INFLUENCE OF STEAM ON COAL DEVOLATILIZATION AND ON THE REACTIVITY OF THE RESULTING CHAR[1]

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ABSTRACT

Improved reactivity of the mild gasification char is highly desirable for the economic viability of a mild gasification process aimed at producing liquid fuel from coal by pyrolysis. In this study, it is demonstrated that devolatilization of coal in the presence of steam atmosphere increases pyrolysis volatile (and liquid) yield and produces a more reactive char. Devolatilization of coal was effected either in a thermogravimetric analyzer or in a slow heating rate organic devolatilization reactor (SHRODR). The chars prepared in steam have a lower oxygen chemisorption capacity than the chars prepared in helium. Fourier transform infra-red (FTIR) spectroscopic studies indicate that the steam char has a higher concentration of hydroxyl groups than the char prepared in He. This implies that pyrolysis of coal in steam may introduce some hydroxyl functional groups which may have a favorable influence during subsequent char gasification/combustion.

INTRODUCTION AND BACKGROUND

It is well known that gasification reactivity of coal char is a strong function of rank of parent coal and pyrolysis conditions used to generate the char (e.g., maximum heat-treatment-temperature, heating rate, and soak time at peak temperature). Numerous studies have been addressed on the influence of thermal history of pyrolysis and the role of the minerals and cations on the reactivity of the resulting char (1-12). However, relatively little attention has been received on the influence of gas atmosphere used during pyrolysis on the reactivity of the resulting char.

Sharma and coworkers (13) studied the low temperature (up to 650°C) pyrolysis of coal in argon, steam, and hydrogen under 1 to 66 atmosphere. Based on very limited studies, it was concluded that pyrolysis gas atmosphere or pressure had <u>no influence</u> on the reactivities of the resulting chars. Christsora and coworkers (14) studied the effect of pyrolysis atmosphere (argon, steam, and hydrogen) on the reactivity (in steam) of produced chars (900°C char) and observed that the

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presence of reactive gases (steam and hydrogen) did not affect the rates of reaction of product chars. It was suggested that the pressure of reactive gases (1 bar) during pyrolysis was too low to effect deeper penetration of the reactive gases into the char structure thus causing changes in the chemical and physical properties of chars that would otherwise affect the reactivity of char.

The purpose of this study is to investigate by means of systematic experiments the effect of steam on the pyrolysis weight loss of coals and on the reactivities of resulting chars. The hypothesis of this study is that pyrolysis of coal under steam atmosphere may introduce oxygen containing functional groups to the coal/char structures which may have positive contribution to the reactivity of char.

EXPERIMENTAL

The coals were devolatilized in a thermogravimetric analysis system (Dupont 1090 thermal analyzer) and in a slow heating rate organic devolatilization reactor (SHRODR) either in He or in steam/He mixture. For the devolatilization in the TGA system, steam was introduced to the TGA system by bubbling He through a filtered dish of a sealed saturator. The temperature of saturator was maintained at a constant temperature of 25°C. The saturation pressure of steam at room temperature is 3 kPa. For the devolatilization in the SHRODR, steam was introduced to the reactor by pumping water to the reactor at the rate of 0.2 cc/min. The analyses of coals used in this study are presented in Table 1. Wyodak coal was acid-washed with 0.1 N HCl solution according to the procedures described by Morgan, et al. (15) to remove exchangeable cations in the coal. The extract solution was analyzed by atomic absorption spectrometry. The exchangeable cation content of Wyodak coal were determined and given in Table 2.

Chemisorption was carried out at 155°C and 0.1 MPa O_2 for 15 h using the TGA. The oxygen chemisorption capacity (OCC) or the active surface area of chars (ASA) were calculated from the amount of oxygen chemisorbed on the chars. Isothermal char reactivities were determined using TGA at 400°C in 0.1 MPa O_2.

The reproducibilities of coal pyrolysis (devolatilization) and char reactivities determination in the TGA system can be seen in Figures 1a and 1b, respectively. It is obvious that the reproducibility of our experiments was very good.

