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## Gas Diffusion and Sorption in Carbon Conversion

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### Abstract

In common carbon conversion models, effective diffusion is considered to describe mass transport of reactive gases in porous char particles. Conventionally, effective diffusion is determined by taking porosity and tortuosity of the solid char into account, however, the tortuosity cannot be determined experimentally. Therefore, values for the tortuosity are mainly chosen to fit the respective model to experimental data. Here, we present the determination of effective diffusion by measuring the sorption kinetics utilizing a volumetric sorption analyzer to circumvent the problem of obtaining proper data for tortuosity. For this purpose, sorption kinetics were determined for carbon dioxide and methane at temperatures of (25 and 50) °C and pressures up to 115 kPa in a synthetic lignite-like solid fuel.

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### 1. Introduction

During combustion and gasification of solid fuels, gas diffusion in the porous structure of the fuel plays a decisive role. Before the gas-solid reaction takes place, molecules from the surrounding gas phase diffuse through a boundary layer into the pore structure. Subsequently, the molecules adsorb on the surface and react with the solid fuel. Since in oxyfuel atmospheres inert nitrogen is substituted by reactive carbon dioxide, the importance of competitive gas diffusion processes becomes even higher than for conventional combustion processes.

The diffusion behavior of the gas molecules can be described by effective diffusion coefficients  $D_{\text{eff}}$ , also known as effective diffusivities. These coefficients describe a combination of different diffusion processes. To consider the diffusion in carbon conversion modeling, the Thiele modulus  $\phi_i$  of all present gas species  $i$  is used. This modulus is

defined as the ratio between reaction rate and diffusion rate [1]:

$$\phi_i = r_p \cdot \left( \rho_p \cdot \nu_{C-i} \frac{n_i + 1}{2 \cdot D_{\text{eff},i}} \cdot \frac{r_{i,S}}{C_{i,S}} \right)^{0.5} \quad (1)$$

Aside from the diffusion coefficient  $D_{\text{eff},i}$  for gas component  $i$ , the radius of the fuel particle  $r_p$ , particle density  $\rho_p$ , stoichiometric factor of the reaction  $\nu_{C-i}$ , reaction order  $n_i$ , reaction rate  $r_{i,S}$  on the surface of the particle and molar concentration  $C_{i,S}$  of the gas component on the surface are required to calculate the Thiele modulus. In advanced conversion models, the effective diffusion coefficient is estimated by a combination of the Bosanquet equation with the parallel-pore model, taking Knudsen diffusion  $D_{\text{Kn}}$  and bulk diffusion  $D_B$  as well as porosity  $\theta$  and tortuosity  $\tau$  into account [2]:

$$D_{\text{eff},i} = \frac{\theta}{\tau} \left( \frac{1}{D_{\text{Kn},i}} + \frac{1}{D_{B,i}} \right)^{-1} \quad (2)$$

Knudsen and bulk diffusion coefficients can be expressed by Knudsen theory and kinetic gas theory [3,4]. To obtain the ratio between porosity and tortuosity, different approaches are suggested in literature [2,5]. However, there is no clear way to determine the tortuosity of char particles, thus, values are mainly chosen to fit the model to experimental data. To circumvent the difficulties of determining porosity and tortuosity, needed to apply eq. (2), effective diffusion coefficients can be determined directly from experimental adsorption data [6,7]. In the present work, we demonstrate the experimental determination of effective diffusion coefficients for  $\text{CO}_2$  and  $\text{CH}_4$  by volumetric sorption measurements on a synthetic hydrochar.

## 2. Materials and methods

### 2.1. HTC char

For this work, a hydrochar was synthesized by hydrothermal carbonization. Thereby, water and cellulose react at a temperature of 200 °C and a pressure of 1.6 MPa and form this lignite-like solid fuel. The synthesis procedure is described in more detail elsewhere [8]. The resulting hydrochar (HTC char) consists mainly of carbon, oxygen and hydrogen (see Table 1) and can be interpreted as a very fundamental designed solid fuel. Influences of catalytically effective minerals are therefore not present. After synthesis, the hydrochar was pyrolyzed at 800 °C in a horizontal tube furnace [9].

