THERMOANALYTICAL INVESTIGATION OF LIGNITE HUMIC ACIDS FRACTIONS

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Abstract

Differential scanning calorimetry (DSC) and thermogravimetry (TG) studies of humic acids (HA) sequentially extracted at pH 7, 8, 9 and 10 by phosphate and pyrophosphate buffers have been carried out. Supplement information were provided by elementary analysis and FTIR spectroscopy to characterize and evaluate in details the thermooxidative behavior of HA fractions. The exothermic DSC profiles of the HA samples extracted by phosphate buffers or by pyrophosphates were shifted to lower temperatures in comparison with the original sample and showed narrow distribution of humic molecules. Experimental data showed dependency of HA fraction composition on the pH used during extraction. DSC experimental data showed 1 endothermic and from 2–5 exothermic peaks associated with mass loss recorded by TG measurement. Higher degree of aliphaticity observed on samples extracted at lower pH did not remarkably affect the DSC peak temperature of the first decomposition step associated with aliphatic moieties and functional groups decomposition and recombination reactions. On the other hand, such dependency was observed in higher temperature range where destruction of aromatic structures took part. The behavior of HA samples (even after separation of specific fractions) showed high complexity of system, which resulted in complicated physical and chemical processes occurred during thermooxidation. Observed stability and released heat were affected by many factors, among them evaporation of volatile part of humic matter and a slight contribution of weak interactions among humic molecules were considered.

Keywords: DSC, lignite humic acids, sequential pH-extraction, TG

Introduction

Lignite or brown coal humic substances (HS) are known to be precursors of coalification of organic matter (OM) which lead to the formation of bituminous coal and finally anthracite. Properties and distribution of HS functional groups are determined by the conditions occurring during diagenesis, e.g. processes leading to either mineralization by microorganisms or alteration to kerogen or coal-like products [1]. As a result of high complexity of decomposition processes and heterogeneity of original OM, humic substances are a complicated mixture of miscellaneous molecules [2]. HS play various roles in many environmental processes; therefore understanding HS

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chemical-physical properties and transformations is crucial in resolving their fundamental behavior. To obtain structural details, many analytical methods and extraction procedures have been applied; however, due to high heterogeneity of HS the problem is far from to be satisfactorily solved [1, 2].

Among modern methods of analysis, thermal investigations are steadily gaining interest. Thermal analytical techniques have been applied with the aim to elucidate structural features, thermal behavior or genesis processes of decayed natural heterogeneous OM for many years [3–13]. Experimental data clearly showed the strong dependence on pretreatment or saturating by cation or on different degree of humification. However, the thermoanalytical methods provide only indirect structural elucidation and therefore they had been frequently coupled with spectroscopic methods [10]. The thermoanalysis of humified organic matter are associated with many problems caused by combination of miscellaneous chemical-physical processes occurring during analysis and those can mislead provided information. In light of above discussion, the fractionation or separation of humic molecules (respecting some criterion) seems to be necessary. Such specification then leads to a 'deeper look' into investigated system. Moreover, some specific humic molecules play an important role in industrial and pharmacological applications [24].

In this work, the clarification of processes occurring during sequential pH-extraction of lignite humic acids and comparison of chemical-physical behavior of obtained fractions by means of thermoanalytical measurement will be given. In past, many extraction techniques and agents have been applied [1, 7], however with few exceptions, the sequential mode has not been used. In previous paper characterization of such fractions was done by means of High Performance Size Exclusion Chromatography [14]; chromatographic methods provided some information about molecular arrangement and dissolved humic molecules behavior. Methods of thermal analysis, on the other hand, under certain measurement condition (atmosphere etc.) can provide more understanding on the organic matter stability (fate) in solid-state. As it was stated previously [14], the sequential pH-extraction does not follow the same mechanism as was originally considered, e.g. in case of polymers separation; more than molecular length the aliphatic/aromatic ratio and oxygen amount dependency was observed and therefore their non-polymeric molecular feature was confirmed. The object of this work is to employ thermal analysis methods DSC and TG and FTIR spectroscopy to investigate analytical profiles (thermooxidative stability/lability) of sequentially extracted lignite HA fractions.

