

# CO<sub>2</sub> and H<sub>2</sub>O Gasification Kinetics of a Coal Char in the Presence of Methane

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The kinetics of CO<sub>2</sub> and H<sub>2</sub>O gasification of a Chinese coal char in the presence of methane has been studied using a thermogravimetric analyzer (TGA) in the temperature range from 1173 to 1273 K. It was observed that the rate of carbon conversion increased with an increasing temperature and decreased with an increasing CH<sub>4</sub> concentration. The rate of carbon conversion during the gasification of the char experienced a maximum without the presence of methane but decreased continuously with carbon conversion in the presence of methane. Carbon deposition from CH<sub>4</sub> cracking reduced the overall rate of carbon conversion during gasification, but this effect was reduced as the temperature and concentration of CO<sub>2</sub> or H<sub>2</sub>O were increased. A gas–solid reaction shrinking core model was developed and applied to the char–CH<sub>4</sub>–CO<sub>2</sub>/H<sub>2</sub>O systems. The experimental results were used to determine the kinetic parameters. The model predictions compared favorably to the measured data. The overall carbon conversion rate has been shown to be a combination of carbon gasification, by CO<sub>2</sub> or H<sub>2</sub>O, respectively, and methane cracking.

## 1. Introduction

The use of coal bed methane (CBM) as an energy source and feedstock for chemical manufacturing has received increased interests in recent years. With a view to co-use coal and CBM, a process combining coal gasification and CBM reforming in a fluidized-bed system to produce syngas has been conceptualized and proven to be feasible on a laboratory scale.<sup>1</sup> The process has been demonstrated to possess at least the following two advantages: (i) the ratio of H<sub>2</sub>/CO of syngas produced is adjustable by adjusting the methane/coal ratio, to suit the downstream synthesis processes, and (ii) there is no need for more expensive metal catalyst because the coal char has been shown to serve as the catalyst while being a reactant. Installation of such combined coal gasification and methane-reforming systems at coal mine mouths seem to make good economic sense because relatively small-scale and scattered CBM would be more difficult for collection and transport.

However, this process involves a very complex heterogeneous–homogeneous reaction system and thus deserves further detailed scientific examination, building on the previous work on the catalytic effect of coal char on methane cracking and methane reforming in the presence of carbon dioxide.<sup>2,3</sup> It has been

confirmed that the coal char has a catalytic effect on methane conversion and carbon dioxide enhances the catalytic ability of coal char during coal char gasification. However, the corresponding coal char gasification rate in the presence of methane has not been established.

The present research focuses on char gasification by CO<sub>2</sub> and H<sub>2</sub>O, respectively, in the combining coal gasification and CBM reforming system. A kinetic model has been developed to simulate the carbon conversion rate in the char–CH<sub>4</sub>–CO<sub>2</sub> (or H<sub>2</sub>O) system.

## 2. Experimental Section

A Chinese bituminous coal (Bin-Xian coal) was employed in this work. The run of mine coal was crushed and sieved to a narrow size fraction of 0.09–0.098 mm. Char used in the gasification experiments in the presence of methane was prepared by devolatilizing the raw coal sample in nitrogen in a fixed-bed reactor at 1173 K for 30 min. The proximate and ultimate analysis data of the coal and char are presented in Table 1.

A thermogravimetric analyzer (TGA) schematically shown in Figure 1 was employed, and high-purity [ $>99.9\%$  (v/v)] methane, nitrogen, and carbon dioxide were used in the experimentation. The gas flow rate was controlled using a mass flow meter.

The flow rate of steam was accurately controlled using a precision microflow pump to deliver distilled water, which was then heated and vaporized in an electrically heated preheater, with its operating temperature maintained at 473 K, prior to entering the TGA furnace.

In an experiment, 5 mg of the char sample was placed in the crucible. A gas stream of known composition flowed through the furnace at a flow rate of 100 mL min<sup>−1</sup>, while the furnace was heated to a desired temperature. Once the furnace reached a preset

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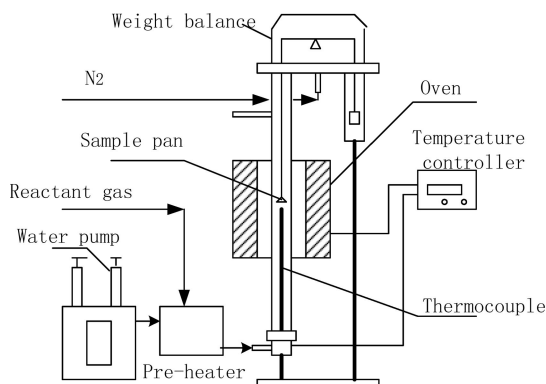
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**Table 1. Proximate and Ultimate Analysis of Raw Coal and Char**

	proximate analysis (wt %)				ultimate analysis (wt %, daf)				
	M (wb)	V (ad)	A (ad)	FC (ad)	C (daf)	H (daf)	O (daf)	N (daf)	S (daf)
Binxian char	0.38	1.32	18.3	80.0	96.1	1.38	1.27	0.92	0.33
Binxian coal	2.6	24.4	10.1	62.9	80.3	4.36	14.4	0.41	0.53

<sup>a</sup> wb, wet basis; ad, air dried; daf, dry ash free.

