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A STUDY OF SULPHONATED AND OXIDIZED COALS BY THERMAL ANALYSIS

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Earthy and xylytic brown coals from Poland have been sulphonated with 98% sulfuric acid at temperatures of 60°, 90° and 140°C. The main exothermic peak shifts to higher temperatures with increase in sulphonation reaction temperature whereas overall weight loss to 1000°C decreases. DTA curves of earthy and xylytic coals sulphonated at higher temperatures are similar, even though DTA curves of the unmodified coals differ appreciably. Thermal decomposition of earthy coal oxidized by nitric acid follows a different pattern. Nitric acid causes oxidation and depolymerization of the organic components and this is reflected in the shapes of DTA and TG curves of oxidized coals. As the nitric acid concentration and reaction temperature increase, the main exothermic peak shifts to lower temperatures (from 330°C for basic coal to 270°C for coal oxidized with 30 and 50% nitric acid). The weight loss is higher for oxidized coal than for coal unmodified by nitric acid.

Keywords: brown coals, sulphonation and oxidation reaction, thermal stability of the coal structure

Introduction

Chemical modification studies of brown coal to produce ion sorbents have proved that coals sulphonated with sulphuric acid of oxidized with nitric acid show very good ion exchange and sorption properties [1]. Sulphonation and oxidation processes of brown coal cause significant changes in chemical structure and may affect considerably the mechanism of thermal decomposition. Shapes of thermal analysis curves and other properties of the samples can be used to determine the degree to which the coal has undergone carbonization [2, 3].

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Experimental

Thermal analysis was carried out on two petrographic types of brown coal (earthy and xylytic from the Polish Coal Basin) and on samples of these sulphonated with concentrated sulphuric acid at temperatures of 60°–140°C, and also oxidized with nitric acid of various concentrations at temperatures of 20°–100°C. Conditions for chemical modification are given in Table 1, and characteristics of the coals before and after modification are presented in Table 2. Thermal analyses were carried out using a derivatograph (MOM Hungary), at a heating rate of 10 deg·min^{-1} in air.

Table 1 Sulphonating and oxidizing conditions for brown coals

Symbol of sample	Concentration and type of acid	Reaction temperature / °C
	E - Earthy brown coal from Konin Coal Mine	
ES – 1	98% H_2SO_4	60
ES – 2	98% H_2SO_4	90
ES – 3	98% H_2SO_4	140
EO – 1	10% HNO_3	20
EO – 2	30% HNO_3	0
EO – 3	30% HNO_3	20
EO – 4	50% HNO_3	100
	X – Xylytic brown coal from Turów Coal Mine	
XS – 1	98% H_2SO_4	60
XS – 2	98% H_2SO_4	90
XS – 3	98% H_2SO_4	140
XO – 1	10% HNO_3	20
XO – 2	30% HNO_3	0
XO – 3	50% HNO_3	100

Results

In sulphonated coals as well as oxidized coals, increase in acid concentration and reaction temperature results in a decrease in carbon and hydrogen contents and an increase in oxygen, sulphur and nitrogen contents of the modified coals [4, 5]. As a result of the action of sulphuric acid on brown coal, sulphonation and oxidation reactions take place, the aliphatic structures undergo aromatization,

Table 2 Chemical characteristics of brown coals and sulphonated and oxidized products

Symbol of sample	Ash	Volatile matter	Ultimate analysis /					Functional groups / mval g^{-1}		Exchange capacity	Mass loss to 1000°C from TG curves /
	A^d/wt%	V^{daf}/wt%	C^{daf}	H^{daf}	S^{daf}	N^{daf}	O^{daf}*	SO_3H^d	$COOH^d$	C_w^d	wt%
E	2.9	53.1	67.4	4.6	1.2	0.9	25.9		2.3	2.3	65.0
ES – 1	1.8	50.7	60.5	3.7	3.5	1.0	31.3	0.7	2.3	3.0	65.0
ES – 2	1.6	51.2	58.2	3.3	4.5	1.0	33.0	1.0	2.3	3.3	63.7
ES – 3	1.1	54.0	55.7	2.9	4.5	1.0	35.9	1.0	2.7	3.7	60.0
EO – 1	2.1	54.0	60.1	4.0	1.0	2.0	32.9	–	3.5	3.5	68.0
EO – 2	1.5	54.0	62.6	4.2	1.0	1.8	30.4	–	3.1	3.1	66.3
EO – 3	1.3	54.7	56.7	3.3	1.0	4.0	35.0	–	4.1	4.1	72.5
EO – 4	1.2	57.5	54.8	3.3	1.0	4.9	36.0	–	4.5	4.5	77.5
X	0.8	60.7	67.4	5.4	1.1	0.2	25.9	–	0.7	0.7	80.0
XS – 1	0.8	55.3	60.5	3.2	5.5	0.2	30.6	1.4	0.7	2.1	63.5
XS – 2	0.7	51.3	59.0	2.9	6.8	0.2	31.1	1.8	0.9	2.7	62.0
XS – 3	0.5	55.1	59.0	2.6	7.3	0.2	32.5	2.0	1.2	3.2	60.0
XO – 1	0.2	61.5	54.7	3.7	1.0	4.5	36.1	–	2.4	2.4	75.0
XO – 2	0.3	65.8	51.3	3.2	0.6	4.4	40.5	–	1.9	1.9	73.6
XO – 3	0.2	68.2	50.2	3.0	0.6	5.4	40.8	–	4.2	4.2	75.0