Materials and methods

Humic samples

South Moravian lignite collected from the Mír mine in the area of Mikulčice, nearby Hodonín, Czech Republic was used. 50 g of previously air-dried and 0.3 mm sieved lignite were mixed with 500 mL of 0.5 M NaOH solution and shaken for 24 h. After centrifugation, the supernatant was treated with concentrated HCl until the value

pH=1 was reached in order to precipitate the humic acid (fraction HA1). HA1 was then treated overnight with 0.5% (*v/v*) HCl-HF solution to remove residual ashes, dialyzed (Spectra/Por® dialysis tubes, 3500 M_w cut-off) against distilled water until chloride-free, and finally freeze-dried.

Table 1 Ash content and ash-free based elemental analyses of HAs, oxygen content obtained by difference 100 – C(%) – N(%) – H(%)

Sample	Ash/%	C/%	H/%	N/%	O/%	C/H	C/O
HA1	2.27	57.2	4.6	1.0	37.2	12.4	1.5
HA2	2.11	53.7	4.7	1.0	40.6	11.5	1.3
HA3	1.17	50.1	6.4	1.3	42.2	7.9	1.2
HA4	3.11	47.6	6.8	1.3	44.3	7.0	1.1
HA5	2.44	50.9	7.2	1.1	40.8	7.1	1.3

The freeze-dried HA1 was further shaken in aqueous buffer solutions to sequentially extract fractions soluble at different pHs. First, 1 L of phosphate buffer with pH=7 (0.062 M NaH_2PO_4 H_2O+0.038 M Na_2HPO_4 $12H_2O$) was added to 2 g of HA1, and the suspension was shaken for 24 h. The supernatant was separated by centrifugation, concentrated HCl was added to pH=1, dialyzed and freeze-dried (humic fraction HA2). The solid residue was again mixed with 1 L of a phosphate buffer with pH=8 (0.014 M NaH_2PO_4 H_2O+0.086 M Na_2HPO_4 $12H_2O$). The resulting humic extract, HA3, was obtained following a similar procedure than HA2. The solid remaining after extraction of HA3 was further mixed with 1 L of a buffer solution with pH=9 (0.002 M NaH_2PO_4 H_2O+0.098 M Na_2HPO_4 $12H_2O$) and the extracted humic acid, HA4, was isolated again by a similar procedure than HA2. Finally, the solid residue from the HA4 extraction was treated with 1 L of sodium pyrophosphate buffer ($Na_4P_2O_7$ $10H_2O$; 0.10 M) at pH=10. The humic acid extract HA5 was obtained as described above. All samples were characterized for their C, N and H contents using a Fisons EA 1108 Elemental Analyzer, whereas the ash content was determined by muffle burning of 50–100 mg of each material at 750°C for 8 h and verified by TG analysis, as well. The oxygen content was determined by difference 100–%C–%N–%H. The sulfur content, usually reported in fossil fuel analysis was ignored. Elemental and ash contents are reported in Table 1.

Thermal analysis

Shimadzu differential scanning calorimeter DSC-60 and thermogravimeter DTG-60 were used for measurements. The temperature as well as heat scale were calibrated using In and Zn. Before measurement, the humic samples were carefully homogenized in agate mortar. The measurements were carried out in open platinum crucible at the rate of heating 10°C min⁻¹ from room temperature to 600°C [6–8]. Although, the sample mass is usually referred up to 100 mg [4, 5, 8], due to oxidative atmo-

sphere, huge amount of heat released and measurement range of Shimadzu calorime-
ter, the mass of sample was approximately 1 mg with accuracy of 0.01 mg. Oxygen
(5.0 purity) was used as a reactive gas with flow rate 20 mL min^{-1}. The measurements
were repeated three times for each sample and standard deviation of peak tempera-
ture, calculated heat as well as mass losses never exceeded 5%. Peak temperatures,
heat values and mass losses are given in Tables 2 and 3, respectively.