**Figure 1.** Schematic diagram of thermogravimetric apparatus.

temperature, the furnace was raised to enclose the crucible containing the char within no more than 5 s. The mass loss of the char because of gasification by CO<sub>2</sub> or H<sub>2</sub>O versus time was recorded on a computer.

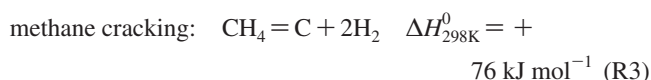
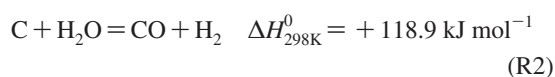
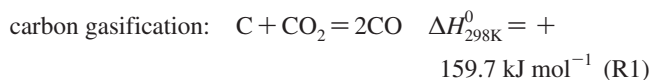
The carbon conversion rate is expressed as

$$x = \frac{w_0 - w_t - w_{\text{ash}}}{w_0 - w_{\text{ash}}} \times 100 \quad (1)$$

where  $x$  is the ash-free carbon conversion,  $w_0$  is the initial mass of the char,  $w_t$  is the instantaneous char mass at time  $t$ , and  $w_{\text{ash}}$  is the mass of ash in the char.

### 3. Kinetic Analysis

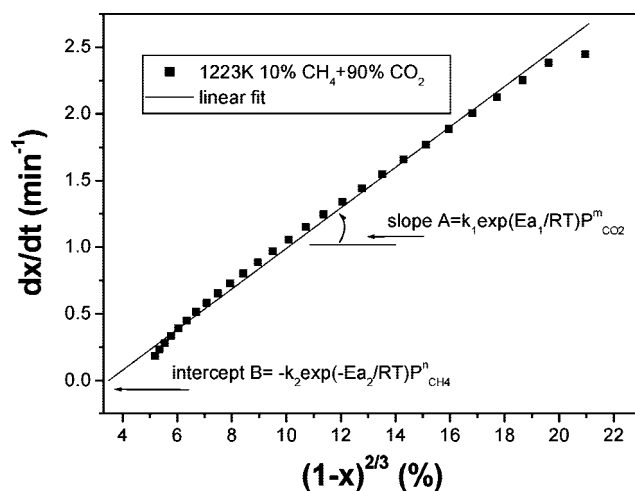
In the present experiments, both mass loss because of char gasification by CO<sub>2</sub> or H<sub>2</sub>O, respectively, and mass gain because of methane cracking on coal char contribute to the observed carbon conversion<sup>2</sup> according to the reactions R1 or R2 and R3 below.



Therefore, the total carbon conversion is the sum of mass changes because of reactions R1 and R3 or reactions R2 and R3, for CO<sub>2</sub> or H<sub>2</sub>O gasification, respectively. The overall rate of carbon conversion,  $-r_A$ , is thus related to temperature  $T$ , the partial pressures of the gasification agent (CO<sub>2</sub> or steam)  $P_i$  and methane  $P_{\text{CH}_4}$ , and the amount of carbon present in the form of

$$-r_A = f\{T, P_i, P_{\text{CH}_4}, \text{carbon}(1-x)\} \quad (2)$$

where  $i$  represents either CO<sub>2</sub> or steam as the gasification agent and  $m$  and  $n$  are the reaction orders in the gasification agent (CO<sub>2</sub> or H<sub>2</sub>O) and methane, respectively.

