Recent development in lignite investigation

Lucia Závodská* - Juraj Lesný†

Abstract

Recently lignite represents mainly and alternatively exploited fuel of lower heating value. Similarly to other naturally occurring raw materials the economical efficiency of lignite mining is strongly influenced by plenty of different economical, technological as well as political factors, all of which are subjects of permanent changes. Fossil materials, including lignite, in general possess some specific properties (as a consequence of their composition), which enable their miscellaneous and often economically very valuable non-energetic utilization. As a rule quantitatively as well as qualitatively rich humic substance and low toxic and heavy metal content, specific physical structure, not negligible sorption properties, suitable sensorial features allow lignite usage as a fertiliser, soil conditioner, bioregulator, regulator of humidity, metal sorbent or agrochemical agent. The presented paper intends to contribute to summarization of recent knowledge concerning lignite - a natural raw material of huge amount and of permanently rising importance.

1 Introduction

Coal is the compressed remains of tropical and subtropical plants, mainly those of the Carboniferous and Permian Periods. Changes in the world climatic pattern explain why coal occurs in all continents, even Antarctica. Coal formation began when plant debris accumulated in swamps, partially decomposing and forming peat layers. A rise in sea level or land subsidence buried these layers below marine sediments, whose weight compressed the peat transforming it under high-temperature conditions to coal; the greater the pressure, the harder the coal. Humification, considered to be the most important chemical process in geochemical transformation, is mainly involved during the early formation stages of these materials [24, 57].

Coals can be classified in various ways. The most widely used classification schemes are based on the degree to which coals have undergone coalification. Such varying degrees of coalification are called coal-ranks (the major ones are lignite, subbitumenous, bituminous and anthracite). While the amount of fixed carbon in a coal increases from lignite to anthracite, the amount of its volatile matter released upon heating decreases. Coal is also classified into rock types on the basis of petrological components called macerals [71].

Coals vary in density, porosity, hardness and reflectivity (the degree to which a coal reflects light) [71]. By the American Society for Testing and Materials lignite is a brownish-black, low-rank coal, which has a heating value less than 19.3 MJ kg$^{-1}$, determined on a moist, mineral-matter-free basis. According to this definition lignite occurs in two subclasses: lignite A (14.7 – 19.3 MJ kg$^{-1}$) and lignite B (less than 14.7 MJ kg$^{-1}$). Outside North America, low-rank coal is classified as brown coal, which includes lignite and subbitumenous, and most high-volatile C bituminous coal of the North American classification system (24.4 – 30.2 MJ kg$^{-1}$). The above mentioned data is summarized in Table 1 [20].

Coals in general are found in many parts of the world. They occur in stratified deposits both, near the Earth’s surface and at various depths. Coals consist of broad range of substances. Owing their origin to the partial decomposition and chemical conversion it contains huge masses of organic matter in a complex, porous, three-dimensional network, which varies from one coal deposit to another and from one location to another within the same seam [4, 71]. Very important components of lignite, humic acids, occur naturally in lignite and can account for an important fraction (10 – 80% depending on the maturity level) of the lignite organic matter [1]. Leonardite is a special type of low-rank and low grade coal. It derives either from lignite that has undergone oxidation during

---

*Department of Projecting & Nuclear and Radiation Safety, Ekosur, SK-919 31 Jaslovske Bohunice, Slovakia, e-mail: zavodskas@ekosur.sk.
†Department of Biotechnology, Faculty of Natural Sciences, University of St. Cyril and Methodius, Nám. J. Herdu 2, SK-917 01 Trnava, Slovakia.
Table 1: Classification of coals by American Society for Testing and Materials [76]

<table>
<thead>
<tr>
<th>Class</th>
<th>Group</th>
<th>Calorific Value Limits (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Anthracite</td>
<td>1. Meta-anthracite</td>
<td>——</td>
</tr>
<tr>
<td></td>
<td>2. Anthracite</td>
<td>32.5 – 34.0*</td>
</tr>
<tr>
<td></td>
<td>3. Semianthracite</td>
<td>26.7 – 32.5</td>
</tr>
<tr>
<td>II. Bituminous</td>
<td>1. Low volatile bituminous</td>
<td>——</td>
</tr>
<tr>
<td></td>
<td>2. Medium volatile bituminous</td>
<td>——</td>
</tr>
<tr>
<td></td>
<td>3. High volatile A bituminous</td>
<td>≥ 32.6</td>
</tr>
<tr>
<td></td>
<td>4. High volatile B bituminous</td>
<td>30.2 – 32.6</td>
</tr>
<tr>
<td></td>
<td>5. High volatile C bituminous</td>
<td>24.4 – 30.2</td>
</tr>
<tr>
<td></td>
<td>2. Subbituminous B</td>
<td>22.1 – 24.4</td>
</tr>
<tr>
<td></td>
<td>3. Subbituminous C</td>
<td>19.3 – 22.1</td>
</tr>
<tr>
<td>IV. Lignitic</td>
<td>1. Lignite A</td>
<td>14.7 – 19.3</td>
</tr>
<tr>
<td></td>
<td>2. Lignite B</td>
<td>≤ 14.7</td>
</tr>
</tbody>
</table>

surface exposure or it represents sediments enriched in humic acids that were leached from top soil or overlain lignite [30].

