REGENERATED HUMIC ACIDS OBTAINED BY THE AIR OXIDATION OF SOUTH MORAVIAN LIGNITE. PART. 2. THERMOANALYTICAL CHARACTERIZATION OF PRODUCTS

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Abstract

A sample of humic acid prepared from parental lignite and seven regenerated humic acids prepared from oxidized ones were extracted from South Moravian lignite. First, the samples were tested for their stabilities and degradabilities using thermogravimetry. It was shown that oxidation of lignite in static reactor at 85 °C produced regenerated humic acids with an increasing content of labile part. The dependency of labile content was exponential-like and reached a constant value after 240 hours of oxidation. Increasing content of labile part in regenerated humic acids was also confirmed by measuring of heat accompanying the thermo-oxidative degradation using differential scanning calorimetry. The previously reported increase in number of ester bonds and the character of surface of prepared humic material was evaluated by moisture uptake measurement. Using thermogravimetry, the determination of the content of moisture adsorbed on the surface of humic samples after 21 days was carried out. In accordance with previous conclusions based on elemental analysis and yield of regenerated humic acids, the highest moisture content was observed for humic sample prepared in fluid reactor from lignite oxidized at 50 °C for 72 hours and a sample extracted from lignite oxidized in static reactor at 85 °C for 456 hours.

Key words: lignite oxidation; regenerated humic acids; moisture uptake; thermal degradation.

1. Introduction

Humic substances (HS), the end product of decayed organic matter, are described as refractory, dark colored, heterogeneous organic compounds [1] which arise from dead plants, organisms and animal tissues [2]. In the next stage, they are supposed to undergo chemical degradation as well as biological degradation by microorganisms, to produce complex chemical structures which are more stable than original materials. As an important fraction of the natural organic matter, HS are present in all natural waters, soils, sediments, peat, bogs and other ecosystems [3, 4]. Physical properties of HS highly depend on their chemical structure, consequently on source materials and isolation conditions. Basically, the published structural models suggest the presence of a biologically relatively resistant and highly substituted core of aromatic nature with presence of heterocyclic structures [5]. The core units are linked to each other via a net of alkyl chains of different lengths, which are highly substituted with functional groups such as carboxylic, aliphatic, aromatic, hydroxyl, and amino groups [6, 7]. In contrast, the recent theory describes humic acids as a mixture of relatively small molecules stabilized predominantly by weak interactions [8]. In the last decade, due to application more sophisticated analytical techniques and approaches, such concept gains a growing attention.

HS play a significant role in environmental and ecological processes by controlling transport and transformation of toxic chemicals in soil and water, metal complexation, nutrient availability, maintenance of soil structure, and carbon and nitrogen exchange between soil and atmosphere [9, 10, 11]. The same function should have HS added into the system artificially, i. e. naturally occurring HS can be supplied by other sources or prepared synthetic reactions. Another option is the application of the so-called regenerated humic acids (RHA) that represent a pool of humic compounds produced by oxidation of lignites or coals of different quality. In comparison with natural HA, RHA are more stable, aromatic, and contain more carboxylic and phenolic groups [12].

The transformation of coal into RHA can be achieved by means of the oxidation using various chemical agents or with air or oxygen [13]. Using oxygen or air, the fragmentation reaction can be controlled, carbon losses can be minimized and almost any coal can be converted in high yields into HA [14]. This method of preparation is very cheap, profitable and mild compared to oxidation in suspension. Despite the differences in fate of RHA and original HA, they have similar characteristics and chemical behavior. They are water insoluble, black, solubility is pH dependent and the dissolution at high pH is related to the presence of many acidic functional groups such as carboxylic and phenolic groups which are responsible for the behavior and performances of these substances in solution [12]. The oxygenated fragments which have been generated (RHA) are held strongly together by hydrogen and/or covalent bonds (e. g. ester groups) [12].

