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Insight into effects of pore diffusion on smoldering kinetics of coal using a 4-step chemical reaction model

Zeyang Song*, Haoran Fan, Jiajia Jiang, Changxin Li

College of Safety Science and Engineering, Nanjing Tech University, Nanjing 211816, PR China

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ABSTRACT

Pore diffusion plays a crucial role in coal smoldering fires, however, its effects have been inadequately investigated. This paper aims to study influences of pore diffusion of oxygen (O_2) on chemical reaction and apparent reaction rate of coal smoldering. Non-isothermal thermogravimetric (TG) tests for two bituminous coal samples at three heating rates (2, 5 and 10 K/min) were conducted, and a 4-step decomposition scheme was constructed. The decomposition schemes contained two competing paths: Coal oxidation → β-Char oxidation → Ash (Path One), and Pyrolysis → α-Char oxidation → Ash (Path Two). A number of kinetic triplets (reaction order, pre-exponential factor and activation energy) and stoichiometric coefficients of the developed decomposition schemes were optimized by a Genetic Algorithm (GA) tool. Emphasis was put on influences of pore diffusion on chemical reactions (e.g. pyrolysis, coal matrix's and chars' oxidation) and on competing paths. Research results show that Knudsen diffusion plays a dominant role in pore diffusion that retards coal oxidation and its successive char oxidation on the Path One, but basically enhances char oxidation on the Path Two. Pore diffusion may exert ignorable influence on pyrolysis as it takes place without O_2. The investigation is beneficial for understanding mechanism of smoldering of coal piles and coal dust layers.

1. Introduction

Smoldering fire is a flameless, low-temperature and slow heterogeneous reaction (Rein 2009, 2013, 2016). Smoldering combustion is an oxygen-limited process via both concentration and transport. It is well-known that smoldering combustion depends on oxygen concentration ($[O_2]$), but critical values of flammability have been still debated. Belcher et al. (2010) reported that smoldering fires would be greatly suppressed below 18.5% O_2, completely switched off below 16% O_2, and rapidly accelerated between 19 and 22% O_2. Hadden et al. (2013) concluded that the oxidation reaction of smoldering has been enhanced with increasing $[O_2]$, resulting in a thinner smoldering front. Oxygen diffusive transport also plays a crucial role in smoldering fires because it drives O_2 from the ambient into external and pore surface areas of solid matrix where chemical reaction takes place. The diffusive transport processes could affect reaction kinetics, burning rate and pollutant release. However, to the best knowledge of the authors, effect of O_2 transport on smoldering fires has been rarely studied.

Coal smoldering, often taking place in coal stockpiles (Song et al., 2014; Zhu et al., 2013) and coal dust layers (Krause and Schmidt, 2001; Krause et al., 2006; Wu et al., 2017), is a significant hazard in industries. It initializes as self-ignition underneath surface (Wu et al., 2017) and propagates into deep inside piles/layers. Compared to flame fires, it is easier to start and harder to be found and extinguished (Hadden and Rein, 2011). Spontaneous combustion of coal has been investigated extensively (Akgun and Essenhigh, 2001; Altun et al., 2003; Schmidt et al., 2003; Wang et al., 2003). However, coal smoldering after self-ignition has been paid less attention and its mechanism has not acknowledged yet. This paper attempts to investigate effects of pore diffusion on coal smoldering kinetics using thermogravimetric (TG) experiments. So far, it is still a big challenge to detect solid-pseudo species produced by heterogeneous reaction. Instead, we will employ an inverse model that has been widely used in the field of smoldering fire (Huang and Rein, 2014; Lautenberger et al., 2006; Rein et al., 2006) to simulate chemical reaction rate and solid-pseudo species formation. The investigation will be helpful for understanding mechanism of smoldering of coal stockpiles or dust layers.

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* Corresponding author.
E-mail address: zeyang.song@njtech.edu.cn (Z. Song).

