

## REACTIVITY OF COAL-STEAM GASIFICATION AT HIGH TEMPERATURE

In-Chul LEE

Fossil Fuel Laboratory, Korea Institute of Energy and Resources, 71-2 Jang-dong, Jung-gu, Daejon 300-32

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**Abstract**—Reactivities and surface areas of coals which were gasified in steam at high temperatures were determined. Reactivities were measured using a TGA and CO<sub>2</sub> adsorption method was used to measure surface areas. The reactivities of coal with steam decrease monotonically as conversion increase while char-steam reactions show a maximum between 5 to 15% conversion. Initial reactivity of coal-steam reaction is much higher than char-steam reaction. Surface areas also decrease as conversion increase. The reactivity change was attributed to variation in surface area.

### INTRODUCTION

Coal gasification mainly involves two steps; initial rapid devolatilization of coal to produce char, tar and gases and subsequent gasification of the char generated. Char gasification, being the slow step, usually controls the overall conversion process, and a better understanding of the kinetics of this step is essential to the optimal design and effective operation of a coal gasifier.

It is well known that devolatilization condition strongly affects the reactivity of char and hence the overall performance of a coal gasifier. In an entrained bed reactor, coal particles in a gasifier undergo devolatilization and gasification continuously under more or less the same condition, at high temperature. Yet most of char gasification data reported in the literature were obtained under gasification conditions that were quite different from the devolatilization conditions under which the chars were prepared. Chars were prepared at slow heating rate, and their gasification temperature was below 1000°C.

When coal particles are rapidly heated, as in a gasifier, chemical and physical properties were changed radically. The resultant properties of the chars are important in determining their subsequent gasification process. Depending on the gasification condition and other factors, the intraparticle diffusional resistance caused by pore structure may become rate limiting. Hence the reactivity of coals and their chars during gasification is closely related to their microstructures.

So the purpose of this work is to gain a better understanding of char-steam reaction under conditions similar to that existed in a number of commercial coal

gasification processes. The reactivities of coals in steam at high temperature were measured. Also surface areas of chars were measured to relate reactivity data.

### EXPERIMENTAL

#### 1. Samples

New Mexico bituminous coal (PSOC 309), Washington subbituminous coal (PSOC 240), and North Dakota lignite (PSOC 1423P), all provided by the Penn. State Coal Bank, were used in this work. The proximate and ultimate analyses of these coals are shown in Table 1.

#### 2. Apparatus

A thermogravimetric analyzer (TGA) which was described by Sears et al. [1] was used in this study. A schematic diagram is shown in Fig. 1. It consisted of a TGA unit, a nitrogen supply line and a steam generator.

The nitrogen supply line included, among other components, a 1" stainless steel pipe which was filled with copper turners and kept at 450°C to remove trace amount of oxygen in the nitrogen gas. It was also connected to a rotameter and a needle valve to measure the nitrogen flow rate to the TGA unit.

An electronic microbalance for weight loss measurement was housed in the upper chamber of the TGA unit where the temperature was maintained below 25°C. The lower chamber of the TGA unit consisted of four electric heating elements supported by zirconia insulating material. The power to the heating elements was controlled by a transformer which was capable of rapidly increasing the temperature of the

**Table 1. Characteristics of coals used.**

|  | North Dakota<br>Lignite<br>(PSOC 1423P) | Washington<br>Subbituminous<br>(PSOC 240) | New Mexico<br>Bituminous<br>(PSOC 309) |
|--|---|---|--|
| <b>Proximate Analysis (wt%, as received)</b> |   |   |  |
| Moisture                                     | 29.53                                   | 18.21                                     | 10.09                                  |
| Ash  | 5.75                                    | 18.39                                     | 18.32                                  |
| Volatile Matter                              | 31.76                                   | 32.00                                     | 33.80                                  |
| Fixed Carbon                                 | 32.96                                   | 31.40                                     | 37.79                                  |
| <b>Ultimate Analysis (wt%, DAF)</b>          |   |   |  |
| Carbon                                       | 69.80                                   | 72.59                                     | 77.08                                  |
| Hydrogen                                     | 4.41                                    | 5.79                                      | 5.75                                   |
| Nitrogen                                     | 1.35                                    | 1.41                                      | 1.70                                   |
| Sulfur                                       | 1.14                                    | 1.30                                      | 1.02                                   |
| Chlorine                                     | 0.00                                    | 0.01                                      | 0.00                                   |
| Oxygen (Diff.)                               | 23.30                                   | 18.90                                     | 14.46                                  |

