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THE KINETICS OF THERMO-OXIDATIVE HUMIC ACIDS DEGRADATION STUDIED BY ISOCONVERSIONAL METHODS

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Humic acids represent a complicated mixture of miscellaneous molecules formed as a product of mostly microbial degradation of dead plant tissues and animal bodies. In this work, lignite humic acids were enriched by model compounds and the model-free method suggested by Šimon was used to evaluate their stability over the whole range of conversions during the first thermooxidative degradation step. The kinetic parameters obtained were used to predict the stability at 20 and 180°C, respectively, which served for the recognition of processes induced by heat and those naturally occurring at lower temperatures. Comparison of the conversion times brought a partial insight into the kinetics and consequently into the role of individual compounds in the thermooxidative degradation/stability of the secondary structure of humic acids. It has been demonstrated that aromatic compounds added to humic acids, except pyridine, increased stability of humic acids and intermediate chars. The same conclusion can be drawn for acetic and palmitic acids. Addition of glucose or ethanol decreased the overall humic stability; however, the char of the former showed the highest stability after 40% of degradation.

Keywords: *DSC, lignite humic acids, isoconversional methods, stability*

Introduction

Humic substances represent unique and the most important components of natural organic matter, the key factor playing a crucial role in stabilization, accumulation and dynamics of carbon. They are also recognized for their beneficial effect on the physical, chemical and biological properties of soils, basically they are one of the factors inevitable for the existence of life on the Earth [1]. Humics content is related to changes in microbial biomass turnover, because it reflects the balance between rates of microbial organic matter accumulation and degradation. The organic matter as a whole reacts less quickly to changes of external conditions than the microbial biomass does. Thus, the nature of the organic matter itself, rather than its concentration, is a more sensitive indicator of the changes in organic matter quality due to changes in environmental conditions. As a result, chemical and structural characteristics of humic substances were shown to be better indicators of natural organic matter properties than soil itself [2]. Humic substances are considered to be stable pool of organic matter since their mean residence time is reported to be hundreds of years [3]. Nevertheless, the contemporary research is aimed at the stabilization of organic carbon bound in that way [3, 4] since, under the influence of oxygen, the humic substances are slowly mineralized and green-house gases are released to the atmosphere. It is noteworthy that the amount of green-house gases released from the soil organic matter is ten times higher than that produced by the anthropogenic activity [5]. Thus, knowledge on the processes concerning the humic stability, mineralization and decomposition is of a great interest.

Humic substances (HS) can be divided into three main groups named fulvic acids, humins and humic acids. The latter are soluble in alkali solutions and insoluble at lower pH [1]. A review of scientific literature shows countless number of papers concerning the humic acid chemical characterization. In the primary humic structure the compounds such as carbohydrates, long chain n-alkanes, alkanoic acids, alkanols, sterols, alkanones, lignin constituents, etc. can be found [6, 7]. Those are assembled together and exhibit a secondary structure, i.e. apparently large molecular mass aggregates stabilized either by weak dispersive forces, H-bonds or by interactions with cations or solid surfaces [8]. Although nowadays the knowledge on primary humic structure is more or less known or attainable, there is a lack of information on the role of individual humic constituents in the humic secondary structure, e.g. on the stability and degradation behavior. Basically, due to the above mentioned molecular interactions, the character and properties of individual constituents cannot be used to predict the behavior of the whole mixture. Therefore, the application of physico-chemical methods (e.g. thermal analysis) to assess the secondary structure behavior, is reasonable and justified.

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Up to date, there have been published several papers on the thermal analysis of humic substances of different origin as well as their parental raw materials, providing many useful correlations and applications [9–18]. Based on the correlations between thermal stability of soil organic matter pools in various temperature ranges and the CO_2 production by classical soil incubations, it has been suggested that their thermal stability can be related to their biological degradability [10]. In another work, the authors demonstrated a possible correlation between the kinetic parameters of thermooxidative degradation and the rate of CO_2 produced by the soils [15]. This correlation is quite reasonable since the organic material bound to mineral particles is hardly accessible to soil microorganisms and exhibits a higher thermooxidative stability. In addition, the stability and microbial resistance is also supported by intrinsic heterogeneity of humic matter itself. Principally, both kinds of degradation of humic molecules proceed gradually from labile aliphatic and polar functionalities to aromatic and heteroaromatic constituents [14]. Recently it has been demonstrated a strong tendency of humic constituents to recombine at elevated temperatures which significantly hampers the possibility to rationalize both the role and content of individual humic molecules. Nevertheless, we assume that the degradation of different humic molecules exhibit different kinetics, and therefore, at least the role of individual molecules in the overall stability of secondary structure can be evaluated on the basis of kinetic parameters of their degradation processes.

