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A Study on the Applicability of Kinetic Models for Shenfu Coal Char Gasification with CO_2 at Elevated Temperatures

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Abstract: In this paper, measurements of the CO_2 gasification kinetics for two types of Shenfu coal chars, which were respectively prepared by slow and rapid pyrolysis at temperatures of 950 ℃ and 1,400 ℃, were performed by an isothermal thermo-gravimetric analysis under ambient pressure and elevated temperature conditions. Simultaneously, the applicability of the kinetic model for the CO_2 gasification reaction of Shenfu coal chars was discussed. The results showed: (i) the shrinking un-reacted core model was not appropriate to describe the gasification reaction process of Shenfu coal chars with CO_2 in the whole experimental temperature range; (ii) at the relatively low temperatures, the modified volumetric model was as good as the random pore model to simulate the CO_2 gasification reaction of Shenfu coal chars, while at the elevated temperatures, the modified volumetric model was superior to the random pore model for this process; (iii) the integral expression of the modified volumetric model was more favorable than the differential expression of that for fitting the experimental data. Moreover, by simply introducing a function: A = A*exp(ft), it was found that the extensive model of the modified volumetric model could make much better predictions than the modified volumetric model. It was recommended as a convenient empirical model for comprehensive simulation of Shenfu coal char gasification with under conditions close to those of entrained flow gasification.

1. Introduction

As an efficient technology for coal utilization, entrained flow gasification has been highlighted in recent years, because of its high gasification efficiency and smooth discharge of molten ash. However, the high temperature in an entrained flow gasifier tends to cause different gasification behaviors of coal chars [1–6]. Accordingly, the clarification of its kinetic characteristics under conditions similar to those of entrained flow gasification becomes very important, particularly for typical Chinese coals. As we know, establishing or choosing a good kinetic model for char gasification makes it possible to improve gasifier design and deficiency. Consequently, one of the problems encountered, particularly for simulation and scaling up of gasifiers, is how to choose an appropriate model to describe, simply and satisfactorily, the char reaction during gasification process.

So far, a number of models dealing with the reaction between gas reactant and carbon in chars have been reported. Some examples are the homogeneous model [7–9], the shrinking un-reacted core model [10,11], the random pore model [12–14], the random capillary model [13,15] and the modified volumetric model [8,16–18], etc. In spite of much research on these models, reliable predictions cannot be made completely for coal char gasification reaction by these models. It is the reason that the applicability of the models is often limited, owing to either semi-empirical simplifications or assumptions made in deriving the models. Therefore, the current work was undertaken to study the applicability of kinetic model and to achieve representative kinetic model for CO_2 gasification of Shenfu coal under conditions close to those of entrained flow gasification.

2. Results and Discussion

2.1. Models

There is no mathematical model that can describe, completely and exactly, both carbon conversion behaviors against time and rate variation with carbon conversion. Consequently, the model selection depends mainly on the purpose of the reactivity determination. In this paper, the applicability of three kinds of kinetic models was discussed and the extension of the modified volumetric model (EMVM) was proposed. The three kinds of models are the shrinking un-reacted core model (SUCM), the random pore model (RPM) and the modified volumetric model (MVM). Their integral and differential expressions are given in Table 1.

The SUCM [10,11] assumes that reacting char particles are spherical grains, the reaction of char particles with gas reactants is initiated on the its external surface and then moves step by step to the its interior, which results in an ash layer formed in its reacted exterior and at the same time an un-reacted core formed in the interior, and the un-reacted core radius decreases as the gasification reaction advances. However, the model does not consider the physical structural changes during the gasification reaction.

The RPM [19] makes the following assumptions for gasification reaction process. The reaction is initiated on the surfaces of pores in chars. As further reaction occurs, a layer of gas product is formed

around each pore which separates the growing reaction surface of the carbon from the gas reactant within the pores. Reactant diffuses through the product layer to reaction surface where chemical change occurs. Although the RPM considers the physical structural changes during the gasification reaction, it does not consider the random pore overlapping and neglects all diffusion resistances in the char reaction.

