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Desulphurization of coals and chars by treatment in various atmospheres between 400 and 600°C

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Desulphurization of fifteen US coals of rank ranging from anthracite to sub-bituminous B and five high-temperature chars by carbon monoxide and other gases and gas mixtures between 400 and 600°C has been studied. The sulphur content of the parent coals ranged between 3.0 and 7.3% and that of the chars between 1.3 and 3.8% by weight. A comparison between air, nitrogen, carbon monoxide, and steam-carbon monoxide mixtures as desulphurizing gases shows the order of desulphurizing ability as air > steam-CO mixture > CO > N₂.

The importance of removal of sulphur from steam coals and metallurgical coals cannot be overemphasized. Attempts have been made in the past to desulphurize coals by hydrogen, steam, and air¹⁻⁴. Desulphurization by hydrogen¹ at low temperatures proceeds at a low rate. Steam does not desulphurize coals significantly at temperatures less than 600°C. At higher temperatures, gasification of coals by hydrogen and steam commences. Any gasification during desulphurization of a metallurgical coal or coke is undesirable as it will reduce the strength of the final coke produced. The low rate of desulphurization by hydrogen at low temperatures may be due to either a low rate of sulphur release from the decomposition of sulphur-bearing species present in the coal matrix or a low rate of dissociation of hydrogen, or both. Carbon monoxide is expected to remove sulphur from coal as carbon oxysulphide; and since carbon monoxide should not have to dissociate to react with sulphur or sulphur-bearing compounds to produce carbon oxysulphide, it is possible that the rate of sulphur removed by carbon monoxide will be greater than with hydrogen. Carbon oxysulphide is a gas at normal conditions of temperature and pressure; and, therefore, can readily be removed from the condensable products (liquid and tar) of coal desulphurization. Sulphur from carbon oxysulphide can be recovered by thermal cracking.

EXPERIMENTAL

Fifteen coals of various ranks ranging from anthracite to sub-bituminous B and five high-temperature coal chars obtained from the Hy-gas⁵ and FMC⁶ processes were selected for this study. Rank, chemical analyses, and the forms of sulphur present in the coal samples, as supplied by Commercial and Engineering Testing, Inc, are given in *Table 1*.

1 g of coal of 70 x 100 US sieve size, dried at 110°C for 1 h, was held in a silica boat 63.5 mm x 12.5 mm (2.5 in x 0.5 in). The boat was introduced into a tube furnace of 38 mm (1.5 in) inside diameter maintained at the desired treatment temperature. Each sample was treated in a flowing stream of the desulphurizing gas for a specified time at a

rectilinear gas velocity of about 200 cm/min. Four temperatures of 400, 450, 500 and 550°C were initially selected for the carbon monoxide desulphurization study. The samples, following their desulphurization treatment, were analysed for total sulphur in a Leco combustion furnace.

RESULTS AND DISCUSSION

Weight losses and total sulphur contents following a 15 min desulphurization by carbon monoxide are presented in *Table 2*. *S*_{original}, reported in *Table 2* and elsewhere, is the sulphur content of the parent coal as ascertained by us on the Leco combustion furnace. Comparison of *Tables 1* and *2* will indicate that in some cases there are slight differences in total sulphur reported. Each sulphur value reported in *Table 2* and onwards is an average of duplicate determinations, differing from each other by less than 10% in all cases.

The general trend is a reduction in the total sulphur following treatment in carbon monoxide for all coals; but the extent of sulphur removed from the coal samples, even at a treatment temperature of 550°C, is not sufficiently large to be of commercial interest. Results on the desulphurization of high-temperature chars by carbon monoxide up to a temperature of 600°C, as presented in *Table 3*, also show that sulphur removal is small.

In order to see if the reduction in sulphur in the coals was due only to the carbonization reactions occurring during treatment with carbon monoxide, the coal samples were treated in nitrogen at corresponding reaction conditions. These results are presented in *Table 4*. A comparison of *Tables 2* and *4* shows that some additional sulphur is removed by carbon monoxide over that removed by nitrogen. This additional removal is significantly high for some coals. However, no correlation between form and type of sulphur distribution and ease of reduction in total sulphur has been found.