RESULTS AND DISCUSSION

Effect of Steam on Pyrolysis Weight Loss of Coals

Tables 3 and 4 summarized the pyrolysis weight loss of Wyodak coal and Pittsburgh No. 8 coal during pyrolysis in He and steam (3 kPa) up to 650° and 950°C. Weight loss (both for temperature up to 650° to 950°C) is a function of coal rank. The weight loss of Wyodak coal (subbituminous coal) is higher than that for the Pittsburgh No. 8 coal (high volatile bituminous coal). The steam gasification process is thermodynamically favorable when the temperature is higher than 500°C. Table 3 shows that pyrolysis of coals in steam up to 650°C increases weight loss by 3.5 percent for Wyodak coal and 7.0 percent for Pittsburgh No. 8 coal. Wyodak coal contains relatively high concentration of exchangeable cations (Table 2) which are excellent catalysts for steam gasification. As shown in Table 4, pyrolysis of Wyodak coal up to 950°C in steam increases weight loss by 28.8 percent. However, weight loss for Pittsburgh No. 8 coal is increased by only 6.0 percent. These results suggest that steam has small but significant effect on the weight loss of coals at lower pyrolysis temperature (Ca 650°C). However, steam appears to have a significant influence on the weight loss of Wyodak (sub-bituminous) coal at higher pyrolysis temperature (950°C). Tables 3 and 4 also indicate that steam has very little effect on the pyrolysis weight loss of acid-washed Wyodak coal both in the high (950°C) and low (650°C) temperature pyrolysis. This demonstrates that the effect of steam on the pyrolysis weight loss of Wyodak coal is mostly due to the catalytic effect of the exchangeable cations present in this low-rank coal.

Table 5 shows the effect of steam and heating rate on the pyrolysis weight loss of Pittsburgh No. 8 coal up to 900°C. The results suggest that heating rate has relatively small influence on devolatilization of coal in He. In contrast, the overall weight loss during pyrolysis of coal in steam is a strong function of heating rate. The weight loss during devolatilization in steam is 37 percent at 50°C/min which increases to 50 percent when a heating rate of 5°C/min was utilized. This increase in weight loss is attributable to gasification of coal/char by steam which is facilitated by longer residence time at slow heating rates.

Influence of Steam Atmosphere on the Reactivities of the Resulting Chars

Table 6 shows the effect of steam on the reactivities of chars prepared at low (650°C) and high (950°C) temperatures. There are several ways to express the reactivity of chars. As continuations of a previous study (5), we are reporting the reactivity data using maximum gasification rate (Rm) and the time for 10 percent char conversion ($T_{0.1}$). It can be seen that the 650° steam-prepared chars have higher Rm and shorter $T_{0.1}$ than those for the 650° helium-prepared chars. The 950° steam-prepared chars also have higher Rm (except for acid-washed Wyodak coal char) than those for the 950° helium-prepared chars. However, the $T_{0.1}$ of 950° steam-prepared chars are longer than $T_{0.1}$ of 950° helium-prepared chars. By viewing the total gasification profiles of 950° chars, it is evident that the 950° steam-prepared chars are less reactive than 950° helium-prepared chars. It appears that Rm does not serve as a good parameter for describing char reactivity in some cases. This is not surprising keeping in mind that char reactivity is a function of char conversion. In order to express the char reactivity properly, we suggest that it is appropriate to report both the maximum gasification rate and the time needed for certain levels of char conversion (e.g., $T_{0.1}$).

Table 7 compares the reactivities and oxygen chemisorption capacity (OCC) for various chars prepared at 650°C. It can be seen that steam-prepared chars have lower OCC and higher reactivity than helium-prepared chars. Long and Sykes (18,19) studied the mechanism of steam-carbon reaction and suggested that steam can dissociate to form an absorbed hydrogen atom and a hydroxyl group which is absorbed on a neighboring carbon atom of the char. They also suggested that the absorbed hydroxyl groups can undergo further reaction to form carbonyl groups and finally desorb as carbon monoxide. Hence, a probable explanation for the lower OCC of steam-prepared chars is that the "newly formed hydroxyl groups" could occupy some of the active sites for oxygen chemisorption and, therefore, lower the OCC of chars. These hydroxyl groups of chars could undergo gasification reaction to form monoxide and, thereby, enhance the reactivity of chars. The FTIR spectra demonstrate that steam-prepared char has slightly higher concentration of hydroxyl groups than those for the helium-prepared char. This implies that the "absorbed hydroxyl groups" (or part of them) serve as surface complexes on the char surface which could have positive contribution to char reactivity. The data shown in Table 7 indicate that the enhanced effect of steam on the char reactivity (Rm) is dominant for the bituminous coal (Pittsburgh No. 8 coal) than for the subbituminous coal (Wyodak coal). This is perhaps due to the higher concentration of cations in Wyodak coal which catalytically promote char gasification. After acid-washing, the catalytic effect became less significant and the effect of steam on char reactivity became more dominant.

