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Chemical Engineering Journal 140 (2008) 1–5

Chemical Engineering Journal

www.elsevier.com/locate/cej

Review

Kinetic study and mathematical modeling of coal char activation

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Received 13 March 2007; received in revised form 28 August 2007; accepted 17 September 2007

Abstract

Kinetic parameters of coal activation with oxidizing gases are depended of coal characters. In this work, activation of Iranian coal char with steam and CO_2 is studied to find kinetic parameters of the reactions. These parameters are determined by unification of thermogravimetric analysis (TGA) data. Mathematical modeling of the reaction with random pore model also is investigated in this study to predict carbon conversion. Formulation of this model in the mixed controlling regime gives coupled partial differential equations, which has no analytical solution. In this work, a new and simple analytical–numerical solution method is presented to solve these complex equations with a good accuracy. The results show good agreement of this solution with the experimental data.

Keywords: Activated carbon; Activation; Kinetic study; Data unification; Random pore model; Quantize solution

1. Introduction

Kinetic studies of different coal chars activation have been subject of many theoretical and experimental works [1–5]. These studies show that reaction rate and kinetic parameters of activation reaction are dependent on type and origin of coal as raw material. The kinetic parameters of this reaction (activation energy and pre-exponential factor) are used to predict carbon conversion and pore development in the char during the reaction.

There are many attempts to modify these dynamic changes through various normalizing parameters such as half-life time ($t_{1/2}$), reactivity (dx_c/dt) or surface area (S_g). According to the unification approach, char activation progresses at different conditions can be unified to a single curve when carbon conversion (x_c) is plotted versus dimensionless time ($\tau = t/t_{1/2}$) [5]. The kinetic parameters of the char activation can be evaluated using this curve successfully.

The activation of char with oxidizing gas is a heterogeneous gas–solid reaction that pore structure and surface area of the solid particle are changing due to the reaction. These structural variations and other phenomena such as film mass transfer, pore diffusion and chemical reaction have to be considered in the modeling of the reaction simultaneously. Several mathematical models are commonly used to describe these specifications of gas–solid reactions [6–11]. Random pore model is an enhanced model to study pore structural variation of char during activation reaction. This mathematical model gives coupled partial differential equations which are mole balances on the gas and solid components of reactants. This formulation has no analytical solution, thus approximate solutions are investigated to account the adequate accuracy and fast calculation.

In the present study, an Iranian coal as a raw material is used for activation experiments. Kinetics of the char activation with oxidizing gases is studied at different temperatures. The kinetic parameters are obtained perfectly by normalizing the parameters and data unification procedure. These parameters are used in the modeling of the activation. We apply a new analytical–numerical solution method to solve the equations of random pore model successfully.

2. Experimental study

An Iranian coal sample from Goltoot coal mine in Kerman region is selected as raw material. Because of high ash content of the as-received coal, this coal sample is washed by heavy media method to reduce its ash content [12]. Comparison of proximate analysis of the as-received and clean coal samples (before and after the coal washing process) is presented in Table 1.

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doi:10.1016/j.cej.2007.09.023

Nomenclature

C	dimensionless gas concentration (C_A/C_{As})
C_A	reactant gas concentration
C_{As}	gas concentration on the external surface of the solid particle
D_e	effective diffusivity
D_{e0}	initial effective diffusivity
D^*	dimensionless diffusivity (D_e/D_{e0})
E	activation energy
h	Thiele modulus ($R_0(k_s\rho_p S_{g0}/12D_{e0})^{0.5}$)
k_m	film mass transfer coefficient
k_s	surface reaction rate constant
k_0	pre-exponential factor
r	solid particle radius
R	initial radius of solid particle
R_c	carbon reaction rate
$\bar{R}_c$	average carbon rate
R_u	unified reaction rate
S_{g0}	initial specific surface area of solid
Sh	Sherwood number ($k_m R/D_e$)
T	reaction temperature
t	reaction time
$t_{1/2}$	half-life time of reaction
x_c	local carbon conversion
X	overall carbon conversion
z_v	ratio of solid volume after reaction to that before

Greek symbols

β	model parameter ($k_s\rho_p(1-\varepsilon_0)/6D_pS_{g0}$)
ε_0	initial porosity of solid
ξ	dimensionless radius (r/R)
ρ_p	particle density
τ	dimensionless time ($t/t_{1/2}$)
Ψ	structural parameter of RPM

The clean coal sample is undergone pre-oxidation at temperature 230 °C for 4 h with air and then carbonized in a nitrogen gas stream at temperature 425 °C for 1.5 h prior activation. These conditions are adequate to avoid char caking and softening at high temperature condition of the activation step [12].

