

STUDY ON MASS TRANSFER PROPERTY OF OXYGEN MOLECULES AND KINETIC REGIMES OF PRESSURED PULVERIZED COAL COMBUSTION

by

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The effects of pressure on diffusion of oxygen molecules during the coal combustion could not be ignored. The compressibility factor of real oxygen is investigated to evaluate the deviation between real and ideal oxygen, and obtain the mean free path of real oxygen. Comparing the Knudsen pore diameter with the minimum pore diameter, it is found that with the increase of pressure, Knudsen diffusion cannot exist at low pressure and may delay to occur at higher temperature. When pressure exceeds 3.5 MPa, no Knudsen diffusion occurs within the whole temperature range of our research. Comparing the diffusion rate at 1 MPa with the burning rate, one can conclude that the combustion mainly take place on the internal and external surfaces, and the reaction is controlled by the chemical kinetics below 1400 K. When temperature is between 1400 K and 1600 K, the reaction is controlled by both the diffusion and the chemical kinetics. When the temperature is more than 1600 K, the combustion primarily happens on the external surfaces and is controlled by the diffusion.

Key words: *Knudsen diffusion, molecular diffusion, mean free path, pressured coal combustion, kinetic regimes*

Introduction

Nowadays, coal has played and continues to play a significant role in meeting the global demand for energy services and needs to be used more efficient and environmentally friendly than ever before. Advanced clean coal technologies, such as pressurized combustion [1] and oxygen-enriched combustion [2, 3], have attracted increasing interests in recent years. Coal is a complex polymeric material which has a highly heterogeneous and complicated pore structure. Pores in coal according to the diameters may be divided into: micro-pores (<2 nm), transitional pores (2-50 nm), and macro-pores (>10 nm) [4]. Pore volume distribution is dependent upon the rank of coal. For different rank coals, pores with diameter of less than 10 nm account for the main portion of the internal coal surface and the available sites for combustion. Many studies [5, 6] have also shown that the pore structure has a significant effect upon the coal combustion. It is now established that pulverized coal (P. C.) combustion is controlled both by oxygen diffusion and chemical kinetics [7]. While extensive experiments and modeling of atmospheric coal combustion have been reported [1], the cases of high pressure are poorly exam-

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ined and lack of systematic study. In high pressure atmosphere, the mean free path of oxygen molecule becomes smaller, meaning that more surfaces of micro-pores can be accessed. Thus the effects of pressure on diffusion of oxygen molecules cannot be ignored.

Diffusion and kinetic regimes

Since the gas molecules may collision with pores walls, Fick's law is inadequate to describe the diffusion in porous media. Within the pores, three different types of diffusion mechanisms have been identified: (1) molecular diffusion, (2) Knudsen diffusion, and (3) transition diffusion. Diffusion occurs via molecular or Knudsen processes, controlled by molecule-molecule or molecule-wall collisions which depending on the mean free path or the relevant pore dimensions. Considering the pressure dependence of mean free path, second virial coefficient over Lennard-Jones (12-6) potential is applied to estimate the deviation between real and ideal gas, and calculate the mean free path of oxygen molecule at elevated pressure. The second virial coefficient $B_2(T)$ is given by [8]:

$$B_2(T) = N_A \cdot 10^{-24} \frac{2\pi\sigma^3}{3} \frac{8\varepsilon}{\sqrt{2}k_B T} \lim_{N \rightarrow \infty} \sum_{k=0}^N \frac{\frac{2\varepsilon}{k_B T}}{k!} \frac{1}{4} \frac{\varepsilon}{k_B T} \Gamma\left(\frac{3}{4} \frac{k}{2}\right) \Gamma\left(\frac{1}{4} \frac{k}{2}\right) \frac{1}{4} \frac{k}{2} \quad (1)$$

where N_A is the Avogadro constant, ε – the depth of the potential wall, k_B – the Boltzmann constant, and σ – the finite distance at which the inter-particle potential is zero. For oxygen molecules, $\varepsilon/k_B = 118$ K, and $\sigma = 3.58 \cdot 10^{-10}$ m. The quantities $\Gamma(\alpha)$ is well known gamma function defined by $\Gamma(\alpha) = \int_0^\infty t^{\alpha-1} e^{-t} dt$.

The compressibility factor, Z , which represents the deviation between real and ideal behavior, is usually obtained by solving equations of state, such as the virial equation. The formula is:

$$Z(P, T) = \frac{Pv}{RT} = 1 + \frac{B_2 P}{RT} \quad (2)$$

where R is the universal gas constant, v – the mole fraction; P [Pa] – the pressure, T [K] – the absolute temperature, and B_2 – the second virial coefficient.

