



## Hydrogen peroxide oxidation of humic acids and lignite



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### HIGHLIGHTS

- Structural information of humic acids and lignite were obtained.
- Malonic acid and succinic acid are formed in high selectivity and high yields.
- Methylene and ethylene chains are main bridge bonds between aromatic rings.
- Optimal conditions were found for the production of malonic acid and succinic acid from lignite.
- The H<sub>2</sub>O<sub>2</sub> oxidation is an attractive route for utilizing South Moravian lignite.

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### ABSTRACT

The H<sub>2</sub>O<sub>2</sub> degradation of humic acids and lignite from Mír mine (South Moravian region, Czech Republic) resulted in oxidation of aromatic structures and cleavage of aromatic units. The hydrophilic fraction largely dominated the oxidation digest in both parental materials. The presence of polycyclic biomarkers  $\alpha$ -Phyllocladane, De-A-lupane confirms the high plant contribution. Hopanoid structures and branched C<sub>15</sub> and C<sub>17</sub> (*iso* and *anteiso*) fatty acids show slight bacterial inputs. Short chain *n*-fatty acids (<C<sub>20</sub>) are ubiquitous in living kingdom, whereas long chain homologs are probably derived from higher plants. Phosphoric acid production through the H<sub>2</sub>O<sub>2</sub> oxidation probably results from hydrolyses of pyrophosphate. From hydrophilic fractions of lignite and humic acids, malonic acid and succinic acid are dominant compounds and could indicate that methylene and ethylene chains are main bridge bonds connecting between the aromatic rings in the structure. The H<sub>2</sub>O<sub>2</sub> oxidation of lignite was very selective for producing malonic acid and succinic acid in high yields and the oxidation degradation method appears to be a suitable new way for utilizing South Moravian lignite. For production of malonic acid and succinic acid, the results indicated that the appropriate condition especially was at 50 °C for 4 h and 40 °C for 4 h, respectively. But oxidation followed by reoxidation of lignite at 30 °C for 1 h could be also a reasonable way to produce that kind of molecules (particularly malonic acid). Lipophilic compounds represented the minor GC-amenable fraction of the total products obtained by oxidation of lignite.

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### 1. Introduction

Humic substances are naturally occurring biomolecules ubiquitous in water, soil, and sediments. The quantity, reactivity and role of humic substances in the biosphere amply justify the intense research on their chemical and biochemical transformation. They are regarded as complex chemical structures which are more stable than their precursors and have lost their chemical

characteristics. They are operationally divided into three classes on the basis of their alkaline and acid solubility (fulvic acids which are soluble under all pH conditions, humic acids soluble at pH > 2 and humin insoluble at all pHs). Humin and humic acids (HAs) generally represent the major fraction of humic substances and appear to display similar analytical characteristics and chemical structure [1]. HAs occur naturally in lignite and can account for an important fraction (10–80% depending on the maturity level) of the lignite organic matter [2–4]. HAs obtained from lignite deposits are further along the diagenetic path of humification. They are considered as containing more condensed aromatic units than soil humic acids [5]. South Moravian lignite contains a relatively high proportion of extractable humic acids of aromatic nature [6–8] which could have

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practical applications due to their binding capacity and stability. As a consequence, the determination of chemical composition and structure of humic acids and lignite at a molecular level is of importance. Chemical degradation of humic acids and lignite (hydrolysis, oxidation, reduction) has been widely used to investigate their structural moieties and has provided evidence of both aromatic and aliphatic constituents [9,10]. Most of the studies involving degradation digest of humic acids has focused on solvent extractable products, while information on water soluble components is limited [11,12].

Lignite is low-rank coal which is formed from original phyto-mass by peatification, followed by coalification and is intermediate between peat and bituminous coal. Unfortunately, composition and structure of lignite is still unclear. Most authors believe that coal macromolecules formed mostly from altered biopolymers found in plants [13]. Lignite is mainly used as fuel for powerplant but its disadvantages are low calorific value and high water content. In this regard, the lignite burning represents wastage of a valuable raw material and a better solution may be to use lignite for non-energy or non-fuel applications. Probably the most attractive way is the use of lignite as sources for humic substances, especially humic acids [6]. Further, it can be used for sorption of heavy metals [14,15], agricultural application for production of coal-based fertilizers, soil conditioners, and humic acids [16,17]. Further, the coal can be used for making composite materials such as coal/polymer composites and coal/conducting polymer composites [17,18].

On the basis of lignite structure, it may be considered as a valuable raw material for the production of a large variety of chemicals such as small molecule acids via liquid phase oxidation [19,20].

Certain carboxylic acids have a variety of applications in industries producing food and pharmaceutical products, surfactants, and detergents [21]. For example, there are four major existing markets for succinic acid [22]. The first and largest is as a surfactant/detergent, extender/foaming agent. The second market is as an ion chelator, where it is used in electroplating to prevent corrosion and pitting of metals. The third is the food market, where it is used as an acidulant/pH modifier, as a flavoring agent, and as an anti-microbial agent. The fourth market is the production of health-related agents, including pharmaceuticals, antibiotics, amino acids, and vitamins [22].