**Table 1.** Proximate and ultimate elemental analysis of the hydrochar (HTC) [8].

Sample	Volatiles [wt.%]	Fixed carbon [wt.%]	Ash [wt.%]	C [wt.%]	H [wt.%]	O [wt.%]
HTC	53	47	0.4	65.0	4.2	30.4

### 2.2. Volumetric sorption system

The volumetric sorption measurements were conducted with an *ASAP 2020* sorption analyzer of *Micromeritics*. In this device, the amount of adsorbed molecules is determined by measuring the pressure drop in a constant gas volume. A certain amount of gas is filled into a known reference volume, represented by the red line in Fig. 1. The pressure in this volume is recorded by four pressure transducers with different measurement ranges and uncertainties, as given in Fig. 1. When valve V12 is opened, the gas flows into the evacuated measuring cell, where the activated HTC char is located. Due to the expansion of the gas, the pressure is reduced, but the number of gas molecules in the system remains constant. During the adsorption of the gas, the gas molecules adsorb on the surface of the HTC char, and a further pressure drop is recorded. Therefore, the amount of adsorbed molecules and, consequently, sorption equilibria as well as diffusion coefficients can be calculated. Changes in pressure can be recorded every 0.4 s, which leads to a maximum resolution in the measured diffusion ratios  $D_{\text{eff}}/r_p^2$  of up to  $1 \text{ s}^{-1}$ . Above this ratio, diffusion velocities are too fast to be measured properly.

The sorption measurements were conducted with carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) at (25 and 50) °C. The equilibrium pressure was increased stepwise from approximately 1 kPa to 110 kPa, using a fixed gas dosing amount of 0.223 mol<sub>gas</sub>/g<sub>s</sub>. Since Xiao et al. [7] described a delay in pressure acquisition caused by the gas expansion, additional measurements with helium (He) were carried out at the same conditions as a benchmark to subtract this delay. CO<sub>2</sub>, CH<sub>4</sub> and He were used with a purity of 99.995 mol-% and were supplied by Coregas, Australia.

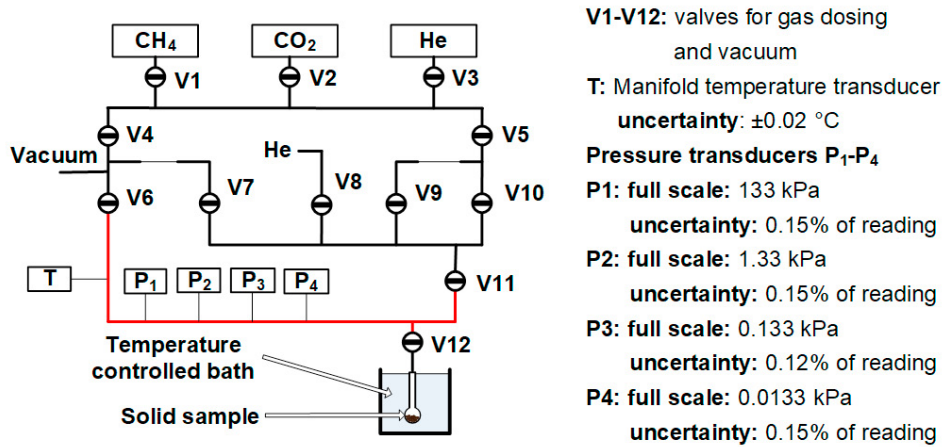


Fig. 1. Schematic of the volumetric sorption analyzer.

### 2.3. Determination of diffusion coefficients from volumetric sorption data

To calculate the diffusion coefficient from kinetic sorption data, the non-isothermal model by *Kocirik et al.* was used [10]. The heat released during the sorption process is not neglected as it is done in common isothermal models. The used model assumes constant-volume and variable-pressure conditions in the measuring cell. Since the measurements were conducted in a volumetric measuring system, both requirements are met. The model of *Kocirik et al.* is a more general form of the well-known constant-pressure model of *Lee and Ruthven* [11]. The analytical solution of the dynamic mass balance to obtain the quotient of the diffusion coefficient  $D_{\text{eff}}$  and the particle radius  $r_p$ , as described by Fick's second law, is given as the following series expression:

$$\frac{m_t}{m_{\text{equi}}} = 1 - \sum_{n=1}^{\infty} \frac{9(1 + \alpha^*) \left( \frac{Y_n}{-q_n^2} \right)^2 \exp\left(-q_n^2 \frac{D_{\text{eff}} t}{r_p^2}\right)}{\frac{1}{\beta_n^*} + \frac{3}{2} \frac{\beta}{\beta_n^*} \left[ q_n \cdot \cot(q_n) \frac{Y_n}{q_n^2} + 1 \right] + \frac{3}{2} \frac{\alpha^* \cdot B_n}{q_n^4 \cdot \beta_n^*}} \quad (3)$$

During the volumetric sorption measurements, the ratio between the actual mass  $m_t$  and the equilibrium mass  $m_{\text{equi}}$  is measured over time  $t$ . In order to obtain the remaining parameters for eq. (3), additional eqs. (4) have to be considered. The local concentration of the adsorbed phase on the surface  $q_n$  can be derived from the following transcendental equation:

$$(-q_n^2 + \alpha) + 3 \cdot \beta \cdot Y_n - \frac{3 \cdot \alpha^* \cdot Y_n}{q_n^2} (-q_n^2 + \alpha) = 0 \quad (4)$$

with:

$$Y_n = q_n \cot(q_n) - 1 \quad (5)$$

$$\alpha = \frac{h \cdot a \cdot r_p^2}{\rho_s \cdot c_s \cdot D_{\text{eff}}} \quad (6)$$

$$\beta = \frac{\Delta h}{\rho_s \cdot c_s} \left( \frac{\partial q^*}{\partial T} \right)_{c_{g(0)}, T_0} \quad (7)$$

Here,  $h$  is the overall heat transfer coefficient between the surrounding gas and the external surface  $a$  of the solid,  $\rho_s$  and  $c_s$  are density and heat capacity of the solid material,  $\Delta h$  is the heat of adsorption and  $q^*$  the concentration of the adsorbed phase in equilibrium at a concentration of the gas phase of  $c_{g(0)}$  and a temperature  $T_0$ . The parameter  $\alpha^*$  can also be derived from the experimental data and is described as the dimensionless ratio between the pressure drop due to adsorption within a single pressure step to the difference of the actual equilibrium pressure to the one in the pressure step before:

$$\alpha^* = \frac{p_{\text{equi}} - p_{\text{initial}}}{p_{\text{equi,before}} - p_{\text{equi}}} \quad (8)$$

To solve eq. (3), additional parameters have to be defined as follows:

$$\frac{1}{\beta_n^*} = \frac{1}{\beta} \left( 1 - \frac{3 \cdot \alpha^* \cdot Y_n}{q_n^2} \right) \quad (9)$$

$$B_n = Y_n [(q_n^2 - \alpha) q_n \cdot \cot(q_n) - 2\alpha] + q_n^2 (q_n^2 - \alpha) \quad (10)$$

