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SOUTH-MORAVIAN LIGNITE – POTENTIAL SOURCE OF HUMIC SUBSTANCES

J. Kučerík, M. Pekař and M. Klučáková

Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
kucerik@fch.vutbr.cz, pekar@fch.vutbr.cz, klucakova@fch.vutbr.cz

Abstract*. South-Moravian lignite (SML) was investigated as a potential source of humic substances (HS). Various extractants were tested as well as lignite oxidizing agents to enhance the extractable content of HS. It was proved that SML contains relatively high amount of HS. HS were characterized by elementary analysis, UV/VIS and FTIR spectroscopies, and ultrafiltration.*

Key words*: humic acids, lignite, oxidation*

Introduction

With the aim to incorporate the Czech Republic among the countries of the European Union, some reforms had to begin in all branches of industry, including chemistry. There is an obvious effort to produce chemicals, for direct and non-direct application, without distinctive influence on the environment. One of the possible ways to do this, is using various sources of raw materials arisen by "the cheapest chemical reaction". An example of these in-nature-formed materials is lignite, which has been used mainly as a not very effective fuel in power plants.

Lignite belongs to the group of the youngest type of humus coal. From the point of view of physical chemistry, lignite can be described as a solid colloidal system with a different surface morphology, dependent on the degree of coalification. Lignite properties are determined by composition of parental phytomass (content of the saccharides, hemisaccharides and lignin) and by intensity of the pressure and thermal conditions during the period of its transformation[1]. Chemical composition of lignite is very heterogenous – plant residues, bitumens, humic substances, mineral inclusions and usually high content of water.

Probably the most attractive way of non-energetic exploitation of lignites is their use as sources for humic substances. These compounds are products of decomposition of plant phytomass and they seem to be the most widely distributed compounds on the earth's surface. They have been studied for long years, yet many questions on, e.g., their structure, function or morphology, have not been fully resolved. Humic substances are usually studied from the standpoint of their function in soil and in natural transport of inorganic and organic substances[2-5]. However, practical applications in various areas (agrochemistry, silicate technology, sorption etc.) are also known. The main goal of our work is to investigate the possible use of South-Moravian lignite (SML) from the locality Mikulčice (Czech Republic) as a source for humic substances. This contribution reports on the first results achieved in this direction.

Typical composition of SML is given in Table 1[6]. High free water content corresponds to the freshly mined material and is typical for SML. We have found that after drying and re-equilibrating under ambient conditions moisture contents is about 5% (by weight).

Elementary composition of combustible matter of SML is given in Table 2 (Lignit Hodonín, Ltd., unpublished data). Comparing with the average composition of solid fuels (Table 3[1,7]), it is confirmed that SML belongs to the group of young brown coals.

Table 1. Typical elementary composition of South-Moravian lignite[6]

Component	weight %
Water	48 – 50
Ash	11.6 – 13.2
Combustible matter	39.1 – 40.3
Hydrogen	~2.15
Carbon	25.91
Oxygen	10.92
Sulphur total	0.81
Sulphur organic	0.48
Sulphur pyrite	0.27
Nitrogen	~0.32
Halogenides	< 0.01

Table 2. Typical elemental composition of combustible matter (ash and moisture free) from South-Moravian lignite (Lignit Hodonín, Ltd., unpublished data)

Hydrogen (weight %)	Carbon (weight %)	Sulphur (weight %)	Nitrogen (weight %)	Oxygen (weight %)
5.0–5.4	64.1–66.3	1.1–1.3	0.8–1.0	27.4–28.5

Table 3. Elemental composition of solid fuels[1,7]

	Carbon (weight %)	Hydrogen (weight %)	Oxygen (weight %)	Nitrogen (weight %)
wood	50	6	43	1
peat	60	6	33	1
brown coal	73	6	19	1
black coal	82	5	10	1
anthracite	94	3	2	1

Elementary composition of ash is given in Table 4. The main part is formed by silicates or aluminosilicates. Content of carbonates is low as the ash content was reduced only by about 10% after lignite treatment by hydrochloric acid, during which no carbon dioxide evolution was observed.

Composition of lignite inorganic particles is very various. XRF spectroscopy revealed almost all basic elements as Fe, Mg, Si, P, K, Ca, for instance, but also Te, U, Ta (traces)[8]. The amount of organic compounds, that means cellulose, hemicellulose, lignin, humic substances and bitumen, is relatively high – it is the reason of high sorption capacity of SML[6,9].