In the present work the mechanism of humic acids degradation was examined using the model-free kinetics method as suggested by Šimon [19–22]. The conversion times were calculated for selected steps of degradation of humic acids enriched with a model compound and compared with values of original humic sample. The model compounds were selected on the base of their presence in raw humic substances or their known influence on the secondary humic structure. We supposed that the addition of a compound promoting changes in the secondary humic structure could be logically associated with changes in thermodynamics of the whole system as well as with changes in kinetics of degradation and therefore it could be easily assessed by a DSC measurement.

Experimental

Humic acids

Humic acids were extracted from lignite mined in 1998 in the mine Mír located in South Moravia (Czech Republic) nearby Hodonín. The details concerning the lignite and extracted humic acids can be found in [12, 14, 18]. Fraction of lignite sieved at 0.2–0.3 mm was mixed with 0.5 M NaOH and 0.1 M $Na_4P_2O_7$ (1:10) and stirred for 3 h. After centrifugation (15 min, 4000 RPM), the supernatant was treated with concentrated HCl to reach pH=1 in order to precipitate the humic acid. That was then treated overnight with 0.5% (*v*/*v*) HCl-HF solution to remove residual ashes, dialyzed (Spectra/Por® dialysis tubes, 3500 Mw cut-off) against distilled water until chloride-free.

HA, still in a gel-like state, was divided into portions of 5 mL. A portion was dried to constant mass to determine the dry humic acids content. A model compound was added to another HA portion to obtain the concentration 10mass/mass%. The following substances were selected as the model compounds: ethanol, glucose, acetic acid, palmitic acid, *p*-cresol, pyridine, pyrocatechol, *p*-xylene. The mixtures of HA and model compounds were shaken for 48 h, dried in an oven at 30°C and homogenized in an agate mortar. A portion of pure HA was treated in the same way and used as a blank. All model compounds (p.a. purity) were ordered from Fluka and used as received.

Thermal analysis

Shimadzu differential scanning calorimeter DSC-60 was employed. The temperature and heat scale were calibrated using In and Zn standards. Measurements were carried out in open aluminum crucibles at heating rates of 3, 5, 7, 10 and 15°C min^{-1}, from the room temperature to 600°C. Sample mass was about 2 mg. Oxygen was used as a purge and reactive gas with the flow rate of 20 mL min^{-1}. All records were corrected by the baseline subtraction (a run without pans under the same conditions). In order to check the reproducibility, measurements of original, glucose and palmitic enriched samples were repeated in triplicate and no significant deviations in the calculated parameters were observed.

Methodology

Stability evaluation

Evaluation of the influence of added compounds on the degradation of humic samples was based on the isoconversional method proposed by Šimon [19–22]. DSC records showed two intense peaks (Fig. 1); in this work only the first (doublet) peak I was subjected to the kinetic analysis. First, the points of zero and 100% conversion (α) detected by DSC were determined. As the point of α=0 the point of the first declination from the baseline was used and the total conversion was supposed to be achieved at the end of the peak (the point of return to the baseline). The total

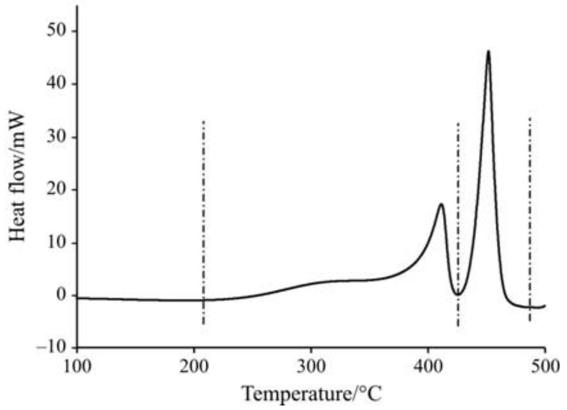

Fig. 1 DSC record of thermooxidative degradation of original HA, heating rate 10°C min^{-1}, under dynamic oxygen atmosphere 20 mL min^{-1}