Because steam gasification reaction is highly favorable at 950°C, the lower reactivity of 950° steam-prepared chars as compared with 950° helium-prepared chars can be attributed to the relatively severe conditions which was utilized for coal pyrolysis.

Table 8 presents the effect of steam on the pyrolysis tar yields of Pittsburgh No. 8 coal in a fixed-bed reactor (SHRODR) and isothermal reactivity of produced char at 400°C. It can be seen that pyrolysis of coal in the presence of steam enhances the tar yield and reactivity of produced chars. Sharma and his coworkers (13) observed that pyrolysis of coal in steam increases the weight loss. However, there was no report regarding the effect of steam on the pyrolysis tar yield. We propose that steam can dissociately sorb on the char surface. This could reduce the recombination reactions and thereby suppress the char formation and increase the tar yield. In order to further confirm the enhanced effect of steam on char reactivity, a non-isothermal reactivity test has also been performed.

Steam-prepared and helium-prepared chars were heated in a TGA unit under 0.1 MPa oxygen at 10°C/min from 400°C to 900°C. Figure 2 shows the non-isothermal gasification profiles of these two chars. It is clear that the steam-prepared char is more reactive than helium-prepared char. Figure 3 shows the non-isothermal gasification rates DTG curves for the two chars. The maximum gasification rate of steam-prepared char is 25 percent higher than that for the helium-prepared char. The temperature for the maximum gasification rate of steam-prepared char is 8°C lower than that for the helium-prepared char. These results again confirm that pyrolysis of coal in the presence of steam at relatively lower temperature (650°C) enhances both the tar yield and reactivity of the resulting chars.

SUMMARY AND CONCLUSIONS

The above results demonstrate that pyrolysis of coal in the presence of steam at relatively lower temperature (≤ 650°C) not only increases the weight loss and tar yield but also enhances the reactivity of the resulting char. Steam can dissociatively absorb on the char surface and thereby inhibit the recombination reactions between tar-free radicals and char-free radicals and, thereby, suppress the retrogressive reactions and increasing tar yield. The newly formed "hydroxyl surface complexes" can undergo further reaction to form carbon monoxide during gasification. Devolatilization of coal in the presence of steam at relatively higher temperature (950°C) enhances the pyrolysis weight loss, primarily due to the steam gasification of coal char. However, the char prepared at elevated temperatures in steam is less reactive perhaps due to loss of volatiles in the presence of steam during the pyrolysis step.

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TABLE 1

Proximate and Ultimate Analysis of
Pittsburgh No. 8 Coal, Wyodak Coal
(PSOC 1520)

	Pittsburgh No. 8 Coal	Wyodak Coal
% C, daf	83.74	73.78
% H, daf	5.46	4.62
% N, daf	1.56	1.11
% S, daf	2.15	1.38
% O, daf (by difference)	7.09	19.11
% Ash (as-received basis)	7.27	9.08
% Moisture	0.57	26.69
H/C Atomic (daf)	0.78	0.75
O/C Atomic (daf)	0.064	0.19

TABLE 2

Exchangeable Cation Content
of Wyodak Coal

Cation	% of Dry Coal
Ca	1.30
Mg	0.275
K	0.005
Na	0.020
Fe	0.275

TABLE 3

Effect of Steam[a] on the Pyrolysis Weight Loss of Coals Up To 650°C (Heating Rate = 20°C/min)

Sample/Pyrolysis Atmosphere	Weight Loss During Pyrolysis Up To 650°C, % of Coal (Dry Base)
Wyodak Coal/He	39.7
Wyodak Coal/Steam	43.2
Acid-Washed Wyodak Coal/He	38.2
Acid-Washed Wyodak Coal/Steam	38.2
Pittsburgh No. 8 Coal/He	30.2
Pittsburgh No. 8 Coal/Steam	37.2

[a] Pressure of Steam: 3 kPa

TABLE 4

Effect of Steam[a] on the Pyrolysis Weight Loss of Coals Up To 950°C (Heating Rate = 20°C/min)

