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Research article

Sorption measurements for determining surface effects and structure of solid fuels

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ABSTRACT

Novel experimental results on temperature dependent diffusion of CO_2 inside porous char particles are provided as well as corresponding data on adsorption of oxygen and carbon dioxide. For this purpose, different chars from a Colombian coal were generated either in a flat flame burner (FFB) under realistic conditions for pulverized coal combustion with heating rates in the order 10^4–10^5 K/s or in a thermogravimetric analyser (TGA) at low heating rates and inert conditions (Ar).

The chars produced are used for kinetic adsorption measurements with a suspension balance to determine temperature dependent diffusion coefficients for CO_2 up to 160 °C. Based on these data the resistance factor for Knudsen diffusion, which describes the influence of the inner particle morphology on gas diffusion, was determined. The results indicate that the diffusion coefficients of the chars converge to the same value with rising temperature, ending in a Knudsen diffusion dominated regime. Furthermore, adsorption measurements for O_2 and CO_2 were conducted up to temperatures of 150 °C and 450 °C, respectively, on coal chars for the first time. Based on the pure component results, multicomponent adsorption has been predicted based on the well-known multi component IAST model. The results indicate that individual species selectivity changes with temperature.

1. Introduction

The combustion or gasification of coal or biomass is subject to ongoing research. For carbon capture, oxyfuel combustion attends continuous interest [1–3]. The reaction rate of heterogeneous combustion or gasification is determined by mass transport and by chemical reactions, which are related to the partial density of species at the surface and thus to the composition of the gas phase at the surface. Detailed knowledge on these compositions is therefore of utmost importance for the understanding of heterogeneous fuel conversion. However, in most cases the major part of the relevant surface is pore surface. Thus diffusion coefficients of the involved gaseous species within the porous structure of the solid fuel need to be known as well, since they determine the accessibility of inner surfaces. In this initial study, CO_2 and O_2 will be considered as major reactants in oxyfuel combustion and gasification; studies on further components generated during the gasification process will follow.

In principal, the essential steps of mass transport from the bulk phase (1) to the surface (4) are well known, see Fig. 1. Transport happens by gas film diffusion (2–3) and by diffusion inside the particle (3–4) [4]. Adsorption measurements can deliver information either about the kinetics and/or about the thermodynamic equilibrium loadings on the surface.

In porous media, the diffusion process determines the kinetics of the adsorption process since the isolated attachment of molecules to the surface (4) is by magnitudes faster than the diffusion process. In the gas phase, the motion of molecules and the formation of boundary layers can be described by gas kinetics reasonably well. However, within the pores of the particle these models fail, because they cannot describe the interaction with an inner structure and with complex surfaces, which are not sufficiently well described by themselves. Thus, experimental data are required to describe the interaction between gas phase and porous particles.

In addition to the influence of particle morphology on the diffusion process, the total mass transfer in a porous particle also depends on the rate at which different species attach to the surface; selective adsorption of species in the pores has to be considered. Besides kinetic and steric selectivity, the mechanism of energetic or thermodynamic selectivity is well known. This mechanism is responsible for deviations between concentrations in the adsorbate phase and in the gas phase close to the surface. This effect can be described by predictive gas mixture adsorption models like the IAST, PRAST, SBM and many others [5–7].

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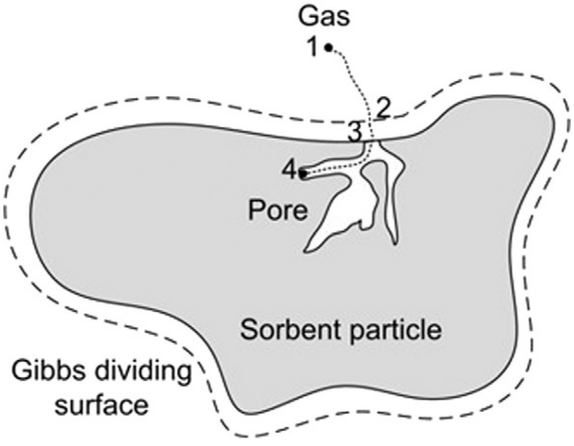

Fig. 1. Schematic of mass transport at a porous particle.

This article will present novel data on temperature dependent diffusion coefficients of CO_2 in the pore structure and on temperature dependant selectivity of the adsorption of CO_2 and O_2 at the char surface.

2. Char production

2.1. Coal petrography

The coal used originates from the coal mine Norte in Colombia. Its maceral and elemental composition is presented in Table 1. After drying at 60 °C, the coal was sieved into a fraction of 90–125 μm.

