

GASIFICATION KINETICS OF COALS AND WOOD

D.P.C. FUNG and Sang D. KIM*

Energy Research Laboratories, CANMET,

Energy, Mines and Resources Canada, Ottawa, K1A 0G1 Canada

*Department of Chemical Engineering, Korea Advanced Institute of
Science and Technology, Seoul 136-791, Korea

(Received 30 September 1989 • accepted 19 January 1990)

Abstract—The chemical reactivity and kinetics of nine Canadian coal samples ranking from lignite to semianthracite and one wood sample were examined in a fixed gasifier in the presence of air and steam at 950-1000°C. The reactivity of the coal and wood samples decrease with an increase in carbon content, but increase with increasing oxygen content of the parent coal. The reaction velocity decreases with an increase in carbon content of the coal. The reaction mechanism based on the shrinking core model for the present gasification has been found to be chemical reaction controlled for the coal-steam-air system and ash-layer diffusion controlled for the wood-steam-air system. The present reaction system favors the water gas shift reaction based on the chemical composition of the product gas from the gasification.

INTRODUCTION

The present research objective is to test the technical and economic feasibility of producing specific gaseous products from coals of different chemical reactivities using the gasification process. The required gasification reactivity data were obtained for various Canadian coals in a laboratory gasifier.

The gasification reactivity and the physical properties of Canadian coals and chars under various experimental conditions were reported previously [1-6]. Kinetic parameters of the reaction model for these solid fuels were evaluated and the shrinking core model was used to explain the gasification mechanism of nine samples of coals and their chars [2,4,8].

This paper reports new gasification reactivity data for nine Canadian coal samples ranking from lignite to semianthracite and one wood sample at 950-1000°C in the presence of air and steam, whereas, previous studies were conducted at 800-840°C. It is hoped that this study will further strengthen the validity of the shrinking core model for the interpretation of the gasification mechanism of carbonaceous materials. Wood is included because it has a lower carbon content but higher reactivity than coal regardless of their

origin. It is an ideal reference material for studying the relationship between the reactivity and the carbon content of solid fuels such as peat, coal and char. The validity of the shrinking core model can be tested at a carbon content from 51 to 92 wt%.

EXPERIMENTAL

1. Materials

Samples were air dried, then oven dried for 2 h at 105°C before gasification. The mean particle size was 4.5 mm with a size distribution which has 8.4 wt% of 5.7 mm, 88.1 wt% of 4.3 mm and 3.5 wt% of 3.6 mm particles, respectively. Chemical analysis of the coal and wood samples are given in Table 1. The wood sample contained 85 wt% spruce and 15% bark.

2. Gasification unit

The gasification procedure in a fixed-bed reactor was detailed in a previous communication [1]. Briefly, a coal sample (50 g) mixed with Berl saddle as an inert material was gasified in a sample holder having a 6-mm diameter opening to receive the incoming reacting gases at the bottom of the holder. The reacting gas was a mixture of air (2.0 dm³/min) and steam (3 g/min-water rate). The gasification temperature ranged from 950-1000°C.

Duplicate experiments were carried out for the

To whom all correspondence should be addressed.

Table 1. Chemical analysis of coal samples (moisture free)

Coal (Rank)	Proximate Analysis (wt%)			Ultimate Analysis (wt%)				
	Ash	Volatile Matter	Fixed Carbon	C	H	S	N	O ^a
Cannmore (semi-anthracite)	15.1	11.9	73.0	78.6	3.6	0.8	1.5	0.4
McIntryre (low vol. bituminous)	8.2	18.1	73.7	83.1	4.3	0.6	1.2	2.6
Devco (high vol. bituminous)	2.9	35.4	61.7	84.7	5.6	1.3	1.3	4.2
Byron Creek (med. vol. bituminous)	15.3	26.2	58.5	74.4	4.3	0.8	1.2	4.0
Prince (high vol. bituminous)	15.6	43.6	49.8	66.0	4.5	4.9	1.4	7.6
Coalspur (sub-bituminous)	9.5	37.1	53.4	71.9	4.7	0.2	1.1	12.6
Bienfait (lignite)	12.5	41.4	46.1	66.1	2.2	0.6	1.3	17.3
Coronach (lignite)	13.4	43.5	43.1	61.1	3.6	1.1	1.0	19.8
Onakawana (lignite)	26.8	40.0	33.2	49.7	3.3	5.4	0.7	14.1
Wood	1.7	76.4	21.9	50.5	5.3	0	0.1	42.4

^aDetermined by difference.

wood and coal samples. After a gasification run of 30 min at atmospheric pressure, the residue in the reactor was cooled with a stream of N_2 (0.9 dm^3/min) for 2 h, then removed and weighed.