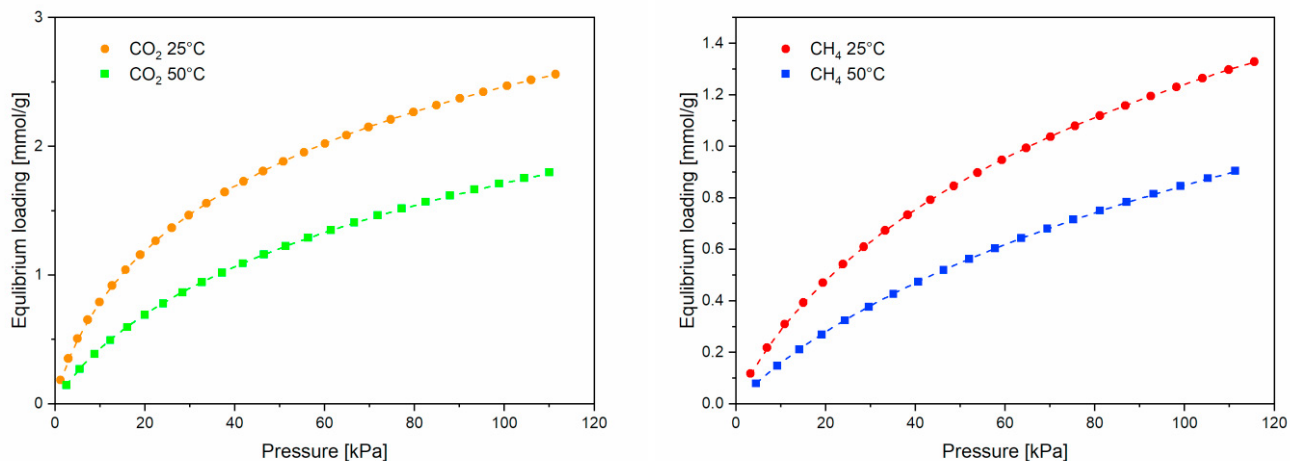
To obtain  $D_{\text{eff}}/r_p^2$  from eq. (3), the model was regressed to the experimental data by adjusting the parameter  $\alpha$  and  $\beta$ . As regression criteria, the root mean square deviation, defined as deviation between experimental data and model, has to be minimized:

$$RMSD = \sqrt{\frac{\sum_{i=1}^N \left[ \left( 1 - \frac{m_t}{m_{\text{equi}}} \right)_{\text{exp}} - \left( 1 - \frac{m_t}{m_{\text{equi}}} \right)_{\text{model}} \right]^2}{N}} \quad (11)$$

### 3. Results

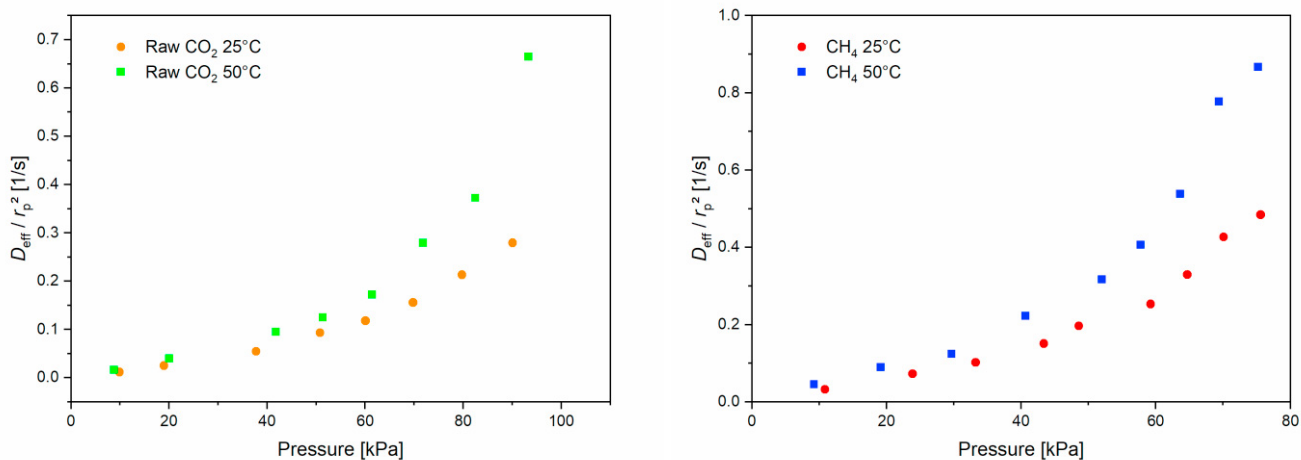
Sorption equilibria loadings of CO<sub>2</sub> and CH<sub>4</sub> at temperatures of (25 and 50) °C are shown in Fig. 2 up to pressures of approximately 115 kPa. For each gas species  $i$ , the equilibria loadings for the gas  $n_{\text{ads},i}$  were regressed using the temperature dependent Toth equation as given in eq. (12), taking the maximal equilibrium loading  $n_{\text{max},i}$ , the Toth adsorption constant  $k_{0,i}$ , the heat of adsorption  $\Delta h_i$ , the gas constant  $R$  and the heterogeneity exponent  $\mu_i$  into account. The fitted isotherms match the experimental data well; for both gases, the coefficient of determination is  $R^2 \geq 0.9999$ . Measured equilibria loadings decrease with increasing temperature. The maximum loadings observed for CO<sub>2</sub> and for CH<sub>4</sub> at a temperature of 25 °C decrease from (2.56 and 1.32) mmol/g to (1.80 and 0.91) mmol/g at a temperature of 50 °C. Heats of adsorption derived from the Toth equation are  $\Delta h_{\text{CO}_2} = 28.4889$  kJ/mol and  $\Delta h_{\text{CH}_4} = 23.0762$  kJ/mol, which means that more heat is released during CO<sub>2</sub> adsorption. For carbon conversion, this heat of adsorption contributes to the overall reaction enthalpy.

