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Gas Yields from Coal Devolatilization in a Bench-Scale Fluidized Bed Reactor

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Abstract−Devolatilization behavior of Australian bituminous coal-gasification was determined in a 0.1 m diameter fluidized bed at 650-900 °C. To predict gas yields from devolatilization, several correlations reported for gas yields were evaluated with the present experimental data. The correlation of Goyal and Rehmat [1993] was found to be good one. Also, a correlation for the product gas yields has been proposed from devolatilization of bituminous coals as a linear function of temperature with constants from the experiment. The experimental yields of product gas show good agreement with the values calculated by the proposed correlation.

Key words: Coal, Gasification, Pyrolysis, Devolatilization, Fluidized Bed

INTRODUCTION

Since a significant amount of product gas originates from devolatilization of coal in the coal gasification process, devolatilization characteristics of feed coal should be determined to design or simulate a coal gasification system. The property of devolatilization product (gas, tar, char and other material) is a function of the structure and composition of the coal as well as the reaction condition (heating rate, residence time, temperature, pressure, gas atmosphere) [Fung and Kim, 1990]. In many gasification processes, coal particles are heated at higher rates. It has been reported that the heating rate in fluidized beds is on the order of 10^4 Ks^{-1} [Tyler, 1979]. The overall weight loss due to devolatilization of coal is characterized by a rapid initial release of about 80-90% of volatiles followed by the slow release of the remaining 10-20%. The early release primarily consists of tar, aliphatic, CO_2, and H_2O, and includes the largest fraction of volatile matter, while the later release includes mainly CO and H_2, with very small amounts of HCN, benzene, etc. A number of correlations have been proposed to predict volatile yields in their specific gasification systems [Loison and Chauvin, 1964; Tsuji and Watkinson, 1990; Gururajan et al., 1992; Goyal and Rehmat, 1993; Lee et al., 1997, 2000]. However, no general correlation is available to predict gas yield for various coal types and pyrolysis conditions. Therefore, a general correlation to predict the gas yields from devolatilization is needed for the design or simulation of coal gasification processes. To find a better correlation for gas yield from devolatilization, the reported correlations have been evaluated and compared with the present experimental data. In addition, our own empirical correlation is proposed.

GAS YIELDS FROM DEVOLATILIZATION

Goyal and Rehmat [1993] presented the empirical correlations for yield and compositions of tar from carbonization of bituminous coals in a fluidized bed reactor as a function of reaction temperature as

$$X_{tar} = -4.95\times10^{-4}\ T + 77.4\times10^{-2} \quad (1)$$

where T in Kelvin, X_{tar} is fraction of feed carbon converted to tar, kg-atom C/kg-atom C in feed. As the temperature increases, tar yield increases up to a maximum value, after which it decreases because of the secondary reaction of tar cracking. Thus, it can be assumed that a certain fraction of tar undergoes partial combustion/decomposition instantaneously according to the following stoichiometric relation:

$$C_\nu H_\alpha O_\beta S_\gamma N_\delta + \frac{1}{2}[\nu - \beta]O_2$$
$$= \gamma H_2S + \delta NH_3 + \nu CO + \frac{1}{2}(\alpha - 2\gamma - 3\delta)H_2 \quad (2)$$

It is assumed that tar is uniformly cracked, hence the composition of remaining tar is unchanged. The fraction of tar cracked to gas may be used as an adjustable parameter for prediction of tar yield. This fraction depends on temperature, pressure, and the presence of limestone and oxygen. The fraction of tar cracked to gas is usually 0.4-0.6 [Song and Watkinson, 2000]. The effect of pressure on product gas yields has been investigated recently [Yun and Lee, 1999]

Goyal and Rehmat [1993] proposed the conversion of oxygen in coal to H_2O, CO, and CO_2 in pyrolysis as

$$Y_{H_2O} = 0.375 \quad (3)$$

$$Y_{CO} = 0.283 \quad (4)$$

$$Y_{CO_2} = 0.167 - 0.0017/(O/C) \quad (5)$$

where Y_{H_2O}, Y_{CO}, Y_{CO_2} are fraction of feed coal oxygen converted to H_2O, CO, and CO_2, kg-atom O/kg-atom O in feed coal. O/C= atomic ratio of O to C in feed coal, respectively. The yields of methane and ethylene are a function of temperature and available hydrogen, where available hydrogen is the excess over that required

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for water formation in Eq. (3) as

$$H_{avail}=(H/C)-2(H_2O/C) \quad (6)$$

where H/C is atomic ratio of H to C in coal, H_2O/C is water yield, kg-mol H_2O/kg-atom C in coal. The methane yields is expressed as

$$Y_{CH_4}=0.085H_{avail}+7.65\times10^{-5}\,T-0.1152 \quad (7)$$

where Y_{CH_4} is fraction of feed coal carbon converted to CH_4, kg-atom C/kg-atom C in feed. Although they also proposed a relation for C_{2+} gases (hydrocarbon larger than ethane), C_{2+} gas yields are neglected in the present study because their contents are usually very small. The hydrogen and nitrogen in the product gas can be determined by elemental balance around the system; and the char yield can be determined by carbon balance around the system.