The chemical character of RHA, produced by air oxidation of South Moravian lignite has already been described [15]. It has been verified that higher temperature during the oxidation supports the production of RHA. Despite the difference in the yield of RHA (extractable part of lignite increase up to 75 % after oxidation) their chemical character was, in all cases, fairly similar. In fact, the elemental content did not show any remarkable changes in composition of RHA. As it was mentioned previously [15], the reason can be seen in the kinetics of oxidation processes as well as in the strength of oxidation agent. Some small differences were revealed using FTIR which showed the increase in number of ester bonds in RHA produced mainly at temperatures above 80°C. As a result a significant increase in apparent molecular weight evaluated by High Performance Size Exclusion Chromatography (HPSEC) was observed [15]. Change in the number of ester bonds caused a change in supramolecular structure of HS, which supported formation of humic aggregates. This structural change is supposed to support the formation of gel-like structure with increased water holding capacity.

Methods of thermal analysis such as thermogravimetry (TGA) and differential scanning calorimetry (DSC) represent a very attractive approach in the study of HS [16, 17]. TGA has been used mainly for quantification of the moisture and ash contents [6] In addition, some authors used this technique also for characterization and study of structural changes in HS [12]. It was concluded that the difference in the thermal decomposition curves of HS samples are caused by different degrees of humification [18] and by different biological and chemical pathways which influence the HS supramolecular structure [19].

The aim of this work is additional evaluation of changes in humic acids structure induced by air oxidation of South Moravian lignite. First, the formation of ester bounds described in the recent paper [15] is evaluated as a moisture uptake studied by TGA. Further, the stability and degradability of humic substances reflecting the character of their supramolecular structure is evaluated by DSC and TGA.

2. Experimental

2.1 Production of RHA

Detailed information on production RHA characterized in this work has already been reported [15]. Briefly, South Moravian lignite of different particle sizes was oxidized by the air flow in either fluid or static reactor at different temperatures and for different time intervals. Further, from oxidized lignite, regenerated humic acids were extracted by alkali extraction, purified and freeze-dried. Unlike in reference [15] in this work, only selected samples were studied. Those are listed in Table 1. Sample denoted as HA represents humic acids extracted from parental lignite, samples produced in fluid reactor are abbreviated as RHA 1–3, and samples prepared in the static reactor as RHA 4–7.

Table 1 List of samples with their respective conditions of preparation.

Mark	Fraction [mm]	Temperature [°C]	Time of oxidation, [hrs]
HA	HA from parental lignite		
RHA 1	1–0.5	20	72
RHA 2			120
RHA 3		50	72
RHA 4	0.5–0.125	85	72
RHA 5			120
RHA 6			240
RHA 7			456

2.2 Moisture affinity evaluation

The samples were stored in a moisturizing container, under controlled 100% relative humidity condition at 25 ± 2°C for 21 days. According to the literature [20], after 21 days the equilibrium between HS and water atmosphere should be achieved. Moisture content in HS was measured by TGA.

2.3 Thermal analysis

Shimadzu differential scanning calorimetr DSC-60 was employed in order to determine the heat of thermo-oxidative decomposition of humic samples. The temperature and heat scale were calibrated using In and Zn standards. Measurements were carried out in open aluminum crucibles at heating rate 10°C min^{-1}, from the room temperature to 600°C. An empty pan was used as a reference. Samples mass was typically around 1.5 mg. The dynamic air atmosphere with the flow rate of 20 ml min^{-1} was used as a reactive gas. Prior the measurement, humic samples were carefully homogenized in an agate mortar. All records were corrected by the baseline subtraction (a run without pans under same conditions). Experimental data were processed by means of Shimadzu TA60 software.

Thermogravimetrical analysis TA Instruments Q5000IR with the dynamic nitrogen atmosphere was used for determination of water content in HS samples previously kept in the moisturizing container. The flow rate of nitrogen was set at 5 mL per minute and the heating rate was 10 °C per minute from the room temperature to 250°C. As a sample holder the open platinum pan was used. Typically, mass of samples was around 5 mg.

Next experiments were conducted again on TGA in order to determine the thermo-oxidative stability and degradability of studied samples. The conditions of measurements were as follows: the heating rate 10 °C per minute from the room temperature to 650°C, samples mass about 5 mg, air was used as a reactive gas with the flow rate of 25 ml min^{-1}.

All obtained results were evaluated by means of TA Universal Analysis 2000 software.

