Thermochimica Acta, 132 (1988) 289–295
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

DESULFURIZATION OF SOME TURKISH LIGNITES DURING OXIDATION BY AIR

SADRIYE KÜÇÜKBAYRAK and ENIS KADIOĞLU

Istanbul Technical University, Faculty of Chemical Metallurgical Engineering, Department of Chemical Engineering, Istanbul (Turkey)

(Received 8 January 1988)

ABSTRACT

The effect of air treatment on the desulfurization of seven Turkish lignites was investigated and the experimental results are presented. Lignite samples were oxidized at 550 ° C for 15 min using particles with diameters in the range 0.1–0.2 mm. The changes in proximate and ultimate analyses, in total sulfur and in forms of sulfur in lignite samples were studied.

INTRODUCTION

The main difficulty in the utilization of Turkish lignites is the emission of sulfur oxides. Many of the lignites of Turkey contain high sulfur and cause air pollution problems. The objective of the present work is the desulfurization of seven lignites from different reserves in Turkey during oxidation by air.

Sulfur occurs in coal as pyrite, organic compounds and sulfates. It has been reported [1,2] that the reaction of pyrite with air is highly complicated and products such as FeS, FeO, Fe_3O_4, Fe_2O_3, $FeSO_4$, $Fe_2(SO_4)_3$, S_n, SO_2, SO_3 and possibly others are produced. Schwab and Philinis [2] reported that in the range 400–500 ° C, with an abundant supply of air, oxidation of pyrite proceeds mainly according to the reaction

$$FeS_2 + 11/2\ O_2 \rightarrow 1/2\ Fe_2O_3 + 2\ SO_2 \qquad (1)$$

Sinha and Walker [1] reported that the removal of organic sulfur during treatment with air occurs as a result of the gasification of the carbon skeleton in the coal. The decomposition of sulfate also occurs in the temperature interval of air oxidation of coal.

EXPERIMENTS

A tubular quartz reactor of 60 cm length and 2.5 cm inner diameter, heated by an electric tube furnace, was used in the experiments. The

0040-6031/88/$03.50 © 1988 Elsevier Science Publishers B.V.

temperature was measured using a chromel–alumel thermocouple, and the heating rate of 10 °C min^{-1} could be controlled by adjusting the voltage with a variable transformer. The gas produced was passed through an ice–water bath, a tar and liquor trap, two absorbers and, finally, into a gas holder. The content of the absorbers were used to determine gravimetrically the sulfur content of the gas [3,4].

3 g of coal with particle diameters 0.1–0.2 mm, dried at 110 °C, was weighed in a silica boat and placed in the center of the quartz reactor. Dry air from a gas cylinder was passed through a preheater at a flow rate of 20 cm^3 min^{-1}. After 15 min at 550 °C the gas flow switched to nitrogen for 20 min and the reactor was cooled. In all experiments the pressure was maintained at atmospheric pressure.

All the analyses of lignite, before and after treatment, were performed according to the ASTM standards [5]. Sulfide sulfur contents of the treated lignite samples were determined gravimetrically [6].

RESULTS AND DISCUSSION

Çayırhan, Soma, Keşan, Çan, Tunçbilek, Mengen and Sorgun lignite samples were used in the experiments. The proximate analyses of the lignite samples are shown in Table 1; the ultimate analyses are given in Table 2 and the forms of sulfur are displayed in Table 3.

In an earlier work we investigated the effects of coal particle size, time and temperature on the desulfurization by air using only Çayırhan lignite [7]. A series of experiments were conducted using samples with particle diameters of 0.200–0.315 mm, 0.125–0.200 mm and < 0.125 mm. In the ranges studied the particle size of coal did not have a significant effect on the desulfurization and weight loss. The effect of time was examined for time intervals of 15, 30, 45 and 60 min at 450 °C. The first 15 min is the

TABLE 1

Proximate analyses of the lignite samples

	Moisture (wt%)	Dry basis			
		Volatile matter (wt%)	Ash (wt%)	Fixed carbon (wt%)	Net calorific value (MJ kg^{-1})
Çayırhan	15.4	49.5	17.9	32.6	21.3
Soma	17.1	51.4	19.8	28.8	19.9
Keşan	16.3	48.1	13.5	38.4	20.7
Çan	16.8	47.4	9.0	43.6	23.0
Tunçbilek	19.6	44.7	10.3	45.0	23.6
Mengen	6.3	55.8	8.9	35.3	27.3
Sorgun	15.7	50.2	3.4	46.4	28.4

TABLE 2

Ultimate analyses of the lignite samples (dry basis)