Two major eras of coal formation are known in geologic history. The older includes the Carboniferous and Permian periods (350 million to 250 million years ago). Much of the bituminous coal of eastern North America and Europe is Carboniferous in age. Most coals in eastern Asia, Siberia and Australia are of Permian origin. The younger era began in the Cretaceous Period (about 135 million years ago) and culminated during the Tertiary Period (about 65 – 2.5 million years ago). From this era came nearly all of the world’s lignites and subbituminous coals. World resources of lignite are difficult to assess because of the different classification systems for low-rank coal in North America and elsewhere. The world’s greatest in-place resources of low-rank coal occur in Russia, Australia, USA and central Europe [71]. EU coal reserves reach > 100 Gt, what represent approx. 10% of the world total. The enlarged EU produces more than 400 Mt/y of brown coal. Figure 1 illustrates the hard coal and brown coal/lignite consumption in EU. The brown coal/lignite production remains centred predominantly in Germany, Greece and Spain (364 Mt/y). The Czech Republic, Hungary, Poland, Slovakia and Slovenia produce annually over 141 Mt [46].

Lignite is one of the first products of coalification and is intermediate between peat and bituminous coal. Its colour is brown to black and it has been formed from peat and under moderate pressure. Dry lignite contains about 60 – 75% carbon. It has been estimated that about 45% of the world’s total reserves are lignitic. However, these reserves have not been exploited to significant extent because comparing lignite with bituminous coal it is of much lower heating value and of deficient storage stability [71].

Lignite is difficult to store and transport because of its high moisture content and its high reactivity, which causes spontaneous combustion. Moreover, experiments with drying, spraying with oil, briquetting and use of a slurry pipeline as alternatives in the transport and storage performance have shown that these techniques are not cost effective. Lignite is used primarily to generate electricity in a short distance localized power plants. Nevertheless, it has been successfully used as a raw material for gasification, liquefaction and pyrolysis. Production of montan wax, activated carbon, as well as its utilization in firing kilns and home heating represent the minor uses of lignite. It is worth mentioning some interesting utilization advantages of lignite over higher-rank coal. Because of its high reactivity (which is due in part to high oxygen content) lignite does not have to be ground as finally as higher-rank coal to ensure complete combustion in pulverised coal systems. Advantages for gasification and liquefaction are high reactivity, low-sulphur content and non-caking properties. Alkali and alkaline-earth elements have catalytic properties in gasification and possibly liquefaction.

Disadvantages of lignite use in combustion, relative to higher-rank coals, are low heating value and the fact that fly ash from lignite may have high electrical resistivity, making it difficult to collect in electrostatic precipitators. Mineral matter in lignite is largely organically bound and inseparable by standard washing techniques. The high sodium content contributes to boiler fouling and slagging problems. The quartz content accelerates erosion of furnace burners. In gasification moisture acts as a diluent [20].
Petrographic composition of lignite

The term **maceral** in reference to coal is analogous to the use of the term **mineral** in reference to igneous or metamorphic rocks. Coal is composed of macerals, which each have a distinct set of physical and chemical properties that control its behaviour. Three basic maceral groups of coal are known: **vitrinite** (huminite used for lignites/soft brown coals), **liptinite** and **inertinite** one. **Vitrinite macerals** are derived from the cell wall materials (woody tissue) of plants, which are chemically composed of polymers, cellulose and lignin. It is the most abundant group and commonly makes up 50 – 90% of most North American coals. The **liptinite macerals** are derived from the waxy and resinous parts of plants such as spores, cuticles and resins, which are resistant to weathering and diagenesis. The **inertinite macerals** are made up from plant material that has been strongly altered and degraded in the peat stage of coal formation. **Huminite** designates a group of medium grey macerals having reflectances generally between those of the associated darker liptinites and lighter inertinites [10, 69].

Petrographic composition of organic fraction from the Rio Maior lignites (Spain) is attributed mainly to macerals of the **huminite** group (73 – 92%) with small percentages of **inertinite** (4 – 14%) and **liptinite** (2 – 18%) groups. Huminite reflectance ranges from 0.16% to 0.30% and indicate that the coals are in an early stage of evolution, corresponding to diagenesis, and in particular to biochemical coalification [68].

Chukurovo (Bulgaria) lignites are assigned to the subgroup of low-rank coals on a basis of maceral composition, where the following ranges were determined: **huminite** (82 – 85%), **liptinite** (8 – 12%), **inertinite** (6 – 7%) [67].

Maceral analysis of two Greek leonardites from Achlada and Zeli open pits shows, that **huminite** is the predominant maceral group (96.7% and 93.7%). **Liptinites** display low values and are higher in Zeli lignite (2.7% and 6.3%), whereas **inertinites** occur only in very low amounts in Achlada lignite (0.6%). Differences in the liptinite macerals are probably due to different organoclastic precursors [30].

Lignite paleoenvironmental study

The petrographic composition of low-rank coals provides useful information regarding peat-forming environments because it is normally possible to identify the plant fragments preserved as macerals. The preservation and the gelification of huminite tissues, the type and content of liptinite present generally reflect the depositional environment as well as its subsequent diagenesis. According to this information Flores reported that the peat biomass of the origin of Portuguese lignite formed from a very diverse vegetation comprising gymnosperms and angiosperms. In some seams Botryococcus algae have also contributed to the biomass [23]. Both gymno- and angiosperms occur in almost all climate zones, their distribution is influenced by climatic conditions. Aromatic biomarkers indicating the occurrence of angiosperms are derivatives of the amyrin triterpenoids. Aromatic diterpenoids of the abietane type are more abundant in the lignite samples from Canada and they represent a gymnosperms (e.g., conifer) dominated
paleovegetation. The aromatic biomarker composition has been used to assess the level of thermal maturity of the organic matter in coal and indicates a prevailing immature character [25].