The experiments of the char gasification are carried out in a thermogravimetric analyzer apparatus (Reometriec scientific, model TGH-1500). An excess gas flow (1 l/min) is found sufficient to eliminate the external mass transfer limitation and ensuring constant bulk gas concentration. High pure CO_2 gas (99.9%) from a pressurized tank is introduced to the system. A glass bubbler floated in hot water bath along with inert gas (N_2) generates water vapor. Partial pressure of water vapor in this gas stream can be controlled with the bath temperature and inert gas flow rate. During the activation, weight loss of the sample is plotted against the reaction time continuously. Figs. 1 and 2 show variation of carbon conversion with time in different temperature of activation with steam and CO_2, respectively.

Table 1
proximate analysis of the as-received and clean coal samples

Coal sample	Moisture	Ash	Volatile matter	Fixed carbon	Sulfur
As-received	2.5	56.5	16	25	1
Clean	1.5	8.5	31	59	0.4

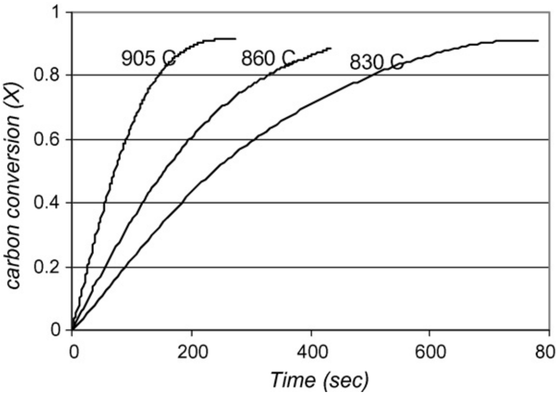

Fig. 1. Experimental data of the char activation with steam at three temperatures.

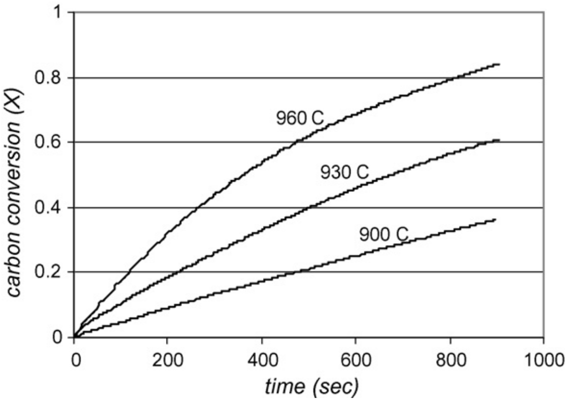

Fig. 2. Experimental data of the char activation with CO_2 at three temperatures.

3. Kinetic parameters determination

The overall reaction rate of activation experiments can be expressed as following general equation, when temperature is only variable parameter:

$$R_c = \frac{dx_c}{dt} = k_s C_A f(x_c) \tag{1}$$

where R_c is activation rate, x_c the carbon conversion, k_s the surface reaction rate constant and C_A is the reactant gas concentration.