Loison and Chauvin [1964] proposed the following correlations to estimate mass fractions of the most important gaseous products in coal pyrolysis. Their correlations require only an approximate analysis of coal, while they do not account for the temperature effects.

$$x_{H_2}=0.157-0.868x_{MV}+1.388x_{MV}^2$$
$$x_{CO}=0.428-2.653x_{MV}+4.845x_{MV}^2$$
$$x_{H_2O}=0.409-2.389x_{MV}+4.554x_{MV}^2$$
$$x_{CH_4}=0.201-0.469x_{MV}+0.241x_{MV}^2$$
$$x_{CO_2}=0.135-0.900x_{MV}+1.906x_{MV}^2$$
$$x_{tar}=-0.325+7.279x_{MV}-12.880x_{MV}^2 \quad (8)$$

where, x_{MV}=the mass fraction of volatile matter in coal on a daf (dry and ash free) basis, x_i=mass fraction of i in the products of pyrolysis, kg/kg.

On the other hand, a number of correlations have been given as function of temperature like

$$M_i/M_{daf}=A_i+B_iT \quad (9)$$

where M_i is the devolatilization yield of species i, kg/h, and M_{daf} is the dry ash free coal feed rate, kg/h. Ma et al. [1989] measured the evolution rate of gases including hydrogen sulfide in a pilot-scale fluid bed coal gasifier and correlated the various gas yields in devolatilization of sub-bituminous coal and lignite. Tsuji and Watkinson [1990] gave their empirical relationship from the pyrolysis of a Canadian coal (Highvale sub-bituminous), in which most gas is given as function of temperature. Lee at al. [1997] and Kim [2000] also measured the gas products in relatively large fluidized beds and correlated their gas yields as a function of temperature as of Eq. (9).

EXPERIMENTAL

A schematic diagram of the bench-scale fluidized bed reactor is shown in Fig. 1. The stainless steel reactor (0.1 m-i.d.) is enclosed by an electric heater of 6 kW and a glass-wool refractory. The proximate and ultimate analyses of Australian bituminous coal are given in Table 1. This coal has very low sulfur content and large amount of SiO_2 in its ash. The coal ground to –6+16 mesh size (average diameter of 2.0 mm) was fed through a screw feeder into the reactor at a flow rate of 1-2 kg/h, depending on the reactor operating condition. It was found that some amount of elutriated fine originates from the screw feeder, so the size distribution of coal fed to the bed will differ from that of coal in the hopper. Preheated air/nitrogen mixture gas is fed through a distributor plate to provide uniform fluidization (0.5-0.8 m/s) of inert sand particles of 0.35 mm diameter in average. Nitrogen to air ratio has been varied a little. Sand particles of 0.3-0.5 kg were loaded in the bed initially and the bed was heated up to ignition temperature of the coal by the ex-

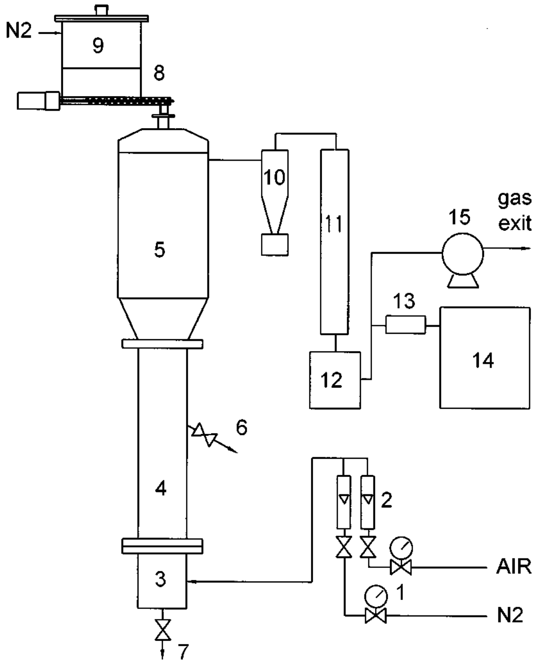

Fig. 1. Schematic diagram of fluidized bed coal pyrolyzer.