The MVM, which is a semi-empirical model, has been developed by Kasaoka *et al.* [16]. It modifies the equation of the homogenous model by adding a new parameter, the time power B. Whereas, A and B, which are determined from the conversion versus time data by the least-squares method, are empirical constants and have no any physical and chemical significance.

Table 1. Integral and differential expressions of SUCM, RPM and MVM.

Models	Integral expression	Differential expression	Notes
SUCM	$X = 1-\left(kt\right)^3$	$\dfrac{dX}{dt} = 3k\left(1-X\right)^{2/3}$	k is the average reaction rate constant.
RPM	$X = 1-\exp\left[-\tau\left(1+\dfrac{\psi\tau}{4}\right)\right], \tau = A_0 t$	$\dfrac{dX}{dt} = A_0\left(1-X\right)\sqrt{1-\psi\ln\left(1-X\right)}$	τ, A_0 and ψ are respectively the dimensionless time, the initial reaction rate and the pore structural parameter.
MVM	$X = 1-\exp\left(-At^B\right)$	$\dfrac{dX}{dt} = \left(1-X\right)A^{1/B}B\left[-\ln\left(1-X\right)\right]^{(B-1)/B}$	A and B are two constants and determined from the conversion versus time data by the least-squares method.

Note: X: the carbon conversion; dX/dt: the apparent reaction rate; t: the reaction time.

In order to predict the gasification reaction much better, the MVM is modified by introducing A which varies with the reaction time. Thus, the equations of the extension of the MVM (EMVM) are as follow: $X = 1-\exp(-At^B)$; $A = A^\star\exp(ft)$. Where $A^\star$ is also an empirical constant and f is a coefficient. It is identified that the EMVM as an empirical model can appropriately describe the gasification reaction for various Shenfu coal chars at elevated temperatures. The details are described in the following parts.

2.2. Comparisons of SUCM, RPM and MVM for Coal Char Gasification

Up to the present, many models have been used to describe the coal char gasification reaction kinetics. However, the hypothetical premises of each model are discriminative, thus their applicative ranges are also different. Here, the comparison of the SUCM, the RPM and the MVM, which are used for simulating coal char gasification, is the main task. Figures 1 and 2 separately show the fitting curves of CO_2 gasification reactions of various Shenfu coal chars at gasification temperatures of 950 ℃ and 1,400 ℃, using the integral expressions of the SUCM, the RPM and the MVM.

Figure 1. Carbon conversion versus gasification time for coal char gasification at the gasification temperature of 950 ℃. Experimental data (■); SUCM (⋯); RPM(---); MVM (—).
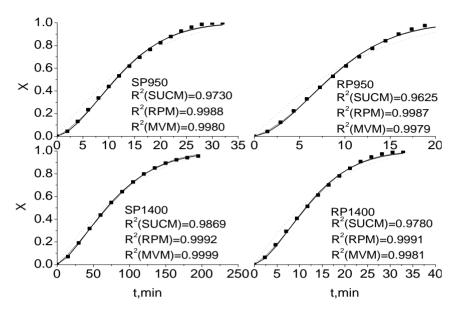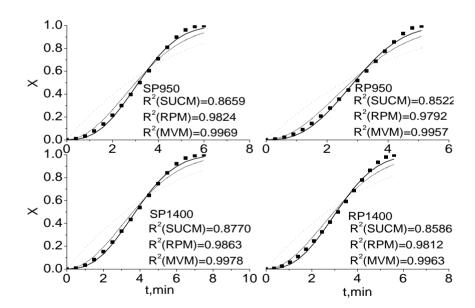

Figure 2. Carbon conversion versus gasification time for coal char gasification at the gasification temperature of 1,400 ℃. Experimental data (■); SUCM (⋯); RPM (---); MVM (—).