Table 2 The temperatures of peaks maxima (T_p/°C) and reaction heat (H/kJ g^{-1}) of the mea-
surements connected with exothermal peaks

Fraction	Peaks					
	II		IIIa	IIIb	H	IV
	T_p	H	T_p	T_p		T_p
HA1	332	0.56	492	–	6.24	–
HA2	319	0.37	432	456	3.82	531
HA3	314	1.57	446	–	4.45	492
HA4	318	1.26	454	–	5.15	507
HA5	313	0.74	456	489	5.10	546

Table 3 Percentage mass losses associated with individual thermooxidative steps; recalculated
for moisture free samples

Fraction	Mass loss (%) at peaks			
	I	II	III	IV
HA1	8.3	18.0	71.4	–
HA2	9.5	21.1	65.7	1.6
HA3	7.5	32.9	57.9	0.5
HA4	6.9	26.2	63.4	0.4
HA5	7.9	24.0	65.1	0.6

FTIR spectroscopy

In order to evaluate humic molecular changes induced by heating and oxidation, FTIR
spectroscopy was employed (Nicolet Impact 400). Conventional KBr pellet technique,
described previously by many authors was used [15]. From 0.5 to 1 mg of humic
samples previously dried at 105°C for 2 h and cooled and stored in desiccator were
mixed in agate mortar with 200 mg of KBr. The spectra of thermally treated samples
were obtained by heating up the humic samples to the chosen temperature and then
cooling to the room temperature in a desiccator under atmosphere of nitrogen.

Results and discussion

The elemental analysis of samples HA1-5 is given in Table 1. Decreasing C/H ratios in the order HA2>HA3>HA4 HA5 can be related to decreasing aromaticity or more specifically to degree of condensation [1]. The HA2 sample, with the largest carbon amount and the lowest hydrogen content among pH-separated fractions, was extracted from HA1 by a buffer solution with pH=7.0. Deducing from elemental analysis and extraction procedure, the composition of this fraction could be described as an aromatic system possessing acidic groups able de-protonation up to pH 7. Fractions HA3 and HA4 were extracted with buffer solutions at pH 8.0 and pH 9.0, respectively. In agreement with literature data, decreasing C/H ratios are attributable to increasing aliphatic contents. Therefore, the aliphaticity of HA3 and HA4 was considered larger than for HA2. The oxygen content of HA2, HA3, and HA4 is in the order HA2<HA3<HA4 and this can be attributed to the increasing polyacidic nature of the humic systems. Fractions HA3 and HA4 are thus not only more aliphatic than HA2, but also more polyacidic. The HA5 fraction revealed the largest amount of hydrogen, whereas carbon and oxygen content was comparable to that of other humic fractions (Table 1). There was assumed that the HA5 fraction was selectively enriched in polyphenols as compared to fractions extracted in phosphate buffers at lower pHs which is supported by previous observation [14, 16].

FTIR spectroscopy measurement of thermally non-treated HA1 and the fractions HA2, HA3, HA4 and HA5 showed typical spectra published and described by many authors [1, 17, 18]. In this work the only FTIR spectra of HA2 sample both thermally non- and treated (Fig. 1) are given. First, some notes to differences among individual samples. Slight shift of peak maxima in the range 3400–3420 cm^{-1} (hydrogen bonded
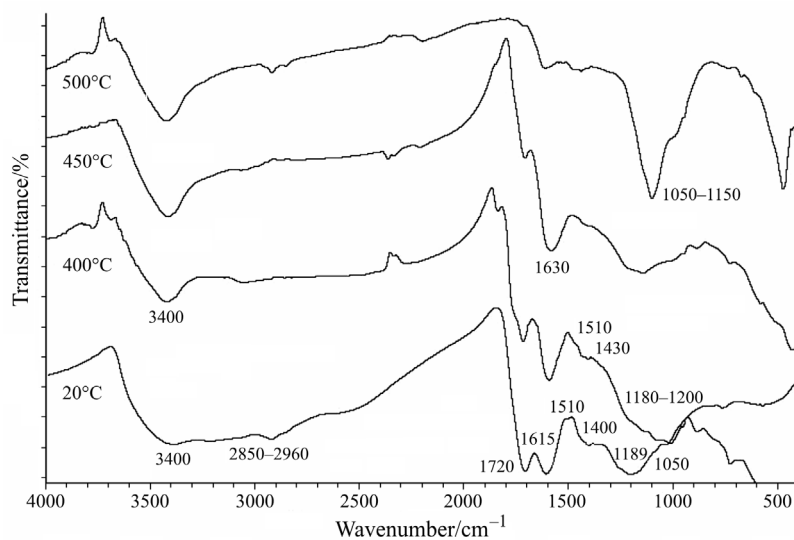