Based on the unification method, when carbon conversion is plotted versus dimensionless time τ ($=t/t_{1/2}$), the curves in different condition (such as temperature, char properties and gas type) can be approximated by a single curve. Because of one-to-one correspondence between carbon conversion and dimensionless time, the reactivity parameter ($dx_c/d\tau$) is a function of only x_c. This means dimensionless reaction rate (R_u) defined in Eq. (2) is a constant for all activation conditions, which has found to be

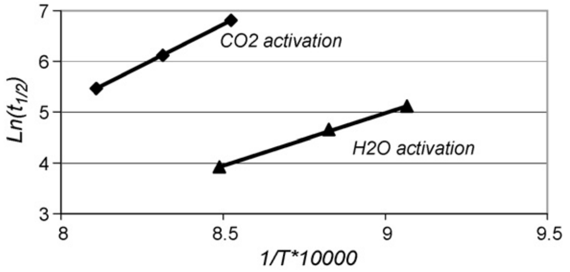

Fig. 3. The Arrhenius plots of half-time in three temperature for two oxidizing gas.

Table 2
The kinetic parameters of the coal char activation with steam and CO_2

	Activation energy (J/mol)	Pre-exponential factor (s^{-1})
CO_2 activation	32,118	327,000
Steam activation	21,153	5,500

around 0.38 [1]:

$$R_u = \int_0^1 \frac{dx_c}{d\tau} dx_c = 0.38 \tag{2}$$

The average reactivity ($\bar{R}_c$) for a particular activation run is as follow:

$$\bar{R}_c = \int_0^1 \frac{dx_c}{dt} dx_c = k_s C_A \int_0^1 f(x_c) dx_c = k_s C_A (A) \tag{3}$$

R_u and $\bar{R}_c$ have the same definition, therefore comparison of Eqs. (2) and (3) and using Arrhenius functionality of the surface reaction rate constant (k_s), gives following expression:

$$t_{1/2} = \frac{0.38}{AC_A} \frac{1}{k_0} e^{E/RT} \tag{4}$$

where k_0 is the pre-exponential factor and E is the activation energy.

Eq. (4) is a perfect relation to evaluate the kinetic parameters from only the half-life data in a few temperatures. The concentration of oxidizing gas is assumed independent of the carbon conversion and is predetermined with N_2 gas stream along the experiments. The value of parameter A in Eq. (4) is determined by using the experimental data numerically. Arrhenius plot of Eq. (4) ($\ln(t_{1/2})$ versus $1/T$) for the TGA data are shown in Fig. 3.

The activation energy and pre-oxidation factor of the coal char activation with CO_2 and H_2O is determined from slope and intercept of the lines in Fig. 3, respectively. The determined kinetic parameters are reported in Table 2.

4. Structural gasification model

There are several regimes such as film mass transfer, pore diffusion and chemical reaction in the activation process which affects on the overall reaction progressing. In addition, changing in the pore structure of char particle makes more complication in the modeling of the process. The mixed control regime, which should be considered both chemical reaction and pore diffusion effects, occur in the most cases of the activation conditions. Mathematical study of this regime is complex. There are several structural models, which are developed to predict the reaction progressing and pore development. Random pore model is widely used in the modeling of char gasification. This model is developed in terms of a pore size distribution with a randomly overlapping set of cylindrical pores. Bhatia and Perlmutter [6,7] have derived equations for non-overlapping surface and volume of the reaction surface with conversion. Then they related these to the overlapping (or actual) properties. The model formulation was derived in two chemical reaction and diffusion controlling regimes. The latter occurs in the most cases of activation condition. The model equations describing gas and solid concentrations within char particle in the dimensionless form are [7]:

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left(D^* \xi^2 \frac{dC}{d\xi} \right) = h^2 \frac{dx_c}{d\tau} \tag{5}$$

$$\frac{dx_c}{d\tau} = \frac{C(1-x_c)\sqrt{1-\psi \ln(1-x_c)}}{1 + \frac{\beta z_v}{\psi}\left(\sqrt{1-\psi \ln(1-x_c)} - 1\right)} \tag{6}$$

The initial and boundary conditions are

$$\text{at } \xi = 1 \quad D^* \frac{dC}{d\xi} = Sh\,(1-C) \tag{7a}$$

$$\text{at } \xi = 0 \quad \frac{dC}{d\xi} = 0 \tag{7b}$$

$$\text{at } \tau = 0 \quad x_c = 0 \tag{7c}$$

where the dimensionless parameters are defined in the nomenclature.