	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)
Çayırhan	45.9	3.9	2.1	23.0	7.2
Soma	50.1	4.1	0.9	23.0	2.1
Keşan	54.1	3.9	1.5	23.1	3.9
Çan	55.4	4.4	2.1	23.4	5.7
Tunçbilek	56.1	4.4	2.7	22.6	3.9
Mengen	58.0	5.3	1.3	12.4	14.1
Sorgun	68.1	4.1	1.9	20.7	1.8

most effective time for removing sulfur from lignite during oxidation by air. Increasing the time only affects the result slightly. The desulfurization of Çayırhan lignite was studied in the temperature range 350–650 ° C, because of the large weight loss at higher temperatures owing to the combustion of the lignite sample in the oxidizing atmosphere. Sulfur removals at 450, 500, 550, 600 and 650 ° C were 29.3, 35.1, 41.7, 45.7 and 47.7 wt%, respectively. As can be seen 550 ° C is the most effective temperature for removing sulfur from Çayırhan lignite by treatment with air.

Since 15 min and 550 ° C were found to be the optimum conditions for Çayırhan lignite, the other six lignite samples were oxidized by air for 15 min at 550 ° C. The proximate analyses of the air-treated samples are given in Table 4; the ultimate analyses are given in Table 5 and the forms of sulfur are given in Table 6.

The removal of the organic sulfur from the lignite samples varies between 3.5% (for Tunçbilek lignite) and 52.5% (for Mengen lignite) depending on the content of volatile matter. The pyrite content of the lignite samples decomposes completely, except in the Mengen lignite which is slightly caking. The removal of sulfate sulfur varies between 3.5% (for Soma lignite) and 100% (for Mengen lignite). Soma lignite contains an unusually high content of basic minerals and Mengen lignite contains the smallest sulfate content (only 0.09%). The total sulfur removal of the lignite samples varies between 28.4% (for Soma lignite) and 52.3% (for Mengen lignite).

Lignite samples do not contain sulfide sulfur. It forms during air treatment as a result of the reduction of sulfates and the reaction of pyrite with air [1,2,8]. Another possibility is the decomposition of pyrite to sulfide and H_2S (similar to the carbonization) owing to the incomplete diffusion of air between coal particles placed in the silica boat (H_2S was detected in the gas produced during air treatment).

The volatile matter content of the lignite samples decreases significantly during air treatment (between 61 and 76% of its original value). The ash content of the lignite samples increases after the air treatment, which reduces their fuel value.

TABLE 3

Sulfur forms of the lignite samples (dry basis)

	$S_{pyritic}$ (wt%)	$S_{sulfate}$ (wt%)	$S_{organic}$ (wt%)	S_{total} (wt%)	S_{ash} (wt%)	$S_{pyritic}$ [a] (wt%)	$S_{sulfate}$ [a] (wt%)	$S_{organic}$ [a] (wt%)	S_{ash} [a] (wt%)
Çayırhan	2.31	0.74	4.14	7.19	0.99	32.13	10.29	57.58	13.77
Soma	0.71	0.36	1.03	2.10	1.54	33.81	17.14	49.05	73.33
Keşan	0.03	0.21	3.63	3.87	0.51	0.78	5.43	93.79	13.18
Çan	0.84	1.63	3.23	5.70	0.09	14.74	28.60	56.66	1.58
Tunçbilek	0.35	1.61	1.95	3.91	0.08	8.95	41.18	49.87	2.05
Mengen	2.48	0.09	11.49	14.06	0.29	17.64	0.64	81.72	2.06
Sorgun	0.23	0.26	1.35	1.84	0.16	12.50	14.13	73.37	8.70

[a] As percentage of total sulfur.

TABLE 4

Proximate analyses of the lignite samples air treated at 550 °C for 30 min (dry basis)

	Volatile matter (wt%)	Ash (wt%)	Fixed carbon (wt%)	Weight loss (wt%)	Net calorific value (MJ kg^{-1})
Çayırhan	28.0	23.8	48.2	31.1	22.6
Soma	26.5	27.2	46.3	29.1	21.3
Keşan	23.4	18.5	58.1	27.1	24.9
Çan	22.3	12.1	65.6	28.4	26.7
Tunçbilek	21.0	13.5	65.5	27.1	25.6
Mengen	21.4	13.5	65.1	37.9	25.2
Sorgun	21.6	4.7	73.7	32.5	29.8

Lignite is a young coal and chemisorption of oxygen occurs easily during air treatment. To keep the chemisorption of oxygen on the lignite samples at a minimum they were cooled in nitrogen at the end of each run.

The heat content of the original lignite samples which remains in the air-treated samples varies between 57.4% (for Mengen lignite) and 87.4% (for Keşan lignite). The highest volatile matter content and the greatest loss of volatile matter occur in Mengen lignite (Table 4). The increase in the ash content of this lignite reduces its fuel value.

The ultimate analyses of the air-treated lignite samples (Table 5) show that the loss of carbon content based on the original lignite samples varies between 13.3% (for Tunçbilek lignite) and 30.7% (for Mengen lignite).