Fig. 1 FTIR spectra of the fraction HA2 before and after thermal treatment

–OH) and differences in regions 2850–2960 cm^{-1} (aliphatic C–H stretching), a sharp peak around 1720 cm^{-1} (C=O of COOH) 1600–1650 cm^{-1}, C=O stretching of COO^-, ketonic C=O and aromatic C=C conjugated with COO^-), a peak in range 1525–1510, 1450–1400 cm^{-1} (aliphatic C–H bending, and COO^- asymmetric stretching), peaks at 1221 cm^{-1} (aromatic C, C–O stretch), at 1189 cm^{-1} (C–O stretch of aliphatic OH), at 1126 cm^{-1} (–C–O stretch and OH deformation of –COOH) and around 1050 cm^{-1} (C–O of polysaccharides and Si–O) were observed. While the weak bands in range 2850–2960 were monitored in spectra of more aromatic HA2, intensity around 1600 cm^{-1} was very strong. Compared to HA3 and HA4, intensity in region 1600 cm^{-1} kept still strong but intensification around 2900 cm^{-1} was noted. The balanced band intensities showed spectrum of HA5 with prominent peak around 760 cm^{-1} related to CH of mono- and/or polysubstituted aromatic rings.

All DSC curves of oxidation of lignite humic acids and separated samples show one endothermic and 2–5 exothermic peaks. Each of heat effects was accompanied with a partial mass loss registered on TG curves. The low-temperature exothermic DSC peaks of HA1–HA5 are given in Fig. 2 whereas the high-temperature ones are shown in Fig. 3. Table 2 reports the peak maxima and enthalpies associated with the thermooxidation steps indicated by the second, third and fourth peaks; in two cases the third exotherm showed splitting and, therefore, it was marked as IIIa and IIIb. The first peak associated with moisture evaporating is briefly described below. The reaction heat was calculated as a sum of both peaks. Experimental results calculated from TG measurement (charts not shown) are summarized in Table 3.

HA1 sample, representing the whole bulk of humic molecules, shows the simplest curve consisting of one endothermic and two exothermic peaks. The broad peak shapes confirmed the high molecular complexity of this sample. On the other hand, higher number and narrower peaks of HA2–HA4, extracted by the mixture of phos-
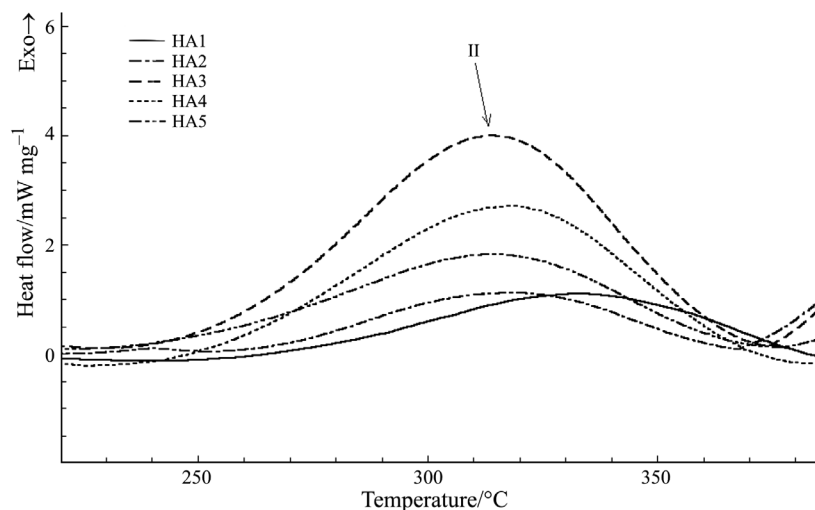

