



Modeling of catalytic gasification kinetics of coal char and carbon

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ABSTRACT

Calcium- and potassium-catalyzed gasification reactions of coal char and carbon by CO₂ are conducted, and the common theoretical kinetic models for gas–carbon (or char) reaction are reviewed. The obtained experimental reactivities as a function of conversion are compared with those calculated based on the random pore model (RPM), and great deviations are found at low or high conversion levels as predicted by theory. Namely, calcium-catalyzed gasification shows enhanced reactivity at low conversion levels of <0.4, whereas potassium-catalyzed gasification indicated a peculiarity that the reactivity increases with conversion. CO₂ chemisorption analysis received satisfactory successes in both interpreting catalytic effects and correlating the gasification reactivity with irreversible CO₂ chemical uptakes (CCU_{ir}) of char and carbon at 300 °C. In details, calcium and potassium additions led to significant increases in CCU_{ir} and correspondent high reactivities of the char and carbon. Furthermore, CCU_{ir} of char and carbon decreased with conversion for calcium-catalyzed reaction but increased for potassium-catalyzed one, corresponded to the tendency of their reactivity. The RPM is extended and applied to these catalytic gasification systems. It is found that the extended RPM predicts the experimental reactivity satisfactorily. The most important finding of this paper is that the empirical constants in the extended RPM correlate well with catalyst loadings on coal.

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1. Introduction

Char gasification is known to be the rate-determining step in coal gasification process. The achievable carbon conversion in the gasifier depends on the gasification rate of char. The use of catalysts in gasification process can accelerate reaction rates and considerably reduce gasification temperature. It is also known that alkali and alkaline earth metals are active catalysts for carbon gasification. Among these potential catalysts, calcium and potassium are the most promising. The former is present in abundance in the mineral matter of coals and forestry wastes [1,2], whereas the latter is abundant in some herbaceous biomass resources [2,3]. From both a fundamental and a technological point of view, the kinetic study for such a system is important.

Gasification reactivity and kinetic modeling of carbon or chars derived from various origins have been widely studied. A great deal of research has been focused on the development of kinetic models to describe the gasification profiles of carbon, based on either gas–solid reaction theory or the concept of the pore surface. However, most of the existing models are not satisfactory for systems in which catalysts play an important role in gasification reaction.

The aim of this paper is to propose a semi-empirical model on the basis of extending the random pore model (RPM) to describe

specific catalytic effects of calcium and potassium on the gasification of chars or carbon. An attempt has been made to correlate the empirical parameters of the extended model with the quantity of catalyst loading.

2. Kinetic models for char gasification reaction

All existing models can be classified into two groups: theoretical and semi-empirical. Well-known examples of theoretical kinetic models include the volumetric model [4], shrinking model [5,6], and random pore model [7]. The volumetric model does not consider the structural changes of the char during gasification, assuming that the gasifying agents react with char at all active sites, which are uniformly distributed on both the outside and inside the particle surface. The rate expression is then given by:

$$\frac{dx}{dt} = k(1 - x) \quad (1)$$

where k is rate constant and x is the conversion.

The shrinking model considers that the gasifying agents react on the surface of nonporous grains or in pore surfaces within the solid. According to different assumptions, the reaction rates in the regime of chemical control can be expressed as:

$$\frac{dx}{dt} = \frac{k_s C^n S_0}{(1 - \epsilon_0)} (1 - x)^m \quad (2)$$

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where k_s is the rate constant for the surface reaction, C is the concentration of the reactant gas, n is the reaction order, S_0 is the initial reaction surface, ε_0 is the initial porosity, m is a shape factor that depends on the shape of the assumed grains (for spheres $m = 2/3$, for cylinders $m = 1/2$ and for flat plate $m = 0$). This parameter has also been used as the reaction order by some researchers. For $m = 1$, Eq. (2) reduces to Eq. (1).

The RPM is developed in terms of a cylindrical pore structure that has arbitrary pore size distributions in the char particle. All pores grow and coalesce as reaction progresses. The reaction rate is expressed as:

$$\frac{dx}{dt} = k_p(1-x)\sqrt{1-\Psi\ln(1-x)} \quad (3)$$

where k_p is a rate constant for reaction on the pore surfaces, and Ψ is the pore surface parameter.

The RPM can represent the behavior of a system that shows a maximum rate at certain conversion levels ($x < 0.393$) as well as one that does not. When $\Psi = 0$, the RPM becomes the same as the volumetric model, and at $\Psi = 1$, it approaches to the shrinking model for the cases of $m \leq 1$. In this regard, the RPM is more flexible than the volumetric and shrinking models. In practice, the model has successfully been used in modeling gasification reactions of coal chars or carbons [8,9]. However, since the structural variables of the char may have a complex and somewhat obscure impact on the reaction, the general applicability of RPM still remains unsatisfactory. For example, the original RPM fails to predict the reactivities accounting for the specific catalytic effect for the chars derived from biomass [2] and low rank coals [10,11].