**Figure 2.** Estimation of the kinetic constants according to eq 5.

The kinetic rate equation (eq 3) of carbon gasification is developed following the shrinking core model in the literature<sup>4-6</sup>

$$-\frac{dx_1}{dt} = -k_1 e^{-\frac{E_{a1}}{RT}} P_i^m (1-x)^{2/3} \quad (3)$$

The kinetic rate equation of methane cracking is shown in eq 4.

$$\frac{dx_2}{dt} = k_2 e^{-\frac{E_{a2}}{RT}} P_{\text{CH}_4}^n \quad (4)$$

Combining eqs 3 and 4 gives the total carbon conversion rate that is expressed as eq 5 below

$$-\frac{dx}{dt} = -k_1 e^{-\frac{E_{a1}}{RT}} P_i^m (1-x)^{2/3} + k_2 e^{-\frac{E_{a2}}{RT}} P_{\text{CH}_4}^n \quad (5)$$

where  $k$  is the pre-exponential factor,  $E_a$  is the apparent active energy in kJ mol<sup>-1</sup>,  $R$  is the universal gas constant of 8.314 J mol<sup>-1</sup> K<sup>-1</sup>,  $i$  denotes carbon dioxide or steam, and subscript 1 and 2 represent carbon gasification and methane cracking reactions, respectively. The term  $(1-x)$  is introduced in this kinetic analysis to account for the dependence of the total carbon conversion on the carbon (char) available in the reaction system.

The various kinetic parameters in eq 5 can be estimated using the experimental data by equating  $r_A$  to  $dx/dt$ . Figure 2 illustrates the method of estimation of the kinetic parameters using a set of typical TGA data of coal char gasification by CO<sub>2</sub> in the presence of methane.

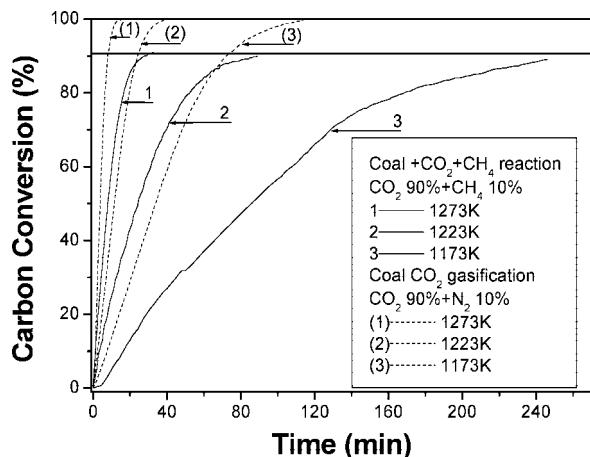
### 4. Results and Discussion

Experiments were performed to determine the rates of CO<sub>2</sub> gasification of the coal char with or without the presence of methane at temperatures ranging from 1173 to 1273 K, with the data of the carbon conversion rate versus reaction time

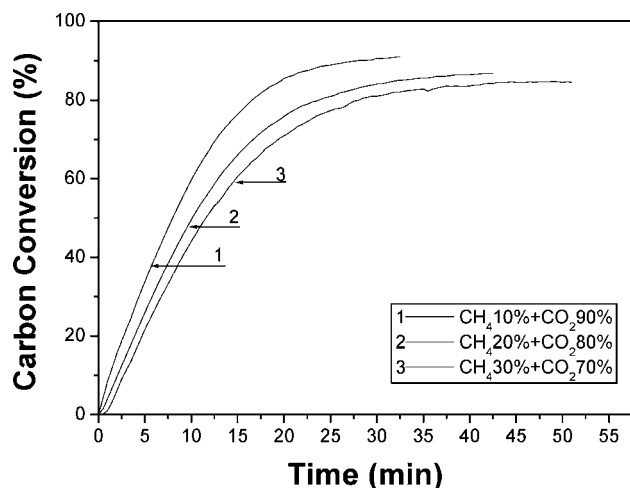
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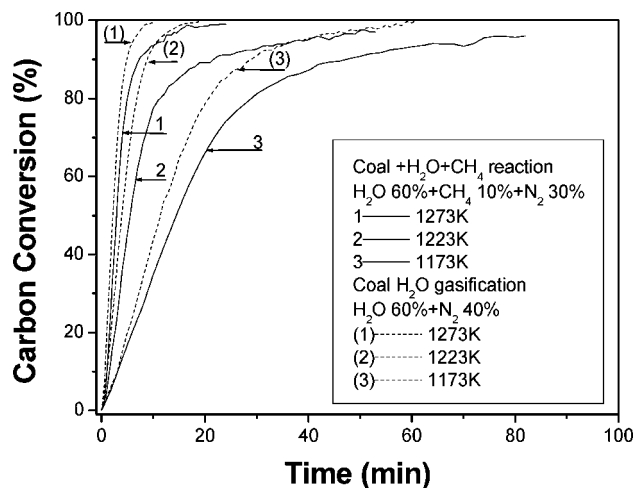
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**Figure 3.** Carbon conversion versus time during  $\text{CO}_2$  gasification of coal char with and without  $\text{CH}_4$  at different temperatures.

