Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 2, 379–383

APPLICATION OF TG-DTG ANALYSIS IN THE STUDY OF THE AMMOXIDISED CARBON MATERIALS

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The effect of ammoxidation on thermal stability of carbonaceous materials characterised by degree of coalification other than that of brown coal (Konin mine, Poland) or sub-bituminous coal (Sośnica mine, Poland) was studied by thermogravimetric (TG-DTG) method. Analysis of TG-DTG curves has shown that coal samples ammoxidised at the higher temperature show slightly lower thermal stability. It has been established the importance of the sequence in the processes of carbonisation and ammoxidation. Both the amount of nitrogen introduced on the surface of studied carbonaceous materials and the thermal stability of nitrogen groups were affected.

Keywords: *ammoxidation, carbon materials, TG-DTG analysis*

Introduction

Nitrogen-enriched carbonaceous materials can be obtained from materials with high content of nitrogen, e.g. some biological materials, certain polymers [1] or chemical modifications of carbons obtained as a result of thermochemical treatment of common raw coal materials [2, 3]. This last procedure involves reactions with different N-reagents such as ammonia or its derivatives (ammonium carbonate, hydrazine, hydroxylamine, urea) [1, 4, 5], nitrogen oxide(II) in the presence or absence of O_2 and/or H_2O [6, 7], mainly with the carboxyl groups naturally occurring in coal [8]. An efficient method of nitrogen enrichment is ammoxidation consisting in a simultaneous oxidation of precursors [4–6].

Recently, active carbons enriched in nitrogen have enjoyed much interest because of their prospective practical application. It has been shown that modification of the active carbon precursor with nitrogen considerably improves its textural properties and the nucleophilous character of its surface [4, 5]. Thanks to these characteristics the modified active carbon can be applied for removal of H_2S, SO_2 [1, 5], HCHO [9], as electrode material in supercapacitors [4, 10–12] as catalysts [13–15] and catalyst supports [16, 17].

The type of nitrogen containing group depends on the method of thermal treatment of the nitrogen-enriched material, however, the main condition necessary for the incorporation of nitrogen into the graphene structure, present in coal materials, is that the temperature is higher than 400°C [18].

The thermal behavior of coal and the possibility of using modified carbon materials in practice are usually studied by the thermal methods such as TG, DTG, DTA, DSC [19–21].

In the study reported the TG-DTG method was applied to investigate thermal behavior of nitrogen-containing functional groups generated by ammoxidation on the surface of selected coals. The main aim of this study was to determine the effect of ammoxidation on the thermal properties of coals of a different degree of coalification and different content of introduced nitrogen.

Experimental

Starting materials

The measurements were performed on two types of coal samples characterised by different degree of coalification: (1) Polish brown coal (lignite) from the Konin colliery and (2) Polish young coking coal (sub-bituminous) from the Sośnica colliery.

The starting raw samples were crushed and sieved to collect the grain size ≤0.01 mm, then subjected to demineralisation by hydrochloric and hydrofluoric acids, according to the Radmacher and Mohrhauer method [22].

Preparation of samples

The raw coal samples were divided into two groups: the first was subjected to ammoxidation and then carbonisation, while the second by carbonisation and then ammoxidation. Ammoxidation was carried out using a mixture of ammonia and air at a volume ratio of 1:3 (250/750 cm^3 min^{-1}) in a flow reactor at 300 or 350°C, for 5 h [4, 11]. The samples were carbonised in the gases evolved during the process, with temperature increasing

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1388–6150/$20.00

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at the rate of 5°C min^{-1} to the final 700°C, maintained for 1 h. Analytical data for the starting coals used in this study are presented in Table 1.

Elemental analysis

The chemical composition of the investigated samples was tested with an Elementar Vario ELIII microanalyser. The apparatus permits determination of the content of carbon, hydrogen, nitrogen and sulphur, separately from oxygen. Results of the elemental analysis are shown in Tables 1–3.

