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Full Length Article

Heat and mass transfer within thermogravimetric analyser: From simulation to improved estimation of kinetic data for char gasification

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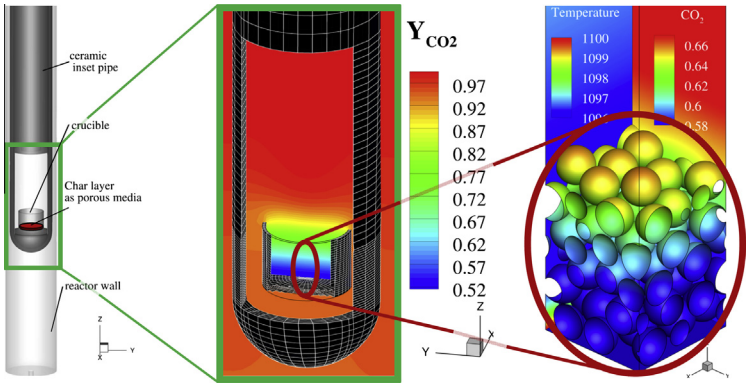
HIGHLIGHTS

- Gasification experiments of HOK lignite char with CO_2 in TGA are conducted.
- CFD reactor simulation of the char gasification in TGA is presented.
- Char conversion including heat and mass transfer near the sample is modeled.
- Detailed particle-resolved simulations of char within crucible validate the model.
- Diffusion limitation are considered for estimation of kinetic parameters.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermogravimetric analysis is a standard experimental method to determine kinetic data for heterogeneous coal char reactions. However, it is necessary to implement a sample holder to weigh the char sample, which may influence the mass and heat transfer towards the crucible. Thus, in this work the heat and mass transfer phenomena in a TGA were investigated. Experiments were carried out with hearth furnace char at temperatures between 1073 and 1273 K and a pressure of 1 bar. Based on the experiments, computational fluid dynamics was utilized to study the macroscopic transport mechanism employing a heterogeneous reaction on the external surface at a temperature of 1100 K. For the species transport it is shown that convection plays a minor role in the crucible and diffusion is predominant. The aim of the work is to present a methodology for evaluating the resultant kinetic data taking the resistances in heat and mass transfer into account. For this purpose, the true species concentration and temperature at the sample were calculated. Therefore, the relevant heat and mass transport phenomena were modeled using a zero-dimensional approach considering spatially uniform concentrations and temperatures in the transient process. The model was validated by detailed CFD simulations of the reacting packed bed of char particles in the range of 900–1250 K. It was found out that the concentration of the gasification agent was about 14% lower than expected as the maximal deviation. Thus, the consideration of diffusional effects within the crucible resulted in higher activation energies and different reaction orders when the kinetic parameters were determined.

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Nomenclature

Symbols

A_R	pre-exponential factor ($mol^{1-n}\ s^{-1}\ m^{-2}$)
A	char layer surface area (m^2)
c_p	heat capacity ($J\ kg^{-1}\ K^{-1}$)
c_i	concentration ($mol\ m^{-3}$)
d_P	particle diameter (m)
D	diffusion coefficient ($m^2\ s^{-1}$)
E_A	activation energy ($kJ\ mol^{-1}$)
h_r	specific reaction enthalpy ($J\ kg^{-1}$)
H	height of crucible (m)
k	reaction constant ($mol^{1-n}\ s^{-1}\ m^{-2}$)
K_{RPM}	random pore reaction rate (s^{-1})
L	height of char layer (m)
L_{ch}	characteristic length (m)
$\dot{m}_C$	carbon mass flow ($kg\ s^{-1}$)
m	mass (kg)
M_i	molar mass ($kg\ mol^{-1}$)
n	reaction order (–)
Pe	Peclet number (–)
$\dot{q}''$	heat flux ($W\ m^{-2}$)
r_{pore}	average pore radius (m)
S'''	specific surface area (m^{-1})
t	time (s)
T	temperature (K)
u	velocity ($m\ s^{-1}$)
X	carbon conversion (–)
Y_i	species mass fraction (–)