The interpretation of the paleoenvironmental peat formation is based on a combination of four indices, namely groundwater index (GWI), vegetation index (VI), gelification index (GI) and tissue preservation index (TPI). GWI indicates the degree of gelification in the peat mire as well as the pH of the water. VI is related to the type of vegetation that dominated the peat mire. GI indicates the level of moisture in the peat-forming environment and is directly related to the rate of peat accumulation and basin subsidence. TPI reflects the degree of humification of the peat-forming materials [44].

Petrographic and geochemical data of gelified and ungelified fossil wood provide evidence that gelification (vitrinitisation), which occurs during the early sub-bitumenous stage, may be governed by microorganisms different from those responsible for decreasing cellulose contents during early diagenetic, aerobic degradation of wood. Generally increasing degree of gelification from the bottom to the top of the lignite seam has been confirmed. It suggests that gelification of plant tissue may be governed by the activity of anaerobic rather than aerobic bacteria [7, 8].

Stefanova et al. [67] reported an organic geochemistry study to establish molecular indicators for the coal-forming paleplant community. Aliphatic fractions isolated from composite bulk coal and analysed by GC and GC-MS show the presence of terrestrial triterpenoids, i.e. defunctionalised, unsaturated and monoaromatic oleanane / ursane. The results imply that dicotyledonous Angiospermae may have had a significant role in studied lignite formation.

Phenolic structures of humic acids may have occurred from lignin in the lignocellulosic materials. Humic acids entering the plants at early stages of development are supplementary sources of polyphenols, which act as respiratory catalysts. Wide range of phenolic substances (including 2, 4-dimethyl phenol, 2-hydroxy benzamide, dimethyl phenol, 4-hydroxy benzaldehyde, α-naphtol, β-naphtol, α-cresol etc.), has been determined in isolated humic acids derivates obtained from the lignite samples by GC-MS. The results confirmed the presence of plant materials in lignite forming process [19].

4 Inorganic matter of lignite

Coal contains various inorganic minerals in addition to the major organic components. Inorganic matter exists in two forms. One is the inherent mineral matter within the coal particles, and the other is adventitious inorganic material remaining external to the coal particles [15]. Minerals in coal vary widely. The approximate order of the amounts present is: the shale group species (comprised of muscovite, illite and montmorillonite) which are principally Na, K, Ca, Al, Mg and Fe silicates; the kaolin group (kaolinite-aluminum silicate) which is most abundant mineral in all the seams. The main clay minerals identified were illite, montmorillonite and illite-montmorillonite [68].

The major mineral phases present in Portuguese lignites are quartz and clay minerals. Quartz is clearly the most abundant mineral in all the seams. The main clay minerals identified were kaolinite, followed by illite, montmorillonite and illite-montmorillonite [68].
5 Lignite organic compounds and extracts

When coal is exposed to water, mostly some organic and inorganic matters in coal may be leached out in wastewater. The degree of total organic carbon in eluents greatly varied with kind of coals and it tended to increase as the O/C value of coal increased. It is also influenced by specific surface areas, what was confirmed by use of heat-treated coals. Extracts gained from hot water extraction of lignite did not show any notable mutagen behaviour, however they were found to give high affinities comparable to typical endocrine-disrupting chemicals [51].

The study of organic matter in coal often requires its isolation. The most common method of organic matter isolation is to dissolve the mineral fraction of the rock by attack with HCl used in combination with HF. This approach results in the highest purity organic concentrates but induces at least some degree of alteration in the organic matter. Robl and Davis [59] compared the HF-HCl and HF-BF₃ maceration techniques. Results indicate that the sample processed with the HF-BF₃ technique does not appear to be altered more than that processed with the more traditional HF-HCl method. The F and Cl data also suggest that the HF-BF₃ procedure actually results in less organic matter alteration.

Alkaline hydrolysates from lignite humic acids markedly differ. Bound lipids from lignite humic acids comprised almost exclusively aliphatic components, largely dominated by long chain alkanoic acids. Lignin-derived fractions consisted predominantly of vanillic and 4-hydroxybenzoic acids indicating a much higher degree of lignin alteration in lignite. Sterols and triterpenols were absent. The high values of the (galactose + mannose) ratios in lignite indicate that carbohydrates are primarily of microbial origin. The absence of hydroxyl proline and the greater abundance of ornithine suggest a higher microbial contribution to the amino acids as the degree of humification increases. The higher contribution of polar amino acids suggests a preferential preservation of these amino acids possibly by interaction with the humic acids surface through hydrogen bonds [1].

Separation methods such as chromatographic methods, techniques based on a size-exclusion effect, GC-MS and electrophoretic methods are widely used to isolate humic substances, to fractionate them before further investigation and to obtain information about their structure and properties. They allow the determination of binding constants and other data necessary to predict the mobility of chemical pollutants in the environment [27]. Novák et al. [53] prepared humic acids from Bohemian lignite using alkaline extraction, sedimentation/filtration and acidic precipitation. Membrane separation was applied to refine some preparatives. They compared the properties of the lignite-derived humic acids with the properties of humic acids prepared from chernozem, peat and commercially available humic acids.

6 Important analytical requirements concerning coal and lignite

Being a complex macromolecular system lignite transformed from the parent plant matter into a material having a specific chemical character, which determines some particular lignite properties: typical void volume (capillars and cracks) and multiple surface with defects containing paramagnetic radicals, free binding sites, ionisable groups [45].