Sample/Pyrolysis Atmosphere	Weight Loss During Pyrolysis Up To 950°C, % of Coal (Dry Base)
Wyodak/He	57.6
Wyodak/Steam	86.4
Acid-Washed Wyodak Coal/He	49.5
Acid-Washed Wyodak Coal/Steam	50.8
Pittsburgh No. 8 Coal/He	41.5
Pittsburgh No. 8 Coal/Steam	47.5

[a] Pressure of Steam: 3 kPa

TABLE 5

Effect of Steam and Heating Rate on the Pyrolysis Weight Loss of Pittsburgh No. 8 Coal Up To 900°C

Heating Rate (°C/min)	Weight Loss During Pyrolysis Up To 900°C	
	He	Steam
5	38.0	50.0
10	37.0	44.5
20	37.0	40.5
50	37.0	37.0

TABLE 6

Effect of Steam on the Reactivities of Chars Prepared at Low (650°C) and High (950°C) Temperature

Sample/Pyrolysis Temperature and Atmosphere	Maximum Gasification Rate at 400°C, %/min (daf)	Time for 10% Conversion ($T_{0.1}$), min
Wyodak/TGA 650/He	10.14	10.0
Wyodak/TGA 650/Steam	10.84	9.0
Wyodak/TGA 950/He	1.58	40.0
Wyodak/TGA 950/Steam	2.81	42.5
Acid-Washed Wyodak/TGA 650/He	3.56	13.0
Acid-Washed Wyodak/TGA 650/Steam	4.06	13.0
Acid-Washed Wyodak/TGA 950/He	1.16	36.7
Acid-Washed Wyodak/TGA 950/Steam	1.05	42.5
Pittsburgh No. 8/TGA 650/He	1.06	30.5
Pittsburgh No. 8/TGA 650/Steam	1.31	28.0
Pittsburgh No. 8/TGA 950/He	0.45	64.5
Pittsburgh No. 8/TGA 950/Steam	0.58	81.0

TABLE 7

Comparison of Reactivities and Active Surface Areas for Various Chars[a]

Sample/Pyrolysis Temperature and Atmosphere	g^b, (% of Char, daf)	Rm^c (400°C) ($g\ g^{-1}\ h^{-1}$, daf)	ASA^d, (g/m^2)	$k^e \times 10^3$ ($g\ m^{-2}\ h^{-1}$)
Pittsburgh No. 8/TGA 650/He	5.73	0.64	172	3.72
Pittsburgh No. 8/TGA 650/Steam	4.93	0.79	148	5.34
Wyodak/TGA 650/He	8.51	6.08	255	23.84
Wyodak/TGA 650/Steam	6.91	6.50	207	31.40
Acid-Washed Wyodak/TGA 650/He	5.62	2.14	169	12.66
Acid-Washed Wyodak/TGA 650/Steam	5.35	2.44	161	15.16

[a] Pyrolysis was performed at 20°C/min.
[b] Chemisorption capacity. Chemisorption was performed at 155°C in oxygen for 15 h.
[c] Maximum gasification rate at 400°C in oxygen.
[d] Active surface area or oxygen chemisorption capacity (OCC).
[e] Reactivity per unit active surface area.

TABLE 8

Influence of Steam on the Pyrolysis Tar Yield for Pittsburgh No. 8 Coal and the Reactivity of the Resulting Chars[a]

Pyrolysis Atmosphere	Tar Yield, % of Coal (daf)	Maximum Gasification Rate at 400°C, %/min (daf)	Time for 10% Conversion, min
He	14.5	1.11	31.6
Steam	16.3	1.36	23.1

[a] Pyrolysis was performed in SHRODR at 500°C, 20 min.