Hydrogen peroxide is a strong oxidative agent. Hydrogen peroxide is decomposed readily by light and/or heat, especially in the presence of trace amounts of transitional metals [23,24], producing reactive radical species [23–31].  $H_2O_2$  reacts as a nucleophile under alkaline conditions [25,26,32,33], and as an electrophile in acidic conditions, where the peroxy acid is formed. The peroxy acid can react as an electrophile with lignine, leading to oxidation and subsequent degradation [31,34–40].

For a brown coal, Miura et al. [41] proposed the mechanism of the  $H_2O_2$  oxidation as follows.

First, weak  $-C-O-$  linkage in coal are broken, producing  $CO_2$  and a large amount of water-soluble organic compounds; simultaneously many carboxylic groups are formed around the condensed aromatic rings of the compound. Then, the aromatics rings with the carboxylic groups gradually decompose to produce small molecule acids. Some of the aromatic rings will also oxidize to produce small molecule acids. Thus, the oxidized coal (residue) becomes rich in aliphatic compounds and carboxylic groups with the progress of oxidation [41,42]. Mechanism of the rupture of aromatic rings may be explained by proton donation through the Fenton reaction due to the catalytic effect of Fe occurring in coal [41].

After oxidation of lignite for 24 h at 60 °C, the average unit structure of water-soluble large-molecule components is presumed to be one aromatic ring attached with carboxylic and aliphatic substituents. The relative amount of carboxylic substituents

to aliphatic substituent was dependent on the condition of the oxidation [19].

$H_2O_2$  oxidation does not cleave ester linkage and therefore has been considered as a method of overestimation of the content of aromatic units in humic substances [43–45].

The aim of this work is twofold. First, the characterization of the South Moravian lignite and humic acids isolated from it at a molecular level by the method of oxidative degradation. Secondly, assessment of the possibility to use the South Moravian lignite oxidation for production of valuable chemicals, primarily low molecular weight organic acids. In the study, we chose the oxidation with  $H_2O_2$  as the degradation method because besides structural information the  $H_2O_2$  oxidation can give interesting chemicals for a industrial sphere from raw lignite. Therefore, we used relatively soft oxidation conditions (temperature and time) to limit overoxidation of digests. In the case of lignite, we also examined the effect of reaction conditions (temperature and time) on the product distribution in view of malonic acid and succinic acid. South Moravian lignite and its organic matter have not been characterized in this way so far. Moreover, coal organic matter in general has not been studied by hydrogen peroxide oxidation under such a broad set of reaction conditions.

## 2. Material and methods

### 2.1. Lignite and extraction of humic acids

The sample of lignite used in this study was obtained from Mír mine located near Hodonín in the south-eastern part of Moravia, Czech Republic. Its detailed characteristic, including geochemical and petrographic description, has been published elsewhere [6,46–49]. Briefly, brown xylite rich lignite was collected from the Dubňany seam in the mine Mír in the South Moravian Lignite Coalfield that and forms northern part of the Vienna basin. Lignite was ground to the size fraction less than 0.2 mm and dried. The extraction with chloroform (under 100 atm at 80 °C,  $3 \times 12$  h) was performed to remove bitumen. Bitumen free lignite was dried under ambient laboratory atmosphere at about 25 °C which resulted in the final equilibrium moisture contents about 7% by weight. Lignite was subsequently used for  $H_2O_2$  oxidation.

Humic acids were isolated from South Moravian lignite following the procedure reported elsewhere [50,51]. Briefly, dried and ground lignite (20 g) was mixed with 1 L of a solution of NaOH 0.5 M and  $Na_4P_2O_7$  0.1 M and stirred for 3 h. The liquid above the sediment was filtered through a 60  $\mu$ m PAD filter and filtrate was acidified by addition of concentrated HCl to pH 1. The precipitated lignite humic acids (HAs) were centrifuged, washed several times by a mixture of HCl 0.25 M and HF 0.3 M, distilled water until chloride-free, dried to constant weight at 50 °C and weighted. Prepared humic acids were extracted with chloroform (under 100 atm at 80 °C,  $3 \times 20$  min) to remove adsorbed bitumen. Bitumen free HA contains 89.5 wt.% of organic matter, 4.5 wt.% of water and 6.0 wt.% of ashes (determined by drying at 105 °C to constant weight and followed by heating 4 h at 700 °C in air).

### 2.2. Hydrogen peroxide oxidation

#### 2.2.1. Oxidation of lignite humic acids

The suspension of HAs (1 g) in aqueous solution of hydrogen peroxide (3 wt.%, 50 mL) was stirred for 6 h at 70 °C. The supernatant was extracted for three times with chloroform to isolate the lipophilic fraction. The solid residue was again oxidized with  $H_2O_2$  until its total disappearing (four  $H_2O_2$  oxidation cycles). Lipophilic fractions were combined, dried over  $MgSO_4$  and evaporated under reduced pressure before methylation with  $BF_3$ -methanol

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