Table 4. Typical composition of ash from the South-Moravian lignite (only main components are given, on oxide base; Lignit Hodonín, Ltd., unpublished data)

Component	weight %
SiO_2	27–48
Al_2O_3	17–22
CaO	10–28
SO_3	8–13
Fe_2O_3	7–8
MgO	3–4

Experimental

Extraction of humic substances. Keeping in mind economy demands of mining company, as simple as possible extraction procedure was employed. Although it inevitably leads to crude humic product, this can be used directly in technical and agricultural applications and will serve as a raw material for production of purified sorts. Moreover, information on maximum extractable amount is obtained. Following procedure, motivated by the Czech standard on determination of content of humic substances in coal[10] and the well-known procedures[2], was used.

20 g of lignite, previously dried to equilibrium moisture content (see above) and retained between 0.2-0.3 mm sieves were mixed with 200 ml 0.1 M HCl. The substrate was then washed with distilled water until free of Cl^- ions. Pretreated lignite was than placed in a beaker and 200 ml of 0.1 M NaOH solution were added in portions at constant temperature. The mixture was stirred and heated at 80°C for a few hours. The remaining solids were removed by 20 minutes centrifugation at 5000 rpm and then rinsed with distilled water. Supernatant solution and the solution obtained during rinsing the remaining solids were mixed and concentrated HCl was added to pH = 1. The coagulated HA were decanted, washed several times, dried and weighted.

Oxidation of SML. It is well-known, that it is possible to enhance natural content of extractable humic substances in original organic-mineral substrate by using undemanding chemical procedures. In this study, oxidation by nitric acid and a mixture of hydrogen peroxide with phosphoric acid was used.

20 g of lignite (equilibrium moisture, particle size 0.2-0.3 mm) were mixed with 200 ml of oxidation agent in reaction vessel and for the desired time; concentration of oxidation agent and oxidation temperature were varied.

Elementary analysis. The ash content was determined by heating at 700°C for 4 hours in air; moisture at 105°C for a few hours to constant weight.

Elemental analysis was kindly made in Pliva-Lachema company, Brno, using standard methods of Carlo-Erba elementary analyzer. Oxygen was calculated by difference.

Characterization of extracted humic substances by UV-VIS and FTIR spectroscopy. UV-VIS spectroscopy was used for both molecular characterization and quantitative analysis. UV-VIS spectroscopy analysis was performed with a Helios-α spectrometer (UNICAM). Humic samples were dissolved in NaOH solutions of varying concentration, transferred to a 1 cm path length quartz cuvette and scanned from 200 to 700 nm. The E_4 (absorbance at 465 nm) and E_6 (absorbance at 665 nm) were also determined. The E_4/E_6 ratio is known as the index of humification and it serves for estimation of degree of condensation [11,12].

IR spectra were measured using KBr technique with Nicolet Impact 400 spectrometer. The pellets for infrared analysis were prepared by mixing of approximately 5 mg of dry humic substance sample with 250 mg of dried KBr.

Determination of molecular weight. Estimates of molecular weights and their distribution were obtained using membrane centrifugation through the polyether sulphone membranes with different pore sizes calibrated in molecular weight cut-offs (Microsep devices, Pall-Gelman company), at 5000 rpm and 5 - 60 min. Concentrations of initial solution and ultrafiltrates were determined by UV-VIS spectroscopy using calibration curve at maximum UV absorbance (about 216 nm). Solutions of humic substances (0.025 g/l) in NaOH of various concentration were used.

Points of differential distribution function (F) were computed from the following relation:

$$F(M_r) = \Delta w_i / (w_0 \Delta M_i) \tag{1}$$

where

$$\Delta w_i = w_i - w_{i+1}, \quad \Delta M_i = M_i - M_{i+1}$$

w_i is concentration of ultrafiltrate from the i-th membrane(g/l), M_i its molecular weight cut-off ($M_i > M_{i+1}$), and w_0 is concentration of initial solution.

Overall average molecular weight was computed from the equation:

$$\overline{M}_r = \frac{\sum_i \Delta w_i M_{ai}}{\sum_i \Delta w_i} \tag{2}$$

where

$$M_{ai} = (M_i - M_{i+1})/2 \tag{3}$$

Of course, fraction retained on the membrane with the largest cut-off could not be included in the computations.

Results and Discussion

Extraction of humic acids. Results of simple extraction procedure made under different conditions are summarized in Table 5. The content of ash was in all samples at most 12%.

Table 5. Dependence of yields of HA on the used extraction agent and temperature

extractant	temperature				
	20°C	50°C	60°C	70°C	80°C
0.5M KOH	12.5	20.7	21.5	24.0	26.4
0.5M NaOH	14.9	21.4	24.5	26.6	30.2
0.1 M NaF	1.6	7.1	8.1	13.1	13.5

It is evident, that the most powerful extractant is 0.5M NaOH. As expected, NaF is a mild extractant, on the other hand, it is supposed to cause minimum alteration of humic substances during extraction. Another alkali extraction agents (LiOH, NH_4OH) were also tested with low efficiency.