Fig. 2 DSC curves of sequential pH-extracted humic samples at lower temperatures
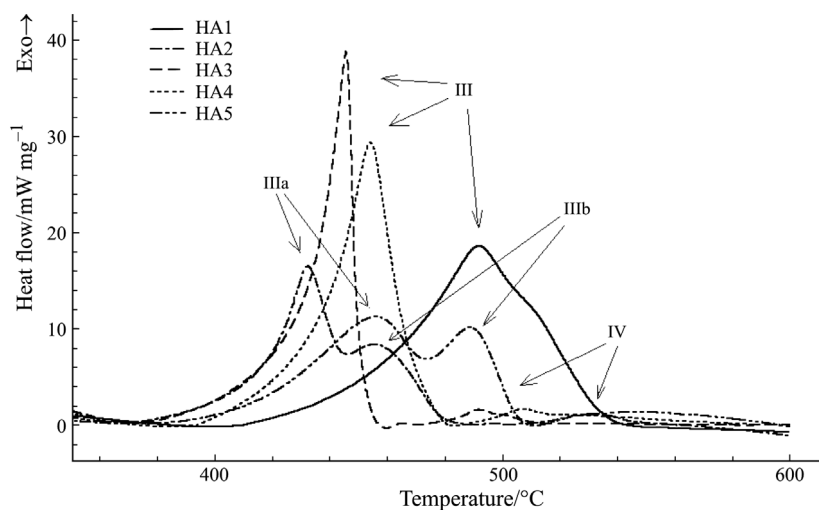
Fig. 3 DSC curves of sequential pH-extracted humic samples at higher temperatures

phates, gave exotherms at lower temperatures; HA5 extracted by the pyrophosphate buffer gave peaks shifted to higher temperatures.

The first endothermic peak occurs in the range 40–110°C for each sample and is obviously connected with gradual moisture evaporating. In all cases, the mass loss connected with the endotherm did not exceed 9% and is in agreement with the data published previously [19].

In the range 110–210°C there appeared a broad but subtle ill-defined peak associated with slight mass loss (Table 3). The mass loss in all curves did not exceed 10% of total mass and this effect may be related to continuing evaporation of water and small organic molecules [20] and/or partial destruction of peripheral aliphatic components [4]. Our FTIR results showed decrease of intensity of broad peak at 3400 cm^{-1} while peaks in area 2900 and 1400 cm^{-1} did not indicate remarkable alteration.

The second broad exothermic peak, with ill-defined maximum for HA2, but well-defined ones for HA1 and HA3-HA5, appeared in the range of 240–380°C (peak II in Fig. 2 and Table 2). According to [4, 7], the thermal degradation indicated by exothermic peak occurring in this temperature range can be attributed to the destruction of aliphatic grouping, CH groups, carbohydrate components and to some extent of oxygeneous (alcoholic, phenolic) and amino groups. Those observations are in agreement with FTIR results. In all cases the 2860 cm^{-1} band disappeared, intensity of 1510, 1430, 1200, 1180 and 1050 cm^{-1} decreased. On the other hand, absorption in range 3400–3600 cm^{-1} as well as at 1650–1740 cm^{-1} slightly increased. As elemental analyses and C/H ratio indicates, HA2 sample possessed the highest content of aromatic carbons in comparison with HA3, HA4 and HA5. Therefore it can be assumed that solely a small part of molecules of HA2 was decomposed and resulted in ill–defined exothermic peak. Moreover, relatively small mass loss as well as

FTIR results indicate, that carboxylic groups are not destroyed, which corresponds with Petrosyan's [4] observations or are decomposed only partially [7]. The difference between samples HA3 and HA4 is remarkable. C/H ratio indicates the slightly higher content of aliphatic groups of HA4, but liberated heat and mass loss occurring in this range is lower than in the case of HA3. Therefore, it is likely that during decomposition reactions some side reactions associated with oxidation of the rest of molecular skeleton occurred. The crucial importance play the type of reactions; if the molecular moiety is only oxidized, partly oxidized or completely decomposed and released as CO_2 and H_2O. Such conclusion is made on the base of the pulse flow calorimetry experimental data, which showed that oxidation reaction of low rank coals (e.g. oxygen richer) produce higher amount of heat in comparison with anthracite etc. [25]. Moreover, the increasing of mass during low temperature oxidation of low rank coal was recorded as well [26]. Hence, above-mentioned contradiction can be put on the account of the extent of oxidation reactions. Although C/H ratio of HA5 is relatively low, because of high content of hydrogen, there was predicted the higher aromaticity degree of the fraction extracted by pyrophosphate [12, 17]. The mass loss 7.9% and total liberated heat 0.74 kJ g^{-1} in range of 240–380°C (Tables 2 and 3), were observed. The thermal behavior of HA1, the original bulk of humic molecules, is interesting showing a higher thermal stability in comparison with its pH-separated fractions resulting in the shift of peak maximum to higher temperatures.

