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EFFECT OF PYROLYSIS ON THE PROXIMATE AND ULTIMATE ANALYSIS OF LIGNITE

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ABSTRACT

The effect of pyrolysis over the temperature range 300–1000 °C on the proximate and ultimate analysis of lignite has been studied and the experimental results are presented here. Seven lignite samples from different reserves in Turkey with particle diameters of 0.1–0.2 mm were subjected to pyrolysis. The volatile matter contents of the lignite samples decreased by about 90%. The fraction of the calorific value remaining in the coke produced varies from 51 to 75%. The oxygen and hydrogen content decrease the most during pyrolysis.

INTRODUCTION

Coal subjected to heat treatment undergoes a series of chemical and physical changes which are of great importance in both the science and the technology of coal. The investigation of the changes in the proximate and ultimate analysis of lignite that take place when it is subjected to the action of heat in the absence of air is the objective of the research described in this study.

Owing to their low calorific values, high ash and sulphur contents, Turkish lignites are classified as low quality lignites. Seven lignite samples were selected for this study from different reserves in Turkey. The Cayirhan, Soma and Tunçbilek lignites are Lower Miocene, the Çan lignite is Upper Miocene, the Sorgun lignite is Lower Eocene, the Mengen lignite is Middle Eocene and the Keşan lignite is Oligocene. The degrees of coalification of some of these lignites are not in accordance with their geological age.

EXPERIMENTAL

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

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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 pyrolysis gas was passed through an ice-water bath, a tar and a liquor trap.

Three grams of coal, dried at 110 °C, were weighed in a silica boat and placed in the centre of the quartz reactor. The reactor and the transfer lines were flushed with nitrogen for 20 min at the beginning of each run to remove air from the system. The system was also purged with nitrogen at the end of each run to remove all of the volatile compounds and the tubular reactor was cooled. Çan and Çayirhan lignite samples with particle diameters of 0.1–0.2 mm were carbonized over the temperature range 300–1000 °C for 30 minutes. The other lignite samples selected for this study with particle diameters of 0.1–0.2 mm were pyrolysed at 900 °C for 30 min. In all of the experiments the pressure was maintained at atmospheric pressure.

All analyses of lignite and coke samples were performed according to the ASTM standards [1].

RESULTS AND DISCUSSION

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

Temperature is the most important variable affecting the composition of pyrolysis products from coal. It affects the decomposition reactions of coal and the secondary reactions of the volatiles released. The analyses of the cokes produced from Çan and Çayirhan lignites pyrolysed at temperatures between 300 and 1000 °C are shown in Table 3. Increasing the temperature causes a decrease in the content of volatile matter, a source of air pollution,

TABLE 1

Proximate analyses of the lignite samples

Lignite sample	Moisture (wt.%)	Dry basis			
		Volatile matter (wt.%)	Ash (wt.%)	Fixed carbon (wt.%)	Net calorific value (MJ kg^{-1})
Çayirhan	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)

Lignite sample	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	S (wt.%)
Çayirhan	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

TABLE 3

Proximate analyses of the cokes produced at different temperatures from Çan and Çayirhan lignites

Temp. (°C)	Çan lignite				Çayirhan lignite			
	Volatile matter (wt.%)	Ash (wt.%)	Fixed carbon (wt.%)	Coke yield (wt.%)	Volatile matter (wt.%)	Ash (wt.%)	Fixed carbon (wt.%)	Coke yield (wt.%)
300	41.4	9.3	49.3	93.1	39.2	19.5	41.3	90.5
400	37.7	10.5	51.8	82.8	35.7	21.8	42.5	80.2
500	26.9	11.7	61.4	74.3	25.8	24.7	49.5	70.7
600	17.3	12.8	69.9	67.9	19.8	26.5	53.7	66.2
700	16.3	13.7	70.0	64.3	18.1	28.0	53.9	60.9
800	12.5	14.4	73.1	61.7	14.1	29.5	56.4	59.1
900	11.4	14.8	73.8	59.5	10.0	31.1	58.9	57.8
1000	11.0	14.9	74.1	59.3	9.4	31.5	59.1	56.8

TABLE 4

Proximate analyses of the coke samples produced following pyrolysis at 900 °C (dry basis)

Lignite sample	Volatile matter (wt.%)	Ash (wt.%)	Fixed carbon (wt.%)	Coke yield (wt.%)	Net calorific value (MJ kg^{-1})
Çayirhan	10.0	31.1	58.9	57.8	22.3
Soma	8.0	32.7	59.3	60.2	23.0
Keşan	7.7	21.7	70.6	62.4	24.8
Çan	11.4	14.8	73.8	59.5	28.2
Mengen	10.3	18.4	71.3	50.6	27.5
Sorgun	10.3	5.6	84.1	58.1	31.2
Tunçbilek	8.4	16.7	74.9	62.9	26.6

but the ash content of the cokes increases. Most of the volatile material is released at temperatures between 400 and 500 ° C.

The proximate analyses of the coke samples produced from the seven lignites pyrolysed at 900 ° C for 30 min are shown in Table 4. The volatile matter contents, compared with the lignite samples, decreased by about 90%. Tunçbilek lignite contains 44.7% and Mengen lignite contains 55.8% volatile matter; the loss of their volatile matter during pyrolysis is 88.2% and 90.6%, respectively. The coke yield decreases with an increase in the volatile matter of the lignite sample. Tunçbilek lignite contains the least volatile matter, therefore the coke yield from it is the highest.