In general coals are analyzed in two main ways: the ultimate analysis determines the total percentages of the elements present (carbon, hydrogen, oxygen, sulphur and nitrogen) and the proximate analysis gives an empirical estimate of the amount of moisture, ash, volatile materials and fixed carbon [57]. Table 2 contains some important analytical data of chosen lignite deposits.

As humic substances are involved in coal formation, information on coal precursors and their transformation during maturation can be gained by their study. The total acidity and carboxyl groups, methoxyl groups, carbonyl groups and quinones are the main oxygen functional groups often determined in lignite humic acids. The diagenetic transformation of oxygen to COOH groups from the parent material follows. It is apparent that in the coalification process, as far as humic substances are involved, COOH groups disappear first, followed by methoxy and carbonyl groups. With increasing rank of the parent material, the content of oxygen as COOH decreases and that as OH increases [66]. The comparison of peat and lignite analysis reveals a degradation of methoxy groups, carbohydrates and carboxylic groups during early coalification, whereas the aliphatic carbons were less affected [31].

Combustion techniques are commonly used in the analysis of coal and lignite in general for the determination of elemental hydrogen, carbon and nitrogen. Unfortunately, pyrolysis does not provide information about the chemical speciation of oxygen in coal. Solomon et al. [64] developed new method for this investigation of coal samples thermogravimetry-Fourier transformed infrared (TG-FTIR). The contributions from H₂O, CO and CO₂ to organic oxygen in American and Canadian lignites show monotonic increase with decreasing carbon content. MacPhee et al. [41] determined the concentration of phenolic and carboxyl functional groups in lignite by methods using very specific reagent n-Bu₄NBH₃ and less specific LiBH₃ in pyridine. Fei et al. [22] studied the total acid
group concentrations and the carboxylic acid content in lignite by pyrolysis and compared them by barium ion-exchange method. Both techniques were for total acid group content in good agreement, only carboxylic acid group concentrations were determined lower by pyrolysis.

Sulphur is ubiquitously present in fossil fuels in a variety of chemical forms. In the same time its amounts vary from traces to more than 10%. A fuller understanding of structures of sulphur-containing compounds present in fossil fuels, their thermal stability and reactivity is important for improving the available processes for removing sulphur or for devising new schemes. Often a combination of several methods is used to determine organic sulphur in coal, including ASTM standard test method D2492, analytical pyrolysis (Py-GC-MS) and scanning electron microscope (SEM) coupled to an energy-dispersive X-ray spectrometer (EDX). Two major non-destructive techniques, X-ray absorption near-edge spectroscopy (XANES) and X-ray photoelectron spectroscopy (XPS), are used to investigate sulphur functionalities, such as pyritic, sulfdic, thiophenic, sulfoxide, sulfone, sulfonate and sulphate forms. Olivella’s study shows that sulphur characterization in coals is not without difficulties and no method is exempt from problems and the introduction of possible artefacts [54].

7 Elements and chemical groups in lignite

Almost all naturally occurring elements, including major elements (C, H, O, N, S, Na, K, Ca, Mg, P, Si, Al, Fe, Ti) and 74 trace elements, have been reported to be present in different coal types using a number of modern analytical techniques [26]. Organogenic elements (H, C, S, N and O) are represented in both organic and mineral matter of coal. The rest of above mentioned elements are typical macrocomponents, whose concentrations generally exceed 1 wt. % in the ash. Nasu et al. [52] reported that the affinity of these elements for inorganic matter decreased in the order: Si>P>Mn>Fe>Ca>Mg>Na>Ti>Al>(S, K). They also presented a new way of determining the proportion of a given element bound to organic or mineral matter.

The distribution of trace elements in coals used for electricity generation is of increasing importance in the assessment of environmental impacts caused by coal-fired power plants. Karayigit et al. [34] studied trace elements in Turkish lignite and found that this lignite is enriched in Zn, Mo and U, in comparison with most coals in the world. Trace elements occur in coal in concentrations of less than 0.1 wt. % (some studies suggest 0.02 wt. % or 0.01 wt. %) and can be analyzed on natural or ashed coal sample. These elements (As, B, Be, Cd, Cl, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Se, U, V, Zn) are associated either with organic (phenolic, carboxylic, amide and sulf-hydroxyl functional groups) or with inorganic material (sulfides, clays, accessory minerals), or they can be affiliated with both fractions of coal. Physico-chemical conditions in the swamp partly control the distribution of certain elements in coal, some of them may be mobilized from the clays and precipitated as authigenic nonsilicate minerals [70].

Sulphur in lignites occurs in inorganic as well as in organic forms. The inorganic sulphur may be present in the form of pyrite, marcasite and other sulfides in very small quantities or as sulphate sulphur, mainly as gypsum but sometimes also as ferrous sulphate. The organic sulphur exists either in aromatic rings or in aliphatic functional groups, usually categorized as mercaptans, aliphatic and aryl sulfides, disulfides and thiophenes. Active sulphur produced primarily from the decomposition of pyrite, sulfates and gaseous sulphurous compounds in lignite may combine with the organic matrix to form new organic sulphur compounds. It has been determined that HCl treatment removes primarily sulphate sulphur from lignites [72]. The morphological structure and pore distribution of coal is pronouncedly affected by sulphur rings or sulphur bonds in coal matrix, depending on the increase of the pyrolysis temperatures. The breaking of these bonds or the removal of rings from coal matrix can modify the surface characteristics of coal. It has been reported that the rise of organic sulphur content of lignite samples at 450 and 500 °C is parallel to the increase in the monolayer capacities [33].