The groups of well-defined but more complicated peaks appeared in range 380–520°C (Fig. 3). While the curve of HA1 shows one simple broad peak with maximum at 492°C, caused by the highest molecular complexity of humic sample, the curves of HA2, HA3, HA4 and HA5 reflected their lower molecular heterogeneity. The HA2 and HA5 plot showed a splitting of the peak with the maxima at 432, 456 and 456, 489°C, respectively. The small shift of the peak maxima and onsets to the higher temperatures was registered in curves of HA3 and HA4 in comparison with HA2. While the peak of HA3 had the maximum at 446°C, the maximum of HA4 sample was showed at 454°C. Peak splitting as in case of HA2 and HA5 was not observed.

According to conclusions drawn by many authors [20], the second group of peaks corresponds to the thermooxidation of aromatic, mono-or polycyclic rings. It is frequently referred to the destruction of COOH groups, as well [4]. Our results obtained by FTIR are in agreement with those observations. Thermally treated samples showed a dramatic decrease in the intensity of FTIR spectra at 1720 cm^{-1}. On the other hand, intensity of 1630 cm^{-1} band did not change, which indicates the fact that chinoidal moiety has not been decomposed yet. The elemental analysis shows (Table 1) the low oxygen amount of HA2 in comparison with HA3 and HA4. The increased stability of oxygen rich humic samples agrees with the results obtained by Peuravuori *et al.* [20] and Griffith and Schnitzer [21]. They found out the higher thermal stability of aquatic fulvic acid samples in comparison with humic samples. It is well known [1] that fulvic acids possess more oxygen-containing functional groups in their molecules, especially carboxylic, and lower amount of aromatic carbon. However, according to experimental data obtained by Peuravuori [20], who deter-

mined the thermal stability of humic and fulvic acids, the higher content of aromaticity alone is not the only implication of the higher stability.

A small exothermic peak appeared in HA2, HA3, HA4 and HA5 DSC curves in the range 480–550°C. TG results of all samples showed only a tiny mass loss (Table 3). According to Petrosyan *et al.* [4], peaks occurring in this temperature range may be attributed to the destruction of the most stable cyclic groupings containing C and N, and the oxidation products of thermooxidation. In HA1 DSC record, this peak did not appear likely due to the highest heterogeneity of this humic sample – exotherm corresponding to this destruction might be hidden in the previous broad one. The non-symmetric shape of the end of this peak supports this conclusion. FTIR results showed a dramatic increase of peak intensity in the range 1050–1150 cm^{-1} (Si–O bonds) and disappearance in region 3400, 1600 and 1400 cm^{-1}. As can be seen in Table 1, the content of nitrogen in all samples varies around 1%. From TG results should be then deduced that most of nitrogen molecules consists of functional groups destroyed at lower temperatures. The highest mass loss showed in this temperature range fraction HA2, which corresponds to the high aromaticity of this sample predicted from elemental analysis results.