3. Gas sampling and analysis

Fifteen samples of the product gas were collected from each run at 2-min intervals over 30 min using a commercial Valco 16-port valve system [7]. Then the samples were analyzed by a gas chromatograph (Perkin-Elmer Sigma 1) with porapak N and molecular sieve 5A columns. Carrier gas was a mixture of helium and hydrogen having the flowrate of 45 cm^3/min with the column temperature programming of 15°C/min from 40 to 75°C.

RESULTS AND DISCUSSION

Gasification and combustion rates were calculated from the ultimate carbon content of the coal samples, the product gas composition and the volume. In a typical plot of carbon conversion vs time, a maximum conversion rate of each fuel sample occurs in the linear region at the initial stage of the reaction as shown in Fig. 1. The conversion versus time, a maximum conversion rate of each fuel sample occurs in the linear portion representing about 20 to 60% conversion.

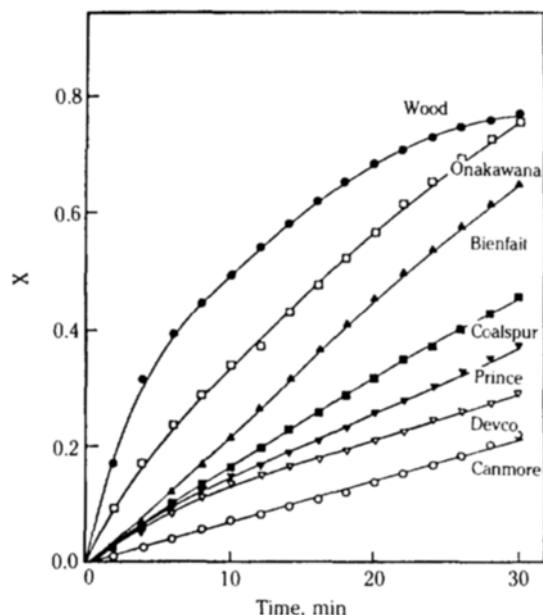


Fig. 1. Carbon conversion of coals and wood versus reaction time at 950-1000°C.

The reactivity, R , can be calculated from the maximum slope of the conversion curve with the following equation [2]:

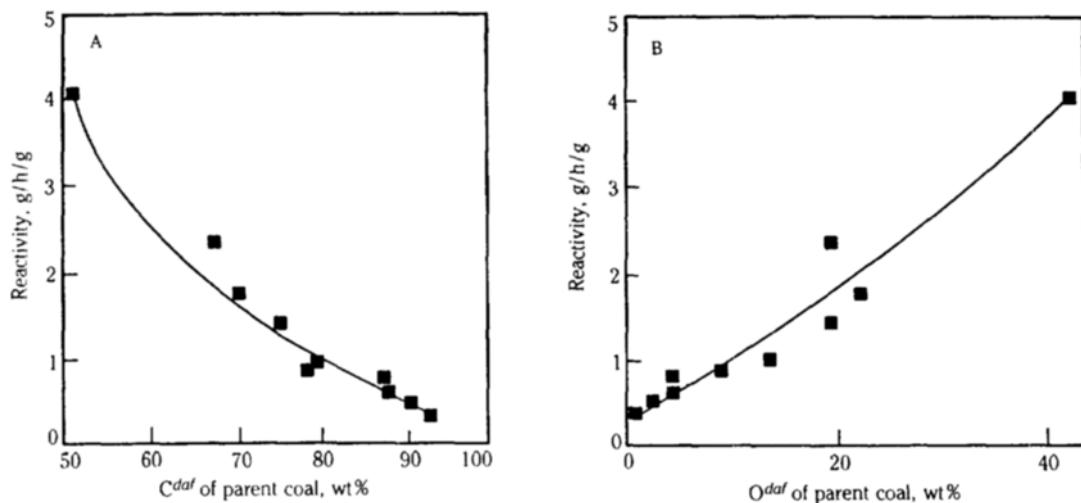


Fig. 2. (a) Correlation between reactivity of coals and wood and carbon content of sample (b) Correlation between reactivity of coals and wood and oxygen content of sample.