By integrating the local values of carbon conversion in the char particle (x_c), the overall carbon conversion (X) can be obtained. This integration is

$$X = 3 \int_0^1 x_c \xi^2 \, d\xi \tag{8}$$

In the chemical reaction control regime, profile of oxidizing gas concentration within the char particle is expected constant and equal to gas concentration on the external surface of the char particle (C_{As}). In this case, Eq. (6) can be solved alone analytically with $C = 1$ and the following equation is derived to describe carbon conversion variation with time during activation:

$$x_c = 1 - \exp\left[\frac{1}{\psi} - \frac{\psi}{\beta^2 z_v^2} \left(\sqrt{1 + \beta z_v \tau} - \left(1 - \frac{\beta z_v}{\psi} \right) \right)^2 \right] \tag{9}$$

When reaction temperature increases, both diffusion and chemical reaction affect on the overall reaction rate. To predict the solid conversion-time behavior of the reaction in this mixed controlling regime, the coupled partial differential equations of the model (Eqs. (5) and (6)) have to be solved simultaneously. Unfortunately, there is no analytical solution of these equations. Numerical solution of these equations is tedious and needs high programming skills and long computational time. Therefore alternative solution method that requires shorter time and provides good accuracy is presented as the quantize solution method.

5. Quantize solution method

Quantize method is a new analytical–numerical approximate solution method which is recently developed to solve coupled partial differential equations. This method was applied in several gas–solid reaction models including particle-pellet model [13,14], volume reaction model [15], nucleation model [16], and single particle model [17] successfully.

Finite difference form of the coupled partial differential Eqs. (5) and (6) leads to a large set of coupled algebraic equations. At these equations $C(i, j)$, $C(i+1, j)$, $C(i-1, j)$, $C(i, j+1)$, $x_c(i, j)$ and $x_c(i, j+1)$ are related to each others where i and j are position and time node counter, respectively. Thus, much computational efforts are required to obtain the results. In quantize method, an independency between the variables at different times and positions is assumed. This means that the variables C and x_c are related only in the node (i, j) state and they are independent in term of $(i-1, j)$ and $(i, j-1)$ states. By replacing $C(i, j-1)$ with $C(i, j)$ in Eq. (6) and $x_c(i, j-1)$ with $x_c(i, j)$ in Eq. (5) as an approximation, this equations can be solve analytically. Treated of Eqs. (5) and (6) with this assumption, the following algebraic equations obtain:

$$C = \frac{1}{a}\frac{\sinh(h\xi)}{\xi\sinh(h)} \tag{10}$$

$$\frac{2}{\psi}\left(1-\frac{\beta z_v}{\psi}\right)\left[\sqrt{1-\psi\ln(1-x_c)}-1\right]-\frac{\beta z_v}{\psi}\ln(1-x_c)=C\tau \tag{11}$$

where

$$a = 1+\frac{1}{Sh}\left[h\cot\left(\sqrt{\left(h^2(1-x_c)\sqrt{1-\psi\ln(1-x_c)}\right)/\left(1+(\beta z_v/\psi)\left[\sqrt{1-\psi\ln(1-x_c)}-1\right]\right)}/(1-(((z_v-1)(1-\varepsilon_0)x_c)/\varepsilon_0)\right)-1\right].$$

The algebraic Eqs. (10) and (11) are used to predict the carbon conversion (x_c) and gas concentration (C) versus activation time within the porous particle when both chemical reaction and pore diffusion regime are affected. By elimination of variable C from Eqs. (10) and (11), an implicit expression is derived to calculate time variable profile of x_c radially. Overall carbon conversion (X) is obtained using this profile and Eq. (8).

6. Results and discussion

The overall reactivity of the coal char is showed in Figs. 1 and 2. Slope of these curves indicates overall reaction rate and it changes with reaction conditions. Rate of steam activation is faster than the CO_2 activation. The kinetic parameters of the reactions describe this dependency. In addition, Activation rate increase with increasing temperature that is because of faster reaction rate in the higher temperature. Mathematical modeling of the overall reaction explains this behavior.