reaction zone from 700°C to 1600°C. The temperature in the reaction zone was monitored by a Pt/Pt-13%Rh thermocouple. The temperatures at various points inside the TGA unit were also monitored with R-type thermocouples.

The steam generator consisted of a distilled water supply tank, a micrometering pump to provide a constant steam flow rate, a 1" stainless steel pipe steam generating unit filled with ceramic beads to generate steam, a furnace with a temperature controller and a steam regulating valve.

A strip chart recorder and a computer data acquisition system was used to record sample weight change during gasification.

### 3. Reactivity Measurement

For each run, 100mg of coal sample was first dried

in air at 105°C for 2 hours in a separate oven before being transferred to a sample pan made of platinum mesh. The TGA with its sample pan in the upper most position where the temperature was kept below 150°C, was then sealed and purged with 2 liter/min (STP) of nitrogen to remove oxygen. After purging for more than 30 minutes, steam was added. Once uniform steam concentration throughout the reaction zone was assured the sample was lowered down by a micromotor to the reaction zone at the bottom of the TGA. The weight loss of the sample due to devolatilization and/or gasification was then recorded by the strip chart recorder and the interfacing microcomputer.

For comparison, reactivities of chars which were prepared in nitrogen were also studied. In this case, char was exposed to devolatilization temperature which is same as gasification temperature in nitrogen for one minute and lifted up to the upper position. As above, when steam concentration is uniform, the sample was re-lowered to the reaction zone to measure the weight loss.

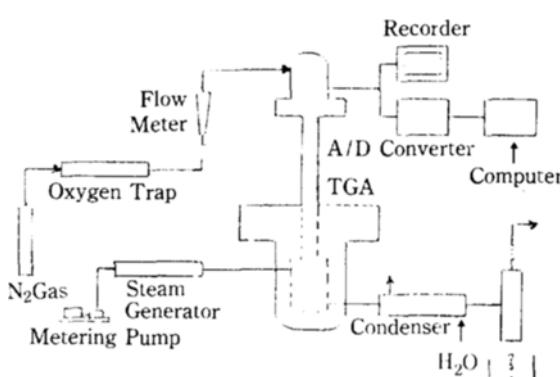
The chars which were obtained in nitrogen are called "Nitrogen chars" to distinguish them from "In-situ chars", which were obtained by devolatilization in steam.

The reactivity of char  $R_c$ , i.e., apparent gasification reaction rate, is defined here according to the following equation

$$R_c = dX/dt = -1/W_o \cdot dW/dt \quad (1)$$

where  $W$  is the instantaneous weight of residual carbon available in char, and  $W$  is equal to  $W_o$  at  $t=0$ .

The effect of coal particle size on the gasification



**Fig. 1. Detailed illustration of the high temperature/pressure TGA system used.**

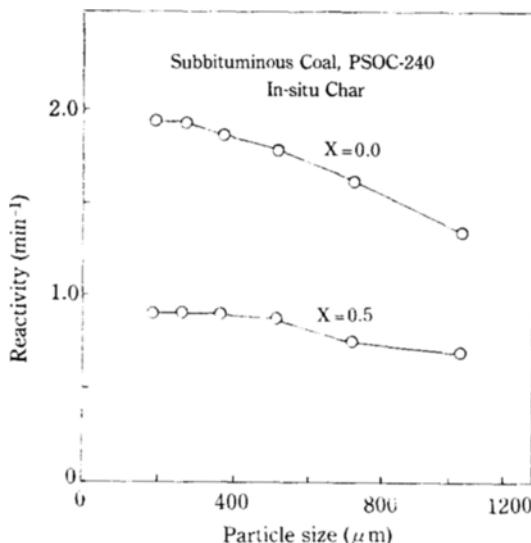


Fig. 2. Reactivity versus particle size at zero and 50% conversions for nitrogen char prepared from subbituminous coal (PSOC-240).