All bituminous coals, ranging from medium-volatile to high-volatile B, and a few high-volatile C coals, more or

Table 1 Chemical analyses of coals

Coal PSOC No.	Rank	Analyses (weight % on dry basis)								
		Ash	C	H	N	Cl	S _{py} *	S _{SO₄} †	S _{org} ‡	O(diff.)
153	A	13.5	75.7	2.5	0.15	0.01	4.36	0.01	0.38	3.3
113	LV	10.6	78.9	4.15	1.03	0.12	2.03	0.16	0.91	2.05
116	MV	12.9	74.2	4.35	1.10	0.11	2.68	0.20	1.16	3.25
208	MV	10.1	70.0	4.9	1.53	0.01	2.68	0.10	1.51	9.0
108	HVA	9.5	75.0	5.05	1.11	0.06	2.06	0.00	1.07	6.15
163	HVA	13.1	70.4	4.9	0.16	0.09	3.97	0.24	1.86	5.25
24	HVB	11.8	70.6	4.85	0.94	0.04	1.94	0.03	1.99	7.75
149	HVB	16.0	65.6	4.35	0.18	0.02	3.94	1.36	1.53	6.9
164	HVB	22.4	60.7	3.3	0.94	0.01	3.79	0.64	2.84	5.3
185	HVB	13.5	66.8	5.05	0.94	0.08	1.63	0.08	1.46	8.4
26	HVC	10.8	68.9	5.0	1.01	0.00	4.23	0.35	2.08	7.55
184	HVC	21.1	60.4	4.4	0.86	0.04	1.43	0.38	0.97	10.2
189	HVC	12.3	66.5	4.95	0.91	0.06	2.57	0.15	2.12	10.3
192	HVC	7.7	72.2	5.3	0.89	0.00	1.31	0.15	1.54	7.75
190	SBB	8.4	69.1	4.9	1.00	0.06	1.05	0.10	1.90	13.3

* Pyritic sulphur

† Sulphate sulphur

‡ Organic sulphur

Table 2 Desulphurization of coals by carbon monoxide for 15 min

Coal PSOC No.1	S _{tot} * (original)	Sulphur content and weight loss (weight %)							
		400°C		450°C		500°C		550°C	
		S _{tot}	Wt loss	S _{tot}	Wt loss	S _{tot}	Wt loss	S _{tot}	Wt loss
153	4.7	4.4	1.0	4.3	1.0	—	—	4.4	2.1
113	3.0	1.7	2.8	1.5	6.7	1.3	10.0	1.4	11.7
116	4.1	3.4	5.0	2.8	9.3	2.8	13.0	2.0	15.1
208	4.3	3.3	17.2	3.6	24.5	—	—	2.8	31.3
108	3.1	2.3	14.0	2.5	25.1	—	—	1.9	30.5
163	6.1	4.5	17.4	3.7	28.1	—	—	3.8	32.0
24	3.8	2.9	14.5	2.4	22.7	2.4	25.9	2.5	28.6
149	6.8	5.9	17.1	4.7	25.0	—	—	3.9	31.6
164	7.3	6.2	17.5	5.1	23.4	—	—	4.9	27.8
185	3.3	2.5	15.6	1.9	23.5	1.7	26.7	1.9	30.0
26	6.9	4.5	16.1	4.2	26.3	3.7	28.1	4.0	30.5
184	3.2	1.9	11.3	1.7	16.5	1.7	19.2	1.8	21.3
189	4.8	3.9	—	3.8	26.0	—	—	3.1	31.6
192	3.2	2.0	16.4	1.7	24.4	1.7	28.5	1.8	31.2
190	3.1	1.9	14.8	1.8	22.3	1.7	26.1	1.8	28.4

* Total sulphur

less sintered, swelled, and caked during treatment in carbon monoxide and nitrogen. An overall low reduction in sulphur during treatment in carbon monoxide could result because of a reduced accessibility to carbon monoxide of the sulphur-bearing species as a result of sintering and caking of the coal. The caking properties of coals can be destroyed by pretreatment in air at low temperatures. Moreover, we have shown⁴ that air by itself is a good desulphurizing gas at low temperatures. It was, therefore, of some interest to investigate the effect of pretreatment in air on the extent of sulphur reduction by carbon monoxide.

Coals were pretreated in air for 5 min at 450°C at a velocity of about 200 cm/min. Following this treatment, carbon monoxide was passed over the sample for 15 min. Pretreatment in air for 5 min completely destroyed the caking properties of the coals. Results on total sulphur following this treatment are summarized in Table 5. A comparison with Table 2 shows that a much greater reduction in sulphur content occurred. The results may be of some technical significance for cases where the weight losses are not excessive.

Table 3 Desulphurization of chars by carbon monoxide for 15 min

Char	Origin	S _{original} (%)	S _{treated} (%)	
			500°C	600°C
HT-154	HY-GAS	1.3	1.2	1.3
POC-130	FMC	1.8	1.6	1.5
POC-135	FMC	3.3	3.1	3.1
POC-141	FMC	2.8	2.7	2.6
POC-145	FMC	1.9	1.8	1.8

It is of interest to determine which of the two gases, air or carbon monoxide, plays a larger role in the desulphurization of coals. Table 6 presents results on total sulphur on coals following treatment at 450°C for 5 min in air alone and for 5 min in air plus 15 min in nitrogen. Comparison of Tables 5 and 6 indicates that treatment in air alone appears most promising. Increase in total sulphur in cases where the air-pretreated samples were held for another 15 min in nitrogen or carbon monoxide is in part due to