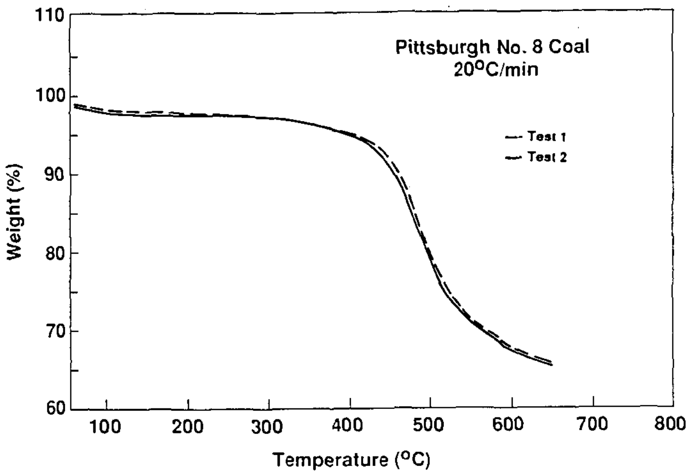

FIGURE 1a. Reproducibility of TGA Devolatilization Runs

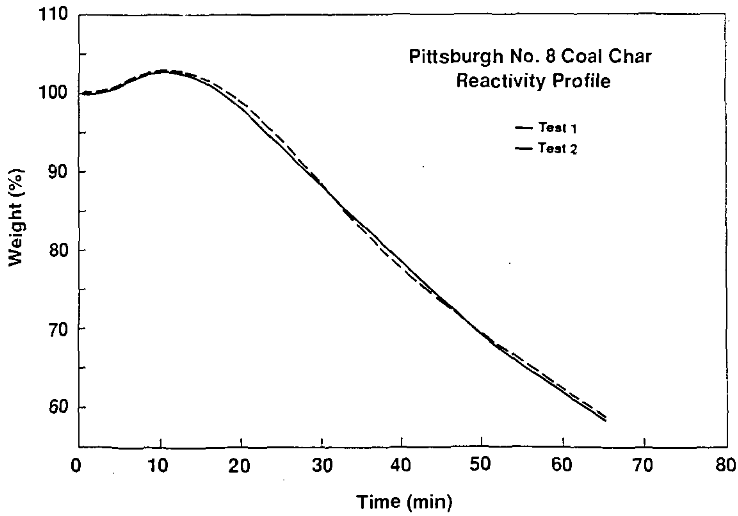

FIGURE 1b. Reproducibility of TGA Reactivity Profiles

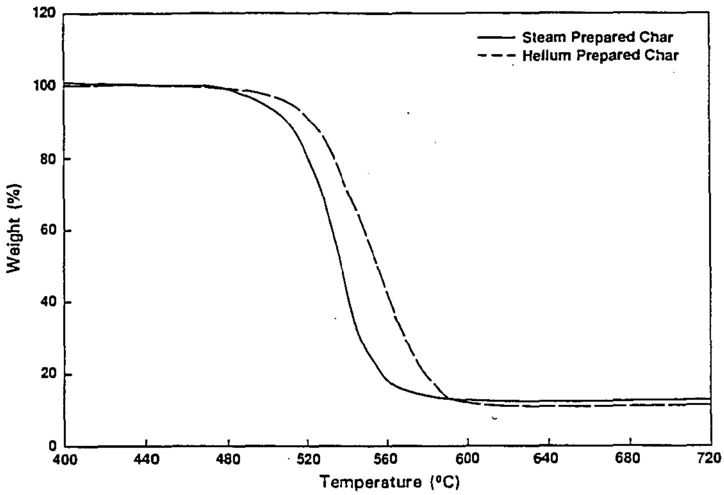

FIGURE 2. Comparison of Non-isothermal Gasification Profiles of Chars Prepared Under Helium and Steam

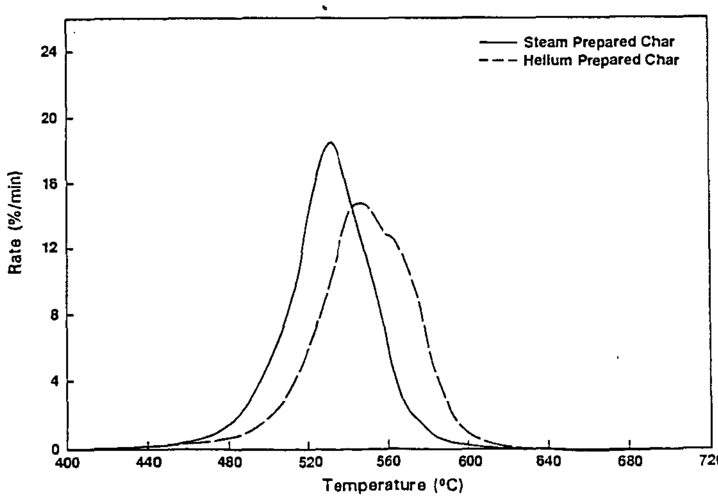

FIGURE 3. Comparison of Non-isothermal Gasification Rates of Chars Prepared Under Helium and Steam