3. Results and discussion

As shown in our previous paper [15], the air oxidation of parental lignite leads to the change of physical-chemical properties of respective regenerated humic acids which was revealed by HPSEC. In contrast, other analysis indicated only small changes in their chemical composition. Therefore, it seems that the differences among samples can be associated rather with their physical (supramolecular) than chemical structure. There exist a range of techniques allowing determination of several parameters useful for study of physical structure of humic substances. In this work, physical structure was assessed by two methods of thermal analysis such as TGA and DSC. Further, moisture uptake as another parameter associated with the character of obtained humic acids was determined.

3.1 DSC thermo-oxidative degradation heat and degradation steps

It is a general agreement that the process of HA thermal or thermo-oxidative degradation proceeds in two or three exothermal degradation steps [21]. Those are preceded by moisture evaporation associated with evaporation and/or sublimation of small amount of volatile humic parts [22]. Next, the exothermal reactions associated with rapid mass loss of samples occur. In the lower temperature range, aliphatic molecules (methyls and other saturated and unsaturated moieties), many functional groups (carboxylic, methylene, alcoholic), polysaccharide C–O bonds and simple aromatics (biodegradable components) are degraded or evaporated [25]. In this step occurring in the temperature range ~200–300°C, recombination reactions complicating the simple determination of individual components may take place [23]. For temperature higher than 300°C the decomposition of carboxylic, phenolic, carbonyl and alcoholic groups from HS occurs [18, 25]. The third step (>400°C) reflects the degradation of aromatic, polyaromatic and further also polyheterocyclic structures (highly humified components and recombination byproducts) [24]. The individual stages of degradation are not always separable, mostly, using thermo-analytical approach, steps are overlapping and only two steps are visible. Hence, it is probable that the character of processes occurring during the first step has a strong influence on the second and third one and the total combustion heat can reveal the differences between specific humic samples [23].

This part of the work was devoted to the evaluation of stability of HA and extracted RHA. The obtained data are summarized in Table 2. The DSC analysis of HA and RHA studied in this work confirmed previous observations concerning the thermo-oxidative degradation of HA from different sources. A typical DSC record of thermo-oxidative degradation of HA is

shown in Figure 1. It can be seen two (or three) pronounced separated peaks generally attributed to the thermo-oxidative degradation of labile (~250–440°C) and stable (~445–510°C) humic acids constituents. The resulting heat is proportional to the peak area and it is a result of both degradation and recombination reactions [26] .

Table 2 The summary of results obtained from DSC and TGA (*recalculated for dry part).

| | | TGA results Δm [%] | | | |
Samples	Combustion heat [kJ g^{-1}]	moisture content	1. step*	2. step*	ash content*
HA	11.3	6.65	77.8	21.1	1.09
RHA 1	10.8	6.44	75.9	23.5	0.58
RHA 2	10.7	6.61	70.0	29.2	0.78
RHA 3	10.3	6.82	75.6	23.8	0.62
RHA 4	11.4	7.87	73.3	25.6	1.18
RHA 5	12.7	7.44	75.5	23.4	1.10
RHA 6	11.8	7.23	79.9	18.9	1.24
RHA 7	11.7	7.16	80.5	18.5	1.00

As can be seen in Figure 2 all the humic samples gave similar DSC records. Nevertheless, some differences appeared comparing the degradation onsets, peak temperatures and peak area (proportional to combustion heat). It seems that increased amount of labile parts as detected by TGA caused the increase in the DSC peaks areas (Figure 2). It can be seen that the peak area around 250–400°C increased confirming the results from TGA. However, it is noteworthy, that the peak increase from 400–500°C occurred as well, but, this region is attributed to the degradation of stable part which was, according to TGA results, partly decomposed by regeneration. Therefore, it implies that the processes in the first step are mostly exothermal recombination of labile part than its degradation.
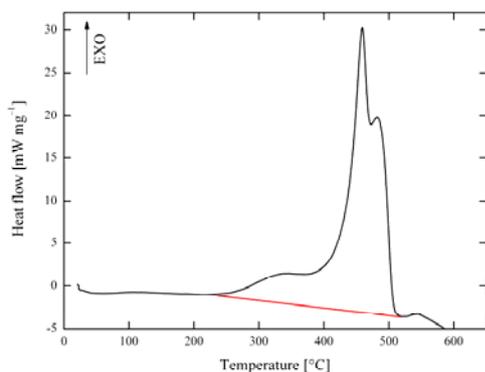