peak area was obtained by integration and assigned to the 100% conversion. Partial peak sub-areas were plotted as a function of temperature and recalculated to conversion scale <0; 1> using the total area. In this way, conversion-temperature curves for different heating rates were obtained. For several selected conversions (given in Tables 1–3) the isoconversional times were calculated as described in [19–22]. Briefly, the calculation considers the linear increase of temperature, combination of general kinetic equation with Arrhenius equation and a plausible assumption on independence of the conversion α_i, corresponding to (the end of) some specific conversion time t_i, on the temperature regime. Two parameters, A and B, are involved in the calculations and defined as follows:

$$A=\frac{F(\alpha_{\text{i}})-F(0)}{A_{\text{k}}} \tag{1}$$

$$B=\frac{E_{\text{a}}}{R} \tag{2}$$

here, A_{k} is the pre-exponential factor in Arrhenius equation, E_{a} is the (effective) activation energy, R stands for the gas constant, and $F(\alpha)$ is the integrated inverted conversion function [19–22]. Due to the above assumption, also the value of the integrated function $F(\alpha)$ at the point α_i, i.e. $F(\alpha_i)$, is independent of temperature. The parameters are related to the applied temperature increase (scan) rate (β) according to the following equation:

$$\beta=\int_{T_0}^{T_{\text{i}}}\frac{\mathrm{d}T}{A\exp(B/T)} \tag{3}$$

T_0 is the starting temperature of the measurement, equal to zero in our case, T_{i} is the isoconversional temperature, i.e. temperature corresponding to the conversion α_i. Calculated parameters A and B are listed in Table 1.

The parameters describe the temperature dependence of the conversion time [19–22]:

$$T_{\text{i}}=A\exp(B/T) \tag{4}$$

The conversion time is the time interval from T_0=0 to the temperature T_{i} corresponding to the selected conversion α_i.

The conversion time t_{i} is the time interval from T_0=0 to reach conversion α_i at the temperature T_{i}. This method has been successfully used for the prediction of stability of various materials at defined temperature [19–22]. In this work, the parameters A and B served for the evaluation of stability at 20 and 180°C. Conversion times calculated for these temperatures using Eq. (4) were compared and served for the estimation of the influence of added compounds on the humic acids stability (Table 2).

All calculations reported here were carried out by software KINPAR [19–22]. The difference between theoretical and measured values never exceeded 2°C.

Results and discussion

The model-free approach avoids the problem with unknown and complex mechanism using the so-called single-step approximation, where the complex set of differential equations describing the kinetics of a complicated solid-state process is approximated by a single-step kinetic equation. It is very useful in our case since humic acids represents a highly complicated chemical system and individual processes in the course of degradation cannot be separated.

Humic acids commonly occurring in natural systems frequently contain, among others, also significant amount of inorganic impurities. Due to the both chemical and physical interactions, the impurities have a significant influence on the stability. The main purpose of this paper was to evaluate degradation profile of humic acids itself, and shed light on the role of mutual interactions among humic constituents and on the stability of intermediates. Thus, humic acids analyzed in this paper were intensively purified by HCl and HF to reduce considerably the ash content. Humic acids prepared by the same procedure were reported having the ash content about 2% [14]. A typical DSC record of thermo-oxidative degradation of HA is shown in Fig. 1. One can see two pronounced separated peaks generally attributed to the thermo-oxidative degradation of labile (~210–420°C) and stable (~425–480°C) humic acids constituents. The resulting heat is proportional to the peak area and it is a result of both degradation and recombination reac-

Table 1 Parameters *A* and *B* obtained using method suggested by Šimon at different conversions of thermo-oxidative degradation of HA and their mixtures with model compounds

