Kinetic study of steam gasification of two mineralogically different lignite chars: An active site/intermediate model

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HIGHLIGHTS

- A novel kinetic model is proposed to describe the kinetics of lignite char gasification.
- The model is based on the active site/intermediate mechanism of char gasification.
- The model fits the kinetic profiles of the Ca-catalyzed and uncatalyzed char gasification.
- The model predicts the changes of the intermediate during the char gasification.

ABSTRACT

A new active site/intermediate model (ASIM) is formulated in terms of a simplified calcium-catalyzed mechanism of char gasification to characterize a conversion-dependent maximum in reaction rate. In a limited case, the model is retrogressed to a common volumetric model (VM). Two sets of kinetic data were experimentally gathered by steam gasification of two lignite chars in a fixed bed reactor with negligible mass diffusion limitation. The gasification behaviors of two chars were, respectively, representative of catalyzed and uncatalyzed gasification as a result of the influences of different mineral components in them. It was found that ASIM intimately fit the kinetic profiles over the entire range of conversion for both catalyzed and uncatalyzed char gasification, demonstrating the good adaptability to varying chars. The model could determine the activation energies for the formation of the total carbon-containing gases and of two individual gases (CO and CO_2) from the oxygenated intermediate. Moreover, for the case of catalyzed gasification, ASIM reasonably predicted the formation, growth and decline of the intermediate with carbon conversion as well as the change in the intermediate concentration with gasification temperature. For the case of uncatalyzed gasification, the model portrayed essentially a linear decline in the intermediate concentration with increasing carbon conversion, similar to VM.

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1. Introduction

Coal gasification is a very old but still ongoing technology. In recent years, coal gasification has been rapidly growing in the world scale of industrial production, as it comparatively provides a clean, efficient, and secure way to use coal for generating a wide range of products, fuel gas, synthetic natural gas or syngas, electricity, hydrogen, and so on. Syngas is available to make into transportation fuels (methanol, gasoline, diesel, etc.) and a diversity of downstream chemicals as a substitute for petrochemicals. Under this circumstance, research interest is resurging more than in the recession period from a climax of the last 70–80 s with respect to

coal gasification, but it seems like the current trend is towards making use of more inferior coal resources such as lignite [1–3] and other untraditional gasification feedstocks [4–6].

The kinetics of char gasification has been ever the subject of a large number of previous studies [7–10], for it is of crucial importance in determining the rate and whole process of coal gasification. It remains a prevalent subject in recent researches [11–13]. The part of reason for this situation is that the char gasification kinetics is complicated by a multitude of influencing factors, particularly by the properties of char such as granularity, porosity, compositions and dispersion of minerals in char, and carbon structures [14]. The complexity also arises from the fact that the properties of char vary kaleidoscopically with the properties of coals such as coal rank, coal mineralogy and coal petrography as well as char formation processes [15,16], and that the properties of char

Nomenclature

$\overline{L}_j$	an average of the relative likelihoods for model j	P_{H_2O}	partial pressure of steam, Pa
m	the number of estimated parameters	t	gasification reaction time, min
n	the number of observations	x	total carbon conversion
k_i	the rate constant of reaction i, min^{-1}		
N_a	the mole numbers of C*–C–CaO (a) per mole of carbon in the char		*Greek letters*
N_c	the mole numbers of CaO (c) per mole of carbon in the char	α	characteristic parameter
		η	the ratio of the mole numbers of C(O)–C–CaO deactivated to C(O)–C–CaO returned to active site
N_o	the mole numbers of C(O)–C–CaO (o) per mole of carbon in the char	θ_a	the dimensionless concentration of C*–C–CaO
N_t	total mole number of calcium per mole of carbon in an original char	θ_o	the dimensionless concentration of C(O)–C–CaO
		θ_c	the dimensionless concentration of CaO
p	a dimensionless kinetic parameter in Eq. (5); the number of temperature points in Eq. (35)	ψ	a dimensionless structure parameter
		φ	a catalysis factor

are even changed with the elapse of char burnout. Therefore, it is hard to establish a universal mathematical expression to correlate the gasification rate of an arbitrary char with the influencing variables. Table 1 tabulates some known kinetic models adapted to char gasification. These models are developed along a long history of research progress but each model is merely asserted from case to case.