Greek symbols

ε_{rad}	emissivity (–)
ε	void space (–)
ε_{part}	particle porosity (–)
λ	thermal conductivity ($W\ m^{-1}\ K^{-1}$)
ψ	structural parameter (–)
Ψ	Weisz-Prater criterion (–)
Φ	Thiele modulus (–)
η	effectiveness factor (–)
ρ	density ($kg\ m^{-3}$)
σ_{SB}	Stefan-Boltzmann constant ($W\ m^{-2}\ K^{-4}$)

Super- and subscripts

0	initial
ax	axial
b	porous bulk
eff	effective
i	species
g	gaseous phase
h	heat transfer
s	solid phase
C	carbon
G	bulk gas
Kn	Knudsen
m	mass transfer
P	particle in char layer
S	surface of char layer
W	crucible wall

1. Introduction

A profound knowledge of the reactivity of carbonaceous feedstock, especially the kinetic parameters of the reactions of char with the gasification agent, is crucial for the development and design of gasifiers. Here, it is important to separate physical processes from chemical processes to gain reliable kinetic data.

Thermogravimetric analysis (TGA) has become a well-established method for studying the kinetics of gasification reactions [1–4]. Nonetheless, the need to have a sample holder may influence the species transport to the sample. Typically, a crucible is filled with char and the flow of the gasifying agent is directed towards the open crucible top. The pore diffusion limitations can be reduced by grinding the particles to a smaller size. To prevent external mass transfer limitations it is not entirely sufficient to increase the fluid flow, since a stagnant gas layer may develop within the crucible.

Ollero et al. conducted investigations on the diffusional effects during char conversion in a TGA [5]. In their experimental study they used different set-ups of char within the crucible confirming diffusion effects on the conversion. Furthermore, the same research group developed a two-dimensional model for reaction-diffusion phenomena within a TGA crucible [6]. They introduced an overall effectiveness factor defined as ratio of reaction rate considering diffusion to the reaction rate for bulk conditions. This effectiveness factor shows that for the conversion of the considered biomass particles this factor is as low as 0.2. Additionally, Gómez-Barea et al. conducted theoretical and experimental studies on the diffusional effects on single particles [7,8]. However, no attempt has been made to apply the model to improve the kinetic data estimation of TGA experiments.

Nowadays, with the progress of computational methods and hardware, numerical simulation and CFD in particular has become a standard tool for predicting and understanding fluid flow and heat and mass transfer in chemical engineering. However, few published works focus on the simulation of TGA reactors. Comesaña et al. [9] simulated the phase change of indium in a TGA. Benedetti et al. [10] applied CFD to study the carbonation of CaO, modeling the heterogeneous reaction as an idealized surface reaction neglecting inter- and intra-particle effects.

Compared with this, detailed numerical studies of reacting single carbonaceous particles are numerous [11–16] due to the commercial importance of entrained flow gasification processes. These numerical simulations can assist the development of submodels in process modeling: For instance, Schulze et al. [17] utilized CFD to develop a submodel for char gasification. With respect to the sample in a TGA, the solid particles are more likely to be found in a packed bed configuration than to be isolated from each other. Despite recent attention paid to particle-resolved simulations of random packed beds [18–23] there are only few published works focusing on packed carbonaceous particles. Mahmoudi et al. [24,25] proposed a model for the heating, drying and pyrolysis of biomass particles. Particle-resolved simulations of char gasification in dense particulate media have been conducted by Schulze and Nikrityuk [26].

Considering these developments in the research on solid fuels, this work demonstrates the path from utilizing numerical simulations on different scales to developing models improving the prediction of TGA experiments.

Therefore, in this work, macroscopic heat and mass transfer in a TGA reactor was studied employing three-dimensional CFD simulation. After the major transport processes had been identified, a simplified model for diffusion and heat transfer within the crucible was developed. The validation of this model was carried out against detailed, particle-resolved CFD calculations of representative packed bed of char particles from the sample. In the first instance, kinetic data from the literature [27–29], which is independent from the kinetic data gained in this work, are applied to carry out reactor simulations and validate the model. Based on the validated model, simulations were conducted to calculate the