Another group of researchers have abandoned the effort to develop theoretical kinetic models, proposing instead the use of semi-empirical models to reconcile experimental data with theory [12–14]. The semi-empirical models are more useful for investigating the catalytic gasification in some cases. However, no attempt has been made to clarify how the empirical parameters correlate with catalyst quantity or char properties.

3. Experimental

3.1. Samples and cation loadings

A low rank coal from Indonesia (denoted by KD) and a coal-based activated carbon (denoted by AC, Diahope 106, Mitubishi chemicals) were used in this study. The properties of the parent KD and AC are listed in Table 1. A KD or AC sample was impregnated with aqueous solutions of two acetic salts ($\text{Ca}(\text{COOH})_2$ and KCOOH). The loading levels of the catalysts on KD or AC were 2.5, 5, and 10 wt.% for calcium and 1, 2.5, and 3.5 wt.% for potassium, respectively (converted according to the respective acetate salt added). The calcium and potassium loaded samples were denoted by KD (or AC)-Ca (or K)_2.5 (or_5_10).

3.2. Char preparation and reactivity measurements

Prior to the gasification reactivity study, all catalyst-loaded samples and the original KD coal were dried at 107 °C for 2 h and then heat-treated in an infrared furnace at a heating rate of 10 °C/s to 900 °C, with 1 min soaking time under a constant argon flow of 200 mL/min. CO_2 gasification of the resulting samples were then performed under isothermal condition using a TG-DTA2000S system (Mac Science Co., Ltd.). In all cases, about 5 mg of the char sample was placed in an alumina pan and heated under a continuous argon flow of 400 mL/min until it reached the desired temperature. Heating was always conducted at a heating rate of 15 °C/min, and the samples were maintained at the desired tem-

Table 1
Properties of KD coal and AC.

Sample	KD	AC
<i>Proximate analysis (wt%, db)</i>		
Volatile	50.0	0.0
Ash	4.2	2.5
Fixed carbon	49.8	97.5
<i>Ultimate analysis (wt%, db)</i>		
C	65.25	94.21
H	4.49	0.12
N	0.74	0.49
(O+S) ^a	25.3	5.18
<i>Ash analysis (wt%, db)</i>		
SiO ₂	22.92	55.89
Al ₂ O ₃	3.99	23.01
Fe ₂ O ₃	34.22	10.34
CaO	17.72	2.78
MgO	11.45	0.67
TiO ₂	0.23	1.35
P ₂ O ₅	0.03	0.67
Na ₂ O	0.11	1.74
K ₂ O	0.20	1.77
SO ₃	5.03	1.41

^a By difference.

perature for a residence time of 30 min. The isothermal gasification of the char was initiated by switching on to CO_2 . The partial pressure of CO_2 was usually 0.1 MPa. All runs were conducted until weight loss was completed. Char conversion (x) and gasification reactivity (r , s^{-1}) were calculated by the following equations:

$$x = (m_0 - m_t)/(m_0 - m_{\text{ash}}) \quad (4)$$

$$r = dx/dt \quad (5)$$

where m_0 denotes the sample mass (mg) at the start of the gasification, m_t the sample mass at gasification time t , and m_{ash} the mass of ash remained after complete gasification.

3.3. N₂ adsorption isotherm and CO₂ chemisorption

N₂ adsorption isotherm at 77 K was measured using a Belsorp max system (BEL Japan INC.). The porosity and surface area of AC and KD derived chars were calculated according to BET equation. The results for selected char and carbon samples are shown in Table 2.

CO_2 chemisorption of KD char and AC related materials was carried out according to the experimental procedures previously described [15], similar to those reported by Solano et al [16]. For a typical run, 20–25 mg of the char or carbon sample was first heated in argon flow at 15 °C/min to 850 °C. At this temperature, char or carbon was either soaked in argon for 10 min only or subsequently gasified by switching argon to CO_2 for a desired reaction time. After that, the sample was cooled down to 300 °C in argon flow until there is no weight change observed. The net weight of the sample used for subsequent CO_2 chemisorption was then obtained by subtracting the weight loss during the above pretreatment from the initial weight of the sample. CO_2 chemisorption of

Table 2
Pore structure, CO_2 chemisorption, and reactivity of KD derived chars and AC related materials.

Char or carbon	S_{BET} (m^2/g)	V_p (m^3/g)	CCU_{ir} (mg/g)	CCU_{re} (mg/g)	$r_{x=0.5} \times 10^{-4}$ (s^{-1})
KD	314	0.11	1.83	1.18	3.9
KD-Ca_2.5	308	0.11	6.06	1.39	8.4
AC	1055	0.63	0.29	1.22	0.3
AC-K2.5	1043	0.62	8.52	2.23	17.9

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