$$R = \frac{1}{W} \frac{dc}{dt} \quad (1)$$

where R is the maximum reactivity, g/h/g, W the initial mass of sample on a dry ash free basis and dc/dt the carbon weight loss rate, g/h. Using Eq. (1), the maximum reactivities of the coal and wood samples were determined at 950-1000°C. The reactivities varied from 4.11 to 0.36 g/h/g from wood to semi-anthracite. In general, the chemical reactivity decreases with increased carbon content or higher rank coal [2,9-11]. This finding is in agreement with two previous gasification studies of coals and chars under different conditions of reacting gases and temperatures [2,4,6]. The low reactivity of the higher rank coal is attributed to poor utilization of the small surface area in the micropores during the gasification reaction [5,6,11]. Conversely, it is believed the higher reactivity of the lower rank coal is caused by the larger pore volume which provides better utilization of the micropore surface area for the reaction [10]. And the higher mineral matter contents of the lower rank coals may act as a catalyst in the gasification reaction [4].

Since the oxidation reaction of the carbonaceous material is involved in the present coal-steam-air gasification system, the oxygen content of the coals and wood influences the chemical reactivity and rate of gasification. As shown in Fig. 2b the reactivity of the carbonaceous material increased with higher oxygen contents of coals and wood [12]. It has been demonstrated that adding oxygen to the steam gasification reaction enhances the chemical reactivity of the higher ranking coals when compared with a similar

Table 2. Chemical composition of product gas from steam gasification

Sample	Chemical composition, vol. % (N ₂ free basis)				
	H ₂	O ₂	CH ₄	CO ₂	CO
Prince	37.3	1.7	1.0	38.6	21.4
Coalspur	53.5	0.8	1.6	25.2	18.9
Bienfait	52.9	0.0	1.5	25.0	20.6
Coronach	48.6	0.7	0.7	28.0	22.0
Onakawana	51.5	0.0	1.5	25.0	22.0
Wood	49.2	0.8	0.8	27.9	21.3

study at 800-840°C having oxygen content in the reacting gas mixture [2].

1. Chemical composition of product gas

Table 2 gives the chemical composition of the product gas of the coal and wood samples from air-steam gasification at 950-1000°C. The gas composition (nitrogen-free basis) is the mean value of 10 compositions sampled from 12 to 30 min of gasification. Relatively large amount of hydrogen, carbon dioxide and carbon monoxide were produced from all the samples. These results suggest that the major reactions involved in the gasification are:



It is believed these two reactions take place at the solid-gas interface while the second reaction may also occur in the gas phase.

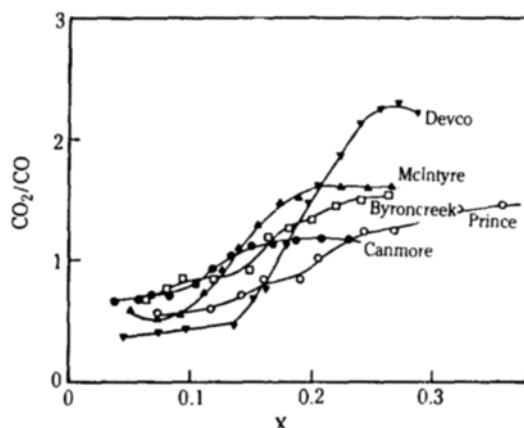


Fig. 3. Variation of the molar ratio of CO_2/CO with carbon conversion.

The relationship between the rank (carbon content dry ash-free basis) of coal and product gas (H_2 , CO_2 , CO and CH_4) is shown in Table 2. Since methane formation from the carbon-steam reaction at atmospheric pressure is not thermodynamically favorable, its formation is therefore independent of the coal's carbon content. In general, CO_2 formation increases somewhat with an increase in carbon content of the coal but decreases with an increase in the oxygen content of the parent coal. However, hydrogen formation decreases slightly with an increase in carbon content of coal. In contrast, the carbon content does not affect the CO formation until it reaches 87 wt% as in the case of the Devco coal. Thereafter, CO formation increases with an increase in the carbon content of the coal. A similar trend of CO formation from coals of various carbon content was also observed at 800-840°C in a previous study [2].