Oxidation of SML. Results of lignite oxidation experiments are given in Tables 6 and 7. Comparing with Table 5, it is evident that the contents of extractable humic matter can be raised up to about 60%, i.e. two-fold. Optimization of oxidation conditions should include both oxidant concentration and reaction time. Thus, either 10% nitric acid for 60 minutes or 20% for 30 minutes can be used. From Table 6 it is seen that hydrogen peroxide in the medium of 10% phosphoric acid is somewhat less active oxidation agent. Using only hydrogen peroxide in the same concentrations as in Table 7 caused substantial reduction in yields (13 – 27% after 18 min. of oxidation). Pure hydrogen peroxide is thus too strong agent causing decomposition of lignite organic matter. The nitric acid and hydrogen peroxide probably did not only show up as an oxidation agent but also as an "opener" of the structure of lignite.

Table 6. Dependence of yields of HA on the concentration of oxidizing agent and time of oxidation

agent	time			
	15 min	30 min	60 min	120 m
5% HNO_3	39.5	48.5	44.3	43.0
10 % HNO_3	43.1	43.6	59.4	43.1
20 % HNO_3	52.5	59.7	48.5	47.4

Elementary analysis of SML and humic acids. Typical results are presented in Table VIII. They correspond with published data of another authors both in general [1,2] and for brown coals from other Czech localities[13]. According to the obtained results, it can be concluded that our HA are probably very aromatic.

Spectroscopic characterization of humic acids. FTIR spectroscopy The main peaks observed in infrared spectra are (see Fig. 1):

- broad band at 3300-3400 cm^{-1} (OH-groups, H-bonds),
- two small but distinct peaks at 2930 and 2850 cm^{-1} (asymmetric C-H stretch of CH_2),
- sharp peak at around 1700 cm^{-1} (C=O of COOH),
- peak at 1620 cm^{-1} (C=C in aromatic structures, COO^-, H-bonded C=O),
- peak about 1221 (aromatic C, C-O stretch),
- composed band in 1000 – 1200 cm^{-1}, attributable to various origins (C-O stretch of aliphatic OH, -C-O stretch and OH deformation of –COOH, C-O stretch of polysaccharides).

Table 7. Dependence of yields of HA on the concentration of H_2O_2 and time of oxidation in the presence of 10% of phosphoric acid

concentration	time	
	30 min	60 min
5% H_2O_2	44.6	41.9
10% H_2O_2	42.7	42.6
20% H_2O_2	42.5	41.9

Table 8. Elementary analysis of extracted humic acids (ash and water free)

Oxygen (weight %)	Carbon (weight %)	Hydrogen (weight %)	Nitrogen (weight %)
37.0	57.2	5.1	0.7

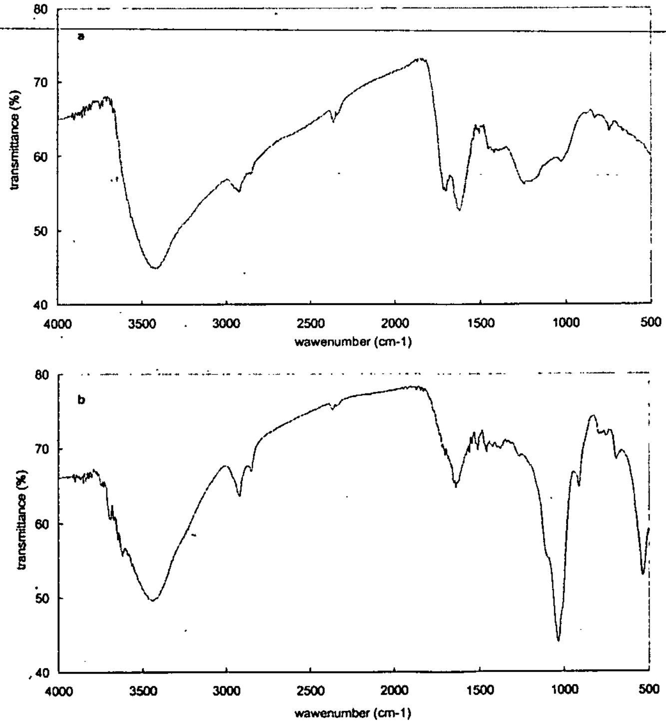

Figure 1. FTIR spectra of humic substances extracted from natural (a) and oxidized (b) lignite.