The pyrolysis causes considerable increase in the ash content of the lignite samples. There is a correlation between the loss of volatile matter and the increase in the ash content as well as the net calorific value which remains in the coke produced. The net calorific value of Keşan lignite is 20.7 MJ kg^{-1} and of the coke produced at 900 ° C is 24.8 MJ kg^{-1}. Comparing the heat content of the coke with that of the original lignite, it is found that 74.8% of the heat content of this lignite remains in the produced coke. Only 51% of the net calorific value of Mengen lignite remains in the coke produced at 900 ° C, because the increase in ash content of this lignite is very high.

The changes in total sulphur and forms of sulphur in the above-mentioned lignite samples following pyrolysis under nitrogen and ammonia atmospheres were discussed in our two recent studies [2,3].

The distribution of carbon, hydrogen, nitrogen and oxygen in the coke produced from pyrolysis of Çan lignite over the temperature range 300–1000 ° C can be seen in Table 5 and the variation in the content of these elements in the coke remaining is illustrated in Fig. 1. The rapid decrease in hydrogen and oxygen content in the coke produced between 300 and 600 ° C is clear. Among the elements studied, hydrogen shows the maximum decrease during pyrolysis of Çan lignite; at 900 ° C, 96% of the hydrogen

TABLE 5

Ultimate analyses of the cokes produced at different temperatures from Çan lignite (30 min; 0.1–0.2 mm) (dry basis)

Temp. (° C)	C (wt.%)	H (wt.%)	N (wt.%)	O [a] (wt.%)	S (wt.%)
300	59.25	3.80	1.65	20.72	5.24
400	61.50	3.00	1.55	18.98	4.47
500	65.45	2.45	1.75	14.27	4.40
600	71.15	1.85	1.60	8.38	4.18
700	72.30	1.35	1.35	7.63	3.69
800	73.70	0.70	1.00	7.14	3.06
900	75.45	0.30	0.45	6.44	2.60
1000	75.65	0.30	0.60	6.05	2.50

[a] %O = 100 − (C + H + N + S + ash) (%).

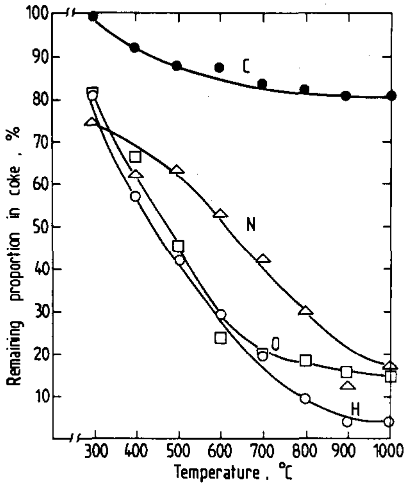

Fig. 1. Variation in the remaining proportion of carbon, hydrogen, nitrogen and oxygen content of Çan lignite in coke with temperature.

content of Çan lignite has been transferred into liquid and gaseous products. As the temperature rises, the coal first loses (400–500 ° C) its loosely bound water, carbon dioxide and carbon monoxide; at higher temperatures a slower evolution of the volatile matter occurs owing to the dehydrogenation of some of the hydroaromatic structures, scission of the molecule at methylene bridges and rupture of the alicyclic rings [4,5].

Nitrogen appears to be more strongly bound and is volatilized over a relatively high temperature range. The nitrogen–carbon ratios are roughly constant over the temperature range 300–600 ° C.

The fraction of the carbon content of Çan lignite remaining in the produced coke does not show any important changes above 500 ° C (Fig. 1). At 500 ° C, the volatile matter content of Çan lignite had decreased by 58%, and 88% of the carbon of the original lignite remains in the coke; at 900 ° C,

TABLE 6

Ultimate analyses of the coke samples produced following pyrolysis at 900 ° C (dry basis)

Lignite sample	C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	S (wt.%)
Çayirhan	61.1	0.5	1.1	2.5	3.7
Soma	63.2	0.6	0.6	0.5	2.4
Keşan	73.4	0.9	1.1	0.8	2.1
Çan	75.5	0.3	0.5	6.3	2.6
Tunçbilek	78.5	0.5	0.9	1.4	2.0
Mengen	73.1	0.8	1.0	0.9	5.8
Sorgun	85.0	0.7	1.0	6.6	1.1

the decrease in volatile matter rises to 86% and 81% of the carbon of the lignite is present in the coke produced. At high temperatures, the volatile fraction is richer in hydrogen than the original coal itself and the coke is richer in carbon. Therefore the hydrogen–carbon ratios of the tar and gaseous products must be much higher than that of the original coal.

The ultimate analysis of the coke samples produced from the seven lignites by heating at 900°C for 30 min is shown in Table 6. The fraction of the carbon content of the lignite samples remaining in the cokes varies between 12 and 36%; the decrease in hydrogen content due to pyrolysis varies between 86 and 96%; the fraction of oxygen which is transferred into liquid and gaseous products varies between 81 and 98% and the decrease in nitrogen content ranges between 55 and 82%. Of the four elements examined, the oxygen and hydrogen decreased the most.

The reason for the decrease in volatile matter content of lignite during pyrolysis is the decrease in its hydrogen, nitrogen and oxygen content.

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