Jennings [9] accurately calculated the real gas mean path of air. This equation can be used to obtain the mean free path of oxygen molecules:

$$\lambda = \frac{\pi}{2} \frac{\mu}{uP} \sqrt{\frac{ZRT}{2\pi M}} = \frac{1}{1.016} \frac{16}{5} \frac{\mu}{P} \sqrt{\frac{ZRT}{2\pi M}} \quad (3)$$

where μ [Pa·s] is the dynamic viscosity, $u = 1.016034 \times (5\pi/32)$ is a numerical factor of order unity proposed by Chapman and Cowling [10]. At high pressure, such as under subcritical or supercritical conditions [11], the formula of viscosity usually contains the residual viscosity term caused by pressure. Considering the residual viscosity, on the basis of Lemmon and Jacobsen [12] summary, values of oxygen molecular dynamic viscosity in different temperature and pressure can be accurately calculated.

In general, molecular diffusion prevails when the pore diameter is ten times greater than the mean free path; Knudsen diffusion may be applicative when the mean free path is ten times greater than the pore diameter [13]. The diffusion coefficient of Knudsen diffusion is:

$$D_{kO_2} = C_k \sqrt{T} d_s \quad (4)$$

where $C_k = 8.57$, d [m] is the pore diameter, and the subscript, s, means the small pores fitting to Knudsen diffusion. Assuming that the concentration of oxygen is zero at the bottom of pores, the flux of oxygen molecules throughout the cross-section of micro-pores by Knudsen diffusion is:

$$J_{O_2,s} = D_{kO_2} \frac{dc_{O_2}}{dz} = \frac{D_{kO_2} P J_{O_2,\infty}}{RTZ\delta_s} = \frac{0.2164537 P d_s}{Z\delta_s \sqrt{T}} \quad (5)$$

where δ [m] is the depth of the hole, $x = 0.21$.

The diffusion coefficient of molecule diffusion is:

$$D_{O_2} = D_0 \left(\frac{T}{T_0} \right)^{1.75} \quad (6)$$

where D_0 is the diffusion coefficient under the standard condition. The flux of oxygen by molecule diffusion is determined by the formula:

$$J_{O_2,l} = \frac{D_{O_2} P \ln(1 - x_{O_2,\infty})}{RTZ\delta_l} = \frac{C_l P T^{0.75}}{Z\delta_l} \quad (7)$$

where $C_l = 1.974 \cdot 10^{-11}$ and the subscripts, l, means the large pores fitting to molecule diffusion.

The flux for the transition diffusion of oxygen molecules is given by the formula:

$$J_{O_2,m} = \frac{D_{O_2} P}{RTZ\delta_m} \ln \frac{1 + \frac{D_{O_2}}{D_{kO_2}}}{1.21 + \frac{D_{O_2}}{D_{kO_2}}} \quad (8)$$

where $D_{kO_2} = 10^{-10} T^{1.25} / d_s$, the subscripts, m, means the middle pores fitting to transition diffusion. Using Taylor series to expand the logarithmic term and ignoring the higher-order terms, eq. (8) is changed to:

$$J_{O_2,m} = \frac{0.2164537 P d_s}{Z\delta_m \sqrt{T}} \quad (9)$$

The controlling mechanism is an important factor when high pressurized coal combustion is investigated. As a general rule of thumb, the rate-control theory is based on comparing the reaction gas diffusion rate with the chemical reaction rate. For coal combustion, three temperature zones, which were, respectively, mainly controlled by chemical kinetics, kinetics-diffusion, and pore diffusion, were identified and categorized on the basis of rate-governing process [14]. Actually the coal combustion rate is typically influenced by all three processes, especially under high pressure. Thermal analysis is widely used to understand the thermal behaviors of solid materials [1-3, 7, 14-16]. Based on simple collision theory (SCT) and the thermogravimetric results of some coal samples, a reaction kinetics model has been proposed and the reaction rate on the surface of P. C. particles and can be given [16]:

$$\frac{d\alpha}{dt} = \frac{k f_s (1 - \alpha) x_{O_2} P}{\sqrt{T} \exp \left(-\frac{E_c}{RT} \right)} \quad (10)$$

where k is the pre-exponential factor and E_c [kJmol⁻¹] – the critical activation energy.

Results and discussions

The values of compressibility factor, Z , of oxygen at different temperatures (600-2000 K) and pressures (0.1-10 MPa) are calculated to evaluate the deviation between real and ideal behavior, fig. 1. Under atmospheric pressure, the compressibility factor is independent of temperature, and very close to 1, which means that the gas can be considered as ideal gas. The effect of pressure is more significant at lower temperatures and cannot be ignored under high pressure.

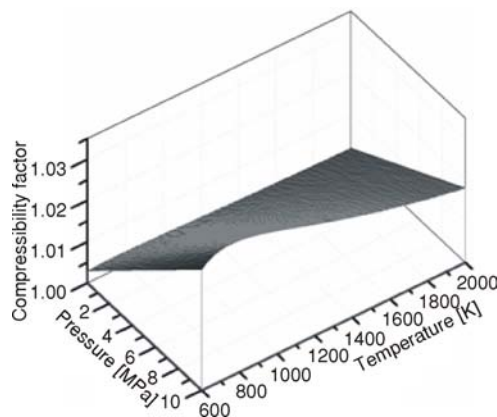


Figure 1. Compressibility factor Z of oxygen (600-2000 K, 0.1-10 MPa)