Both heating rate and pressure affect swelling characteristics during lignite pyrolysis. At low heating rates (1 K/s) volatiles can diffuse through the pores without causing an internal pressure high enough to cause the particle to swell. At moderate heating rates (10³ K/s), the volatiles formed in the particle interior are formed faster than they can escape through the pores and swelling occurs if the particle has softened. At high heating rates (10⁵ K/s), the volatiles are formed faster than the swelling process can accommodate and the bubbles burst [78].

8 Differences in humic acids of various origin

Organic matter of peats, leonardites and lignites containing a high amount of humic substances has been characterized using electroscopic techniques, such as laser fluorescence, ¹³C-NMR, ²H-NMR, FT-IR, surface enhanced Raman spectroscopy, etc. The degree of humification (DH), humification rate (HR) and humification index (HI) belongs to the main humification parameters used to evaluate the humification level in organic materials and fer-
tis. Cavani et al. [11] found that only partial characterization of peat, Leonardite and lignite is possible with above mentioned parameters. With HR is possible to distinguish Leonardite from peat and lignite, but not peat from lignite; with DH and HI it is possible to distinguish peat from Leonardite and lignite, but not Leonardite from lignite.

Humic acids extracted from lignite have some characteristics that are comparable to humic acids in soil organic matter and peats including the presence of polyphenolic cores, phenolic, hydroxyl and carboxyl groups with pH dependent dissociation [75].

Novel understanding of the nature of humic substances indicates that, rather than being high-molecular weight polymers, they are associations of small heterogeneous molecules held together by relatively weak forces in contiguous hydrophilic and hydrophobic domains of apparently high molecular sizes. It has been revealed that humic acids isolated from lignite have higher hydrophobicity than humic acids from compost [65]. It is reported that soil humic substances are more aromatic in character and more hydrophobic than humic substances originated from the marine environment [56]. Humic acids of different origin differ in their chemical properties. This influences the stability of the metallo-humic complexes as well as the transport mechanisms of the concerning metals [63].

The present practice to characterize humic substances is to use chemical parameters describing the quality of organic carbon, humification parameters and relationship between atomic ratios. The need to obtain structural details during the diagension of natural organic carbon or the structural changes in humification led to the use of some additional analytical techniques. The quantitative distribution of the hydrogen atoms obtained using the NMR technique may complement the qualitative information about the structural units. Differential thermal analysis has been proposed as a method to characterize the genesis of coal and humic substances from different environments [24].

Lignite humic acids (LHAs) differ from that of soil humic acids (SHAs) in being highly condensed and possessing fewer side chains and functional groups [6]. The elemental composition of the LHAs substantially differs from the forest and agriculture SHAs, too. The greatest observable differences between SHAs and LHAs are the decrease in O and N contents, which is consistent with the higher degree of maturity of LHAs and the increase in S, P and ash contents from SHAs to LHAs. The H/C atomic ratio in LHAs is generally smaller than one, although some H/C atomic ratio values > 1 have been reported as well. The high value of H/C atomic ratio in LHAs suggests that they are of low degree of maturity [1]. The origin of the humic acid influences its C/N ratio. Lower ratios usually indicate the presence of not decomposed organic matter [62]. C/N atomic ratio for LHAs is significantly higher than those observed for the SHAs and indicates a relatively high stage of coalification [60].

The differences between the composition of LHAs and oxidized bituminous coal are mainly in much higher values of O, H, dissociation constants and some metal binding capacities and lower values of C and aromaticity index in LHAs and/or oxidized lignite samples [37].

9 Lignite and microorganisms

It is generally accepted that microorganisms have played a prominent role in the process of coal formation. Coal, as a product of plant fossilization, still preserves some molecules derived from lignin, which could be susceptible to degradation by extracellular fungal enzymes. Also biological solubilization of coal has become a subject of increasing interest because it could occur at ambient temperatures and pressures. Nowadays, it is accepted that at least three mechanisms are possible for biosolubilization of low rank coal such as lignite: enzymatic attack, basic metabolites and microbial chelators. Liquefaction of higher rank coal as bituminous and subbituminous coal has been rarely achieved [32, 38]. In some humates or in several materials containing humic acids large populations of Actinomyces microorganisms, that share the properties of both fungi and bacteria, are present. They are capable to degrade a wide range of substances including cellulose, hemicellulose, proteins and lignin by enzymes carried on the lignin degradation (ligninase, Mn-peroxidase and laccase) [18].

In many mine soils, lignite carbon is present as a potential carbon source for microorganisms. It was shown in laboratory studies that lignite (Lusatia, Germany) can be degraded by microorganisms, because lignite carbon was a part of the humic acids fraction. The peroxidase system responsible for lignite biodegradation was found to be produced by soil-inhabiting basidiomycetes. Carbon derived from lignite and recent organic matter can be quantitatively estimated by $^{14}$C analyses. A decrease of microbial activity with increasing age of mine soils was also observed and explained by the accumulation of compounds, which are stabilised against decomposition [60].

Microorganisms were also isolated from lignite freshly excavated in coal mine (Záhorie, Slovakia) under conditions excluding contamination with either soil or air-borne microorganisms. The isolates represented both Prokaryota and Eukarya (fungi). Bacteria belonged to the genera Bacillus, Staphylococcus and Rhodococcus. The presence of anaerobic bacteria was also documented, although they have not yet been identified. Fungal isolates belonged to the
genera *Trichoderma* (*Hypocrea*), *Penicillium*, *Epicroccum*, *Matarrizium* (*Cordyceps*) and *Cladosporium*. Results demonstrated that microorganisms were able to survive in the low-rank coal over a long period of time [58].