* calculated by difference

and the degree of condensation of the aromatics increases. The action of nitric acid on brown coal causes oxidation, nitration and depolymerization. The intensity of these processes depends on both acid concentration and reaction temperature.

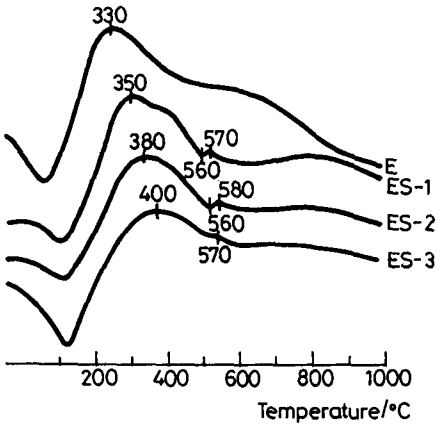

Fig. 1 DTA curves of earthy brown coal and sulphonated products

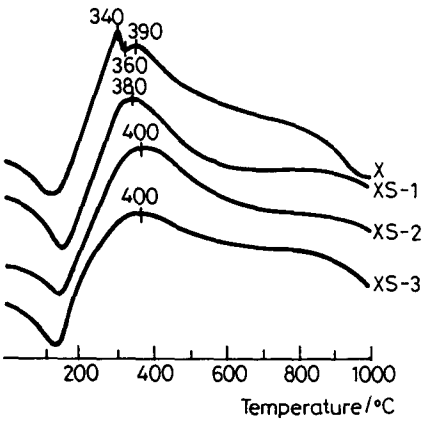

Fig. 2 DTA curves of xylytic brown coal and sulphonated products

Figures 1–4 show DTA curves of original and modified coal samples. A common characteristic is a low-temperature endothermic peak which begins at 60°–80°C, reaches its maximum at 120°–140°C and ends at 200°–220°C. This effect corresponds to a weight loss on the TG curve attributed to loss of adsorbed

water. For the non-modified earthy brown coal, thermal destruction starts at 200°C, reaches its maximum at 420°C and ends at about 550°C. On the DTA curve a wide exothermic peak with a maximum at 330°C can be observed. It can be seen distinctly from the DTA curves of sulphonated coals that increase in temperature of sulphonation reaction in the range 60°–140°C causes the main exothermic peak to undergo a systematic shift towards higher temperatures, reaching 400°C for coal sulphonated at 140°C. The total weight loss decreases systematically with increase in sulphonation temperature.

It is likely that these phenomenon result from an increase in extent of aromatic condensation of the brown coal structure with increase in sulphonation temperature. On DTA curves of sulphonated earthy brown coals an additional small exothermic peak at 560°C occurs. However this peak does not appear on DTA curves of sulphonated xylytic brown coals. The origin of the peak is very difficult to explain. The DTA curve of non-modified xylytic brown coal has a somewhat different shape compared with that of earthy brown coal. The DTA curve of xylytic brown coal results from a combination of typical basic components such as cellulose and lignin. Cellulose characteristically shows an endothermic peak at 360°C and lignin an exothermic peak at 400°C [6]. Increase in sulphonation temperature is followed by complete loss of the endothermic peak while the exothermic peak at 400°C remains unchanged. The DTA curve of xylytic brown coal sulphonated at 140°C is nearly the same as the DTA curve of earthy brown coal sulphonated at the same temperature. As a result of the sulphonation process the organic component of the brown coals undergoes thermal decomposition at higher temperatures than non-modified coals. The maximum weight loss accompanying thermal decomposition of earthy brown coal to 1000°C is 65 wt% whereas for coal sulphonated at 140°C the weight loss is only 60 wt%. The max-

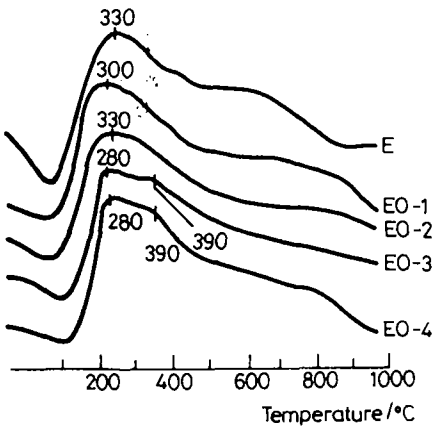

Fig. 3 DTA curves of earthy brown coal and oxidized products

imum weight loss of xylytic brown coal during carbonization to 1000°C is considerably higher (reaching 80 wt%) compared with earthy brown coal. However xylytic brown coal sulphonated even at lower temperatures has a much lower weight loss (about 63 wt%). This results from the fact that sulphuric acid destroys the cellulose structure but leaves the structure of lignin intact; this is thermally more stable.