From the two figures, two results can be deduced. The one thing is that as a whole the simulations of both the RPM and the MVM are better than that of the SUCM. Experimental data from the two figures show that the curves of carbon conversion versus gasification time present S-shaped. That is to say, the reaction rate initially increases up to a maximum and then decreases during the gasification reaction (see Figures 3 and 4). The expressions of both the RPM and the MVM are fit for S-shaped curves. Moreover, the SUCM does not consider the physical structural changes during the gasification reaction. Thereby, both the RPM and the MVM are superior to the SUCM. Another thing is that the fitting

degree of the MVM is almost as good as that of the RPM at the gasification temperature of 950 ℃ (Figure 1), while better than that of the RPM at the gasification temperature of 1,400 ℃ (Figure 2). Many literatures [6,13,14,19] found that the application of the RPM was relatively befitting for the reaction process, during which the reaction rate presented a maximum where carbon conversion was below 20% or slightly higher. In this paper, the reaction rate is up to a maximum at the carbon conversion of about 20–30% at the gasification temperature of 950 ℃ (see Figure 3), while up to a maximum above the carbon conversion of 50% at the gasification temperature of 1,400 ℃ (see Figure 4). Moreover, with the increase of gasification temperatures, the carbon conversion at the point of the maximal reaction rate becomes larger and larger [20]. Based on these facts, it should be showed that experimental data are fitted better by the MVM than the RPM at elevated gasification temperatures. Therewith, this result can be also proved by comparing the square value of correlation index (R^2) presented in the two figures. Above all, it is concluded that among the three models, the MVM is the best to simulate the CO_2 gasification reaction for Shenfu slow and rapid heating chars.

2.3. Comparison of Integral and Differential Expressions of the MVM for Coal Char Gasification

In general, a kinetic model can be expressed in two forms, which are the integral equation (carbon conversion versus gasification time) and the differential equation (reaction rate versus carbon conversion). In this part, the integral expression of the MVM is compared with its differential one for simulating the gasification reaction of coal chars. Figures 3 and 4 separately present that the experimental data are fitted by the differential equation of the MVM at gasification temperature of 950 ℃ and 1,400 ℃.

Figure 3. Reaction rate versus carbon conversion for coal char gasification at the gasification temperature of 950 ℃. Experimental data (■); MVM (—).
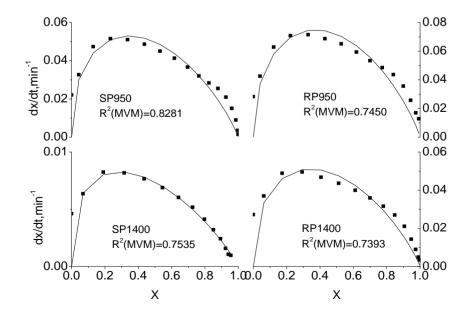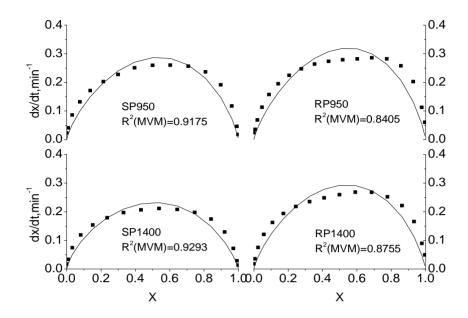
Figure 4. Reaction rate versus carbon conversion for coal char gasification at the gasification temperature of 1,400 °C. Experimental data (■); MVM (—).

Comparing Figures 1 and 2 with Figures 3 and 4, these can be seen that the fitting curves resulting from the integral expression of the MVM are closer to the experimental data than those resulting from the differential expression of the MVM, and the value of R^2 acquired by fitting the experimental data with the integral equation of the MVM, is correspondingly larger than that with the differential equation of the MVM at gasification temperature of both 950 °C and 1,400 °C. This result suggests that the fitting extent of the integral expression is higher than that of the differential one. Thereby, it is very favorable that the integral expression is chosen for fitting the experimental data. Theoretically, the fitting extent of the integral equation should be the same as that of the differential one. However, the difference of the fitting extent is resulted. The following is the main cause. The data fitted by the integral expression are carbon conversions which are obtained directly from the experimental measurement, while those fitted by the differential expression are reaction rates which are obtained indirectly from the approximate derivative calculation of carbon conversion versus gasification time instead of the direct measurement. Thereby, this results in the deviation of the value of reaction rate.