1. Pressure regulator
2. Valve and flow-meter
3. Gas plenum
4. Fluidized bed
5. Freeboard
6. Overflow
7. Bed solid drain
8. Screw feeder
9. Coal hopper
10. Cyclone
11. Condenser
12. A collector
13. Dust filter
14. Gas chromatography
15. I.D. fan

Table 1. Analyses of Australian bituminous coals (as received basis)

	wt%		wt%
Ultimate analysis		Ash composition	
Carbon	72.3	SiO_2	65.50
Hydrogen	4.3	Fe_2O_3	2.24
Nitrogen	0.4	CaO	0.19
Sulfur	0.2	P_2O_5	0.30
Oxygen	11.7	MgO	0.35
		TiO_2	1.50
Proximate analysis		Al_2O_3	27.94
Volatile	27.4	Na_2O	0.43
Fixed carbon	57.2	K_2O	1.40
Moisture	7.1	MnO	0.02
Ash	8.3	Cr_2O_3	-

Table 2. The experimental variables and ranges

Variable	Range
Coal feed rate (kg/h)	1-2
Coal diameter (mm)	1-5 (average=2.0)
Bed temperature (°C)	650-900
Air flow rate (m^3/hr)	0-1
Nitrogen flow rate (kg/hr)	0.05-1.00
Fluidizing gas, U_g/U_{mf}	2

ternal electric heater. Thereafter, coal was fed to the reactor to maintain a desired reaction temperature. The temperatures, pressures and flow rates of various parts in the system were monitored continuously through a recorder and a data acquisition board. When the reactor reached steady state, a portion of product gas was continuously sent to an HP5890A gas chromatograph through a dust filter and a mini-pump. A gas sample of 0.25 ml was intermittently injected into the column of the gas chromatograph by help of an auto-injection unit for analysis of the gas composition. Both 'Molecular sieve 5A' and 'Carboxen 1004' column have been used for the gas analysis. The content of moisture, carbon, and ash was determined in the bed material and cyclone ash after completion of one reaction run. The experimental variables and their ranges used in this study are summarized in Table 2.

RESULTS AND DISCUSSION

Devolatilization of coal was carried out in a fluidized bed reactor at 650-900 °C. The nitrogen to air ratio was varied a little to simulate the condition of a real coal gasifier. Most runs have been carried out with nitrogen content of 50%. One result for the product gas composition is represented in Fig. 2. The symbols are raw experimental data and they seem to be largely scattered. On the other hand, the composition of product gas has been calculated by both the correlations of Goyal and Rehmat [1993] and Tsuji and Watkinson [1990]. For calculation purposes, the tar is assumed to be formed by Eq. (1) and after that 50% of tar is being cracked according to Eq. (2). The calculated predictions are also shown in the figure. As can be seen in the figure, hydrogen production is below 10 vol% in the present fluidized bed pyrolysis system. This is much lower than the predicted value from both of the above correlations. Also the yield of carbon monoxide shows lower than the predicted value. These phenomena could be due to the dilution of nitrogen feed gas (almost 50%). Many other investigators have used pure nitrogen carrier gas for the pyrolysis of coal in their laboratory scale fluidized bed or fixed beds. On the other hand, the predictions are not bad for the content of methane and carbon dioxide. It can be said from this comparison that it will be somewhat difficult to find very appropriate correlation from literature to describe one's product yield from devolatilization of coal.

The various correlations in the literature for the devolatilization gas yields have been evaluated with the present experimental data. The coal type and pyrolysis conditions of each correlation have been summarized in Table 3. The prediction ability of those correlations has been tested with the data of product gas at 50% nitrogen feed, and the result is represented in Fig. 3 and Fig. 4. All the correlations in Fig. 3 [Ma et al., 1989; Lee et al., 1997; Kim, 2000] are given as a linear function of temperature like Eq. (9). Although they used similar scale fluidized bed reactors, the proposed constants are very different for each other. Such differences may be from the corresponding coal type and their specific devolatilization system-operating conditions like feed gas concentration. Therefore, it can be said that the correlations in Fig. 3 are somewhat specific to coal type and etc. not general. Furthermore, they could not predict the present experimental data well as represented in Fig. 4. The experimental data of gas yields are relatively low compared to the corre-