rate was first studied. The average particle size was reduced from 1000  $\mu\text{m}$  to see the particle size effect. A typical experimental results obtained is presented in Fig. 2. It can be seen that the initial and half-life reactivities increase as the mean particle size is reduced from 1000  $\mu\text{m}$ , and then level off at 178  $\mu\text{m}$ . This result suggests that the coal particles of 178  $\mu\text{m}$  used in this work are small enough to be considered free of major transport resistances. So in this study, -70 + 100 mesh size coal was used as sample. All experiments were conducted at 76 mole% steam concentration.

#### 4. Surface Area Measurement

Surface areas of the three coals and their chars were determined by gravimetric adsorption method using  $\text{CO}_2$  as an adsorbate. The apparatus for measuring  $\text{CO}_2$  adsorption gravimetrically consists of a electronic microbalance, a vacuum pump, a U-tube manometer and two pressure detectors. The overall system provides the capability to continuously record the weight gain from adsorption of  $\text{CO}_2$ .

Approximately 300mg of sample were used for each measurement. The sample was first outgassed to remove moisture which might otherwise block entrances to some micropores. This was done by keeping the sample overnight at approximately 110°C and 0.001 torr until weight loss became negligible.

After degassing, the system was allowed to cool to 25°C before starting a series of adsorption runs, each conducted at 25°C and at different pressure range from 60 to 700 torr. At each  $\text{CO}_2$  pressure, the weight

gain curve of sample was continuously recorded in a strip chart recorder until adsorption equilibrium was reached. Depending on the type of coal involved, the time required to reach equilibrium varied. For lignite coal, 8-10 hours were normally needed for both the coal and its chars. On the other hand, it took about 24 hours for the subbituminous coal but only 2-3 hours for its chars. For the bituminous coal, the times needed were only 4-5 hours for coal but about 24 hours for chars.

Specific surface areas were determined by means of Dubinin-Polanyi (D-P) equation [2-5]:

$$\ln W = \ln W_o - D \ln n(P/P_o) \quad (2)$$

where  $W$  is the weight of  $\text{CO}_2$  adsorbed per unit weight of sample at pressure  $P$ .  $P_o$  is the vapor pressure of  $\text{CO}_2$ , whose value is 63.5 atm at 25°C [5], and the corresponding  $W$  is designed as  $W_o$ .  $D$  and  $n$  are constants whose values are determined from experimental data. For most of the cases,  $n$  is equal to 2.0. The molecular cross-sectional area of  $\text{CO}_2$  at 25°C was taken as 25.3  $\text{\AA}^2$  [5]. The relative pressure employed in all measurements were less than 0.015 to avoid capillary condensation [6].

## RESULTS AND DISCUSSION

Reactivities for six different chars at five temperatures from 1000 to 1400°C as function of conversion are illustrated in Fig. 3. Obviously, for both types of chars, the reactivities of chars increase as gasification temperature is raised. The difference in kinetic behavior between in-situ and nitrogen chars is clearly demonstrated in this figure. For nitrogen chars the gasification reactions proceed slowly during the initial stage of gasification ( $X < 0.15$ ) and their reactivities first increase, pass through a maximum at conversions between 5 to 15% and then gradually decline. On the other hand, for in-situ chars, initially the gasification reactions proceed more rapidly than the nitrogen char, but their reactivities decrease monotonically throughout the whole period of gasification. It is generally believed that prolonged heat treatment destroyed the active sites in chars rendering them less reactive. On the contrary, chars formed by rapid heating at high temperatures are very reactive perhaps due to a more open pore structure thus created. The fact that the in-situ char has a much higher reactivity than that of the nitrogen char, also indicates that, annealing time during devolatilization/gasification can significantly affect char reactivity. As mentioned before, in-situ chars were exposed to the reaction time only, but nitrogen chars were experienced one minute more in addition to the reaction time. So nitrogen chars which exper-