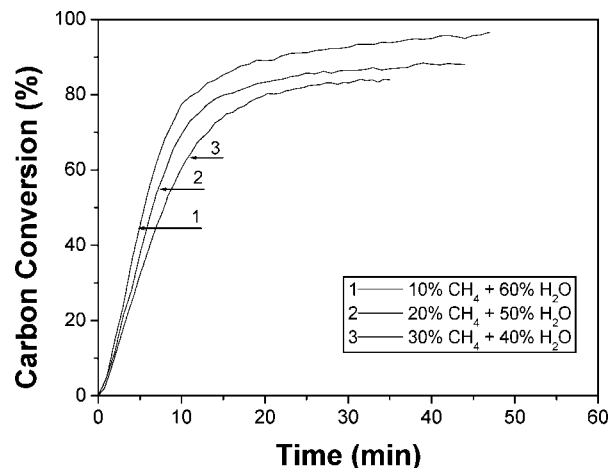


**Figure 4.** Carbon conversion versus time during  $\text{CO}_2$  gasification of coal char in the char- $\text{CH}_4$ - $\text{CO}_2$  system with different  $\text{CH}_4/\text{CO}_2$  ratios (1273 K).

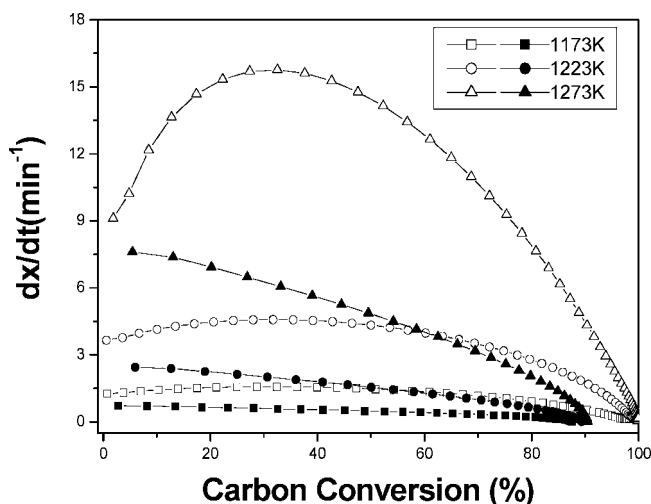


**Figure 5.** Carbon conversion versus time during  $\text{H}_2\text{O}$  gasification of the coal char with and without  $\text{CH}_4$  at different temperatures.

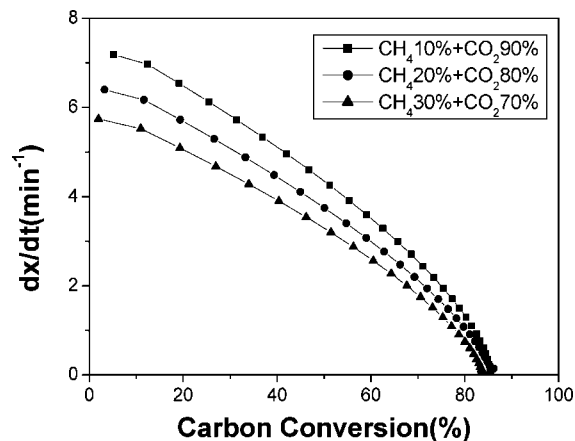
shown in Figure 3. It can be seen that the total time required to complete the  $\text{CO}_2$  gasification without the presence of methane decreases with an increasing temperature and is 1173 K at 120 min, 1223 K at 30 min, and 1273 K at 12 min ( $\cdots$ ), respectively. In the presence of methane, the  $\text{CO}_2$  gasification of the coal char is also dependent upon temperature; however, the total time required to achieve the same carbon conversion



**Figure 6.** Carbon conversions versus time during  $\text{H}_2\text{O}$  gasification of the coal char in the char- $\text{CH}_4$ - $\text{H}_2\text{O}$  system with different  $\text{CH}_4/\text{H}_2\text{O}$  ratios (1223 K).