Table 7 shows the percentage distribution of sulfur in the solid, liquid and gaseous products of air oxidation based on the total sulfur originally present in the lignite samples.

The amounts of sulfur dioxide which are released per 4186 MJ (10^6 cal) heat during combustion of the original and air-treated lignite samples are shown in Table 8. The combustible sulfur contents and the net calorific values of the lignite samples before and after air treatment were used to calculate the values in Table 8.

TABLE 5

Ultimate analyses of the lignite samples air treated at 550 °C for 30 min (dry basis)

	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)
Çayırhan	56.9	2.1	1.6	9.5	6.1
Soma	58.8	2.4	1.1	8.4	2.1
Keşan	62.2	2.5	2.1	11.3	3.4
Çan	65.6	2.1	1.6	13.9	4.7
Tunçbilek	66.7	2.1	2.5	12.1	3.1
Mengen	64.8	2.1	1.6	7.2	10.8
Sorgun	76.6	2.6	2.2	12.5	1.4

TABLE 6

Sulfur forms of the lignite samples air treated at 550 ° C for 30 min (dry basis)

	S_{pyr} (wt%)	$S_{sulfate}$ (wt%)	$S_{sulfide}$ (wt%)	$S_{org.}$ (wt%)	S_{total} (wt%)	S_{ash} (wt%)	$S_{pyr.}$ [a] (wt%)	$S_{sulfate}$ [a] (wt%)	$S_{sulfide}$ [a] (wt%)	$S_{org.}$ [a] (wt%)	S_{ash} [a] (wt%)
Çayırhan	–	0.57	1.00	4.51	6.08	1.51	–	9.38	16.45	74.17	24.84
Soma	–	0.49	0.40	1.23	2.12	1.90	–	23.11	18.87	58.02	89.62
Keşan	–	0.25	0.22	2.91	3.38	0.73	–	7.40	6.51	86.09	21.60
Çan	–	0.23	0.25	4.21	4.69	0.16	–	4.90	5.33	89.77	3.41
Tunçbilek	–	0.26	0.07	2.77	3.10	0.16	–	8.39	2.26	89.35	5.16
Mengen	1.31	–	0.70	8.78	10.79	0.42	12.14	–	6.49	81.37	3.89
Sorgun	–	0.09	0.07	1.24	1.40	0.22	–	6.43	5.00	88.57	15.71

[a] As percentage of total sulfur.

TABLE 7

The distribution of the eliminated sulfur of lignites in the oxidation products

	Solid products (wt%)	Gaseous products (wt%)	Liquid products (wt%)
Çayırhan	58.29	31.38	10.33
Soma	71.56	27.61	0.83
Keşan	63.67	25.64	10.69
Çan	58.89	28.40	12.71
Tunçbilek	57.77	27.87	14.36
Mengen	47.66	32.51	19.83
Sorgun	51.36	24.65	23.99

TABLE 8

The amount of SO_2 which is released during combustion per 4186 MJ (10^6 cal) heat

	Air-treated lignite (kg SO_2 per 4186 MJ)	Original lignite (kg SO_2 per 4186 MJ)	Difference (%)
Çayırhan	16.92	24.34	30.48
Soma	0.86	2.36	63.56
Keşan	8.92	13.56	34.22
Çan	14.21	20.46	30.55
Tunçbilek	9.63	13.61	29.24
Mengen	34.47	42.28	18.47
Sorgun	3.31	4.94	33.00

To determine the amount of sulfur removal the formula given below is used

$$\text{Sulfur removal (wt\%)} = \frac{S_{\text{lignite}}\ (\text{wt\%}) - S_{\text{coke}}\ (\text{wt\%}) \times \text{coke yield}}{S_{\text{lignite}}\ (\text{wt\%})} \times 100$$

REFERENCES

1 R.K. Sinha and P.L. Walker, Fuel, 51 (4) (1972).
2 G.M. Schwab and J. Philinis, J. Am. Chem. Soc., 69 (1947).
3 R.D. Snow, Ind. Eng. Chem., 24 (3) (1932).
4 S.S. Block, J.B. Sharp and L.J. Darlage, Fuel, 54 (4) (1975).
5 Annual Book of ASTM Standards, Part 26, Methods D 3175-77, D 3177-75, D 2492-77, D 3174-73, D 3286-73, D 3178-73, D 3179-73, D 1757-62, D 3302-74, 1977.
6 R.E. Brewer and J.K. Ghosh, Ind. Eng. Chem., 41 (9) (1949).
7 S. Küçükbayrak, F. Basmacı and E. Kadioğlu, J. Therm. Sci. Technol. (Turkish), 9 (3) (1986).
8 R.A. Powell, Ind. Eng. Chem., 12 (11) (1920).