



The characterization of South Moravian lignite in its natural and treated forms using thermal degradation methods



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ABSTRACT

Thermal degradation experiments were performed on South Moravian lignite in its natural and treated forms primarily to investigate the changes taking place during pyrolysis, and, secondarily, to determine the structural characteristics of lignite using thermal degradation methods. The lignite was treated by extraction with chloroform, demineralization, and the remineralization or sorption of calcium ions on the demineralized lignite. The analysis of pyrolysis products was performed in solid and gaseous states using FTIR analysis and the thermogravimetric technique coupled with FTIR (TG-FTIR). Experiments were complemented by thermochemolysis with tetramethylammonium hydroxide (TMAH). South Moravian lignite was characterized by the bimodal distribution of saturated fatty acids, with two maxima at $n\text{-C}_{16}$ and at $n\text{-C}_{28}$, and the dominance of guaiacyl units indicating a gymnosperm origin. FTIR analysis of the examined sample set showed that lignite contains different functional groups with various thermal stabilities degrading to the evolution of gases such as H_2O , CO , CO_2 and CH_4 . Precursors of the gaseous products generated and an analysis of functional groups in the samples are discussed in the paper. The results show that treatments of lignite may be reflected in their thermal behaviors during pyrolysis.

1. Introduction

Lignite is a low-rank coal which is formed from original phytomass by peatification followed by coalification and is considered as an intermediate form between peat and bituminous coal. Lignite is mainly used for energy and fuel production, even though it has low calorific value and high water content. Alternative applications of low rank coals are subject to intensive research and may include, for example, use as a sorbent of heavy metals and dyes [1,2]; uses in agriculture as a source of humic acids [3], as organic and organomineral fertilizers (generally coal-based fertilizers), and as soil conditioners [3]; and material for the production of low molecular weight acids by chemical treatments [4].

The improvement and development of these applications are closely linked with an understanding of coal structure. Chemical information on coaly organic matter can be obtained either by non-destructive methods, or destructive methods, while coal can be studied in its original form, or modified through various process such as demineralization, extraction etc. Destructive methods are based on the fragmentation of macromolecular organic matter by chemical and/or pyrolytic degradation and subsequent analyses of the low molecular weight products. Secondary reactions (rearrangement, cracking,

hydrogenation, and polymerization) in a heterogeneous mixture cannot be excluded, and it is logical that conclusions regarding the original structure of coal in the macromolecular phase have to be drawn with caution. In contrast, the main advantage of non-destructive methods lies in the fact that the sample can be analyzed without drastic pretreatment. The sample can be examined as a whole and secondary reactions can be avoided. Non-destructive methods include, for example, nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray near edge absorption spectroscopy (XANES), and scanning electron microscopy (SEM) coupled to energy-dispersive X-ray analysis (EDX). Most of these methods, however, are relatively insensitive and reveal low resolution. Although these techniques can give good results concerning total chemical composition, specific compounds are difficult to identify [5].

The present study is focused on lignite from the South Moravian Lignite Coalfield located in the northern part of the Vienna basin. The Vienna basin extends into the Czech Republic from the northern tip of Austria. A part of the basin is located on the territory of Slovakia. Some of the abovementioned analytical approaches have been used to characterize the macromolecular organic matter of South Moravian lignite.

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Table 1

Ultimate and proximate analyses of natural lignite (NL), extracted lignite (EL), demineralized lignite (DL), and remineralized lignite (RL).

Sample	Moisture (wt.%)	Ash (wt.%)	Elemental composition (at.%)					Atomic ratios		
			C	H	N	S	O ^{diff.}	H/C	O/C	N/C
NL	15.0	11.3	33.8 ± 0.2	40.5 ± 0.1	0.6 ± 0.0	0.3 ± 0.0	24.9 ± 0.3	1.20 ± 0.01	0.74 ± 0.01	0.02 ± 0.00
EL	21.7	11.4	32.0 ± 0.3	38.1 ± 0.6	0.6 ± 0.0	0.3 ± 0.0	29.0 ± 0.5	1.19 ± 0.03	0.91 ± 0.02	0.02 ± 0.00
RL	9.2	11.9	35.6 ± 0.0	41.5 ± 0.2	0.6 ± 0.0	0.3 ± 0.0	22.0 ± 0.3	1.17 ± 0.01	0.62 ± 0.01	0.02 ± 0.00
DL	6.5	1.4	39.6 ± 0.5	41.6 ± 0.9	0.6 ± 0.0	0.3 ± 0.0	17.9 ± 1.3	1.05 ± 0.01	0.45 ± 0.04	0.02 ± 0.00

However, the studies focused mainly on the spectrometric characterization of structural features in South Moravian lignite using ¹³C NMR and FTIR spectrometers [6]. Doskočil et al. [4] applied hydrogen peroxide oxidation to lignite in order to obtain structural information and to find interesting new applications for this coal. Havelcová et al. [7] analyzed soluble organic compounds in a suite of coals including that from the South Moravian Coalfield using gas chromatography/mass spectrometry (GC/MS). With regard to potential applications, water-extractable fractions from South Moravian lignite were characterized by spectrometric methods and further analyzed at the molecular level [8]. However, no thermochemical methods have so far been used or reported in the literature with respect to this low-rank coal or any other coals from the Vienna basin.

