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Research Paper

Study on the anisotropy of mass transfer for oxygen in the ash layer of extremely low calorific oil shale semi-coke

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HIGHLIGHTS

- The anisotropy of mass transfer for oxygen in the ash layer of oil shale semi-coke is confirmed.
- The oxygen diffusion rate along the direction perpendicular to the bedding plane is slower than that parallel to the bedding plane.
- The ash layer diffusivities along the direction perpendicular and parallel to the bedding planes are respectively 0.25×10^{-6} m^2/s and 2.36×10^{-6} m^2/s.
- The ash layer diffusion resistance is the major control factor during the combustion of oil shale semi-coke.

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ABSTRACT

Oil shale semi-coke produced from the oil shale retorting process causes great hazards to the environment due to its high phenol and polycyclic aromatic hydrocarbons content. A good solution of the current of semi-coke is to burn it as feedstock. In the present work, the anisotropy of mass transfer for oxygen in the ash layer of extremely low calorific oil shale semi-coke that is featured in laminated structure was investigated by using the one-dimensional unreacted model of unchanging size. Results indicated that the severe anisotropy of mass transfer for oxygen in the ash layer of semi-coke was confirmed, and the oxygen diffusion rate along the direction perpendicular to the bedding plane was much slower than that parallel to the bedding plane. This difference was attributed to different porous characters in the ash layer of semi-coke along different directions. When the burning temperature was 900 °C, the average ash layer diffusivities were 0.25×10^{-6} m^2/s and 2.36×10^{-6} m^2/s, respectively, along the direction perpendicular and parallel to the bedding planes. Furthermore, an unreacted shrinking sphere model of unchanging size was established to describe the combustion of extremely low calorific oil shale semi-coke, and it could be concluded that the ash layer diffusion resistance was the major control factor during the combustion of oil shale semi-coke, and the relative resistance of ash layer diffusion monotonously increased.

1. Introduction

In China, abundant oil shale (OS) resources are mainly used by retorting for the production of shale oil to alleviate the shortage of petroleum [1–3]. Currently, its prevailing method is still using Fushun-type retorts [4], thus resulting in that around 10–30 tons of oil shale semi-coke (SC) per ton of shale oil is left after production [5]. Owing to the absence of available techniques, landfill is always adopted to dispose of SC. However, this method occupies a lot of land, but also causes great hazards to the environment [6–9].

The recommended processing approach to deal with low calorific SC in an environmental-friendly way is co-combustion with some high calorific fuels at a certain rate in the circulating fluidized bed combustor [10–13]. The heat value of blended fuels is usually required to be at least 5000 kJ/kg, and the treatment cost is relatively high. Consequently, a harmless treatment scheme that SC is directly burnt in the fluidized bed combustor is proposed, and the key to carry out this scheme is accurately confirming combustion behaviors of SC, including its oxygen diffusion characteristics.

Until now, there are many systematic experimental researches and theoretical analyses about the oxygen diffusion resistance during the combustion of low calorific fuels at home and abroad. Charlton [14] investigated combustion kinetics of SC from seven major Australian deposits using a fluidized bed batch technique, and a generalized form of the grain model was employed to

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Nomenclature

OS	oil shale
SC	oil shale semi-coke
C_1	oxygen concentration in the ambient medium, mol/m^3
C_2	oxygen concentration at the external surface of the ash layer, mol/m^3
C_3	oxygen concentration at the interface between the ash layer and the unreacted char, mol/m^3
$J^1_{O_2}$	mass-transfer rate of oxygen transferred from ambient medium to the external surface of the ash layer, mol/s
$J^2_{O_2}$	inward net diffusion rate of oxygen through the ash layer, mol/s
$J^3_{O_2}$	consumption rate of oxygen at the reaction interface, mol/s
k_1	external convective mass-transfer coefficient, m/s
D_e	ash layer diffusivity, m^2/s
k_3	rate constant of the carbon-oxygen reaction, m/s
Do_2	molecular diffusivity of oxygen, m^2/s
M_c	molar mass of carbon, kg/mol
r_0	radius of the spherical oil shale semi-coke particle, m
r	radius of the reaction interface, m
ρ_c	carbon density, kg/m^3
X	combustion conversion rate
t	burning time, s
L	feature size of oil shale semi-coke particle, m
Sc	Schmidt number
Re	Reynolds number
A	pre-exponential factor
E	activation energy
R	gas law constant
T	reaction temperature, k
δ	ash layer thickness at a certain moment, m
δ_f	total ash layer thickness, m
Δm	mass loss at a certain moment, kg
Δm_f	total mass loss, kg
β	heating rate, k/min
α	conversion rate
$De_{average}$	weighted average ash layer diffusivity, m^2/s
De_1	ash layer diffusivity along the direction perpendicular to the bedding plane, m^2/s
De_2	ash layer diffusivity along the direction parallel to the bedding plane, m^2/s
A_1	external surface area parallel to the bedding plane, m^2
A_2	external surface area vertical to the bedding plane, m^2

