Thermochimica Acta, 126 (1988) 299–306
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DESULFURIZATION OF SOME TURKISH LIGNITES DURING CARBONIZATION BY AMMONIA

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(Received 8 July 1987)

ABSTRACT

The aim of this study is to examine the sulfur removal efficiency of carbonization by ammonia from seven Turkish lignites. The effects of carbonization time and temperature were investigated together at 700, 800 and 900 °C for time intervals of 5, 15 and 30 min using one lignite: the other lignite samples were then carbonized under the most suitable conditions.

INTRODUCTION

Fossil fuels contain sulfur in varying concentrations, depending primarily on the source of the fuel. Coal contains generally 0.2–7.0% sulfur by weight and the high-sulfur coals are defined as those which have more than 3% sulfur [1]. Turkish lignites contain especially high sulfur. The sulfur oxides are the most important atmospheric pollutants in big cities, because coal combustion sources are concentrated in and around them. The aim of the present study is the desulfurization of seven Turkish lignites from different reserves during carbonization by ammonia. Lignite samples from Çayırhan, Soma, Keşan, Çan, Tunçbilek, Mengen and Sorgun were used in this study. The geological age of Çayırhan, Soma and Tunçbilek lignites is Lower Miocene, that of Çan lignite is Upper Miocene, that of Sorgun lignite is Lower Eocene, that of Mengen lignite is Middle Eocene, and that of Keşan lignite is Oligocene. The coalification degrees of some of them are not in accordance with their geological age.

EXPERIMENTAL

A tubular quartz reactor, 60 cm in length and 2.5 cm inner diameter, heated by an electric tube furnace, was used in experiments. The temperature was measured by using a chromel–alumel thermocouple and the heating

0040-6031/88/$03.50

rate of 10 °C $\min^{-1}$ could be controlled by adjusting the voltage with a variable transformer. The carbonization gas was passed through an ice–water bath, a tar and liquor trap and two absorbers containing a mixture of water, hydrogen peroxide and concentrated ammonium hydroxide and finally into a gas holder. The contents of the absorbers were used to determine the sulfur content of the gas gravimetrically [2,3].

Three grams of coal, dried at 110 °C, was weighed out in a silica boat and placed in the center of the quartz reactor. Anhydrous ammonia from a gas cylinder was passed through a preheater at a flow rate of 25 $\text{cm}^3 \min^{-1}$. After holding the lignite sample at the treatment temperature for the desired period of time, the gas flow was switched to nitrogen for 20 min and the tubular reactor was cooled. In all of the experiments the pressure was maintained at atmospheric pressure.

Time and temperature were the parameters tested for their effects on desulfurization during carbonization by ammonia gas. These experiments were carried out using lignite samples with particle diameters in the range of 0.1–0.2 mm. The effects of carbonization time and temperature were investigated together at 700, 800 and 900 °C for time intervals of 5, 15 and 30 min. Çan lignite, a high-sulfur Turkish lignite, was used to determine the optimum conditions of time and temperature, and other six lignite samples from different reserves in Turkey were carbonized accordingly.

All of the analyses of lignite and coke samples were performed according to the American Society for Testing and Materials standards [4].

RESULTS AND DISCUSSION

The proximate analyses of the lignite samples are shown in Table 1; the ultimate analyses are given in Table 2, and the sulfur forms in Table 3. The

TABLE 1

The proximate analyses of the lignite samples

Lignite	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

The ultimate analyses of the lignite samples (dry basis)

Lignite	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

volatile matter varies between 44.7 and 55.8%, the ash content between 3.4 and 19.8%, and the total sulfur content between 1.84 and 14.06%. Soma lignite differs from the others in that 73.33% of its total sulfur content is retained by ash during combustion (Table 3). Because of its interesting property this lignite sample was also used in this study although it does not need desulfurization.