$$n_{\text{ads},i} = \frac{n_{\text{max},i} \cdot k_{0,i} \cdot p \cdot \exp\left(-\frac{\Delta h_i}{RT}\right)}{\left(1 + \left(k_{0,i} \cdot p \cdot \exp\left(-\frac{\Delta h_i}{RT}\right)\right)^{\mu_i}\right)^{1/\mu_i}} \quad (12)$$



**Fig. 2** Equilibria loadings of CO<sub>2</sub> (left) and CH<sub>4</sub> (right) in HTC char for all pressure steps at temperatures of (25 and 50) °C. Loadings were fitted to the Toth equation with the following parameters: CO<sub>2</sub>:  $n_{\max, \text{CO}_2} = 6.0550 \text{ mmol/g}$ ,  $k_{0, \text{CO}_2} = 0.338 \cdot 10^{-6} \text{ 1/kPa}$ ,  $\Delta h_{\text{CO}_2} = 28.4889 \text{ kJ/mol}$ ,  $\mu_{\text{CO}_2} = 0.4914$ ; CH<sub>4</sub>:  $n_{\max, \text{CH}_4} = 3.7055 \text{ mmol/g}$ ,  $k_{0, \text{CH}_4} = 1.067 \cdot 10^{-6} \text{ 1/kPa}$ ,  $\Delta h_{\text{CH}_4} = 23.0762 \text{ kJ/mol}$ ,  $\mu_{\text{CH}_4} = 0.5906$ .

Diffusion coefficients were derived from the sorption kinetics as  $D_{\text{eff}}/r_p^2$  by applying the model of *Kocirik et al.* [10]. In dependence of the constant particle radius, this ratio directly matches with eq. (1) to determine the Thiele modulus. In Fig. 3, these diffusion ratios are presented for different equilibria pressures of CO<sub>2</sub> and CH<sub>4</sub>. For CH<sub>4</sub>, diffusion coefficients can only be derived for pressures below 80 kPa. Above this pressure, diffusion velocity is already so fast that the pressure transducers cannot measure the pressure change properly. For both gases, the diffusion ratio increases with increasing temperature and pressure because of faster molecular motions. The determined diffusion coefficients for CH<sub>4</sub> in the hydrochar are slightly higher than for CO<sub>2</sub>. With further measurements at higher temperatures, the temperature dependence of the diffusion behavior can be predicted [12].



**Fig. 3** Effective diffusion coefficients over particle radius of CO<sub>2</sub> (left) and CH<sub>4</sub> (right) in HTC char plotted versus experimental pressure at temperatures of (25 and 50) °C.

#### 4. Outlook

In this work, a method to determine effective diffusion coefficients for the integration in carbon conversion models has been shown. Values for tortuosity and porosity, which are usually needed for the determination of effective diffusion coefficients are not required for application of this method. To obtain more detailed information on the diffusion behavior, further investigations on the gas diffusion behavior in fundamental designed hydrochars is required. Besides measurements at higher temperatures, the diffusion of other gases like oxygen, water vapor and hydrogen are of utmost importance to understand the comprehensive diffusion process during oxyfuel combustion. The hydrochar we investigated in the present work was almost free from minerals like iron, calcium, sodium or silica, whereas small amounts are normally present in natural solid fuels. Diffusion experiments with different mineral-doped hydrochars to investigate the influence of the doped minerals are part of our ongoing research.

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