A microbial study of Spanish coals has confirmed presence of 150 different bacteria and fungal strains, which were isolated in pure culture. *Penicillium sp.* has been largely isolated microorganisms strain with liquefaction and/or solubilization effect on lignite from Galicia. When lignite was pretreated with nitric acid or chelating agents, a more intensive and rapid liquefaction was achieved [48].

Rumpel and Kögel-Knabner [61] examined the importance of two organic matter types as substrates for soil microbial biomass in mine soils containing organic matter with a contrasting degree of humification. Their results indicated mineralization and humification of lignite under laboratory as well as field conditions and suggesting that lignite carbon is an active compartment in the carbon cycle of studied soils.

10 Treatment and utilization of lignite and lignite ash

Energetic utilization and related problems

Brown coal is one of the abundant natural resources in some countries, but its effective utilization except fuel for power generation actually has not been developed yet [50]. In recent time an overall increase in gas fired electricity generation and a corresponding reduction of coal and lignite fired electricity generation on a trans-national level has been noticed. This is a result of the CO$_2$ tax, which mainly caused a shift towards fuels with lower carbon content. According new model study in some zones (The Netherlands, Belgium/Luxemburg, Italy) the emissions will rise whereas in others (Germany, France and Spain) they will decrease [74].

Gas exhalation

Direct combustion of coal with high sulphur content, especially lignites, produces flue gases containing large amounts of SO$_2$, which is one of the major atmosphere pollutants. Harmful SO$_2$ emissions can be controlled by taking precautions such as coal desulphurization (physical, chemical and biological methods), oxydesulphurization (both pyretic and organic sulphur can be eliminated), sorbent injection into combustion systems (limestone, dolomite, soda ash, trona, fly ash, activated carbon etc.) and removal of SO$_2$ from flue gases (during combustion or from flue gases after combustion). Demirbas investigated the usage of aqueous alkaline solution derived from wood ash for desulphurization of lignite. By this process high sulphur removal from lignite was possible [17].

Removal of impurities from low-rank coals by physical cleaning is necessary prior to combustion of the coal. Conventional physical cleaning of lignite can only remove a portion of the pyritic sulphur but cannot reduce the organic sulphur. Although chemical, bacterial and postcombustion gas scrubbing are capable desulphurization techniques, they are relatively expensive or not amenable to the utilization of volatiles in subsequent processes. A processing route involving low temperature carbonization followed by dry magnetic separation is put forward for the desulphurization and deashing of lignite. Under optimum conditions, a remarkable decrease in both ash and more importantly in total and particularly organic sulphur was achieved. A systematic study of the mechanism of the sulphur removal reveals the formation of iron-sulphur coordination compounds in coal [12].

The sulphur compounds in coal are during desulphurization decomposed, reduced and hydrocracked. Most sulphur goes into the gas phase in the form of H$_2$S, which is easily recovered as sulphur. Chen et al. [14] studied the transformation of sulphur during pyrolysis under nitrogen and hydropyrolysis of Chinese lignite. The main volatile sulphur-containing gas was H$_2$S in both methods. Elemental analysis and XPS results indicate that more sulphur was removed in hydropyrolysis than in pyrolysis under nitrogen. Thiophenic sulphur is thermally stable up to 650 °C and can be partially hydrogenated and removed in hydropyrolysis. Pyrite can be reduced to a ferrous sulphide completely even as low as 400 °C in hydropyrolysis, while in pyrolysis the reduction reaction continues up to 650 °C.

Several authors have studied coal desulphurization using oxidative treatments. Alvares et al. [2] reported that the nitric acid cause effective nitration of the Spanish coal, the nitrogen being incorporated especially as aromatic nitrogen. The substitution is easily produced (50 °C), when there are two adjacent aromatic hydrogens per ring. Nitration increases with an increase in temperature, in acid concentration and length of time. Nitric acid acts as an oxidant, producing a significant increase in carbonyl groups. They are more and more located within increasingly electrophilic molecules. Nitric acid also causes organic matter solubilization and rapid sulphate and pyritic sulphur reduction in range of 92 – 93%.

The sulphur content is a decisive evaluation parameter of coal quality for its next utilization. It becomes quite obvious that it is always preferable to keep the sulphur levels in coal at a minimum. Bacterial oxidation of the sulphur present in coal by *Thiobacillus ferroxidans*, *Thiobacillus thioxidans*, *Thiobacillus acidophilus*, *Thiobacillus thioparus* could well be thought of as an effective alternative of biological desulphurization. This
environmental friendly treatment of coal is considerable long-lasting process, what increases its economic costs. Biological lixiviation has caused relatively significant change in FeS$_2$, in some cases full or part elimination of dispersed framboids at mineralised detrite as well as at huminite macerals resulting in empty holes and FeS$_2$ grains were slightly disintegrated at the surface or dike-pyrite was released irregularly after lixiviation [40].

**Lignite radioactivity**

The lignite combustion results in the release of a considerable amount of naturally occurring radionuclides into the atmosphere. Aycık and Ercan [3] concentrated mainly to measure the level of natural radioactivity in the environment due to the operation of coal fired power plants and to search for the related external radiation doses to the population. They found out that the external gamma radiation exposure to the public from these power plants is small, as compared with the variation of radiation exposure from natural sources.