Conv.	Original		Ethanol		Glucose		Acetic acid		*p*-Cresol		Pyridine		Pyrocatechol		Xylene		Palmitic acid	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
0.00	1.19E-08	9.32	1.12E-08	9.29	1.96E-08	8.48	1.34E-08	9.48	1.14E-08	9.45	1.35E-08	9.10	1.18E-08	9.46	1.14E-08	9.45	1.01E-08	9.47
0.02	1.67E-08	10.01	1.39E-08	9.98	3.48E-09	10.03	4.25E-08	9.95	1.97E-10	11.41	6.15E-09	10.14	5.50E-09	10.52	1.12E-08	10.22	3.36E-08	10.00
0.06	2.86E-08	10.18	1.56E-08	10.37	8.09E-09	10.04	8.08E-09	10.94	5.61E-10	11.80	6.33E-09	10.66	2.42E-10	12.14	3.22E-09	11.23	9.45E-09	10.77
0.12	3.09E-08	10.53	1.65E-08	10.73	1.74E-08	10.12	4.17E-10	12.50	2.09E-10	12.97	8.53E-09	10.94	4.25E-10	12.51	3.06E-09	11.85	6.22E-09	11.45
0.22	1.07E-07	10.23	2.24E-08	11.02	1.72E-08	10.76	1.92E-09	12.20	5.14E-10	13.00	1.49E-08	11.16	1.10E-09	12.52	2.80E-09	12.11	1.90E-09	12.23
0.32	4.86E-07	9.86	4.83E-08	11.01	2.66E-09	12.49	4.98E-09	12.11	1.13E-09	13.01	5.06E-08	10.94	5.98E-10	13.31	3.33E-09	12.45	2.87E-09	12.41
0.42	5.00E-07	10.21	9.78E-08	11.02	1.96E-10	13.99	5.52E-09	12.50	2.33E-09	13.05	6.81E-08	11.24	9.54E-10	13.52	6.31E-09	12.51	4.01E-09	12.62
0.52	1.52E-08	12.65	1.25E-08	12.65	1.70E-11	15.69	6.53E-09	13.79	1.11E-09	13.94	9.33E-09	12.87	1.60E-10	15.08	2.00E-09	13.61	1.41E-09	13.64
0.62	6.06E-10	14.93	5.74E-10	14.89	2.57E-12	17.43	2.97E-11	16.55	6.99E-11	16.04	2.57E-10	15.45	1.76E-11	16.87	1.11E-10	15.76	3.53E-10	14.86
0.72	3.32E-11	16.99	3.22E-11	16.96	4.29E-12	18.03	8.40E-13	19.10	3.99E-12	18.15	1.04E-11	17.75	2.50E-12	18.42	2.87E-12	18.36	2.36E-11	16.87
0.82	2.34E-10	15.87	4.87E-12	18.35	1.51E-12	18.90	1.26E-13	20.54	2.49E-13	20.18	4.22E-13	20.01	1.44E-12	18.98	1.54E-12	18.99	6.14E-12	17.98
0.92	9.57E-13	19.52	9.90E-13	19.53	8.92E-13	19.57	2.60E-12	18.74	8.85E-14	21.00	5.37E-13	20.02	3.86E-14	21.51	8.69E-13	19.53	4.93E-12	18.33
1.00	5.83E-14	21.83	5.05E-15	23.44	5.46E-14	22.03	2.74E-13	20.65	1.04E-14	22.91	1.03E-12	20.02	1.60E-15	24.17	1.65E-12	19.53	4.25E-13	20.44

A parameter/min, *B* parameter·10^3/K

Table 2 The comparison of conversion times of HA and their mixtures at 20 and 180°C at different conversions. The number refers to the ratio of conversion times of derivates to HA