DTA curves of brown coals oxidized with nitric acid are quite different. With increase in acid concentration as well as reaction temperature, the basic exothermic peak temperature of oxidized earthy brown coal shifts towards lower temperatures, i.e. from 330°C for unmodified brown coal to 280°C for coal oxidized with 30 and 50% nitric acid. Simultaneously, an additional exothermic peak with a maximum at 390°C appears. Weight losses increase systematically from 65 wt% for non-modified coal to 77.5 wt% for coal oxidized with 50% HNO_3. The DTA curves of oxidized xylytic brown coal are similar to those of earthy brown coal. Two exothermic peaks with maxima at 280° and 390°C can be observed on the DTA curves. The typical peaks for non-modified xylytic coal (exothermic at 340°C and endothermic at 360°C) disappear for modified coals. It is likely that nitric acid oxidizes cellulose to oxycellulose and lignin to humic acid of nitrohumic acid which are thermally more thermostable than cellulose and these determine the shape of the DTA curve. The first exothermic peak at 280°C may be connected with split-off of carboxylic groups. It is likely that in this temperature range the low molecular weight fragments of the brown coal structure which are formed as a result of the depolymerizing action of nitric acid un-

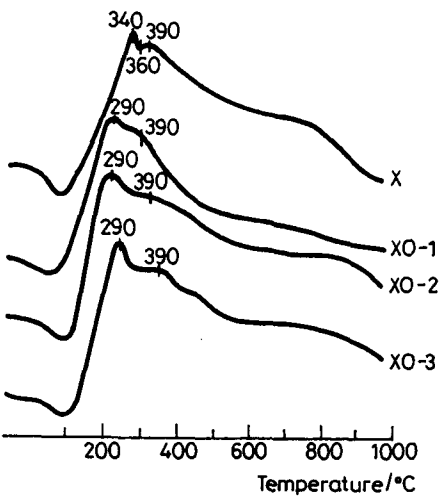

Fig. 4 DTA curves of xylytic brown coal and oxidized products

dergo condensation. Maximum weight losses up to 1000°C accompanying pyrolysis of oxidized xylytic coals are considerably lower compared with non-modified xylytic coals and are all about 75 wt% regardless of the conditions used; which this is evidence that the oxidized xylytic structure is more resistant to thermal decomposition. The sulphonation and oxidation processes cause fundamental changes in the chemical structure of xylytic brown coal, making this similar to the structure of earthy brown coal.

Conclusions

Investigations of the thermal decomposition of brown coals using thermal analysis have proved the chemical changes of the organic substance of coal during sulphonation affect the thermal stability of the coal structure. Factors responsible for this phenomenon are the aromatization of aliphetic structures as well as condensation of aromatic structure which result from the action of sulphuric acid upon brown coals.

Depolymerization reactions accompanying the oxidation of brown coals with nitric acid render their structure less thermally stable. The main exothermic peaks shift towards lower temperature, from 330°C for non-oxidized coal to 280°C for oxidized coal.

As a result of sulphonation with sulphuric acid or oxidation with nitric acid, the chemical structure of xylytic brown coal becomes similar to that of earthy brown coal in terms of thermal stability.

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Zusammenfassung — Aus Polen stammende Erd- und xylitische Braunkohle wurde bei einer Temperatur von 60°, 90° und 140°C mit 98%-iger Schwefelsäure sulfoniert. Der größte exotherme Peak verschiebt sich in Richtung höherer Temperaturen, wenn die Sulfonierungsreaktionstemperatur erhöht wird., während der Gesamtgewichtsverlust bis 1000°C abnimmt. Die DTA-Kurven von bei höheren Temperaturen sulfonierten Erd- und xylitischen Braunkohlen ähneln einander, wenn sie auch von den DTA-Kurven der nicht modifizierten Kohlen beträchtlich abweichen. Die thermische Zersetzung von mittels Salpetersäure oxidierter erdiger Kohle zeigt einen anderen Verlauf. Salpetersäure verursacht eine Oxidierung und Depolymerisierung der

organischen Komponenten und dies spiegelt sich in den Verläufen der DTA- und TG-Kurven der oxidierten Kohlen wieder. Steigen Salpetersäurekonzentration und Reaktionstemperatur an, verschiebt sich der höchste exotherme Peak in Richtung niedrigerer Temperaturen (von 330°C für die Basiskohle auf 270°C für die mit 30 und 50%-iger Salpetersäure oxidierte Kohle). Der Gewichtsverlust ist für die mit Salpetersäure modifizierte Kohle höher als bei der unmodifizierten Kohle.