**Fly ash**

Approximately 100 million tons of lignite fly ash is produced annually worldwide after combustion of lignite, in the respective power station, as a waste product. Fly ash particles are considerable to be highly contaminated since their high surface area leads to enrichment in potentially toxic trace elements, which condense during the cooling of the combustion gases. Moutsatsou et al. [49] deal with the hydrothermal treatment of two Greek lignite fly ashes in order to examine their ability of giving rise to zeolitic product. Classic alkaline conversation of fly ash is based on the combination of different activation solution/fly ash, with temperature (80 – 200 °C), pressure (atmospheric and water vapor) and reaction time (3-96 h) to obtain different zeolite types. The synthesis of zeolite products from fly ash is analogous to the formation of natural zeolites from volcanic deposits or other high Si, Al- materials. Chareonpanich et al. [13] used lignite ash from Thailand and rice husk ash as raw materials with addition of sodium silicate solution for ZSM-5 zeolite synthesis. They reported that the yield for synthetic zeolite was as high as 59 wt. % by following conditions: SiO$_2$/Al$_2$O$_3$ mole ratio 40, the holding temperature 210 °C, the holding time 4 h and the initial pressure 400 kPa. The catalytic performance for CO$_2$ hydrogenation reaction of studied zeolite was preliminary tested and compared with the commercial one. It was observed that there was no significant difference.

**Sorption agent**

**CO2 & VOCs**

The adsorption capacity of Malaysian lignite, studied by Azmi et al. [4], shows an inverse relationship with temperature. These findings open an interesting platform for CO$_2$ sequestration to be implemented in Malaysia. It was observed that the untreated lignite sample exhibited the highest CO$_2$ gas adsorption as compared to the three treatment coal samples that had undergone pre-treatment in acidic (pH 1), alkaline (pH 12) and near neutral (pH 6) condition. Among the three treatments, acidic one was found to have the higher CO$_2$ gas adsorption rate. For the particle size variation, it was found that the CO$_2$ gas adsorption rate was the highest for smaller coal particles (1000 μm) as compared to larger particles (2000 μm). This is due to the larger surface area of the smaller particles.

Man many materials like granulated active carbons and active carbon fibers are nowadays studied with the aim to reduce pollutant emissions from gaseous or aqueous media. Burg et al. [9] investigated the usage of other low-cost adsorbent for this purpose. Lignite as a raw and cheap material was treated by an inexpensive reagent urea, before the activation step. The aim of the chemical treatment was to introduce nitrogenated surface functional groups able to give to the final active carbon a selective character, different from the selectivity of the parent activated coal, towards pollutants such as volatile organic compounds. Nitrogen groups are interesting for their thermal stability. The lignite selectivity is modified while keeping the ability to adsorb large quantities of pollutants. Activated lignites show high selectivity for pair of two VOCs namely methanol and dichloromethane.

**Metallic ions**

The special merit of brown coal is that this material contains many oxygen-containing functional groups. Among these groups, carboxyl groups are considered to play the most important role in cation exchange. Cation exchange characteristics of brown coal show promising potentiality for selective removal of heavy metallic ions from industrial wastes or for treatment of radioactive wastes. Brown coal is inexpensive and its treatment after adsorption is considered to be easily realisable. The adsorption process on brown coal (Victoria, Australia) exhibited Langmuir behaviour, the temperature at exchange reaction had a marginal influence on the adsorbed amounts of metallic ions, which increased by addition of organic solvent [50]. Recovery of heavy metals present in wastewaters in relatively low concentration (< 10 mmol dm$^{-3}$) is rather difficult. The common methods (conventional ion-exchange, electrolytic or liquid extraction, electrodialysis, precipitation, reverse osmosis) are in this case either economically unfavourable or technically complicated. Usage of lignite adsorbents for removal of heavy and toxic metals from water has following advantages: the coal is not sensitive to organic impurities, no regeneration is required and the sorbent is highly selective for heavy metals. Adsorption properties of lignite can be markedly improved by chemically fixed calcium. Such modified raw material shows high removal effectiveness of pollutants especially for their low concentrations in wastewater. The
sorption is relatively slow and the recommended optimal flow rate is rather low. The selectivity of the sorbent decreases in the sequence: \( \text{Pb} > \text{Cr}^{3+} > \text{Fe}^{2+} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Co} \geq \text{Ni} \) [29].

It is interesting to compare the sorption rate of metal cations with solid humic acids in batch experiments. The examined cations can be arranged in the following order \( \text{Pb} > \text{Cu} > \text{Cd} > \text{Ba} > \text{Ni} \sim \text{Zn} \sim \text{Co} \sim \text{Mn} > \text{Mg} > \text{Ca} \). The order of the metal-humate binding strength is based on the stability constants of metal-humate complexes. The sorption of metals on the surface of humic acids depends strongly on the pH, sorption decreases with decreasing pH value [16]. Further column experiments confirmed the real possibility of the practical application of humic acids for the separation of heavy metals from waste water. The sorption efficiency of tested metals is also dependent on the composition of the solution. It is important that already sorbed metals are not washed out by demineralised water and remain sorbed [42]. The sequential extraction test (BCR procedure) was used to assess a leachability of heavy metals (\( \text{Zn}, \text{Cd}, \text{Pb}, \text{Cu} \)) from the metallo-organic sorbent-iron humate-loaded with these metals. It was proven that the heavy metals are bound mainly to Fe oxides and organic matter and thus they may be relatively hardly liberated into the environment. The iron-humate sorbent is suitable for removing of \( \text{Zn}^{2+}, \text{Pb}^{2+} \) and \( \text{Cu}^{2+} \) ions from waters, while the sorbent is less suitable for removing of cadmium [28].