Experimental data indicate, that the highest heat released during thermooxidation of sequential pH-extracted humic samples was observed for the samples richer in oxygen content. This result is quite unexpected since it is known that oxygen-containing groups bring a decrease of heat liberated during thermal degradation. In the light of the above discussion it is evident that many physico-chemical processes can occur during thermal treatment of humic substances. As stated by Buurman and Aran [22], the evaporation of highly oxygenated low-molecular organic acids as well as the loss of heat used in reconfiguration reactions were the most important processes which complicated the elucidation of thermooxidative behavior and misrepresent calculated values of reaction heats. Recent knowledge [2] obtained on the basis of HPSEC results suggested that the heterogeneous humic molecules self-assemble in supramolecular conformations stabilized only by weak forces such as dispersive interactions (van der Waals, – , and CH– bonds) and hydrogen bonding. The latter are relatively strong linkages since they involve an energy gain from 10 to 20 kJ mol^{-1} in comparison to van der Waals bonds [23]. In this work, the fraction HA4 possesses the highest amount of oxygen atoms potentially taking part in H-interactions and showed relatively high amount of liberated heat in comparison with the other fractions. It seems to be likely, although slightly, the contribution of weak interactions, especially hydrogen bonding, can affect thermoanalytical results as well. Buurman *et al.* [6] did similar conclusion based on observations of DTA and TG curves shifted to higher temperatures after treatment of cation saturated humic extracts with relatively polar organic compounds.

As can be also seen, the original sample HA1 did not show an 'average behavior' of its sequential pH-extracted samples. The applied extraction procedure likely affected rearrangement of conformations and the chemical change of humic molecules occurring during the preparation could not be neglected, as well.

Conclusions

Thermooxidative behavior of lignite humic fractions obtained by sequential extraction at pH 7, 8, 9 and 10 has been evaluated by DSC, TG and FTIR spectroscopy provided information indicating their different physical-chemical properties. DSC curves supported by TG measurement showed 1 endothermic and from 2 to 5 exothemic peaks resulted in gradual decomposition of humic molecules. In low temperature range (e.g. up to approximately 210°C), the FTIR spectra indicated evaporation of physically bounded water. The first intensive exothermic peak appeared in all cases in range 240–380°C and it was ascribed to decomposition of aliphatic moieties and functional groups. Very likely recombination reactions producing the chinoidal structures occur in this temperature range. In range of 380–520°C the second intensive exothermal peaks were recorded. Humic fractions extracted at pH 7 by phosphate buffer (0.062 M NaH_2PO_4 H_2O+0.038 M Na_2HPO_4 $12H_2O$) and at pH 10 by pyrophosphate buffer (0.1 M $Na_4P_2O_7$ $10H_2O$) showed splitting of peaks, which indicated extraction of more specific molecules. Fractions obtained at pH 8 and 9, extracted by phosphate buffer consisting of 0.014 M $NaH_2PO_4 \cdot H_2O$+0.086 M Na_2HPO_4 $12H_2O$ and 0.002 M $NaH_2PO_4 \cdot H_2O$+0.098 M Na_2HPO_4 $12H_2O$, respectively, showed similar DSC curves; the shift to higher peak temperature of latter was observed. On the other hand, the original HA sample (extracted by 0.1 M NaOH) showed very broad peak that lined out the high-complicated system of humic molecules and showed its highest thermal stability. Therefore small exothermal peak seen on all pH fractions DSC profiles in range of 480–550°C, has been covered by strong exothermal peak. FTIR spectra suggested the decomposition of cyclic grouping containing N and C atoms.

To sum up, exothermic DSC peaks of the samples extracted by phosphate buffers and by pyrophosphate were shifted to lower temperatures in comparison with the original one and showed narrow distribution of humic molecules. The ratio of aliphatic/aromatic carbon along with oxygen content seems to be an important factor playing role in stability/lability degree. Higher degree of aliphaticity observed at samples extracted at lower pH did not show some dependency on the peak temperature of the first decomposition step associated with decomposition of aliphatic moieties and functional groups. On the other hand, such dependency was observed in higher temperature range where destruction of aromatic structures took part and lower C/H degree of HA samples shifted maxima to higher temperatures. Apparently, the employed oxidative atmosphere strongly affected and complicated the evaluation of experimental data. However, few reactions take place in inert atmosphere and humic matter behavior is in presence of oxygen very frequently affected. Nevertheless, the obtained results along with calculated heats lead to the conclusion that thermooxidative stability and released heat were affected by processes such as evaporation of oxygen-rich low-molecular organic acids, recombination, side and partly oxidative reactions and possibly by weak interactions among humic molecules.

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