TG-DTG analysis

TG/DTG analysis of the investigated coal samples was conducted with a Setsys 12 (Setaram) instrument. The samples of about 10 mg and particle size below 0.01 mm were heated in helium atmosphere in temperature range from 20 to 1000°C at the heating rate of 3°C min^{-1}.

Results and discussion

The results of the elemental analysis of the main materials under study subjected to demineralisation are presented in Table 1. The differences in elemental carbon and total oxygen and sulphur results from different degree of coalification of the raw coal samples.

Ammoxidation of coal leads to decrease in elemental carbon content in both samples (first demineralised and carbonised (Table 2)) while a significant increase in the content of nitrogen can be observed in the samples. The content of introduced nitrogen in non-carbonised samples was also two times higher than in those previously carbonized.

This difference can be explained by the surface structure of materials subjected to ammoxidation containing functional groups characterised by different reactivity towards the ammonia–air mixture.

Increased ammoxidation temperatures lead to increase in the amount of introduced nitrogen. Small

Table 1 The elemental analysis of starting materials (mass%)

Sample code	C		H		N				(O+S)	
	E	F	E	F	E	F	E	F	E	F
SD	77.8	68.4	5.2	3.0	0.9	12.4	–	–	16.1	16.2
SD	77.8	69.1	5.2	2.9	–	–	0.9	13.1	16.1	14.9
SDK	90.9	84.2	2.1	1.9	0.0	5.9	–	–	7.0	8.0
SDK	90.9	80.7	2.1	1.8	–	–	0.0	7.7	7.0	9.8

S – hard coal, *D* – material demineralised, *K* – after carbonization, T_1 – ammoxidation in 300°C, T_2 – ammoxidation in 350°C, *E* – before ammoxidation, *F* – after ammoxidation

Table 2 Effect of ammoxidation on elemental composition of investigated samples (mass%)

Sample code	C		H		N		(O+S)	
	G	I	G	I	G	I	G	I
SD	77.8	90.9	5.2	2.1	0.9	0.0	16.1	7.0
SDN_1	68.4	83.2	3.0	2.0	12.4	9.0	16.2	5.8
SDN_2	69.1	82.9	2.9	2.3	13.1	9.2	14.9	5.6

S – hard coal, *D* – material demineralised, *K* – after carbonization, N_1 – ammoxidation in 300°C, N_2 – ammoxidation in 350°C, *G* – before carbonization, *I* – after carbonization

Table 3 Effect of carbonisation on elemental composition of investigated samples (mass%)

Sample code	C		H		N		(O+S)	
	J	L	J	L	J	L	J	L
SDK	90.9	93.1	2.1	1.1	0.0	0.0	7.0	5.8
SDN_1	68.4	91.1	3.0	1.2	12.4	2.3	16.2	5.4
SDN_2	69.1	90.2	2.9	1.2	13.1	2.7	14.9	5.9
SDN_1K	83.2	89.7	2.0	1.2	9.0	3.6	5.8	5.5
SDN_2K	82.9	90.3	2.3	1.1	9.2	2.7	5.6	5.9
$SDKN_1$	84.2	92.5	1.9	1.0	5.9	1.9	8.0	4.6
$SDKN_2$	80.7	91.1	1.8	1.3	7.7	2.9	9.8	4.7

B – hard coal, *D* – material demineralised, *K* – after carbonization, N_1 – ammoxidation in 300°C, N_2 – ammoxidation in 350°C, *J* – before activation, *L* – after activation differences in the contents of the other elements are caused by changes in their proportions as a result of nitrogen introduction or their loss during the process of ammoxidation.

Carbonisation of the earlier ammoxidised samples leads to decrease in the content of nitrogen from 12.4 (SDN_1) and 13.1 (SDN_2) to 9.0 and 9.2 mass%, respectively (Table 3). As a result of release of volatile components, the total content of oxygen and sulphur decreases, and this decrease is accompanied by an increase in the content of elemental carbon as a consequence of carbonisation.