Char was produced for the raw coal in two different ways. On the one hand, chars were produced under fast heating rates similar to real combustion systems in a so-called flat flame burner. On the other hand, slowly pyrolysed chars were generated using a thermogravimetric apparatus.

2.2. Flat flame burner chars

The char was produced in a laminar flow reactor based on a non-premixed Hencken-type flat flame burner (FFB) design. Methane was injected through 199 tubes evenly distributed over the base plate into a carbon dioxide/oxygen mixture serving as oxidizer. A ceramic honeycomb was used to hold the fuel tubes in position and to distribute the oxidizer homogenously. The generated exhaust gas is guided in a reactor tube, which provides a laminar flow field.

Two operating points were set in the FFB, with 17 vol% and 34 vol% oxygen exhaust gas. The exhaust gas compositions are given in Table 2. The gas temperature was measured with radiation corrected Type S thermocouples and amounts to approx. 1300 °C in the concerned reactor region. The temperature profile along the reactor centerline is depicted in Fig. 2. Typical particle heating rates are in the order 10^4–10^5 K/s [8]. Single coal particles were injected through a central tube using carbon dioxide as carrier gas. The coal feed rate was kept low (~200 mg/h) to provide single isolated burning particles.

Table 1
Maceral and elemental analysis.

Maceral analysis	
Vitrinite [%]	76.6
Liptinite [%]	2.0
Inertinite [%]	16.6
Minerals [%]	4.8
Elementary analysis	
Ash content wf[a] [%]	10.64
Volatile matter waf[b] [%]	41.29
C waf[b] [%]	78.61
H waf[b] [%]	5.34
N waf[b] [%]	1.39

[a] wf = water free.
[b] waf = water and ash free.

Table 2
Reaction atmosphere composition.

	O_2 [vol%]	CO_2 [vol%]	H_2O [vol%]
Oxyfuel 17%O_2	16.9	61.7	21.4
Oxyfuel 34%O_2	33.5	45.6	20.9

The test rig is equipped with a water cooled particle sampling probe (PSP) [9]. The burning char particles are quenched upon entering the PSP by a cold nitrogen flow of 10 l/min N_2. In that manner the particles are rapidly cooled down below 400 °C and the char burnout is interrupted. Further the particle loaded quench gas flow is conducted through the inner tube of the PSP to a temperature-resistant filter (polyphenylene sulfide and polyimide, 140–160 °C), where the sample is separated from the gas. By varying the distance between particle outlet and the inlet of PSP different residence times can be achieved. In the present work, the char samples were collected at flight distances (105 and 150 mm) in the reactor, which are denoted in Fig. 2. The respective residence time of the particles in the reactor varies with the reaction atmosphere because of small differences in gas velocity and is given in Table 3. Further information on the flat flame burner operation and design can be found in [8]. The elemental composition and the BET surface area of the chars are presented in Table 3. The BET surface areas were obtained by applying the theory of Brunauer, Emmett and Teller to the N_2 adsorption and indicate the area of the outer surface and of the large pores.

2.3. TGA char

Alternatively, the generation of coal chars was carried out with a thermogravimetric analyser (TGA) *Dyntherm* by *Rubotherm* including a magnetic suspension balance. The pyrolysis inside this TGA was defined by a heating ramp of 10 K/min up to a temperature of 1100 °C.

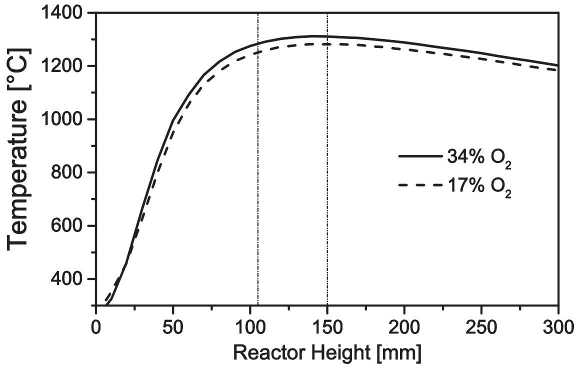

Fig. 2. Gas temperature vs. reactor height measured with 30 μm type S thermocouples.

Table 3
Elemental analysis and BET surface of FFB and TGA chars.

Sample	C [wt.%]	H [wt.%]	N [wt.%]	BET surface [m^2/g]
34%O_2 OXY 105 mm–88 ms	63.67	2.83	1.84	11.0
34%O_2 OXY 150 mm–114 ms	57.68	3.00	1.42	6.0
17%O_2 OXY 105 mm–96 ms	68.99	0.51	2.18	33.0
17%O_2 OXY 150 mm–124 ms	62.20	3.41	1.56	6.0
TGA-char	79.22	0.75	1.70	2.6