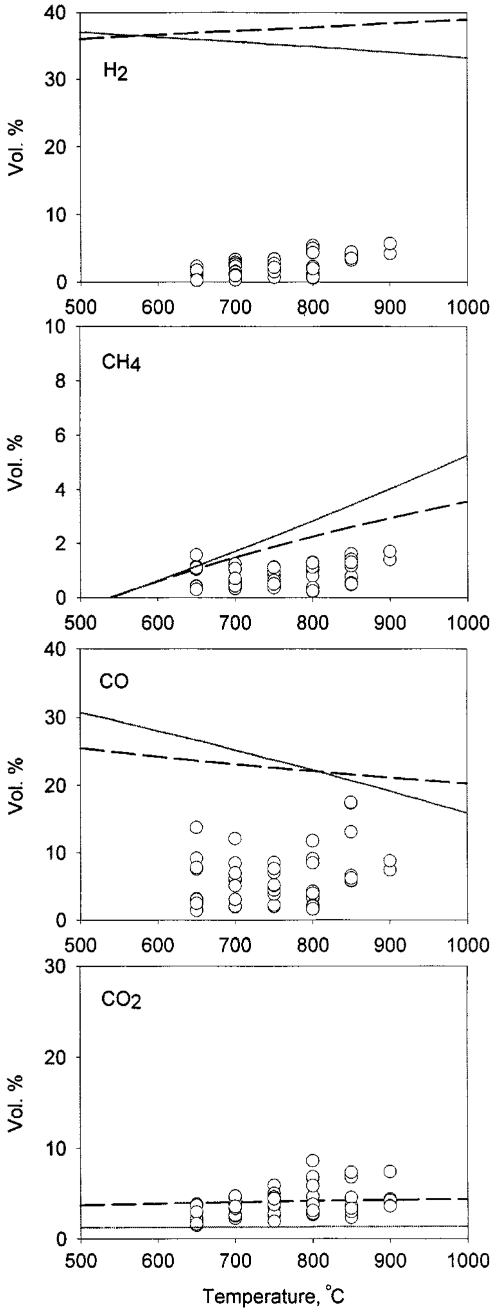

Fig. 2. The model prediction and experimental data for the gas composition in the coal devolatilization (solid line=Goyal & Rehmat; dashed=Tsuji & Watkinson, coal feed=1.5 kg/h, nitrogen feed=50 vol%, extent of tar cracking=50%).

Table 3. The correlations for the gas yield from coal devolatilization

Authors	Coal	Temp., °C	Feed gas	Reactor	Correlation	Parameter*
Loison and Chauvin [1964]	Various	-	N_2	-	Eq. (8)	C
Tsuji and Watkinson [1990]	Canadian Sub-B	-	-	Spouted bed	Similar to Eq. (9)	C, T
Goyal and Rehmat [1993]	Bituminous, Lignite	760-870	N_2/air	Pilot carbonizer**	Eq. (3)-(7)	C, T
Ma et al. [1989]	Sub-B, Lignite	744-1008	N_2	0.15 m i. d. fluid bed	Eq. (9)	T
Lee et al. [1997]	Australian Sub-B	750-900	N_2	0.1 m i.d. fluid bed	Eq. (9)	T
Kim [2000]	Senwha Bituminous	750-900	N_2/air	0.1 m i.d. fluid bed	Eq. (9)	T
This study	Australian Bituminous	700-900	N_2/air	0.1 m i.d. fluid bed	Eq. (9)	T

*C : coal properties, T : temperature.

**Pressurized fluid bed, coal feed rate=500 kg/h

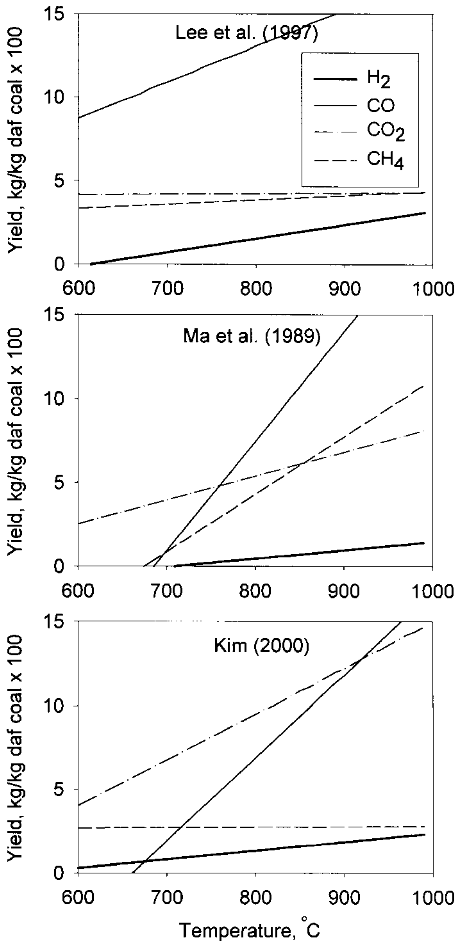

Fig. 3. The prediction of gas yields from coal devolatilization by several correlations (Australian bituminous coal, coal feed= 1.5 kg/h, nitrogen feed=50 vol%, extent of tar cracking= 50%).