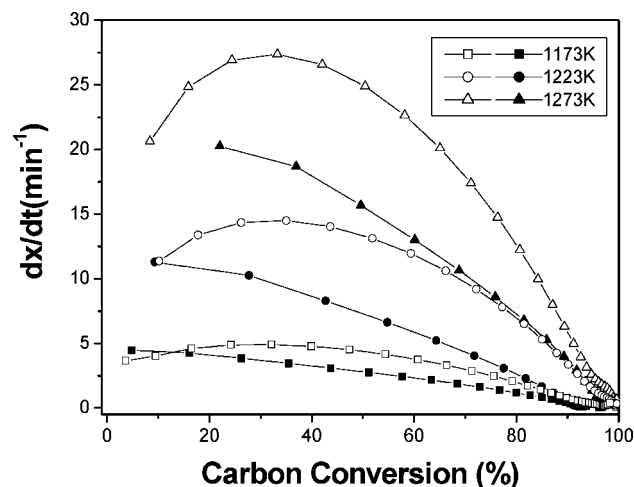


**Figure 7.** Rate of carbon conversion versus carbon conversion during  $\text{CO}_2$  gasification of coal char with and without  $\text{CH}_4$  at different temperatures. Open symbols are for  $\text{CO}_2$  gasification of coal char alone, 90%  $\text{CO}_2$  and 10%  $\text{N}_2$ . Close symbols are for  $\text{CO}_2$  gasification of coal char in the presence of  $\text{CH}_4$ , 90%  $\text{CO}_2$  and 10%  $\text{CH}_4$ . The total gas flow rate is  $100\text{ mL min}^{-1}$ .

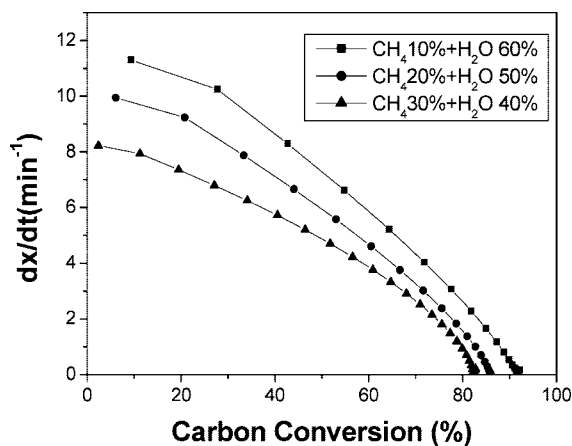


**Figure 8.** Rate of carbon conversion versus carbon conversion during  $\text{CO}_2$  gasification of coal char with different  $\text{CH}_4/\text{CO}_2$  ratios (1273 K).

is nearly doubled, and the final carbon conversion does not reach 100% ( $-$ ) within the limitation of the experiment times. This is because the overall carbon conversion in the presence of



**Figure 9.** Rate of carbon conversion versus carbon conversion during H<sub>2</sub>O gasification of coal char with and without CH<sub>4</sub> at different temperatures. Open symbols are for H<sub>2</sub>O gasification of coal char alone, 60% H<sub>2</sub>O and 40% N<sub>2</sub>. Close symbols are for H<sub>2</sub>O gasification of coal char in the presence of CH<sub>4</sub>, 60% H<sub>2</sub>O, 30% N<sub>2</sub>, and 10% CH<sub>4</sub>. The total gas flow rate is 100 mL min<sup>-1</sup>.

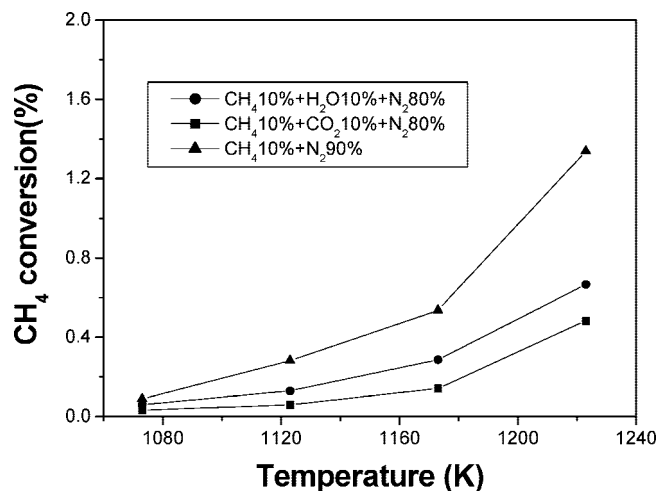


**Figure 10.** Rate of carbon conversion versus carbon conversion during H<sub>2</sub>O gasification of coal char with different CH<sub>4</sub>/H<sub>2</sub>O ratios (1223 K).