2.4. Extension of Modified Volumetric Model for Coal Char Gasification

Figures 5 and 6 show the fitting curves of the MVM and the EMVM for CO_2 gasification of Shenfu slow and rapid heating coal chars at gasification temperatures of 950 °C and 1,400 °C, respectively. From the two figures, it can be seen that under the conditions of slow or rapid heating and low or high gasification temperatures, the fitting curves of the EMVM are closer to the experimental data than that of the MVM, especially at higher carbon conversion, and the value of R^2 resulted from the fit of experimental data by EMVM is correspondingly larger than that resulted from the fit of the same experimental date by MVM. Moreover, under the condition of gasification temperature ranged from 950 °C to 1,400 °C, the value of R^2 was also calculated using the data of the literature [20] and is presented in Table 2. From this table, the same result can be also obtained. These results tell us that after the constant A was empirically modified with a function: $A = A^{\star}\exp(ft)$, the prediction by the

EMVM agrees much better with experimental results than the prediction by the MVM. That the MVM is correct as a mathematical model has been approved by many researchers [8,16–18]. However, it is a semi-empirical model. Accordingly, the parameter A is only as an empirical constant in the expression and does not imply any physical or chemical significance such as pore structure, crystal structure, chemical structure and active surface area so on. Form Table 3, which is obtained from the literature data [20], it can be seen that both A and A* present irregular changes with the increasing gasification temperature. Consequently, like the parameter A, A* also has no any physical or chemical significance and can be only taken as an empirical constant in the EMVM. Consequently, the EMVM should be a purely empirical model.

In a word, the EMVM obtained by modifying the MVM with a simple function can make much better predictions than the MVM. The reason for this improvement is not clear and needs to be studied further for the future. But it can be concluded that the EMVM as an empirical model is convenient for the comprehensive simulation of Shenfu coal char gasification at elevated temperatures, particularly at high carbon conversions.

Table 2. Comparison of the square value of correlation index (R^2).

Gasification temperature (℃)	SP950		RP950		SP1400		RP1400	
	MVM	EMVM	MVM	EMVM	MVM	EMVM	MVM	EMVM
950	0.99799	0.99932	0.99787	0.99940	0.99991	0.99991	0.99805	0.99963
1,000	0.99783	0.99949	0.99815	0.99975	0.99994	0.99996	0.99922	0.99986
1,100	0.99742	0.99968	0.99754	0.99964	0.99989	0.99990	0.99897	0.99991
1,200	0.99730	0.99976	0.99769	0.99964	0.99953	0.99986	0.99854	0.99980
1,300	0.99734	0.99961	0.99702	0.99931	0.99841	0.99981	0.99725	0.99940
1,400	0.99690	0.99948	0.99574	0.99890	0.99775	0.99954	0.99627	0.99922

Table 3. The values of A and A* calculated by the fit of experimental data respectively using the MVM and the EMVM.

	Gasification temperature （℃）					
	950	1000	1100	1200	1300	1400
Constant A						
SP950	0.01261	0.02110	0.02817	0.03290	0.02956	0.03501
RP950	0.01839	0.0302	0.03446	0.03055	0.03879	0.04363
SP1400	0.00141	0.00501	0.02272	0.02335	0.02191	0.02428
RP1400	0.01404	0.02464	0.03434	0.03362	0.03751	0.03725
Constant A*						
SP950	0.02413	0.03656	0.04266	0.04426	0.03966	0.04217
RP950	0.03230	0.04786	0.04690	0.03994	0.04408	0.04564
SP1400	0.00146	0.00544	0.02183	0.03031	0.03289	0.03475
RP1400	0.02772	0.03549	0.04457	0.04354	0.04483	0.04319