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Nomenclature

A	pre-exponential factor
E	activation energy
m	mass
m'	mass loss rate
M	mass fraction based on proximate analysis
n	reaction order
r	reaction rate
R	universal gas constant
T	temperature
Y	oxygen mass fraction

Greeks symbols

γ	weight coefficient of the objective function
ν	stoichiometric coefficient
Φ	objective function

Subscripts

0	initial
a	ash
g	gas
i	solid pseudo species number
ig	ignition
k	reaction number
max	maximum
min	minimum
o	coal oxidation
p	pyrolysis
sim	simulation
t	time
α	α-char
αo	α-char oxidation
β	β-char
βo	β-char oxidation
∞	final
$\sum$	cumulative mass

2. Experimental

2.1. Coal samples

Two bituminous coal samples were collected from Changcun and Xin'an Coal Mines in Henan Province, China. Fresh coal samples were maintained in well-sealed stainless-steel cylindrical containers to prevent weathering. Coal samples were pulverized into five diameters (<74, 86.5, 111, 160.5, and 550 μm). Proximate and ultimate analyses of both bituminous coal samples are presented in Table 1. Also, the surface areas and average pore sizes shown in Fig. 1(a) were measured by the Autosorb-1 analyzer (Quantachrome Instruments) (Song et al., 2017), which proves that pore surface area of CC coal sample is smaller than that of XA coal sample. It is clear that total area of pore surface steeply increases with pore diameter when the pore diameter is smaller than ~12 nanometer (nm) and the total pore surface area reaches a plateau when the pore diameter approaches 30 nm. Interestingly, for both CC and XA coal particles, most of pores are very tiny (<32 nm) and large pores merely concentrate on a diameter of ~200 nm, as shown in Fig. 1(a). Surface areas of tiny pores (<32 nm) account for ~90% of total pore surface areas. It indicates that the Knudsen diffusion plays a dominant role in pore diffusion, which agrees with previous theoretical models (Huo et al., 2014; Wang et al., 1999).

TENSOR27 FTIR (Fourier Transform Infrared Spectroscopy) spectrometer (Bruker Optics, German) was used to examine the functional groups and the reactivity of raw coal samples. FTIR spectra of two raw coal samples are presented in Fig. 1(b) (Song et al., 2017). The absorbance of CC coal sample is much higher than that of XA coal sample within the range between 1700 cm^{-1} and 1000 cm^{-1}, which suggests that CC coal sample contains higher concentrations of function groups of C=O, anhydride, aromatic C=C, C-O, carboxylic acids, etc. and is easier to react with O_2.

2.2. TG-FTIR experiments

Coal particles (~0.5 mg) were homogeneously put on a round aluminum-oxide plate as a monolayer bed to exclude interparticle and external diffusions (Ollero et al., 2002; Song et al., 2017). Five particle sizes (Test (I_1)-Test (I_5): <74, 86.5, 111, 162.5 and 550 μm) were considered. Only pore diffusion was involved in these tests. Each scenario was carried out at least twice to guarantee the repeatability. Mass-loss-rate data difference between two TG tests <3% was acceptable in this paper. Mass difference between repeated tests was less than ±0.1 mg.

STA449-F3 apparatus (NETZSCH, accuracy of 10^{-7} g) was used for non-isothermal TG tests for both pre-dried coal samples as follows:

With nitrogen as the purging gas (100 ml/min), coal sample was first heated from 30 °C to 105 °C at the rate of 10 K/min, then kept isothermal for a half hour to further eliminate the water, and was cooled back to 30 °C at the rate of −10 K/min. Subsequently, nitrogen (N_2) (80 ml/min) and O_2 (20 ml/min) were simultaneously purged into the furnace, and the sample temperature was elevated

Table 1
Properties of studied coal samples.

Basic properties		Changcun (CC)	Xin'an (XA)
Proximate analysis (%)	Moisture	2.860	1.740
	Volatile	34.750	12.330
	Ash	14.840	14.120
	Fixed carbon	47.550	71.810
Ultimate analysis (%, Dry ash-free basis)	Carbon	71.104	88.077
	Hydrogen	5.438	4.752
	Oxygen	21.880	3.990
	Nitrogen	1.313	1.680
	Sulfur	0.265	1.501
Pore surface area (m^2/g)		0.289	1.118
Average pore size (nm)		1.780	1.727

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