Conversion	Ethanol		Glucose		Acetic acid		*p*-Cresol		Pyridine		*p*-Xylene		Pyrocatechol		Palmitic acid	
	20	180	20	180	20	180	20	180	20	180	20	180	20	180	20	180
0.00	0.86	0.88	0.10	0.26	1.90	1.59	1.51	1.29	0.54	0.71	1.51	1.29	1.61	1.59	1.64	1.35
0.02	0.75	0.77	0.23	0.22	2.09	2.23	1.40	0.96	0.58	0.49	1.40	0.67	1.91	1.19	1.98	1.97
0.06	1.06	0.83	0.18	0.21	3.77	1.51	4.24	1.12	1.16	0.64	4.12	0.91	6.93	1.20	2.52	1.22
0.12	1.08	0.83	0.14	0.23	11.19	1.05	28.46	1.48	1.14	0.68	9.12	0.99	12.05	1.31	4.74	1.53
0.22	3.16	1.20	1.00	0.52	14.85	1.39	62.31	2.17	3.38	1.08	16.27	1.66	25.85	1.93	16.61	1.46
0.32	5.12	0.93	44.02	1.34	22.10	1.08	110.90	1.80	4.23	0.83	48.13	1.53	162.82	2.24	36.23	1.21
0.42	3.16	2.61	159.58	3.67	27.24	3.86	76.95	5.50	4.66	2.95	32.95	4.51	156.43	7.73	30.46	3.65
0.52	0.84	5.47	36.59	6.10	20.96	4.73	6.06	8.32	1.33	6.62	3.55	7.25	42.99	18.66	2.77	5.47
0.62	0.85	5.29	22.08	6.45	12.30	10.69	5.23	8.16	2.57	8.16	3.19	6.97	22.38	16.47	0.47	3.04
0.72	0.90	4.69	4.63	6.63	33.81	13.78	6.49	8.03	4.30	8.63	9.56	9.19	10.22	11.98	0.49	2.81
0.82	0.10	2.96	0.20	3.08	4.29	9.64	2.56	8.59	2.43	10.00	0.27	3.85	12.25	4.63	0.03	1.65
0.92	0.87	1.06	0.89	1.04	0.15	0.49	11.68	2.43	2.50	1.69	0.76	0.93	29.07	4.48	0.07	0.37
1.00	0.77	3.03	1.93	1.46	0.08	0.35	7.42	1.94	0.04	0.32	0.01	0.18	55.78	6.88	0.07	0.34

Table 3 The comparison of effective activation energies; the values express the ratio of activation energy of spiked sample *vs*. original sample at the relevant conversion

Conversion	Ethanol	Glucose	Acetic acid	*p*-Cresol	Pyridine	*p*-Xylene	Pyrocatechol	Palmitic acid
0.00	1.00	0.91	1.02	1.01	0.98	1.02	1.01	1.02
0.02	1.00	1.00	0.99	1.14	1.01	1.05	1.02	1.00
0.06	1.02	0.99	1.07	1.16	1.05	1.19	1.10	1.06
0.12	1.02	0.96	1.19	1.23	1.04	1.19	1.13	1.09
0.22	1.08	1.05	1.19	1.27	1.09	1.22	1.18	1.20
0.32	1.12	1.27	1.23	1.32	1.11	1.35	1.26	1.26
0.42	1.08	1.37	1.22	1.28	1.10	1.32	1.23	1.24
0.52	1.00	1.24	1.09	1.10	1.02	1.19	1.08	1.08
0.62	1.00	1.17	1.11	1.07	1.03	1.13	1.06	1.00
0.72	1.00	1.06	1.12	1.07	1.04	1.08	1.08	0.99
0.82	1.16	1.19	1.29	1.27	1.26	1.20	1.20	1.13
0.92	1.00	1.00	0.96	1.08	1.03	1.10	1.00	0.94
1.00	1.07	1.01	0.95	1.05	0.92	1.11	0.89	0.94

tions. It has been demonstrated that in the area (I) molecules are partially degraded and partially recombined creating more stable, probably highly aromatic structures decomposed in the area II [16]. Since the shape of DSC records of modified HA samples were at first sight similar to that reported in Fig. 1, they are not shown. On the other hand, the mathematical treatment of integrated peak areas and the application of incremental method resulted in changes of obtained values of the parameters *A* and *B* with conversion α in comparison with the original HA (Table 1).

Calculated parameters *A* and *B* were used for the calculation of (isothermal) conversion times using Eq. (4). Such an Arrhenius-like treatment was used for calculation of the conversion times by extrapolation to high (180°C) and low (20°C) temperatures. Since 180°C is very close to the temperatures used for the calculations of conversion times it is more reliable for extrapolation because the potential deviations should have tendency to be more evident at low temperature. It is necessary to keep in mind that detection of conversion temperatures strongly depends on the technique used for the analysis. Thus, it is likely that some processes occur in the interval preceding the conversion temperature; however, by means of technique used in this work it is impossible to determine their real conversion.