**Table 2. Kinetic Parameters of CO<sub>2</sub> and H<sub>2</sub>O Gasification of Coal Char with and without of Methane**

Char-CH <sub>4</sub> -CO <sub>2</sub> System					
$k_1$	$k_2$	$E_{a1}$ (kJ mol <sup>-1</sup> )	$E_{a2}$ (kJ mol <sup>-1</sup> )	$m$	$n$
$4.7 \times 10^{10}$	$2.8 \times 10^{11}$	283	318	0.63	0.11
Char-CH <sub>4</sub> -H <sub>2</sub> O System					
$k_1'$	$k_2'$	$E_{a1}'$ (kJ mol <sup>-1</sup> )	$E_{a2}'$ (kJ mol <sup>-1</sup> )	$m'$	$n'$
$5.8 \times 10^8$	$6.4 \times 10^{11}$	223	302	0.23	0.71
char CO <sub>2</sub> gasification		char H <sub>2</sub> O gasification			
$E_{aco2}$ (kJ mol <sup>-1</sup> )		239		$E_{ah2o}$ (kJ mol <sup>-1</sup> )	
				221	

methane is a net result of carbon consumption because of CO<sub>2</sub> gasification and carbon formation as a result of methane cracking. The final reachable overall carbon conversion is about 90% and increases with an increase in the reaction temperature as shown in Figure 3. The effect of the CH<sub>4</sub>/CO<sub>2</sub> ratio on the final carbon conversion was also examined with the results shown in Figure 4. The rate of carbon conversion and the final carbon conversion all decrease with an increasing CH<sub>4</sub>/CO<sub>2</sub> ratio. It indicates that the carbon deposition is increased as the ratio of CH<sub>4</sub>/CO<sub>2</sub> increases. These observations suggest that



**Figure 11.** Methane conversion as a function of the temperature during methane cracking, reforming by carbon dioxide (or steam) over a bed of quartz particles in a fixed-bed reactor (residence time, 1 s; total flow, 250 mL min<sup>-1</sup>).

there is a balance point between carbon consumption because of gasification and carbon formation in the reaction process that determines the final carbon conversion, depending upon the temperature and CH<sub>4</sub>/CO<sub>2</sub> ratio.

Similar experiments were performed on the steam gasification of the coal char with or without the presence of methane in the temperature range from 1173 to 1273 K, and the results are shown in Figure 5. A similar trend to that observed in the CO<sub>2</sub> gasification is evident, although higher overall carbon conversions were achieved in the H<sub>2</sub>O gasification (Figure 5) than in the CO<sub>2</sub> gasification (Figure 3). It can also be seen from Figure 5 that the addition of 10% of methane in the reactant gas slowed down the carbon gasification rate by nearly 50% compared to the case without methane. The effect of the CH<sub>4</sub>/H<sub>2</sub>O ratio on the final carbon conversion was also examined with the results shown in Figure 6. Again, it can be seen that the rate of carbon conversion and final carbon conversion all decrease with an increasing CH<sub>4</sub>/H<sub>2</sub>O ratio.

The rate of carbon conversion versus the overall carbon conversion during the CO<sub>2</sub> gasification of the char, with and without the presence of CH<sub>4</sub> at different temperatures is depicted in Figure 7. It can be seen that, without the presence of CH<sub>4</sub>, the rate of carbon conversion as a function of the overall carbon conversion always presents a maximum value. This is because, in the initial stages of the gasification, there is an increase in the total surface area of the char particles because of the opening of previously inaccessible or closed pores in the char structure,<sup>7-10</sup> but as the reaction progresses, the total surface area decreases because of coalescence of the pores, resulting from the consumption of the carbonaceous materials. This will reduce the observed rate of gasification. As a result, the rate of carbon conversion experiences a maximum. In the presence of 10% CH<sub>4</sub>, in addition to carbon consumption because of the gasification of CO<sub>2</sub>, carbon is also formed as a result of CH<sub>4</sub> cracking. In addition, the reforming of CH<sub>4</sub> also consumes part of CO<sub>2</sub>, thus reducing the amount of CO<sub>2</sub> for carbon gasification reactions, and the reaction between CH<sub>4</sub> and CO<sub>2</sub> is prone to carbon deposition,<sup>3</sup> resulting in a reduction in the overall rate of carbon conversion.