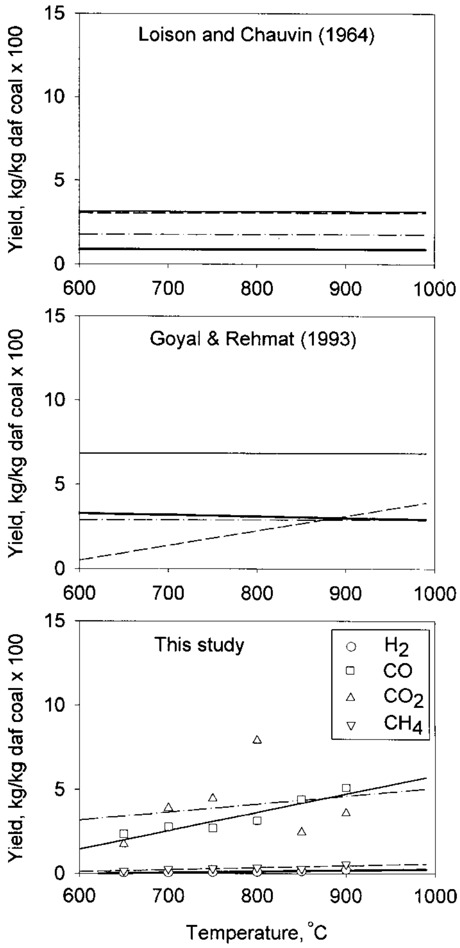

Fig. 4. The prediction of gas yields from coal devolatilization by several correlations (conditions are same in Fig. 3, symbols are experimental data).

lations in Fig. 3.

In this study, the experimental data of gas yields can be readily represented as a form of Eq. (9), where the constants A_i and B_i for the present Australian bituminous coal have been determined through linear regression analysis. The resultant correlation of Eq. (10) is in very good accord with the experimental data as seen in Fig. 4.

$$M_{H_2}/M_{daf}=-6.052\times10^{-3}+6.763\times10^{-6}\,T$$

$$M_{CO}/M_{daf}=-0.053+6.763\times10^{-6}\,T$$

$$M_{CO_2}/M_{daf}=-9.627\times10^{-3}+4.749\times10^{-5}\,T$$

$$M_{CH_4}/M_{daf}=-9.169\times10^{-3}+1.178\times10^{-5}\,T \qquad (10)$$

However, a more general relationship for product yields will be needed in order to simulate or design a coal gasification reactor. Thus, two other correlations have been evaluated which have some generality for coal type and the result is shown in Fig. 4. The correlation of Loison and Chauvin [1964] has been used widely since they require only approximate analysis of coal. One disadvantage is that they do not account for the temperature effects - they give constant gas yields for a given coal regardless of devolatilization temperature as can be seen in the plot. However, their predicted value is much better compared to those in Fig. 3. Goyal and Rehmat [1993] reported that gas species from coal pyrolysis are independent of temperature, except for methane as shown in the figure. Their prediction seems to be well in accord with the present experimental data. The relatively higher predictions of the correlations in Fig. 3 may be attributed to the difference in feed gas concentration: This study and Goyal and Rehmat [1993] used air-nitrogen mixture, whereas Lee et al. [1997] and Kim [2000] used pure nitrogen feed gas. In view of modeling purpose, the correlation of Goyal and Rehmat [1993] is most appropriate because they also give the relationship for tar formation and composition simultaneously.

CONCLUSIONS

Devolatilization of Australian bituminous coal was carried out in a fluidized bed reactor. The yields of most gas components increased with temperature, but the mode of increase differed for each gas. The various reported correlations for the product gas yields have been evaluated with the experimental data. The best correlation describes the gas yield as a linear function of temperature with constants from experiment. The correlation of Goyal and Rehmat [1993] may be used to predict variables in devolatilization stage in a gasification process for bituminous coal.

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