It is necessary to point out that, especially at higher conversions (i.e above 0.5), the extrapolated data gave quite unrealistic values. Nevertheless the conversion times calculated for selected conversions were compared with results obtained for the original HA sample and obtained ratio served for the evaluation of the role of added compound on the stability and consequently on the kinetics of degradation. It is a similar approach as used in reference [22] where that ratio was called 'protection factor' and served for the similar purpose. Thus values listed in Table 2 are the indicators of higher or lower stability which at the same time indicate the kinetics of studied processes.

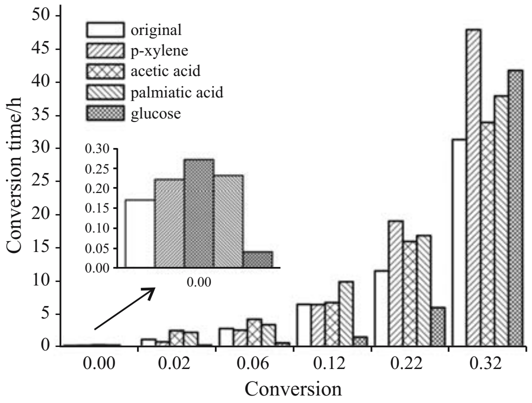

Fig. 2 The extrapolated conversion times of original HA and four selected humic derivates at 180°C

Many problems can appear when data obtained at higher temperatures are extrapolated to lower temperatures [23]. It can be found for example in [17] where the regenerated humic acids were tested and the order of stability after extrapolation did not correspond to the order of onsets at higher temperatures. As it was stated by Šimon [23], the reason can be seen among others in morphological differences at high and low temperatures or simply in introduction of different reactions occurring exceptionally at elevated temperatures. In our work the lowest temperatures at which no baseline deviation was detected for temperature lower than 180°C and therefore to assess the temperature influence the extrapolations were done to 180 and 20°C, respectively. Their mutual comparison can serve as a tool to answer the question if and when some morphological changes, non-typical reactions etc., occur. If the ratio is proportional at both temperatures, one can assume that the processes at low temperatures are similar to those occurring at high temperatures.

The extrapolation of values at zero conversion to both temperatures resulted in similar ratios regarding to the original HA. Although the conversion times obtained using higher heating rates (i.e. above 1°C min^{-1}) are frequently unrealistic [17], in this case the stability obtained for humic acid showed realistic data 1.46 years and 0.17 h for 20 and 180°C, respectively. Values corresponding to the modified samples can be easily calculated from Table 2 and all of them are in a reasonable time range. To sum it up, it is highly probable that in the period preceding the main degradation processes, only (pre)oxidation processes similar to those at room temperatures play a crucial role.

The ratios listed in Table 2 or in Fig. 3 for conversions from 0.02 to 1 showed a different pattern, which is understandable regarding to the countless number of recombination reactions induced and sup-

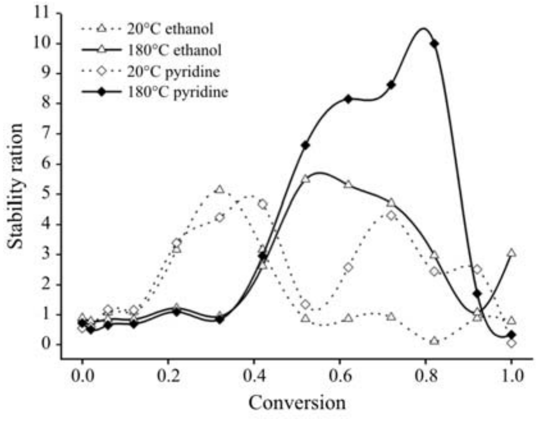

Fig. 3 The comparison of stabilities of ethanol and pyridine enriched samples in the course of thermooxidative degradation when extrapolated to 20 and 180°C. Value '1' means the same stability as the original HA sample

ported by heat and oxygen and which have already been suggested to take part in the degradation process [18]. The highest differences between low and high temperature extrapolation have been induced by aromatic compounds. Whereas at lower temperatures they showed increasing effect on the humic stabilization, the same conversions extrapolated to higher temperature resulted in a lower stability than in the case of original sample.