Brewer and Ghosh [5] reported that ammonia gas, when brought in contact with hot coke at 700 °C or higher undergoes marked decomposition into nascent hydrogen and nascent nitrogen, from which nascent hydrogen reacts with the sulfur compounds to form volatile sulfur compounds. Therefore the experiments which were made to examine the effects of time and temperature started from 700 °C. Table 4 shows the effect of time and temperature on the course of the desulfurization of Çan lignite and on the coke yield. There is no significant increase in the desulfurization above 800 °C, because the decomposition of ammonia does not show a significant increase above this temperature [5]. The major part of the sulfur lost at 700, 800 and 900 °C is lost in the first 5 min. At 800 °C for 5 min the desulfurization of Çan lignite is 67.1%, but for longer carbonization periods such as 15 and 30 min the desulfurization increases up to only 69.3 and 71.2%, respectively. It can be concluded that 800 °C and 5 min are the most suitable conditions to desulfurize this lignite during carbonization by ammonia. Therefore the other six lignite samples were carbonized at 800 °C for 5 min. The total sulfur and sulfur forms of the produced cokes are seen in Table 5.

As can be seen in Table 5 pyrite decomposes completely. Only the coke produced from Mengen lignite still contains pyritic sulfur. Mengen lignite is slightly caking during carbonization. The mass transfer limitations as a result of the reduction in coal surface area might be the reason that 5.9% of its pyritic sulfur could not decompose.

The decomposition of the sulfate content of the lignite samples is also almost complete; it varies between 85 and 100%.

TABLE 3

Sulfur forms of the lignite samples (dry basis)

Lignite	$S_{pyritic}$ (wt%)	$S_{sulfate}$ (wt%)	$S_{organic}$ (wt%)	S_{total} (wt%)	S_{ash} (wt%)	$S_{pyritic}^{*}$ (wt%)	$S_{sulfate}^{*}$ (wt%)	$S_{organic}^{*}$ (wt%)	S_{ash}^{*} (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

* As percentage of total sulfur.

TABLE 4

Effect of carbonization time and temperature under ammonia on the total sulfur removal and coke yield of Çan lignite

Temperature (°C)	5 min		15 min		30 min	
	Sulfur removal (wt%)	Coke yield (wt%)	Sulfur removal (wt%)	Coke yield (wt%)	Sulfur removal (wt%)	Coke yield (wt%)
700	61.7	62.0	64.0	61.0	67.6	60.3
800	67.1	59.0	69.3	58.9	71.2	58.1
900	69.5	55.0	71.2	54.1	75.1	53.7

$$\text{Sulfur removal} = \frac{S_{\text{lignite}} - S_{\text{coke}} \times \text{coke yield}}{S_{\text{lignite}}} \times 100.$$

Lignite samples did not contain sulfide sulfur. It forms during carbonization as a result of the decomposition of pyrite, the reduction of sulfates and the reaction of hydrogen sulfide with carbonaceus materials. The coke produced from Çayırhan lignite contains the most sulfide sulfur, because the sum of the pyritic and sulfate sulfur contents of this lignite is the highest. The sulfide sulfur content of the produced coke samples is smaller than the amount of sulfur lost by the pyrite and sulfate of the lignite samples. It is possible that some of the sulfide sulfur is transformed to a sulfur–carbon combination and is removed along with gases produced [6–8].

The organic sulfur removal of the lignite samples is also significant. The maximum organic sulfur removal (76.1%) was achieved for Mengen lignite. The elimination of the organic sulfur is dependent on the volatile matter content of the lignite sample, because it is removed during volatilization of the organic material. On the other hand the sulfide sulfur formed hinders the decomposition of the organic sulfur compounds [9].

The total sulfur removal of the lignite samples varies between 26.7 (for Soma lignite) and 75% (for Mengen lignite). Soma lignite contains unusually high basic minerals. Therefore most of the sulfur content of this lignite sample is retained in the coke. The combustible sulfur decreases from 26.67 to 16%, because as a result of volatilization, the percentage of the basic minerals increases. The organic sulfur content increases as a result of the transformation of the sulfide sulfur to a sulfur–carbon combination.

Table 6 shows the percentage distribution of sulfur in the solid, liquid and gaseous products of carbonization based on the total sulfur originally present in the lignite sample.