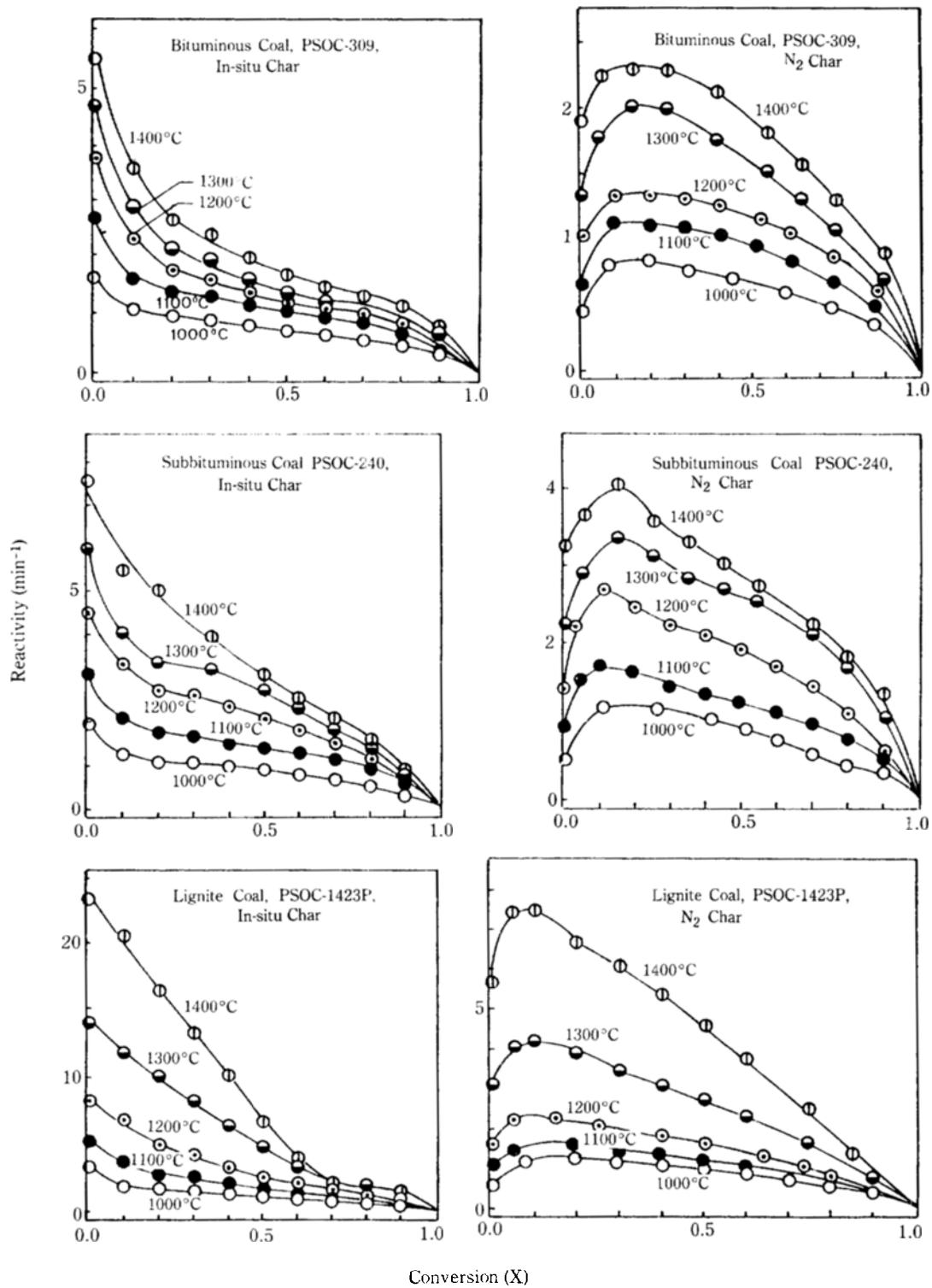


Fig. 3. Reactivity versus conversion for in-situ and nitrogen chars of three coals (bituminous, PSOC-309; subbituminous, PSOC-240; lignite, PSOC-1423P).