Figure 5. Carbon conversions versus gasification time for coal char gasification at the gasification temperature of 950 °C. Experimental data(■); MVM (···); EMVM (—).
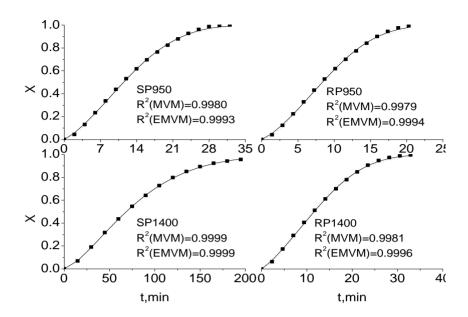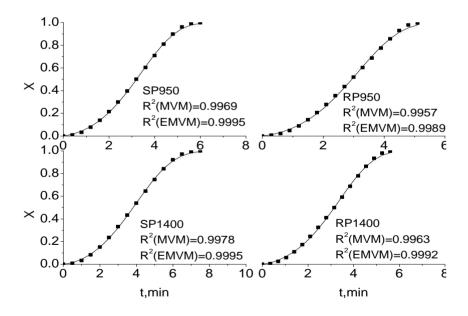

Figure 6. Carbon conversions versus gasification time for coal char gasification at the gasification temperature of 1,400 °C. Experimental data (■); MVM (···); EMVM (—).

3. Preparation of Chars and Gasification Experiments

A typical coal, Shenfu coal, from China was employed in this paper. A thorough characterization of the coal has been provided in the literature [20]. Slow heating char samples were prepared by devolatilization of parent coal in the muffle. A small-scale falling reactor [20] was employed to prepare rapid heating char samples. The preparation procedures of slow and rapid heating chars were the same as those in the literature [20]. Slow heating char samples prepared at pyrolysis temperatures of 950 °C and 1,400 °C, were respectively termed as SP950 and SP1400. Rapid heating char samples

prepared at pyrolysis temperatures of 950 ℃ and 1,400 ℃, respectively were termed as RP950 and RP1400. The proximate and ultimate analysis data of various slow and rapid heating chars are shown in Table 4.

Table 4. Proximate and ultimate analysis of slow and rapid heating chars.

Samples	Proximate analysis (wt%, d)			Ultimate analysis (wt%, d)			
	A	V	FC	C	H	S_t	N
SP950	10.30	3.22	86.48	87.00	0.64	0.38	0.30
SP1400	10.56	1.07	88.44	89.53	0.11	0.38	0.02
RP950	10.41	6.14	83.45	83.68	1.73	0.33	1.04
RP1400	11.32	3.07	85.61	87.05	0.51	0.38	0.08

Note: d: dry basis; A: ash content; V: volatile matter content; FC: fixed carbon content; C: carbon content; H: hydrogen content; S_t: total sulphur content; N: nitrogen content.

Char samples were ground up to the particle diameter ⩽73 μm and were stored for gasification experiments. Measurements of coal char gasification were performed in a SETARAM TG-DTG/DSC thermo-gravimetric analyzer using an isothermal method. The procedure of measurements can be seen in the authors' paper [20]. Due to the gas diffusion especially in high temperatures, distinguishing intrinsic and effective reaction rate is indeed particularly difficult. No matter what any measurements are used, this is always an issue. Therefore, the paper used the apparent reaction rate as the char gasification reactivity index. The apparent reaction rates (dX/dt) are obtained indirectly from the derivative calculation of carbon conversion (X) versus reaction time (t).

4. Conclusions

The applicability of kinetic models for Shenfu slow and rapid heating coal char gasification with CO_2 was investigated at elevated temperatures. The following conclusions were reached. The MVM was the most superior among the three models, used for the CO_2 gasification kinetic model of Shenfu coal chars (slow and rapid heating) at elevated temperatures. It was very much favorable that the integral expression of the modified volumetric model is chosen for fitting the experimental data. The EMVM proposed in the paper gave better predictions than the MVM. It was recommended as a convenient empirical model for comprehensive simulation of coal char gasification, particularly for Shenfu coal under conditions close to the entrained flow gasification.