Overall reaction rate of the coal char activation is studied with random pore model (RPM) by using the calculated kinetic parameters. The model equations of CO_2 activation are solved with both analytical solution (in chemical reaction control regime) and quantize solution and then compared with experimental data. This comparison is presented in Figs. 4–6 at different temperatures.

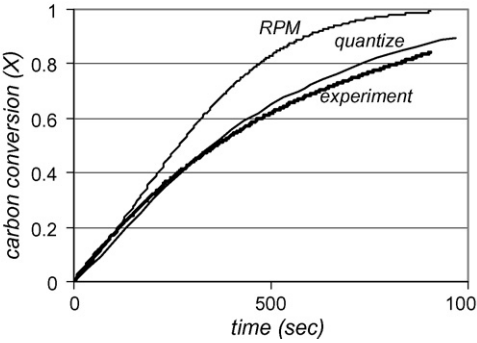

Fig. 4. The comparison of the solutions of RPM with experiment of CO_2 activation at 960 °C.

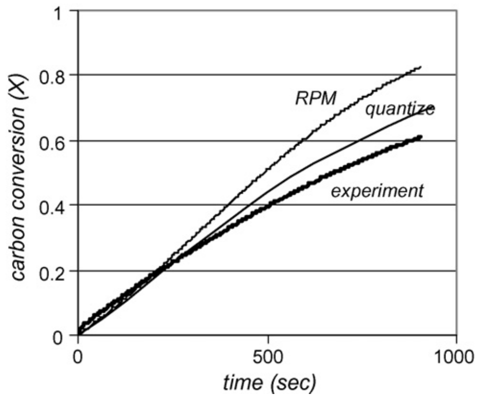

Fig. 5. The comparison of the solutions of RPM with experiment of CO_2 activation at 930 °C.

In these figures, it is clear that the quantize solution presented more accurate prediction of the reaction behavior than the solution of the equations models in the kinetic control regime. In addition, this accuracy increases with temperature increasing.

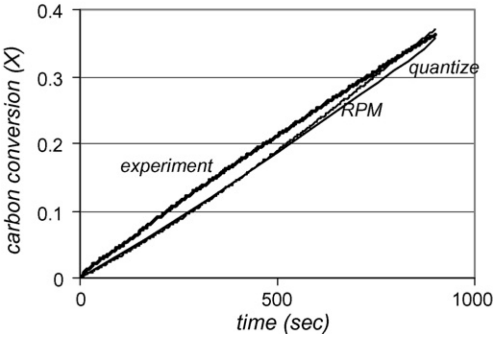

Fig. 6. The comparison of the solutions of RPM with experiment of CO_2 activation at 900 °C.

Table 3
Maceral analysis of the coal sample

Maceral analysis	vol.%
Vitrinite	80.1
Liptinite	0.0
Inertinite	1.8

The modeling of activation in the chemical reaction control regime gives an analytical expression (Eq. (9)) which does not consider diffusion effect and therefore this expression has less validation especially at the high activation temperature. In this temperature range, the pore diffusion resistance increases and therefore it should be considered, but the problem is solution of the model equations (Eqs. (5) and (6)). Quantize method is a good solution method to consider both effects of chemical reaction and pore diffusion during the char activation successfully. This is reason of adequate precision of quantize method. In addition, a part of the deviation is assumption of the model regardless of the solution (such as pore geometry). Another advantageous of quantize method is simplicity of calculation that is clear with comparison of Eqs. (10) and (11) with Eqs. (5) and (6).

Comparison of kinetic parameters determined in this work (Table 2) with those reported in the literature shows that values of these parameters are different with coal type and origin. The heterogeneity of coal and variation of coal components specially coal maceral clarify the difference. Because of oxygen rich and moderately aromatic structure of Vitrinite and carbon rich and highly aromatic structure of Inertinite, the reaction behavior of these maceral groups with oxidizing gas is different. The Liptinite maceral group has hydrogen rich and highly aliphatic structure but the Liptinite content of the coal is close. Maceral composition of the coal sample determined with XRF analyzer is reported in Table 3.

In addition, the trace elements such as sulfur and chlorine are affects on the reaction rate.

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