**Table 2. Comparison of initial reactivities and reactivities at X=0.5 of coal chars.**

(-70 + 100 mesh coal, 76 mole% steam, 1 atm)

| Temperature<br>(°C) | In-situ Char                          |   | N <sub>2</sub> Char                   |   | $\frac{(R_c)_{0,i}}{(R_c)_{0,N}}$ | $\frac{(R_c)_{0.5,i}}{(R_c)_{0.5,N}}$ |
|---------------------|---------------------------------------|---|---------------------------------------|---|-----------------------------------|---------------------------------------|
|                     | $(R_c)_{0,i}$<br>(min <sup>-1</sup> ) | $(R_c)_{0.5,i}$<br>(min <sup>-1</sup> ) | $(R_c)_{0,N}$<br>(min <sup>-1</sup> ) | $(R_c)_{0.5,N}$<br>(min <sup>-1</sup> ) |                                   |                                       |
| <b>PSOC 309</b>     |                                       |   |                                       |   |                                   |                                       |
| 1000°C              | 1.59                                  | 0.70                                    | 0.46                                  | 0.65                                    | 3.44                              | 1.07                                  |
| 1100°C              | 2.66                                  | 1.04                                    | 0.65                                  | 0.95                                    | 4.13                              | 1.10                                  |
| 1200°C              | 3.77                                  | 1.21                                    | 1.01                                  | 1.17                                    | 3.73                              | 1.04                                  |
| 1300°C              | 4.70                                  | 1.47                                    | 1.32                                  | 1.61                                    | 3.55                              | 0.87                                  |
| 1400°C              | 5.48                                  | 1.64                                    | 1.90                                  | 1.91                                    | 2.89                              | 0.86                                  |
| <b>PSOC 240</b>     |                                       |   |                                       |   |                                   |                                       |
| 1000°C              | 1.93                                  | 0.90                                    | 0.50                                  | 0.92                                    | 3.85                              | 0.98                                  |
| 1100°C              | 3.06                                  | 1.39                                    | 0.91                                  | 1.25                                    | 3.38                              | 1.11                                  |
| 1200°C              | 4.51                                  | 2.08                                    | 1.40                                  | 1.92                                    | 3.21                              | 1.09                                  |
| 1300°C              | 5.97                                  | 2.72                                    | 2.25                                  | 2.61                                    | 2.66                              | 1.04                                  |
| 1400°C              | 7.56                                  | 3.09                                    | 3.25                                  | 2.91                                    | 2.33                              | 1.06                                  |
| <b>PSOC 1423P</b>   |                                       |   |                                       |   |                                   |                                       |
| 1000°C              | 3.41                                  | 1.16                                    | 0.59                                  | 1.01                                    | 5.78                              | 1.15                                  |
| 1100°C              | 5.29                                  | 1.86                                    | 1.09                                  | 1.24                                    | 4.85                              | 1.51                                  |
| 1200°C              | 8.33                                  | 2.65                                    | 1.66                                  | 1.67                                    | 5.03                              | 1.58                                  |
| 1300°C              | 14.0                                  | 4.93                                    | 3.18                                  | 2.77                                    | 4.39                              | 1.78                                  |
| 1400°C              | 23.3                                  | 6.81                                    | 5.68                                  | 4.67                                    | 4.17                              | 1.46                                  |

perienced longer heat treatment were less reactive than in-situ chars.