Chemical composition of the samples of brown coal from KWB Konin colliery, Poland subjected to the same procedure as discussed in this paper was investigated earlier [4]. Subjecting brown coal sample to the same procedures as those applied to sub-bituminous coal permits introduction of 22 mass% of nitrogen into the former samples.

Figures 1–4 show results of TG-DTG analysis of the investigated carbonaceous samples.

The DTG curves presented in Figs 2 and 4 show, in all cases, the presence of the first peak at about 100°C, assigned to elimination of water molecules. For samples subjected demineralisation the second peak appearing in the temperature range 360–420°C is related to primary devolatilisation, that is the release of volatile substances and tar components. With increased degree of coalification of the initial material the peak temperature is shifted towards higher values. The third peak in the temperature range 560–620°C is assigned to the secondary devolatilisation involving mainly a release of hydrogen and methane [21, 23, 24].

The second and third peaks do not occur in the DTG curves of the samples which were preliminary subjected to carbonisation as the volatile components were already removed in this process. As coal contains small graphitic ring clusters during carbonisation, all lower aliphatic and hydroxyl groups, together with hydrogen, carbon monoxide and alkyl aromatics, start to disappear leaving behind all the aromatic ring structures [23].

In the case of the samples first subjected to carbonisation and next ammoxidation, the mass loss within the temperature range 640–720°C is higher which can be assigned to the release of weakly bonded nitrogen species. For brown coal samples the mass loss is greater, which indicates smaller thermal stability of the nitrogen surface functional groups relative to that of the groups in the sub-bituminous coal.

TG curves of the studied samples are given in Figs 1 and 3, while quantitative aspects of the observed processes are summarised in Tables 4 and 5. The samples of both brown and sub-bituminous coals subjected

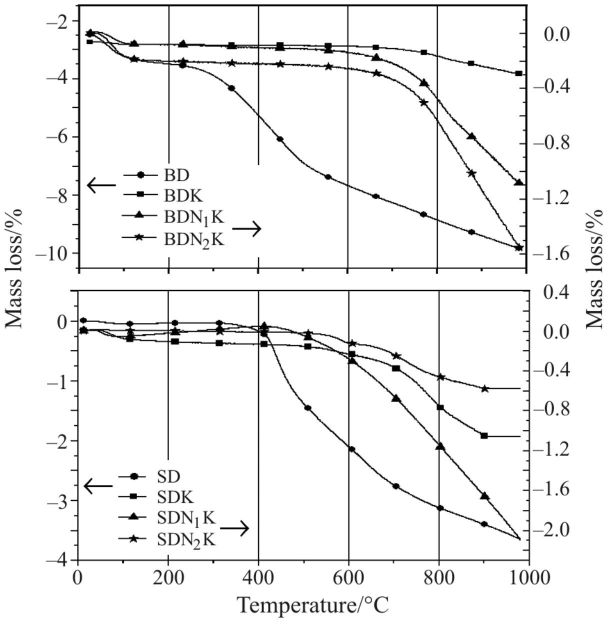

Fig. 1 TG curves of brown coal demineralised (BD), demineralised and carbonised (BDK), demineralised, ammoxidised in 300°C and carbonised (BDN_1K), demineralised, ammoxidised in 350°C and carbonised (BDN_2K) and sub-bituminous coal demineralised (SD), demineralised and carbonised (SDK), demineralised, ammoxidised in 300°C and carbonised (SDN_1K), demineralised, ammoxidised in 350°C and carbonised (BDN_2K)

