initial mass of particles can lead to inaccurate measurements due to limited accuracy of the balance. Additionally, the effect of fluid flow on the balance can negatively affect its measurement. At the same time, for the prevention of external mass transfer limitations it is not entirely sufficient to increase the fluid flow since a stagnant gas layer may develop within the crucible [16].

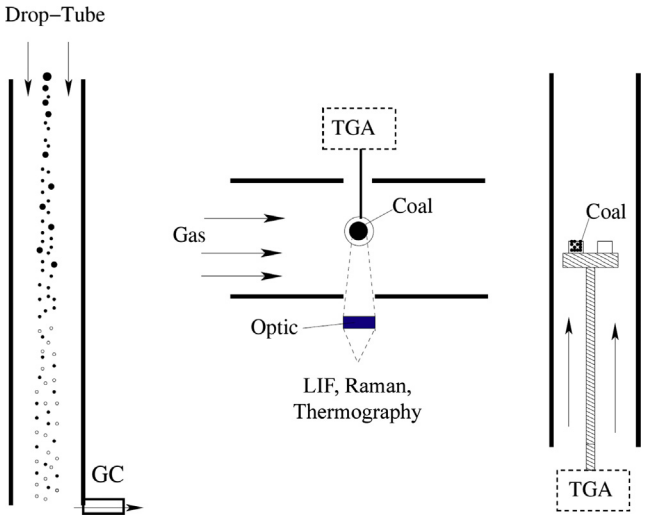

Fig. 1. Principal scheme of devices used to measure kinetics of high temperature conversion of materials: left – drop tube reactor (particle size < 200 μm, particle velocity is limited); right – a standard TGA (mass transport limited); center – a new TGA (particle velocity and mass transport is not limited).

Finally, it is evident that using TGA or DTF only gives indirect information about the processes occurring on the particle surface. For example by changing the gas composition or the particle weight, the changes in gas composition on the particle surface is unknown. Only the use of computational models of processes occurring inside TGA or DTF can help detect the kinetics, e.g. see the works [16,17]. However, often some inadequate simplification compared with the real process must be taken into account to determine final parameters as heterogeneous kinetics at the exist-