Comparison of initial reactivities ( $R_c)_0$  and reactivities at X=0.5,  $(R_c)_{0.5}$  of both in-situ and nitrogen chars at various gasification temperatures for the three coals investigated are presented in Table 2. It can be seen, the initial reactivities of in-situ chars are 2 to 4 times higher than that of corresponding nitrogen chars of New Mexico bituminous coal (PSOC 309) and Washington subbituminous coal (PSOC 240) whereas for

North Dakota lignite (PSOC 1423P) increase in reactivity as high as 6 times. Tamhanker et al. [7] have also observed that the reactivities of continuously reacted North Dakota lignite chars (PSOC 246) are 2 to 10 times higher than that of the chars prepared separately under the inert atmosphere. On the other hand, the difference in  $(R_c)_{0.5}$  are not as significant. The activation energy and the pre-exponential factor obtained from the Arrhenius equation are presented in Table 3. It can be seen from this table that the activation ener-

**Table 3. Activation energies and frequency factors of char gasification reaction.**

(-70 + 100 mesh coal, 76 mole% steam, 1 atm)

| Parent<br>coal | Type of<br>char     | $(R_c)_0$                     |                    | $(R_c)_{0.5}$                 |                    |
|----------------|---------------------|-------------------------------|--------------------|-------------------------------|--------------------|
|                |                     | $k_p$<br>(min <sup>-1</sup> ) | $E_a$<br>(kJ/mole) | $k_p$<br>(min <sup>-1</sup> ) | $E_a$<br>(kJ/mole) |
| PSOC 309       |                     | 344                           | 56.82              | 24                            | 36.51              |
| PSOC 240       | In-situ             | 611                           | 60.63              | 207                           | 57.20              |
| PSOC 1423P     |                     | 9300                          | 84.67              | 2031                          | 79.66              |
| PSOC 309       |                     | 165                           | 62.63              | 60                            | 47.64              |
| PSOC 240       | N <sub>2</sub> char | 1212                          | 82.40              | 152                           | 54.11              |
| PSOC 1423P     |                     | 6071                          | 98.52              | 499                           | 67.40              |

gies of types of char decrease as the carbon contents of their corresponding raw coals increase. This trend is consistent with that reported previously by Johnson [6]. The values of activation energy obtained in this work for both types of char are at lower end of all the activation energies reported previously.

Specific surface area data are shown in Fig. 4. In Fig. 4, specific surface areas decrease monotonically with temperature. This implies that, the decrease in specific surface area, as gasification proceeds, is mainly due to the collapsing of pore walls between neighboring micropores. The dependence of specific surface area on conversion, as observed here, is quite different from that by Toda [8] and Harper [9], who reported that specific surface area first increased, reaching a maximum and then decreased, as gasification proceeded. It is, however, worthwhile to point out that the chars used in those previous works were prepared separately in an inert atmosphere at a temperature which was either the same or lower than the gasification temperature. Hence one would expect that those chars, which experienced both heating and cooling before gasification started would have quite different microstructure compared to the in-situ chars used here. The variations in gasification reactivities with conversion

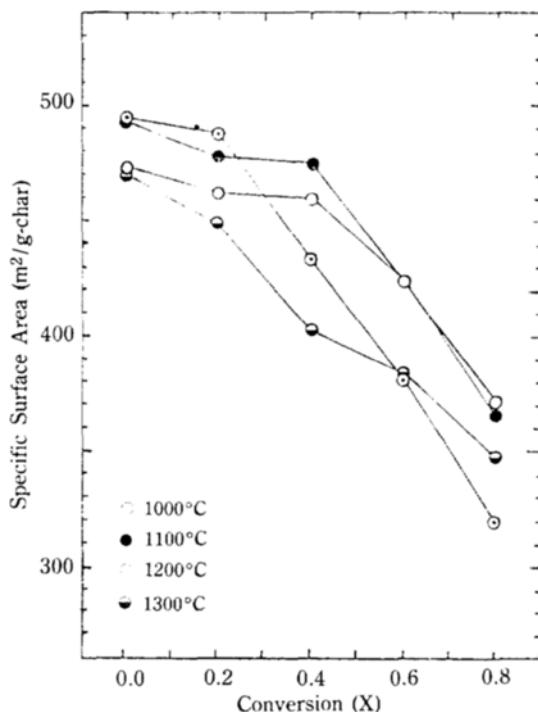


Fig. 4. Effect of conversion on the specific surface area of in-situ char prepared from subbituminous coal (PSOC-240).