Ethanol and glucose enriched samples showed lower stability of the samples and char intermediates up to the conversion of 0.22. During this interval, we suppose that the compound added takes part in recombination/degradation processes and decreases the stability of humic acid. Reactions occurring in this interval are quicker than those in the original sample which can be attributed to the lower thermo-oxidative stability of the added molecules as well as to the changes in the secondary humic structure. Alcohols for instance were demonstrated to cause the partial disruption or alteration of weak hydrophobic interactions [13]. On the other hand, above the conversion of 0.22, the stability of char increased and in the case of glucose the stability was higher than 100 times.

Addition of acetic acid to humic sample is associated with a re-aggregation of hydrophobic domains and H-bonds become more important in the stabilization of humic secondary structure [13]. H-bonds represent relatively strong linkages in comparison to van der Waals bonds since they involve an energy gain in tens of kJ mol^{-1} [24]. As a result the stability of that sample significantly increased in comparison with the original HA.

Aromatic compounds added to humic acids generally increased stability of both humic secondary structure and intermediate chars. It is noteworthy that extrapolation to 180°C in the case of *p*-cresol and *p*-xylen brought lower stability of intermediate than that of original sample. Increase of the stability induced by the presence of aromatic compounds was highest at the conversion 0.32.

Addition of palmitic acid induced a slight increase of humic acid stability with the maximum at the conversion 0.32. However, the influence on the stabilization was not as strong as in the case of *p*-xylen, *p*-kresol and pyrocatechol. It is quite obvious since the latter compounds act as antioxidants in synthetic organic materials as well as in living organisms [25, 26].

In the case of pyridine, mixing with humic acids resulted in a significant decrease of the stability. The main reason can be probably seen in the disruption of dispersive weak interactions (hydrophobic) among humic molecules and destabilization of the whole system. Intermediates of the thermo-oxidative degradation showed the highest stability at the conversions 0.42 and 0.82 for 20 and 180°C, respectively.

Equation (2) allows calculation of the effective activation energy of processes under study. In fact, the dependence of activation parameters on conversion is believed to be one of the ways which can disclose the complexity of a process and shed light on the kinetic scheme of processes in condensed phase [27–31]. However, as it was demonstrated by Šimon [32] the physical meaning of activation parameters cannot be interpreted mechanistically and used in terms of the free energy barrier. The main strength of the single-step approximation is that it enables a mathematical description of kinetics of solid-state reactions, however, without a deeper insight into the reaction mechanism [33].

The trends seen in Table 3 are quite inconsistent with those shown in Table 2 or displayed in Fig. 3. The reason can be seen in the above-mentioned fact that the activation parameter E_α does not represent the energy free barrier but it is just an 'apparent' parameter. It has a major significance for processes modeling, however, without a deeper knowledge of the process mechanisms. Therefore, to evaluate the kinetics of a process it is more advisable to employ parameters with a clear physical meaning, i.e. the conversion time as demonstrated here.

Our results point out the other attribute of single step approximation. In line with previous observation [33], the far-reaching extrapolation can result in meaningless values of conversion times. Further, the adjustable parameters occurring in the temperature and conversion functions can vary with the range of experimental data and thus the extrapolation of the results measured too far outside the experimental range cannot be considered trustworthy. To sum it up, the kinetics obtained by extrapolation to 180°C can be considered more reliable and trustworthy.

Conclusions

In this work, lignite humic acids were enriched by model compounds and model-free kinetics suggested by Šimon was used to evaluate their stability over the whole range of conversions during the first thermooxidative degradation step. Obtained parameters were used to predict the stability at 20 and 180°C, respectively, which served for the recognition of the processes induced by heat and those naturally occurring at lower temperatures. Comparison of obtained conversion times brought a partial insight into the kinetics and consequently into the role of individual compounds in the thermo-oxidative degradation/stability of secondary humic acids structure. It has been demonstrated that aromatic compounds added to humic acids, except pyridine, increased the stability of humic acids and intermediate chars. The same conclusion can be drawn for acetic and palmitic acids. Addition of glucose and ethanol decreased the overall humic stability, however, the char of the former showed highest stability after 40% of degradation.

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