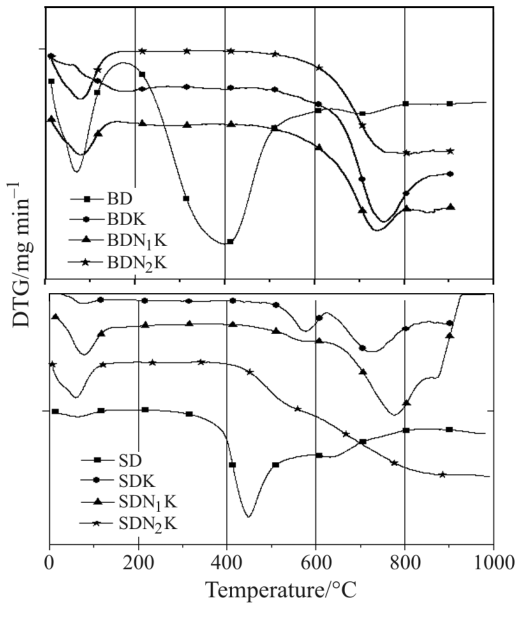

Fig. 2 DTG curves of brown coal demineralised (BD), demineralised and carbonised (BDK), demineralised, ammoxidised in 300°C and carbonised (BDN_1K), demineralised, ammoxidised in 350°C and carbonised (BDN_2K) and sub-bituminous coal demineralised (SD), demineralised and carbonised (SDK), demineralised, ammoxidised in 300°C and carbonised (SDN_1K), demineralised, ammoxidised in 350°C and carbonised (BDN_2K)

to demineralisation are characterised by a three-stage process of thermal decomposition. The TG curves of the samples first carbonised and then ammoxidised do not show the peak in the range 360–420°C, which is a result of the devolatilization of the samples during the above processes. In the range 820–860°C the TG curves of the nitrogen modified samples show an additional peak corresponding to mass loss, which can be related to the release of the more stable nitrogen groups. The TG curves of the brown coal samples ammoxidised in the higher temperature (BDN_2K) show the mass loss by about 3 mass% greater than that obtained for the samples ammoxidised in the lower temperature (BDN_1K). For the corresponding samples of sub-bituminous coal, the relation is reverse. It has been established that the sequence of the processes of carbonisation and ammoxidation affects both the amount of nitrogen introduced on the surface of the

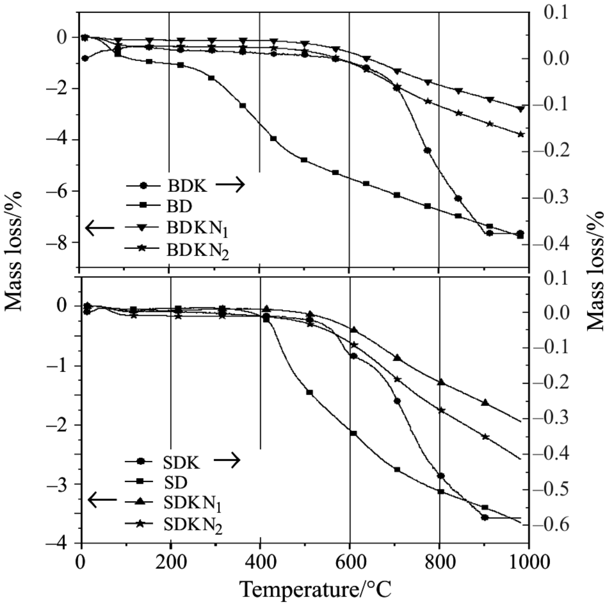

Fig. 3 TG curves of brown coal demineralised (BD), demineralised and carbonised (BDK), demineralised, carbonised and ammoxidised in 300°C ($BDKN_1$), demineralised, carbonised and ammoxidised in 350°C ($BDKN_2$) and sub-bituminous coal demineralised (SD), demineralised and carbonised (SDK), demineralised, carbonised and ammoxidised in 300°C ($SDKN_1$), demineralised, carbonised and ammoxidised in 350°C ($BDKN_2$)