The comparison of the proximate analysis of the lignite samples and of cokes produced shows that the decrease in the volatile matter content varies between 87.5 and 91.9% (Table 7). The ash content of the lignite samples increases considerably during carbonization. After converting the heat content of the coke samples on the original lignite base we can see that 66.8% of

TABLE 5

Sulfur forms of the produced coke samples from carbonization at 800 ° C for 5 min by ammonia

Lignite	$S_{pyr.}$ (wt%)	$S_{sulfate}$ (wt%)	$S_{sulfide}$ (wt%)	$S_{org.}$ (wt%)	S_{total} (wt%)	S_{ash} (wt%)	$S_{pyr.}^{*}$ (wt%)	$S_{sulfate}^{*}$ (wt%)	$S_{sulfide}^{*}$ (wt%)	$S_{org.}^{*}$ (wt%)	S_{ash}^{*} (wt%)
Çayırhan	–	0.05	1.59	3.22	4.86	1.71	–	1.03	32.72	66.25	35.19
Soma	–	0.07	0.67	1.90	2.64	2.22	–	2.65	25.38	71.97	84.09
Keşan	–	0.05	0.18	2.43	2.66	0.83	–	1.88	6.77	91.35	31.20
Çan	–	0.05	0.38	2.75	3.18	0.22	–	1.57	11.95	86.48	6.92
Tunçbilek	–	0.03	0.13	2.40	2.56	0.17	–	1.17	5.08	93.75	6.64
Mengen	0.29	–	1.21	5.48	6.98	0.44	4.15	–	17.34	78.51	6.30
Sorgun	–	0.02	0.09	1.34	1.45	0.32	–	1.38	6.21	92.41	22.07

* As percentage of total sulfur.

TABLE 6

The distribution of the eliminated sulfur of the lignite samples in the carbonization products

Lignite	Coke (%)	Gaseous products (%)	Liquid products (%)
Çayırhan	39.5	47.6	12.9
Soma	73.3	26.0	0.7
Keşan	43.1	46.5	10.4
Çan	32.9	47.3	19.8
Tunçbilek	39.8	46.1	14.1
Mengen	24.9	54.1	21.0
Sorgun	45.0	45.2	9.8

TABLE 7

The proximate analyses of the coke samples produced from carbonization at 800 °C for 5 min by ammonia

Lignite	Volatile matter (wt%)	Ash (wt%)	Fixed carbon (wt%)	Coke yield (wt%)	Net calorific value (MJ kg^{-1})
Çayırhan	7.9	26.5	65.6	58.4	24.4
Soma	9.7	32.0	58.3	58.3	23.9
Keşan	9.4	21.2	69.4	62.7	25.6
Çan	10.0	14.6	75.4	59.0	27.5
Tunçbilek	8.9	16.4	74.7	60.8	27.3
Mengen	9.0	16.9	74.1	50.1	27.8
Sorgun	9.0	5.8	85.2	57.1	31.8

the heat content of Çayırhan lignite, 69.9% of Soma lignite, 77.5% of Keşan lignite, 70.6% of Çan lignite, 70.4% of Tunçbilek lignite, 51% of Mengen lignite, and 63.8% of Sorgun lignite remains in the cokes produced.

TABLE 8

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

Lignite	Coke [kg SO_2 (4186 MJ)$^{-1}$]	Lignite [kg SO_2 (4186 MJ)$^{-1}$]	Difference (%)
Çayırhan	10.81	24.34	55.59
Soma	1.47	2.36	37.71
Keşan	5.97	13.56	55.97
Çan	9.02	20.46	55.91
Tunçbilek	7.33	13.61	46.14
Mengen	19.73	42.28	53.33
Sorgun	2.98	4.94	39.68

The amount of sulfur dioxide which is released per 4186 MJ (10^6 cal) of heat during combustion of the lignite and coke samples produced can be seen in Table 8. The combustible sulfur content and net calorific values of the lignite and coke samples were used to calculate the values in Table 8.

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