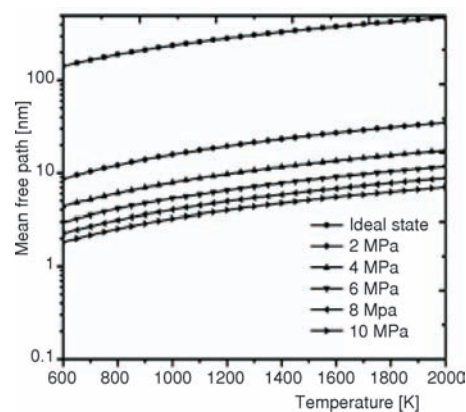


Figure 2. Real gas mean path of oxygen (600-2000 K, 0.1-10 MPa)

Considering the real gas effect, the real gas mean path of oxygen is obtained by eq. (3). As shown in fig. 2, at the same temperature, the mean path of oxygen in pressured atmosphere is 1-2 order smaller than the standard atmosphere. Thus pressure term was taken into account in this study, and it also can be seen that the free mean path enlarges with the increasing temperature, while declines with the decreasing pressure. With the increasing pressure, Knudsen diffusion cannot exist at low pressure and delay to occur at higher temperature. The smallest pore in this research is 2 nm. Let the critical pore diameter for Knudsen diffusion equal 2 nm and the value of temperature equal 2000 K, pressure with a value of 3.5 MPa can be obtained. It means that when pressure exceeds 3.5 MPa, the diameter of the smallest pore is bigger than the Knudsen pore diameter; hence no Knudsen diffusion occurs within the whole temperature range.

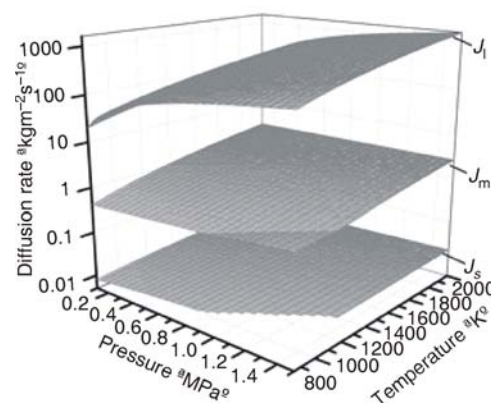


Figure 3. Diffusion rate of oxygen (650-2000 K, 0.1-1.5 MPa)

Rates of three diffusions are shown in fig. 3. It clearly shows that as the pressure increases, Knudsen diffusion disappears at low temperature. The oxygen diffusion rate under 1.5 MPa is compared with the burning rate calculated from the SCT model as shown in fig. 4. It can be concluded that when temperature is below 1400 K, the rate of diffusion in micro-pore is much more

than the burning rate. The combustion takes place mainly on the internal and external surfaces. Thus the reaction is controlled by the chemical kinetics, which is so called the chemical kinetics regime. When temperature is between 1400 K and 1600 K, the diffusion rate is close to the burning rate. Hence, the reaction is controlled both by the diffusion and the chemical kinetics. This is the chemical-diffusion regime. When temperature is more than 1600 K, the rate of diffusion occurring at macro-pores and transitional pores is close to the burning rate, meaning that the combustion mainly happens on the external surfaces and controlled by the diffusion. Thus it is called the diffusion controlled regime.

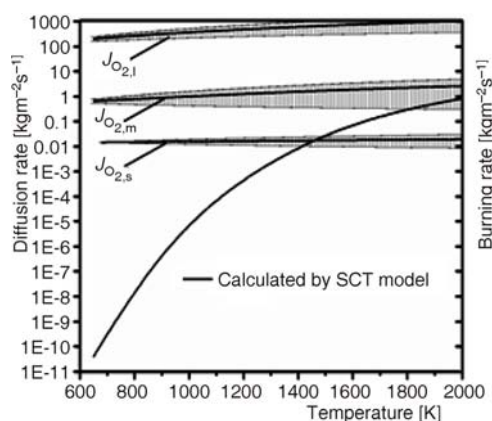


Figure 4. Comparison of the pressured oxygen diffusion rate (1.5 MPa) with the burning rate

Conclusions

The present study demonstrates the following conclusions: (a) Changes of compressibility factor with the pressure indicate that oxygen cannot be considered as ideal gas under the pressured atmosphere, especially at low temperature and high pressure; (b) The mean path of oxygen in pressured atmosphere is 1-2 order smaller than the standard atmosphere. Moreover, it increases with the temperature and decreases with the pressure conversely. When pressure is elevated upon 3.5 MPa, the diameter of the smallest pore considered in this article is bigger than the Knudsen pore diameter. Hence no Knudsen diffusion occurs over the whole temperature range; (c) When temperature is below 1400 K, the combustion takes place mainly on the internal and external surfaces. Thus the reaction is controlled by the chemical kinetics, which is so called the chemical kinetics regime. When temperature is between 1400 K and 1600 K, the reaction is controlled both by the diffusion and the chemical kinetics. This is the chemical-diffusion regime. When temperature is more than 1600 K, the combustion mainly happens on the external surfaces and controlled by the diffusion. Thus it is called the diffusion controlled regime.

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