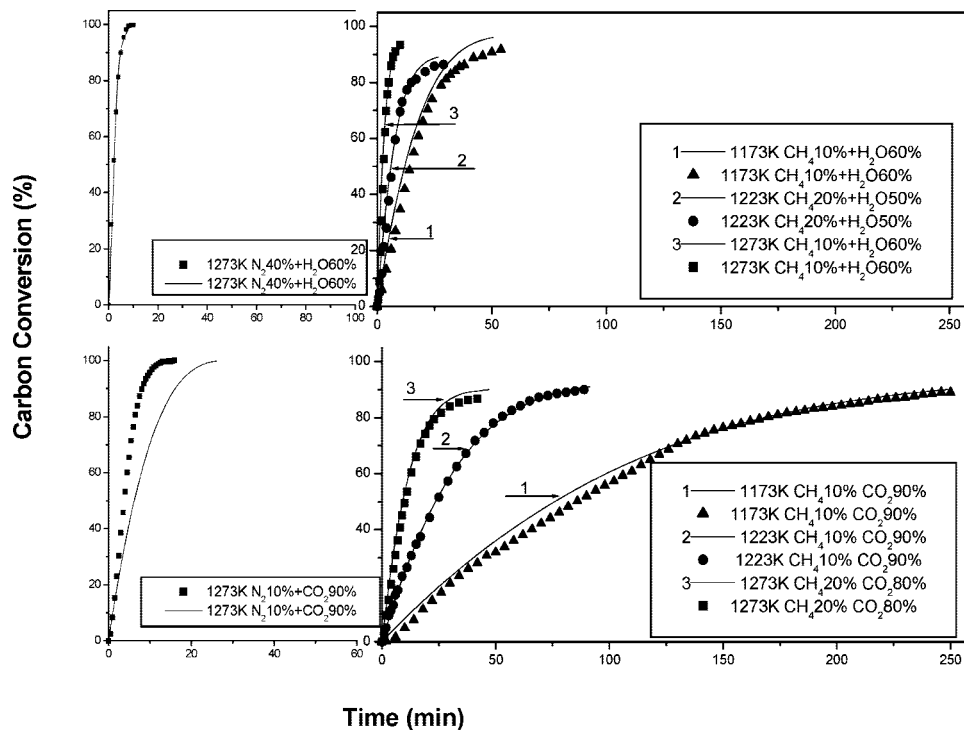
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**Figure 12.** Comparison of the kinetic model simulation results with experimental data for the char-CH<sub>4</sub>-CO<sub>2</sub> (lower right), char CO<sub>2</sub> gasification (lower left), char-CH<sub>4</sub>-H<sub>2</sub>O (upper right), and char H<sub>2</sub>O gasification (upper left) systems (closed symbols are for the experimental results, and lines are for the simulation results).

In the presence of CH<sub>4</sub>, furthermore, the rate of carbon conversion seems to always decrease with the overall carbon conversion, as shown in Figure 8, and the higher the CH<sub>4</sub>/CO<sub>2</sub> ratio, the lower the rate of carbon conversion. This is because, with the increasing CH<sub>4</sub>/CO<sub>2</sub> ratio, carbon deposition becomes more severe and the carbon formed from the CH<sub>4</sub> cracking is less reactive than the coal char, resulting in a reduced carbon reaction rate. Compounded with the reduction in the CO<sub>2</sub> concentration, the observed rate of carbon conversion therefore decreases with carbon conversion, as clearly demonstrated in Figure 8.

Similar results were obtained for the char-CH<sub>4</sub>-H<sub>2</sub>O reaction system as shown in Figures 9 and 10. Figure 9 shows that the steam gasification of the coal char alone experiences a maximum rate without the presence of CH<sub>4</sub> and the gasification rate increases with an increasing reaction temperature. In the presence of 10% CH<sub>4</sub>, however, the rate of carbon conversion is greatly reduced and seems to always decrease with an increasing carbon conversion. Increasing the CH<sub>4</sub>/H<sub>2</sub>O ratio further reduces the rate of carbon conversion as shown in Figure 10.

Comparisons between Figures 7 and 9 and between Figures 8 and 10 further confirm that, at the same CH<sub>4</sub> concentrations, between 0 and 30%, the H<sub>2</sub>O gasification of the coal char is faster than the CO<sub>2</sub> gasification. A further inspection of the results in Figures 8 and 10 reveals that, in the presence of CH<sub>4</sub>, there seems to be a “stagnant” point for each set of experiments at which the overall rate of carbon conversion drops to zero, indicating that the rate of carbon consumption because of gasification by CO<sub>2</sub> or H<sub>2</sub>O is counter-balanced by the rate of carbon deposition as a result of CH<sub>4</sub> cracking. This “stagnant” point is clearly dependent upon the reaction temperature and the CH<sub>4</sub>/CO<sub>2</sub> or CH<sub>4</sub>/H<sub>2</sub>O ratios.