determine chemical and diffusion kinetics. Results showed that chemical rate constants and ash layer diffusivity varied widely as a result of different mineral and chemical compositions among the shales. Sadhukhan [15] studied the combustion characteristics of a single-particle high ash coal char at elevated pressure through a fully transient shrinking reactive core model, incorporating a simple mechanistic kinetic scheme. The char combustion model predicted the mass loss profiles and burnout time of the char particle at different oxygen concentrations and temperatures, and the computed results were found to agree well with the published experimental findings of pressurized combustion of high ash coal char. Charlton [16] investigated combustion characteristics of Nagoorin carbonaceous spent shale using a fluidized bed batch technique, and according to the experimental results, an empirical equation was derived to calculate the burnout time for a given particle size between 600 °C and 700 °C. On the other hand, after retorting and burning, SC and its ash layer still maintain the laminated structure of OS, which destines the anisotropy of mass transfer for oxygen along different directions in the ash layer of SC. However, thus far, there has been little work in the literature regarding the anisotropy of extremely low calorific SC, as well as the quantitative analysis of its oxidation resistance during the combustion process, which is considered to be useful to clarify its combustion mechanism in depth.

Consequently, in this work, the anisotropy of mass transfer for oxygen in the ash layer of SC was firstly investigated by burning the cuboid SC particles with different open surfaces at 900 °C, and then, an unreacted shrinking sphere model of unchanging size was established to describe the combustion of SC and predict its burning time. What's more, the relative oxidation resistance during its combustion process was also compared.

2. Theoretical section

As is known to all, during the combustion of fuel particle, it roughly undergoes the following four successive variation or partial overlap stages [17]: (1) moisture evaporation. (2) Devolatilization and combustion of volatile matter. (3) Char combustion. (4) Carbonate decomposition. Generally speaking, the consumption time of char combustion occupies most of the total combustion time. Therefore, char combustion was mainly studied in this paper, and according to the conventional viewpoint [18], the mass transfer for oxygen during the combustion of char particles with high ash content includes the following procedures: (1) the mass transfer for oxygen from ambient medium to the external surface of the ash layer. (2) The diffusion of oxygen toward the reaction interface through the ash layer. (3) The reaction between oxygen and carbon at the reaction interface. Also, some assumptions were implicit in this work: (1) SC particle was an ideal spherical shape, and its particle size remained unchanged during the combustion. (2) Ash and carbon were uniformly distributed in the SC particle. (3) The combustion reaction at the reaction interface was first-order, and only the reaction $C + O_2 \rightarrow CO_2$ took place [19]. (4) The ash layer diffusivity was considered to be irrelevant to the ash layer thickness, and it was constant. (5) The system was at a quasi-steady state.

C_1, C_2 and C_3 represented the oxygen concentration in the ambient medium, at the external surface of the ash layer, and at the interface between the ash layer and the unreacted char, respectively. Then, the mass-transfer rate of oxygen transferred from ambient medium to the external surface of the ash layer could be described as

$$J^1_{O_2} = k_1 \times (C_1 - C_2) \times 4\pi r_0^2 \tag{1}$$

where $J^1_{O_2}$ is the molar rate of oxygen from ambient medium to the external surface of the ash layer. k_1 is the convective mass-transfer coefficient, and r_0 is the radius of SC particle.

According to Fick's first law, the inward net diffusion rate of oxygen through the ash layer was

$$J^2_{O_2} = 4\pi \times D_e \times \frac{C_2 - C_3}{\frac{1}{r} - \frac{1}{r_0}} \tag{2}$$

where $J^2_{O_2}$ is the molar rate of oxygen through the ash layer. D_e is the ash layer diffusivity, and r is the radius of reaction interface.

The consumption rate of oxygen at the reaction interface could be expressed as