The spectrum corresponds with spectra of humic substances of different origin published throughout the vast literature on this matter[2,14,15]

Spectra of humic acids prepared by extraction of oxidized lignite were also measured and compared with humics obtained from the raw lignite. Spectra differ from those measured with HA prepared from the natural lignite mainly in much higher intensity of bands between 1000 – 1200 cm^{-1} and diminishing the peaks at 1600 – 1750 cm^{-1}. The former is attributable to new C-O stretch vibrations of aliphatic alcohols formed during oxidation and probably also to C-O vibrations of formed karboxyls (shoulder close to 1200 cm^{-1}). Smaller peak at 1600 – 1750 cm^{-1} probably points to partial destruction of original carboxyls under reaction conditions. Oxidation process forms primarily hydroxylic groups.

UV–VIS spectroscopy

Experimental results suggest that all UV-VIS spectra of HA from different sources are similar[2,5,14]. Typical spectrum of humic acids extracted from the South-Moravian lignite is given in Figure 2. It resembles spectra given in literature. The index of humification, determined as the ratio of absorbancies at 465 and 665 nm, was about 3.9. In accordance with FTIR results and elementary analysis, there is evidence for a high level of aromatic C structures[2].

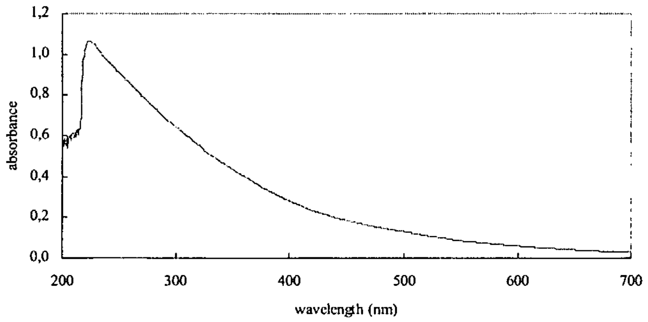

Figure 2. UV/VIS spectrum of lignite humic substances in NaOH solution.

Molecular weight distribution. Quantitative reproducibility of ultrafiltration experiments is rather problematic, particularly in the case of membranes with the lowest molecular weight cut-off. As the permeate volume was constant after seven repetition cycles, the main cause should be the adsorption of humic substance on membrane. Nevertheless, qualitative features of distribution were reproducible and at least estimates of some numerical values were obtained.

Results of two repetitions with solution in 0.01 M NaOH are given in Figure 3 (values of M_{ai}, see Equation (3), are indicated as tick labels on the M_r axis). The same shapes were obtained also for other concentrations of NaOH solvent. Molecular weight distribution is, at least, trimodal. The highest peak is observed at the lowest values of M_r, about 1 000. Second peak occurs at M_r of several thousands and in some experiments is observed only as a tail of the former (cf. Figure 3). Last maximum is located at about 40 000. It should be pointed that some part of humics was retained even on the largest used membrane, i.e., with 1 000 kDa cut-off. Distribution curve over 100 kDa is not shown as it is close to the molecular weight axis and lowers readability of the figure.

Trimodal distribution was observed regardless alkali concentration. However, NaOH concentration affects estimates of the overall average molecular weight. The lower the alkali concentration, the higher the average weight. In fact, the molecular weight in ultrafiltration is a measure of pore size that is of molecular dimensions. Higher concentration of sodium counterions thus probably reduces electrostatic repulsion of humic macromolecules, which can pack into more favorable smaller conformations.

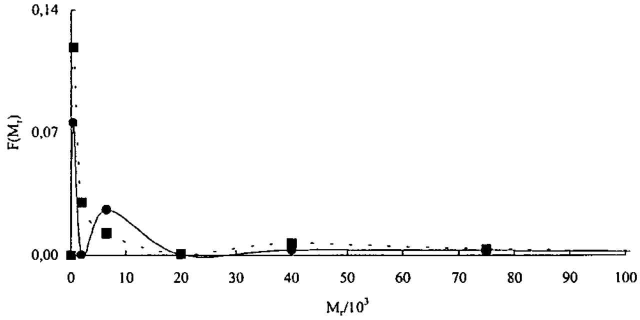

Figure 3. Molecular size distribution of humic substances estimated from ultrafiltration (two replicates).

Conclusion

South–Moravian lignite was verified to be a potential source of humic substances. Their content is relatively high and can be further increased by simple oxidative procedures. It is evident that the lignite combustion is waste of high-quality raw material from which valuable substances can be obtained by relatively undemanding processes. Work is in progress to open new application areas of South-Moravian lignite both on technical and speciality chemical levels.

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