Table 4 Effect of heat treatment in nitrogen for 15 min on sulphur in coals

Coal PSOC No.	Sulphur content and weight loss (weight %)					
	400°C		500°C		550°C	
	S _{tot}	Wt loss	S _{tot}	Wt loss	S _{tot}	Wt loss
153	4.2	1.0	—	—	4.2	2.2
113	2.0	3.2	1.7	—	1.6	11.6
116	3.8	4.1	3.4	—	2.9	14.5
208	5.0	15.0	4.5	—	3.3	30.6
108	3.6	15.0	3.1	—	2.4	31.0
163	4.5	15.5	4.5	—	4.6	31.7
24	3.2	13.7	3.0	—	2.7	27.6
149	6.8	16.7	6.2	—	5.2	30.6
164	7.1	16.7	6.4	—	4.3	27.5
185	2.4	15.7	2.4	—	2.2	28.2
26	5.7	15.1	5.2	—	4.5	29.5
184	2.0	12.1	1.8	—	1.9	21.0
189	4.0	19.0	3.9	—	3.5	32.7
192	2.5	16.2	1.9	—	1.9	21.0
190	2.0	14.3	1.9	—	1.9	—

Table 5 Desulphurization of coals by air followed by carbon monoxide at 450°C (air, 5 min; CO, 15 min)

Coal PSOC No.	S _{tot} (%) (original)	After treatment	
		S _{tot} (%)	Wt loss (%)
113	3.0	0.8	10.8
116	4.1	1.2	12.4
208	4.3	1.5	26.3
108	3.1	1.3	24.0
163	6.1	2.8	28.2
24	3.8	1.8	25.8
149	6.8	3.4	29.1
164	7.3	3.5	19.6
185	3.3	1.5	26.3
26	6.9	2.6	44.2
184	3.2	1.5	28.7
189	4.8	2.8	31.1

the removal of chemisorbed oxygen picked up by coals during the air pretreatment. Carbon monoxide acts as an oxygen scavenger; and, consequently, the total sulphur and weight losses are the highest following 15 min holding of the air-pretreated samples in carbon monoxide.

Vestal and Johnston¹ found very little removal of sulphur from coals by hydrogen treatment below 500°C. This may in part be due to an insufficient rate of dissociation of hydrogen to atomic species at temperatures lower than 500°C. We studied the extent of desulphurization of the coals at 450°C in steam-carbon monoxide mixtures. The thought was that a steady-state and significant concentration of hydrogen atoms might be produced as a result of the reaction of water with carbon monoxide (the water-gas shift reaction). Two ratios, H₂O/CO = 1/6 and H₂O/CO = 1 by volume, were used for this study. Results shown in Table 7 reveal that, although the extents of sulphur removed from coal in water-carbon monoxide mixtures

Table 6 Desulphurization of coals by air and air plus nitrogen at 450°C

Coal PSOC No.	5 min in air		5 min in air + 15 min in N ₂	
	S _{tot} (%)	Wt loss (%)	S _{tot} (%)	Wt loss (%)
113	0.8	7.9	0.6	9.0
116	0.9	10.9	1.0	11.5
208	1.5	25.0	1.6	25.3
108	1.3	21.8	1.2	25.4
163	2.8	25.9	2.4	28.1
24	1.6	22.8	2.0	23.0
149	3.3	27.0	3.8	27.7
164	2.6	23.8	4.0	23.1
185	1.2	25.8	1.3	27.1
26	2.5	30.3	3.2	31.3
189	2.3	28.7	2.8	31.3
192	1.2	26.5	1.6	27.3

Table 7 Desulphurization of coals in steam-carbon monoxide mixtures at 450°C for 15 min

Coal PSOC No.	S _{tot} (%) (original)	P _{H₂O} /P _{CO} = 1/6		P _{H₂O} /P _{CO} = 1/1	
		S _{tot} (%)	Wt loss (%)	S _{tot} (%)	Wt loss (%)
153	4.7	—	—	4.4	1.5
113	3.0	1.8	6.7	1.7	6.8
116	4.1	2.6	8.5	2.6	8.4
208	4.3	3.7	22.7	3.6	21.7
108	3.1	2.5	23.5	2.5	23.6
163	6.1	4.5	25.5	4.2	23.2
24	3.8	2.6	21.8	2.5	20.8
149	6.8	4.7	25.2	4.6	—
164	7.3	5.5	22.5	5.3	22.2
185	3.3	2.0	22.8	2.0	21.4
26	6.9	4.0	26.0	4.1	24.4
184	3.2	1.8	18.0	1.8	16.2
189	4.8	3.7	25.6	3.8	27.0
192	3.2	1.9	24.1	1.8	24.4
190	3.1	1.8	22.4	1.8	22.0

were slightly greater than those removed by carbon monoxide alone (Table 2), results at 450°C are not technically promising.

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