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An investigation into the thermal behaviour of Bangladeshi coals

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Abstract

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) studies have been carried out to investigate the thermal behaviour of Bangladeshi coals. On heat-treatment in an inert atmosphere up to 600°C, 20-27% weight loss occurs due to the removal of various volatile materials. DTA results indicate the chemical reactivity of the coal samples initially at 80-110°C, due to loss of water, and two other major reactions at around 420 and 530°C, due to primary and secondary devolatization. Primary devolatization takes place as the coal melts under the action of heat, and the secondary devolatization represents the resolidification of the coal samples. The DTA curves also indicate the coking ability of the coals.

Keywords: Coking coal; DTA; Free swelling index; TGA

1. Introduction

Coal is a physically heterogeneous and chemically complex mixture of organic and inorganic species. Coals undergo appreciable physico-chemical changes when heat-treated in the temperature range 350-600°C, during which reactive molecules break along the weakest bonds, forming free radicals which subsequently recombine with other radicals or molecules to form more highly condensed species and volatile

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compounds. Coals are broadly classified into two types: coking and non-coking. Coking coals usually pass through a plastic or softening state in the temperature range 350-450°C depending on the rank [1]. The strength of the coke residue largely depends on the degree of plasticity in the softening zone.

Prior to coke formation, bituminous rank [2] has the same characteristics as coking coals, because bituminous coals possess a greater degree of orientation and consequently a greater tendency towards parallel stacking of structural units than low rank coals, and there are also less cross-links and fewer pores. Prime quality coking coals, having volatile contents in the range $20-32%$ (dry ash free, daf), become plastic before active decomposition occurs [3,4]. A coal with a free swelling index of \geq 4 may have good coking properties.

Differential thermal analysis (DTA) [5] was the first thermoanalytical tool used in studying the thermal behaviour of coal. Although various investigators [6,7] have observed similar qualitative effects for coals of the same rank, there are still few quantitative data available to distinguish one from another. DTA is another important aid to the study of decomposition reactions in coal. The use of thermogravimetry in coal research was pioneered by van Krevelen and his followers [8-10] in the study of coal degradation to measure weight change.

The DTA thermograms of coal are recognized by initial, primary and secondary devolatization. In good coking coal, primary devolatization must occur within the same temperature range as softening. Coals undergoing excessive initial devolatization do not, in general, have adequate softening and binding capacity. However, strong secondary devolatization increases the formation of cracks and undesirable reduction of the coke to small size [4].

Superior quality coals have a greater practical application in power generation and also in the metallurgical industries, especially the steel industry. In view of the World energy situation, Bangladesh is faced with a dual energy problem. Over recent years about 250 million tonnes of coal have been found in the north-western part of Bangladesh. The main objective of this research is to characterize the rank of Bangladeshi coals and to attain a better understanding of the coking process on the basis of their thermal behaviour.

2. Experimental

2.1. Coal sample specification

Coal samples were collected from different depths of Barapukuria and Khalaspir coal deposits found in the north-western part of Bangladesh. Barapukuria and Khalaspir coals are specified by GDH-39 $(160-450 \text{ m depth})$ and GDH-45,46 (287-442 m depth) respectively. The samples were sun-dried and ground into fine powder by pestle and mortar, and then passed through a I00 mesh screen. The powder was immediately stored in an air-tight container to avoid water absorption.

Coal		Rank (ASTM	Elemental analysis (wt%, daf)					Moisture $(wt\%, db)$	Volatile matter	Free swelling
Bore hole no.	Depth to top in ft	class- ification)	C	H	N	О	S		$(wt\%, daf)$	index
GDH-39	625	mv B	82.34	5.23 2.14		9.70	$0.59 - 3.25$		26.72%	5.5
GDH-39	638	mv B	81 22	5.07	1.83	11.23	0.65	3.82	25%	5.0
GDH-45	989	mv B	85.77	5.16	1.83	6.39	0.85	3.50	22.76%	7.5
GDH-45	1026	my B	85.11	5.09	1.83	7.21	0.76	3.25	20.71%	4.5
GDH-46	1055	mv B	90.64	2.34	1.64	4.58	0.80	7.23	21.86%	7.0

Table 1 Characterization of Bangladeshi coals

db: dry basis, daf: dry ash free basis.