The experimental data presented in Figures 7–10 have been employed to estimate the kinetic constants according to the kinetic model (eq 5) and the methodology articulated in Figure

2 for the char-CH<sub>4</sub>-CO<sub>2</sub> and char-CH<sub>4</sub>-H<sub>2</sub>O systems, respectively. The results are given in Table 2. The activation energy of R2 in the char-CH<sub>4</sub>-H<sub>2</sub>O system is 223 kJ mol<sup>-1</sup>, which is a little higher than that (221 kJ mol<sup>-1</sup>) of the H<sub>2</sub>O gasification of the coal char alone. Likewise, the activation energy of R1 in the char-CH<sub>4</sub>-CO<sub>2</sub> system (283 kJ mol<sup>-1</sup>) is also higher than that (239 kJ mol<sup>-1</sup>) for the CO<sub>2</sub> gasification of the coal char alone. Two factors contribute to these results: (1) the carbon deposition because of methane cracking covers the surface of the coal char, hampering the reaction between CO<sub>2</sub> (or H<sub>2</sub>O) and coal char, and (2) the deposited carbon is less reactive than the coal char in gasification by CO<sub>2</sub> or H<sub>2</sub>O. The activation energy of carbon deposition because of methane cracking is 302 and 318 kJ mol<sup>-1</sup> for the char-CH<sub>4</sub>-H<sub>2</sub>O and char-CH<sub>4</sub>-CO<sub>2</sub> systems, respectively, which compares favorably lower than the C-H bond energy of methane (435 kJ mol<sup>-1</sup>).<sup>11</sup>

In the presence of CO<sub>2</sub> or H<sub>2</sub>O, methane may undergo reforming, which may then consume a certain amount CO<sub>2</sub> or H<sub>2</sub>O. To ascertain this effect, experiments of methane reforming by CO<sub>2</sub> or H<sub>2</sub>O were performed in a fixed-bed reactor<sup>2</sup> without the presence of char, and the results are shown in Figure 11. It can be seen that the potential influence of a reduced CO<sub>2</sub> (or H<sub>2</sub>O) concentration because of methane reforming can be ignored. Furthermore, methane cracking in the gas phase can also be ignored on the basis of the results of methane cracking on quartz as shown in Figure 11.

Integrating the overall carbon conversion rate equation (eq 5) gives the relationship of carbon conversion  $x$  versus time  $t$ , as shown by the following equation:

(11) Atkins, P.; de Paula, J. *Atkins' Physical Chemistry*, 7th ed., 2002; p 1095.

$$t = -\frac{3}{A}(1-x)^{1/3} + \frac{3B^{1/2}}{2A^{3/2}} \ln \frac{\left(\frac{A}{B}\right)^{1/2} (1-x)^{1/3} + 1}{\left(\frac{A}{B}\right)^{1/2} (1-x)^{1/3} - 1} + \frac{3}{A} - \frac{3B^{1/2}}{2A^{3/2}} \ln \frac{\left(\frac{A}{B}\right)^{1/2} + 1}{\left(\frac{A}{B}\right)^{1/2} - 1} \quad (6)$$

$$\text{where } A = k_1 e^{\frac{E_{a1}}{RT}} P_i^{m_i}; \quad B = k_2 e^{\frac{E_{a2}}{RT}} P_{\text{CH}_4}^n$$

Using the kinetic constants in Table 2, the curves of  $x \sim t$  for the char-CH<sub>4</sub>-H<sub>2</sub>O and char-CH<sub>4</sub>-CO<sub>2</sub> systems, respectively, at different temperatures and different CH<sub>4</sub>/CO<sub>2</sub> or CH<sub>4</sub>/H<sub>2</sub>O ratios are obtained and shown in Figure 12. It can be seen that the kinetic model simulation results compare quite well to the experimental data.

## 5. Conclusions

CO<sub>2</sub> and H<sub>2</sub>O gasification of the coal char in the presence of methane has been studied using a TGA in the temperature range from 1173 to 1273 K. The rate of carbon conversion increases

with an increasing temperature and decreases with an increasing CH<sub>4</sub>/CO<sub>2</sub> or CH<sub>4</sub>/H<sub>2</sub>O ratio. The rate of carbon conversion during the gasification of the char by CO<sub>2</sub> or H<sub>2</sub>O alone experiences a maximum without the presence of methane but always decreases with an increasing carbon conversion in the presence of methane. Carbon deposition from CH<sub>4</sub> cracking reduces the overall rate of carbon conversion during gasification, but this effect is reduced as the temperature and concentration of CO<sub>2</sub> or H<sub>2</sub>O are increased.

A gas-solid reaction kinetic model has been developed and applied to the char-CH<sub>4</sub>-CO<sub>2</sub> and char-CH<sub>4</sub>-H<sub>2</sub>O systems. The model predictions compare favorably to the measured data. The overall carbon conversion rate has been shown to be a combination of carbon gasification, by CO<sub>2</sub> or H<sub>2</sub>O, respectively, and methane cracking.

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