Volumetric model (VM), as shown in Table 1, is a simple model. It is based on an assumption that the active site distributed uniformly on the surface of coal char over the process of gasification. Thus, the reaction rate decreases linearly with reaction time. This model can predict the char conversion as a function of reaction time for uncatalyzed gasification, but an acceptable fit is usually limited to a range of char conversion smaller than 75% or a more narrow range [21].

The shrinking core model (SCM) is described in detail by Levenspiel et al. [20]. This model assumes the homogenous distributions of mass and porosity in the char particle and a spatial shrinking of char with the char burnout. The amount of active sites is proportionate to the char surface area exposed to gasifying agents through the pores of char. In the regime of chemical reaction control, SCM expresses the reaction rate as Eq. (2) (Table 1), where m is a shape factor that depends on the geometry of the grains, and for spheres, $m = 2/3$, for cylinders, $m = 1/2$, and for flat plates, $m = 0$. This model, particularly with $m = 2/3$, is widely used to describe the char gasification rate.

Nevertheless, neither VM nor SCM is supposed to characterize a char conversion-dependent maximum of gasification rate. The VM and SCM models are invalid to express the kinetics of char gasification for some cases, especially for catalyzed char gasification [21,25,26]. In dealing with this problem, some researchers ever introduced a function of char conversion, $g(x)$, into the VM or SCM rate expression [23,24]. An example is the Johnson model, as shown as Eq. (3) (Table 1), where $g(x) = f_1 \exp(-\alpha x^2)$. Although the introduction of $g(x)$ makes it possible for the gasification rate to have a maximum at a point of char conversion and thus allows for better fit to the profiles of gasification rate with time, the selection

of $g(x)$ is almost a sheer mathematical excise without its chemical meanings being rendered.

The random pore model (RPM) is initially proposed by Bhatia and Perlmutter [21], as shown in Table 1. RPM assumes that char holds a cylindrical pore structure with random pore size distributions in char particle, and the surface area changes with the growth and coalesce of pores by the mass loss of char. Compared to SCM, RPM is capable to describe a complex change in the surface area of char particle during char gasification and it allows a maximum of gasification rate to appear in a range of carbon conversion between 0 and 0.393 depending on a dimensionless structure parameter of char, ψ. This model was reported to success in fitting the char gasification kinetics in some instances [26,27].

However, Liu et al. [22] and Zhang et al. [25] found that RPM was quite unsatisfactory for fitting the catalytic char gasification. RPM could collapse into VM with $\psi = 0$ when it was applied for the catalytic char gasification. In this case, by no mean could RPM predict the characteristic appearance of maximum gasification rate. Their work was then going to explore an extended random pore model (ERPM) by incorporating a function of char conversion, $g(x) = 1 + (cx)^p$ or $g(x) = 1 + [c(1-x)]^p$, into the original RPM equation, as shown in Table 1. ERPM behaved indeed well in denoting a maximum at a lower or higher carbon conversion [12]. Kopyscinski et al. [11] further validated the high accuracy of ERPM to fit the uncatalyzed and K_2CO_3-catalyzed char gasification of ash-free coal char by comparing with RPM and other models. Despite the above success, the drawback of ERPM is apparent due to the introduction of two more parameters into RPM, c and p, either of which has no chemical meanings. Therefore, ERPM is at most a semi-empirical formula.

In the present work, we undertake to develop a new kinetic model (abbreviated to ASIM), based on a simplified mechanism of calcium-catalyzed char gasification. The model has been verified to be highly accurate in fitting the gasification kinetics of two lignite chars, which are, respectively, representative of calcium-catalyzed char gasification and uncatalyzed char gasification. The model is expected to have the adaptability to various chars. The

Table 1
The typical models applied for char gasification.

Eq. no.	Model name	Differential formula	References
1	Volumetric model (VM)	$\frac{dX}{dt} = k(1-X)$	[17,18]
2	Shrinking core (SCM)	$\frac{dX}{dt} = k(1-X)^{\frac{2}{3}}$	[19,20]
3	Random pore (RPM)	$\frac{dX}{dt} = k(1-X)\sqrt{1 - \psi \ln(1-X)}$	[21,22]
4	Modified VM or SCM	$\frac{dX}{dt} = k(1-X)^{2/3}g(x)$	[23,24]
5	Extended random pore (ERPM)	$\frac{dX}{dt} = k(1-X)\sqrt{1 - \psi \ln(1-X)}g(x)$	[11,25]