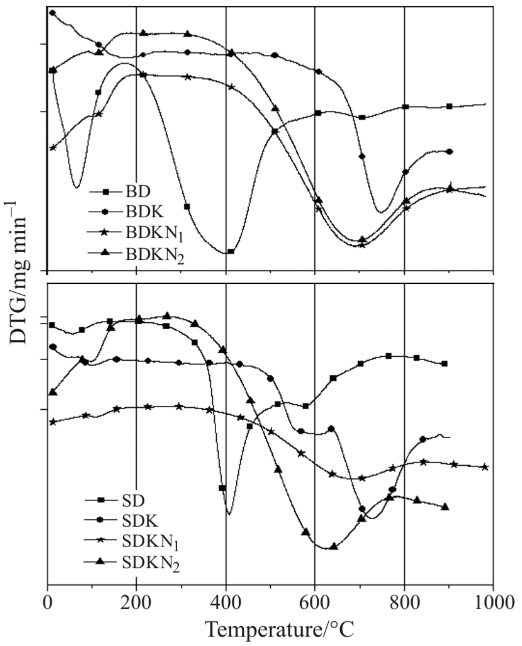

Fig. 4 DTG curves of brown coal demineralised (BD), demineralised and carbonised (BDK), demineralised, carbonised and ammoxidised in 300°C ($BDKN_1$), demineralised, carbonised and ammoxidised in 350°C ($BDKN_2$) and sub-bituminous coal demineralised (SD), demineralised and carbonised (SDK), demineralised, carbonised and ammoxidised in 300°C ($SDKN_1$), demineralised, carbonised and ammoxidised in 350°C ($BDKN_2$)

Table 4 Temperature ranges in which maximum mass loss of first carbonised and then ammoxidised coal samples are observed (mass%)

Sample code	Temperature range/°C			
	90–110	360–420	640–720	820–860
BD	10.2	37.2	9.2	–
SD	0.7	21.3	–	–
BDK	–	–	–	4.1
SDK	0.6	–	1.6	3.7
$BDKN_1$	0.7	–	14.1	–
$SDKN_1$	0.7	–	9.9	–
$BDKN_2$	2.5	–	17.6	–
$SDKN_2$	1.2	–	11.8	–

B – brown coal, *S* – bituminous coal, *D* – material demineralised, *K* – carbonised, N_1 – ammoxidation in 300°C, N_2 – ammoxidation in 350°C

Table 5 Temperature ranges in which maximum mass loss of first ammoxidised and then carbonised coal samples are observed (mass%)

Sample code	Temperature range/°C			
	90–110	360–420	640–720	820–860
BD	10.2	37.2	9.2	–
SD	0.7	21.3	–	–
BDK	–	–	–	4.1
SDK	0.6	–	1.6	3.7
BDN_1K	1.5	–	–	6.1
SDN_1K	1.7	–	–	7.3
BDN_2K	2.8	–	–	9.9
SDN_2K	0.6	–	1.2	3.2

B – brown coal, *S* – bituminous coal, *D* – material demineralised, *K* – carbonised, N_1 – ammoxidation in 300°C, N_2 – ammoxidation in 350°C studied carbonaceous materials and the thermal stability of nitrogen groups (Figs 3 and 4).

If the process carbonisation of coal material follows its ammoxidation, then DTG curves show a peak in the range of 820–860°C, its presence may be explained by decomposition of more stable nitrogen-containing functional groups formed during the carbonisation process.

Conclusions

The presented results have proved that the processes of carbonisation and ammoxidation significantly change the proportion of elemental composition of the studied brown and sub-bituminous coals. The increasing temperature of the ammoxidation process of the coal samples from 300 to 350°C results in the increase in nitrogen introduced onto their surfaces. The coal samples ammoxidised at the higher temperature show slightly lower thermal stability. The amount of the nitrogen introduced also depends on the sequence of the processes of carbonisation and ammoxidation. Moreover, the samples first ammoxidised and then carbonized are characterized by a greater thermal stability of nitrogen groups.

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Received: March 20, 2005
Accepted: August 26, 2005

DOI: 10.1007/s10973-005-6987-y