Thermogravimetric analysis (TGA) is a widely used method providing information on the mass loss and pyrolysis rate through the thermogravimetric curve and the differential thermogravimetric curve, respectively. A gas analyzer connected to TGA provides information on the volatiles evolved during the process and information on the pyrolysis behavior. Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) is one of the most common methods enabling the study of functional-group decomposition [9]. Gaseous products such as CO₂, CO, H₂O, CH₄, C₂H₄, NH₃, COS, SO₂ are the most commonly detected gases during coal pyrolysis using TG-FTIR [10]. MacPhee et al. [10] reported that TG-FTIR can also be reliably used for determination of the organic oxygen content in coals. Thermochemolysis is an analytical pyrolysis, which allows the analysis of both free and bound carboxylic and alcoholic moieties [11]. The result of thermochemolysis with tetramethylammonium hydroxide (TMAH) is the formation of less polar and methylated low molecular weight units which are amenable to gas chromatography analysis [12]. Even though thermochemolysis with the reagent TMAH is well known and used for the molecular analysis of natural organic matter such as soils and sediments, this procedure has, so far, been applied to whole coals to a lesser extent [13–15].

The aim of this work was primarily to investigate the changes taking place during pyrolysis and, secondarily, to determine the structural characteristics of lignite using thermal degradation methods such as thermogravimetric analysis (TGA), a thermogravimetric technique coupled with FTIR (TG-FTIR), and thermochemolysis with TMAH. These methods were applied to South Moravian lignite from the Vienna basin before and after treatments including extraction with chloroform, demineralization, and the remineralization or sorption of calcium ions on the demineralized lignite. Although the pyrolysis of lignite has been widely studied, in most cases pyrolysis products are analyzed in either a solid or a gaseous state. In our work, we performed an analysis of residues together with the evolved gases, thereby allowing a complementary and comprehensive view of pyrolysis.

2. Materials and methods

The sample of lignite used in this study was obtained from the Mír mine in the locality of Mikulčice, Czech Republic; the mine belongs to the Dubňany seam in the South Moravian Lignite Coalfield, which forms the northern part of the Vienna basin. This was a representative sample of the standard product of this mine; its detailed characteristics,

including its geochemical and petrographic description, have been published elsewhere [7,8,16]. Before use, the lignite was dried at 105 °C for 24 h and left to equilibrate in the ambient laboratory atmosphere at about 25 °C, which resulted in a final equilibrium moisture content. Then, the milled lignite was sieved to the size fraction of less than 0.2 mm.

The lignite sample was extracted with chloroform for 36 h in a Soxhlet apparatus. The extracted lignite was dried and then allowed to equilibrate in the ambient laboratory atmosphere at about 25 °C.

Demineralization of the lignite sample was done by treatment with hydrochloric and hydrofluoric acids under conditions described in the literature [17]. Briefly, hydrofluoric acid was added to the lignite and the suspension was maintained at 55 °C for 45 min. After filtration, the procedure was repeated with HCl instead of HF. Demineralized lignite was washed with hot water, dried, and then left to equilibrate in the ambient laboratory atmosphere at about 25 °C.

The preparation of remineralized lignite was performed according to Murakami et al. [18]. Briefly, demineralized lignite was immersed in a calcium acetate solution with a pH of 8.3. This value of pH was based on reports that protons of all carboxyl groups were exchanged with calcium ions at this pH [19,20]. Remineralized lignite was washed with ultrapure water, dried, and then allowed to equilibrate in the ambient laboratory atmosphere at about 25 °C.

Elemental compositions of the samples were determined using a CHNS-O EA 3000 Elemental Analyzer. The oxygen content was calculated by difference and the data obtained were corrected for moisture and ash content. The results are presented in Table 1.

Thermal degradation of the prepared samples was performed using a Q5000IR TG analyzer (TA Instruments) with ± 1 °C temperature accuracy and ± 0.1% mass accuracy. Twenty mg of examined sample was introduced into a platinum cup. The sample was heated at a heating rate of 20 °C min⁻¹ to different temperatures in the range 300–800 °C under a flow of nitrogen (20 cm³ min⁻¹). The solid residue obtained after degradation at different temperatures was analyzed using an FTIR spectrometer.

FTIR spectra were recorded on pellets prepared by pressing a mixture of 1.5 mg of sample and 400 mg of dried spectrometry grade KBr using a Nicolet iS50. Spectra were recorded in the range 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ and 256 scans were performed on each sample.

For the analysis of evolved gases, 20 mg of lignite sample was introduced into a platinum cup. The crucible was inserted into a Q600TG-DTA analyzer (TA Instruments) connected with the measuring cell (TGA/FT-IR Interface, Thermo Scientific) of a Nicolet iS10 FTIR spectrometer (Thermo Scientific) by means of a heated capillary (200 °C). The sample was heated at a heating rate of 20 °C min⁻¹ under a flow of argon (100 cm³ min⁻¹) to 900 °C. A set of 651 infrared spectra was collected in the wavenumber region from 600 to 4000 cm⁻¹.

Thermochemolysis was based on the off-line procedure developed by Grasset and Amblès [21]. Sample (350 mg) was placed in a ceramic boat and thoroughly soaked with 2 ml of a 50% w/w solution of tetramethylammonium hydroxide (TMAH; Acros Organics, New Jersey, USA) in methanol. After 1 h of impregnation, the sample was transferred into a Pyrex tube and heated at 400 °C (30 min isothermal). Thermochemolysis products were swept using N₂ to a trap containing

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