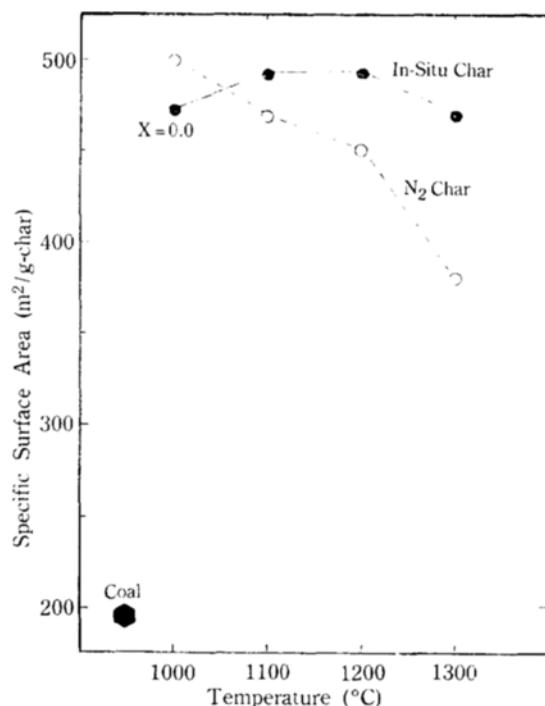


Fig. 5. Specific surface areas of nitrogen and in-situ chars versus devolatilization temperature --- subbituminous coal (PSOC-240).

have same tendency as surface area change with conversion. Thus, changes in reactivities of chars can be attributed to change in surface area.

Before proceeding to correlate the data of specific surface areas of in-situ chars with conversion, it is worthwhile to compare the values of the specific surface areas of in-situ chars at zero conversion with that of nitrogen chars. As shown in Fig. 5, both are higher than that of the original coal and in general both have the same order of magnitude, although overall the values associated with in-situ chars are larger. One possible explanation is that the blocking of micropores by free carbon produced by secondary decomposition of heavy tarry material is reduced in the case of in-situ chars because of its reaction with steam during devolatilization. One also notices from Fig. 5 that the specific surface areas of the in-situ chars at zero conversion are not as sensitive to variation in devolatilization temperature as that of the nitrogen chars. This is certainly a reflection of the significant effect of reactive steam, in addition to temperature, on the evolution of microstructure of in-situ char during devolatilization.

To develop appropriate correlations for the specific surface area data obtained in this work, the most suitable functional form to use is

$$S = S_o [1 + \phi \ln(1 - X)]^{1/2} \quad (3)$$

where  $S$  is surface area per gram of char (ash-containing basis),  $S_o$  is  $S$  at zero conversion and  $\phi$  is a constant. The parameters estimated from this equation are follows

| Temp. (°C) | $S_o$ | $\phi$ |
|------------|-------|--------|
| 1000       | 483   | 0.25   |
| 1100       | 501   | 0.29   |
| 1200       | 495   | 0.38   |
| 1300       | 449   | 0.26   |

They predicted the change of  $S$  with respect to conversion very well, with deviation from experimental data being less than  $\pm 5\%$  for all ranges of conversion considered. As shown in the above table, all the  $S_o$  estimated from the linear plots also appear to be close to that obtained experimentally.

## CONCLUSION

A significant feature of this work was that of devolatilization and gasification of coals in steam at very high temperatures, as opposed to most of the previous studies of devolatilizing coals first in the inert media and then measuring the reactivities of the remaining chars under totally different gasification environments.

The results obtained in this work indicate that the reactivities of the resulting in-situ chars are up to six times higher than that of the corresponding nitrogen chars. Furthermore, the reactivities of all the in-situ

chars decrease monotonically as carbon conversion of the chars increase, whereas maximum reactivities exist for nitrogen chars at carbon conversion less than 0.15. The decrease in reactivities was related to the surface areas which also decrease as conversion increase.

The activation energies of the in-situ chars obtained are in the range of 56-85 J/mole. As expected the values of the activation energy increase as the carbon content of the corresponding parent coals decrease.

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