2.2. DTA and TGA apparatus

All DTA and TGA scans were carried out from 30 to 900°C under argon flow at a heating rate of 10 K min⁻¹. DTA was performed using a Shimadzu micro DTA system model DT-30. A Mettler M3 balance TG 50 furnace and microprocessor TA-3000 system were used for TG analysis. The methods of thermal analysis used in this study have been described elsewhere $[11-13]$.

3. Results and discussion

Results of the elemental analysis of the coal samples are tabulated in Table 1. They show that Bangladeshi coals can be specified as being of the high quality bituminous type according to the ASTM standard method [14]. Fig. 1 shows the DTA traces of the coal samples. All the DTA traces show the same trend in behaviour, having three endothermic peaks followed finally by an exothermic peak. The first small endothermic peak around 100° C is expected to be due to elimination of water molecules. The second endothermic peak appearing in the temperature range $400-435^{\circ}$ C is related to primary devolatization [15], during which compounds containing carbon, hydrogen and oxygen are released. The third endothermic peak in the temperature range $525-550^{\circ}$ is caused by the secondary devolatization, during which mainly hydrogen is removed.

The last exotherm is expected to be due to the greater degree of orientation of carbon hexagonal planes. As coal contains small graphitic ring clusters, in the carbonization of coals [16] all lower aliphatic and hydroxyl groups, together with hydrogen, carbon monoxide and alkyl aromatics, start to disappear leaving behind all the aromatic ring structures. These ring structures become aligned in a parallel array to form an anisotropic structure at higher temperatures. The peak areas of primary and secondary devolatization are found to be more or less equal.

Fig. 1. DTA **traces of Barapukuria and Khalaspir coal deposits:** (a) GDH-39, depth 638 ft; (b) GDH-45, depth 989 ft; (c) GDH-45, depth 1026 ft; (d) GDH-46, depth 1055 ft; (e) GDH-39, **depth** 625 **ft.**

Compared to the thermal study of German rank classification of Illinois coals by Glass [1], the behaviour of Bangladeshi coals is found to have very little difference. The primary and secondary devolatization peaks occur within the temperature range 410-550°C in the case of Bangladeshi coals. Melting and resolidification start earlier in Bangladeshi coals than in Illinois coals. Inexcessive amounts of volatile materials are released in the primary devolatization and as a result the coals have adequate softening and binding capacities, good characteristics of suitable coking coals. As the secondary devolatization peak is not very strong, coke formation will be mostly uniform.

Fig. 2. Thermogravimetric study of Khalaspir coal: (a) GDH-45, depth 989 ft; (b) GDH-45, depth 1026 ft; (c) GDH-46, depth 1055 ft.

Fig. 3. Thermogravimetric study of Barapukuria coal: (a) GDH-39, depth 638 ft; (b) GDH-39, depth 625 ft.

This thermal behaviour of the coal samples can be correlated with the standard German classification of rank and coking property [1]. The Bangladeshi coal samples occur as Fettkohle coking type coals (i.e. coals which contain 22–28% volatile matter) and are naturally of coking type. Values of the free swelling index indicate the nature of good coking coal, and Bangladeshi coals may be valuable for use as metallurgical coke.

Figs. 2 and 3 show the TG weight loss curves of the coal samples. There are two temperature ranges observed: one in the low-temperature region from 80 to 110° C, where water loss is expected and the total moisture content is calculated to be about

 $3-8\%$, and the other mainly in the $300-600^{\circ}$ C region, where maximum loss of volatile materials of about $20-27%$ occurs due to primary and secondary devolatization.

4. Conclusions

The Bangladeshi coals are specified as medium volatile bituminous coal having low sulphur content according to the ASTM standard. On the basis of differential thermal analysis, they are identified as coking coal. The thermal curve gives a graphic representation of the relative extents of primary and secondary devolatization.

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