2. Reaction kinetics

When the rates of diffusion through a fluid-film and a porous solid are both fast, the overall rate of a solid-fluid reaction is entirely controlled by the inherent chemical reactivity of the solid reactant [2,8,13]. Since the reaction between coal-steam and coal-oxygen are controlled by the chemical reactivity, the shrinking core model [2,6,13-15] can be used to interpret the present conversion data of coals and wood.

In the shrinking core model, where chemical reaction is the rate controlling step, the following equation can be applied [13,15]:

$$t/t^* = 1 - (1 - X)^{1/3} \quad (2)$$

where t is the reaction time, X the carbon conversion fraction and t^* the time for complete conversion as defined by:

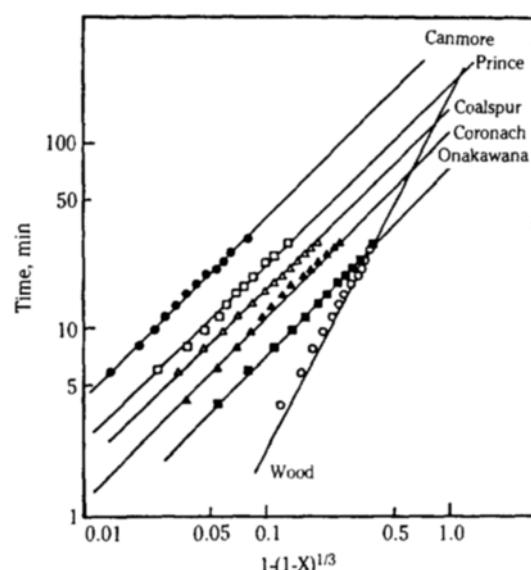


Fig. 4. Carbon conversion versus reaction time in shrinking core model.

$$t^* = r C_{so} / KP^n \quad (3)$$

where r , C_{so} , K , and P are mean radius of the particles, initial concentration of carbon, specific velocity per reaction surface and pressure, respectively. The order of reaction (n) for fluid reactant is one. When ash layer diffusion is the controlling step, the following can be applied:

$$t/t^* = (1 - (1 - X)^{1/3})^2. \quad (4)$$

From Eqs. (3) and (4) it can be determined that, when a log-log plot of $[1-(1-X)^{1/3}]$ versus time is made, the slope of the line determines whether the reaction is chemical controlled or ash layer diffusion controlled. If a straight line is obtained with a slope of unity, the chemical reaction is a rate controlling step. A slope of 2 indicates that the reaction is controlled by ash layer diffusion.

Figure 4 is a log-log plot of the reaction time, t , versus $[1-(1-X)^{1/3}]$. The solid line represent model lines. It can be seen that the carbon conversion data points of the coals falls on the lines of chemical reaction controlled having a slope of 1. But, the slope of the line is 2 for the carbon conversion of wood and thus the reaction is controlled by ash layer diffusion. This means that the gasification mechanism for wood is different from that of coal in which chemical reaction control predominates. One may say that the char ash layers formed during wood gasification increase diffusion resistance to the reacting gas passing through the layers as postulated by the shrinking core model.

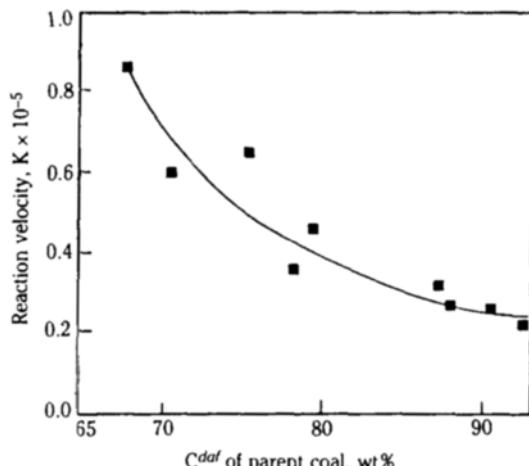


Fig. 5. Correlation between reaction velocity and carbon content of coal.

[13].

The value of t^* for each sample can be obtained by extrapolating the model lines to complete conversion ($X = 1.0$) in Fig. 4. From the t^* values, the specific reaction velocity per reaction surface, K , of each sample, can be determined from Eq. (3) with the knowledge of R , C_{so} and P . It can be seen from Fig. 5 that the specific reaction velocity K of the coal samples decreases with higher carbon content of the coal.