Acknowledgements

References and Notes

1. Liu, G.; Tate, A.G.; Bryant, G.W.; Wall, T.F. Mathematical modeling of coal char reactivity with CO_2 at high pressures and temperatures. *Fuel* **2000**, *79*, 1145–1154.
2. Luo, C.; Watanabe, T.; Nakamura, M.; Uemiya, S.; Kojima, T. Gasification kinetics of coal chars carbonized under rapid and slow heating conditions at elevated temperatures. *J. Energy Resour. Technol.* **2001**, *123*, 21–26.
3. Nowok, J.W; Hurley, J.P.; Bensen, S.A. The role of physical factors in mass transport during sintering of coal ashes and deposit deformation near the temperature of glass transformation. *Fuel Process. Technol.* **1998**, *56*, 89–101.
4. Zhou, J.; Zhou, Z.J.; Gong, X.; Yu, Z.H. Study of char-CO2 gasification (I) by isothermal thermogravimetry. *Coal Conversion* **2002**, *25*, 66–69, (in Chinese).
5. Liu, H.; Kaneko, M.; Luo, C.; Kato, S.; Kojima, T. Effect of pyrolysis time on the gasification reactivity of char with CO_2 at elevated temperatures. *Fuel* **2004**, *83*, 1055–1061.
6. Kajitani, S.; Hara, S.; Matsuda, H. Gasification rate analysis of coal char with a pressurized drop tube furnace. *Fuel* **2002**, *81*, 539–546.
7. Ye, D.P.; Agnew, J.B.; Zhang, D.K. Gasification of an Austrailian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies. *Fuel* **1998**, *77*, 1209–1219.
8. Yang, Y.; Watkinson, A.P. Gasification reactivity of some Western Canadian coals. *Fuel* **1994**, *73*, 1786–1791.
9. Li, S.F.; Sun, R.Z. Kinetic studies of a lignite char pressurized gasification with CO_2, H_2 and steam. *Fuel* **1994**, *73*, 413–416.
10. Li, S.F.; Liu, H.B. The application of unreacted-core shrinking model to coal chars with CO_2 pressurized gasification reaction. *Gas & Heat* **1993**, *13*, 3–9, (in Chinese).
11. Wen, C.Y. Noncatalytic heterogeneous solid fluid reaction models. *Ind. Eng. Chem.* **1968**, *60*, 34–54.
12. Chi, W.; Perlmutter, D.D. The effect of pore structure on char-steam reaction. *AIChE J.* **1989**, *35*, 1791–1802.
13. Gavalas, G.R. A random capillary model with application to char gasification at chemically controlled rates. *AIChE J.* **1980**, *26*, 577–585.
14. Liu, H.; Luo, C.H.; Kaneko, M.; Kato, S.; Kojima, T. Unification of gasification kinetics of char in CO_2 at elevated temperatures with a modified random pore model. *Energy Fuels* **2003**, *17*, 961–970.
15. Ochoa, J.; Cassanello, M.C.; Bonelli, P.R.; Cukierman, A.L. CO_2 gasification of Argentinean coal chars: a kinetic characterization. *Fuel Process. Technol.* **2001**, *74*, 161–176.
16. Kasaoka, S.; Sakata, Y.; Tong, C. Kinetic evaluation of the reactivity of various coal chars for gasification with carbon dioxide in comparison with steam. *Int. Chem. Eng.* **1985**, *25*, 160–175.
17. Lee, W.J.; Kim, S.D. Catalytic activity of alkali and transition metal salt mixtures for steam-char gasification. *Fuel* **1995**, *74*, 1387–1393.
18. Song, B.H.; Sang, D. Catalytic activity of alkali and iron salt mixtures for steam-char gasification. *Fuel* **1993**, *72*, 797–803.
19. Bhatia, S.K.; Perlmutter, D.D. A random pore model for fluid-solid reactions: I isothermal, kinetic control. *AIChE J.* **1980**, *26*, 379–386.

20. Wu, S.Y.; Gu, J.; Li, L.; Wu, Y.Q.; Gao, J.S. Variation of the crystalline structure and CO_2 gasification reactivity of Shenfu coal chars at elevated temperatures. *Energy Fuels* **2008**, *22*, 199–206.