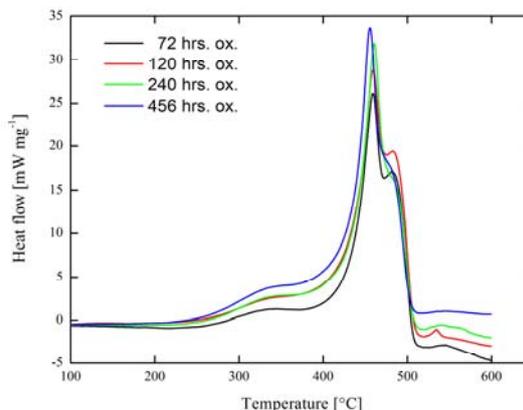Fig. 1. DSC record of thermooxidative degradation of RHA 4

Fig. 2. DSC record of thermooxidative degradation of samples RHA 4–7

Fig. 3 shows a typical TGA record including the first derivative (DTG). In all samples, the progressive mass loss which occurred up to 125°C was caused mainly due to the loss of adsorbed water. In general, the first derivative of thermogravimetric curves showed two degradation rate peaks. One peak occurred between 300 and 440°C and is associated with a mass loss from 70 to 80 % of the total sample mass. A second peak occurred between 480 and 520°C and gave 18 to 30% of mass loss. Thermogravimetric results conformed results obtained by DSC measurements.

The parameters obtained from the DTG, TGA and DSC measurements are summarized in Table 2. HA analyzed in this paper were intensively purified by HCl and HF to reduce the ash content. As it can be seen, the ash content was relatively low, in all cases it was determined about 1%. Moisture content was determined in the interval from 6.6 to 7.9%. It seems that the greater moisture content had samples prepared in the static reactor (RHA 4–7). This increase can be associated with the physical and chemical changes in humic samples as a result of structure alteration which occurred in the course of oxidation periods. TGA measurement of humic samples further showed two mass loss steps. The first step can be related to decomposition of labile parts and the second one to the stable parts of humic acids. Comparison of the values from samples prepared in the static reactor

(RHA 4–7) indicates an increase in labile component content and simultaneously a decrease of stable fraction. Evidently, during oxidation the partial decomposition of stable humic part occurred and therefore the RHA extracted from oxidized lignite contained larger pool of labile molecules. Further decomposition is then easier which can be related to the change of stabile/labile parts ratio. Nevertheless, these results are not confirmed by DSC measurement. Total heat evolved was obtained by the DSC peak integration (Fig. 1). The largest value of 12.7 kJ g^{-1} was observed for sample RHA 5. In this case, no significant correlation was observed.
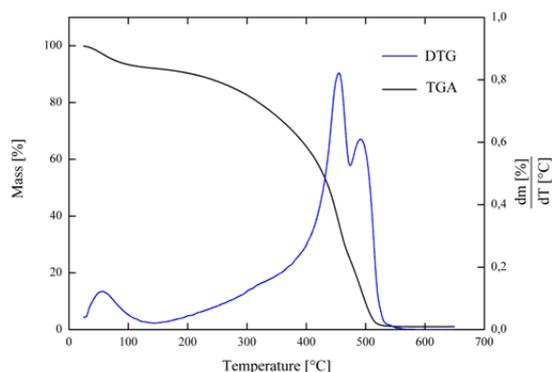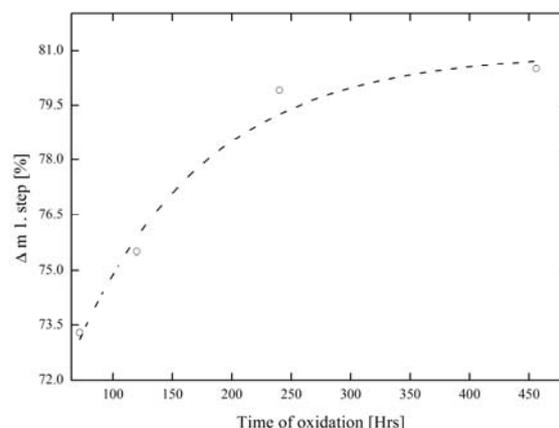

Fig. 3. TGA and DTG record of RHA 4

Fig 4. Dependence of the loss of mass in the first step of RHA 4–7 on the time of oxidation

Figure 4 shows the correlation between the mass loss of humic acids in the first step and the time of respective lignite oxidation. It seems that amount of mass decomposition in the TGA first step increases with the time of oxidation. Increasing of labile parts in RHA is also confirmed by DSC measurement as mentioned above. As it can be seen the increase reaches the limit which implies that at approximately 240 hours of oxidation the lignite structure was completely changed a no further conversion can be obtained by extended period of oxidation. Apparently, that statement is valid only for conditions used in this work, i.e. for South Moravian lignite and oxidation by air at 85°C.