Figure 6 is a model line plot between the carbon conversion fraction, X , and the reaction time, t , of the coal and wood samples. The carbon conversion was calculated from Eqs. (2) and (3) using t^* value (in bracket) extrapolated from the plot in Fig. 4. One can see that agreement exists between the experimental data points and the model (Fig. 6). This shows that the shrinking core model can be utilized for predicting the carbon conversion for various coals and wood samples from their conversion completion time (t^*).

CONCLUSIONS

From the present experimental study, the following conclusions can be drawn. The reactivity of nine Canadian coals and one wood samples decrease with increasing carbon content, but increase with an increase in oxygen content of the parent coal. The reaction velocity decreases with higher carbon content of the coal. With the shrinking core model, the coal-steam-air systems have been found to be under chemical reaction control; the wood-steam-air system, however, were found to be ash-layer diffusion controlled. The present reaction system favors the water gas shift reac-

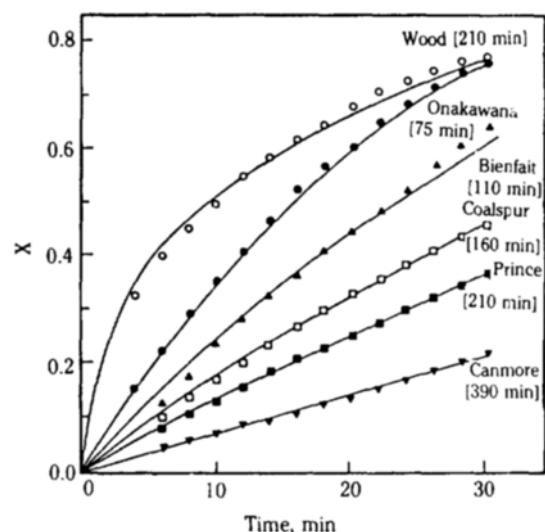


Fig. 6. A comparison of the model and experimental data on carbon conversion with time.

tion based on the chemical composition of the product gas from the gasification.

NOMENCLATURE

c	: carbon weight [g]
C_{so}	: initial concentration of carbon [mol/cm ³]
K	: specific velocity per reaction surface [mol cm ⁻² atm ⁻ⁿ min ⁻¹]
P	: pressure [atm]
r	: mean radius of the particles [cm]
R	: maximum reactivity [g/h/g]
t	: time [s]
t^*	: time for complete conversion [s]
W	: initial mass of coal sample [g]
X	: carbon conversion fraction

REFERENCES

1. Fung, D.P.C.: *Fuel*, **61**, 139 (1982).
2. Fung, D.P.C. and Kim, S.D.: *Fuel*, **62**, 1337 (1983).
3. Fung, D.P.C.: *Chemistry in Canada*, **32**, 25 (1981).
4. Fung, D.P.C. and Kim, S.D.: *Fuel*, **63**, 1197 (1984).
5. Ng, S.H., Fung, D.P.C. and Kim, S.D.: *Fuel*, **67**, 700 (1988).
6. Kwon, T.W., Kim, S.D. and Fung, D.P.C.: *Fuel*, **67**, 530 (1988).
7. Fung, D.P.C. and Channing, M.W.: *J. Chromat.*

Sci., **20**, 188 (1982).

- 8. Kwon, T.W., Kim, J.R., Kim, S.D. and Park, W.H.: *Fuel*, **68**, 416 (1989).
- 9. Solano, A.L., Mahajan, Om. P. and Walker, P.L. Jr.: *Fuel*, **58**, 32 (1979).
- 10. Hippo, E. and Walker, P.L. Jr.: *Fuel*, **54**, 245 (1975).
- 11. Jenkins, R.G., Nandi, S.P. and Walker, P.L.Jr.: *Fuel*, **52**, 288 (1973).
- 12. Dutta, S., Wen, C.Y. and Belt, R.J.: *Ind. Eng. Chem. Process Des. Dev.*, **16**, 31 (1977).
- 13. Wen, C.Y.: *Ind. Eng. Chem.*, **60**, 34 (1968).
- 14. Jensen, G.A.: *Ind. Eng. Chem. Process Des. Dev.*, **14**, 308 (1975).
- 15. Schmal, M., Montelvo, J.L.F. and Castellan, J.L.: *Ind. Eng. Chem. Process Des. Dev.*, **21**, 256 (1985).