3.2 Moisture uptake

Some differences in chemical character among samples have already been revealed using FTIR which indicated a small increase in the number of ester bonds in RHA [15]. Results of HPSEC showed the increase in the apparent molecular weight with increasing time of lignite oxidation of respective samples prepared in the fluid reactor [15]. Thermal analysis techniques such as DSC and TGA confirmed the difference in physical structure. In order to evaluate the changes in detail, the capacity of surface area to uptake moisture was tested using moisturizing container.
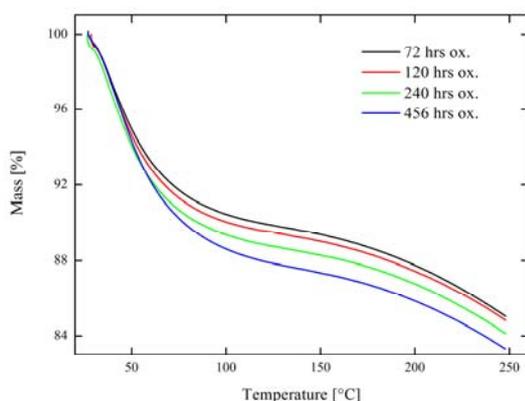

Fig. 5. Evaporation of moisture from samples RHA 4–7

Table 3 Moisture content in RHA samples

Sample	Δm – moisture content [%]
HA	12.9
RHA 1	12.9
RHA 2	11.8
RHA 3	13.5
RHA 4	10.0
RHA 5	10.8
RHA 6	11.2
RHA 7	13.1

Fig 5 shows selected TGA curves, which resulted from the evaporation of moisture adsorbed on the surface of samples RHA 4–7, placed into the moisturizing chamber for 21 days. As

it can be seen all the records gave similar curve shapes which imply similar mechanisms of moisture release. Water content was determined as a mass loss recorded up to 125°C. The results regarding the determination of moisture content in RHA samples are summarized in Table 3. Amount of evaporated moisture was determined in the range from 10 to 13%. In fact, water content increases with increasing time of lignite oxidation. The evaporation of water molecules from RHA is governed by the strength of polar groups on the surface of humic material. The greatest rate of evaporation occurred at the beginning of the experiment where the records had steepest slopes, while at approximately 100°C the kinetics decreased and at between 150 and 200°C degradation started.

As could be seen, moisture content was higher in samples which were prepared at lower temperatures and also increased at longer period of oxidation at 85°C. This trend corroborate with yield of humic substances extracted from oxidized and parental lignite published recently [15] and can be probably attributed to the content of COOH and phenolic OH groups in humic material.

4. Conclusion

Thermal analysis was used to study properties of humic acids and RHA produced from lignite oxidized by air under different conditions. The influence of these conditions on moisture uptake and thermal stability were studied. Our recent results indicated an increase in number of ester bonds in RHA [15]. Further, by means of HPSEC it was demonstrated the increase in the apparent molecular weight with increasing time of oxidation for samples prepared in static and the fluid reactor.

It has been verified that higher temperature during the oxidation supports the production of more "cross-linked" RHA. Moisture content in samples placed into the moisturizing chamber for 21 days (relative humidity is 100%) increased with increasing time of parental lignite oxidation. Comparison of the TGA values from samples prepared in the static reactor (RHA 4–7) indicates an increase of labile component content, and, simultaneously, a decrease of a stable fraction. The increase reached the limit which implies that at approximately after 240 hours of oxidation the structure was completely altered a no further transformation of humic matter took place by further oxidation (for conditions used in this work, oxidation by air at 85°C). No significant correlation was observed for samples extracted from lignite oxidized in fluid reactor. Increasing content of labile pool in RHA was also confirmed by a DSC measurement.

Acknowledgements

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