**Catalytic activity & Chemical modification**

Bai et al. [5] reported that using of low-cost lignite char as a catalyst is a promising method for hydrogen production by methane decomposition both economically and environmentally. Hydrogen has been considered as the ideal energy source for the future because of the uncontaminated combustion product. Methane is preferred source of hydrogen, but non-catalytic methane decomposition requires high temperatures (1200–1700 °C). Lignite catalyst shows several advantages over metal catalyst, such as low cost, easy availability and no requirement of regeneration of catalyst etc. Also, the lignite, which is more volatile, forms more pores of suitable geometry during devolatilization than bituminous coal and anthracite, which is favourable for the methane adsorption. It should be pointed out that the surface area and the catalytic activity of chars obtained at experimentally tested temperatures is not linearly proportional.

Erçin et al. [21] treated Turkish lignite with I2 and studied its effect on lignite structure. They found that I2 attachment to the lignite structure obeyed Langmuir-type of adsorption model. I2 treatment also created charge transfer complexes. Increase in the free radical concentrations of the I2-treated lignite was due to the formation of charge transfer complexes between I2 and aromatic systems in the coal by single electron extraction from the donor to the I2. FTIR spectra of I2-treated coals towards lower wavelengths also indicated the creation of charge transfer complexes in the lignite after I2 treatment where the I2 acted as the electron acceptor.

**Humic substances**

Lignite is commonly used as an organic amendment in soil restoration, too. Experiments suggest that prior dispersion may enhance the stabilising effect on soil structure. Application in aqueous ammonium might be a suitable mean of adding a humic acid fraction to artificial top soils. Increasing stability was only observed for materials already containing a clay mineral fraction [75]. Martinez et al. [43] have prepared calcium humate phosphates by direct interaction of humic acids from Spanish lignite, calcium ions and phosphate at pH 5 and 7. The study of phosphorous availability indicated that in these complexes, it is in available form. In acid soils the ions \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) from colloidal oxides and hydroxides react with soluble phosphates forming \( \text{FePO}_4 \) and \( \text{AlPO}_4 \), insoluble in acid medium. In alkaline soils, soluble phosphates react with calcium hydroxide and calcium carbonate forming dicalcium or tricalcium phosphate that is transformed to hydroxylapatite, insoluble in alkaline pH. Low-rank coals are usually used for the production of humic acids, which are in the form of alkali-soluble humate salts. Nitrogen-rich coal humic acids are valuable fertilizers acting as growth stimulators. The improve plant resistance under unfavourable conditions, accelerate ripening and influence favourably biochemical processes during plant growth [77].

The absorption of humic substances requires a material with a well-developed mesoporous texture due to large sizes of their molecules. Lorenc-Grabowska and Gryglewicz [39] describe the adsorption of different lignite-derived humic acids on a bituminous coal-based mesoporous activated carbon. Humic acids derived from Polish lignite show a similar affinity toward the surface of demineralised and non-demineralized carbons. From both carbons the Freundlich capacity decreases with an increase in the carbon content of humic acids. For the pH range of 5.4-12.2 with lowering pH, a decrease in the amount of adsorbed humic acids was observed.

11 **Acknowledgement**

We gratefully acknowledge the support provided by Slovak Research and Development Agency within the frame of the Czech-Slovak intergovernmental R&D project No. SK-CZ-12206.
Table 2: Review of chosen lignite deposits in the world and lignite characteristics

<table>
<thead>
<tr>
<th>Country</th>
<th>Deposit / Type</th>
<th>H_{2}O %</th>
<th>Ash %</th>
<th>C wt.%</th>
<th>H wt.%</th>
<th>N wt.%</th>
<th>O wt.%</th>
<th>S wt.%</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>Victoria Light type1</td>
<td>0.6</td>
<td>72.7</td>
<td>5.9</td>
<td>0.5</td>
<td>20.7</td>
<td>0.2</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>Victoria lignite Loy Yang</td>
<td>0.6</td>
<td>69.57</td>
<td>5.0</td>
<td>0.6</td>
<td>26.2</td>
<td></td>
<td></td>
<td>[22, 51]</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>Chokarovo</td>
<td>8.8</td>
<td>20.5</td>
<td>67.9</td>
<td>5.6</td>
<td>1.2</td>
<td>24.9</td>
<td>0.4</td>
<td>[67]</td>
</tr>
<tr>
<td>Canada</td>
<td>Sofia</td>
<td>7.2</td>
<td>24.6</td>
<td>67.1</td>
<td>5.8</td>
<td>1.3</td>
<td>22.1</td>
<td>3.7</td>
<td>[73]</td>
</tr>
<tr>
<td>Czech rep.</td>
<td>Jíří mine</td>
<td>37.4</td>
<td>18.8</td>
<td>72.9</td>
<td>5.82</td>
<td></td>
<td></td>
<td>2.13</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Mr. Mihulčice</td>
<td>7.13</td>
<td>28.87</td>
<td>42.27</td>
<td>43.69</td>
<td>0.64</td>
<td>12.86</td>
<td>0.54</td>
<td>[17]</td>
</tr>
<tr>
<td>Germany</td>
<td>typical lignite</td>
<td></td>
<td></td>
<td>57.3</td>
<td>5.5</td>
<td></td>
<td></td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>Greece</td>
<td>Drama 1</td>
<td></td>
<td></td>
<td>56.7</td>
<td>4.2</td>
<td>2.4</td>
<td>33.0</td>
<td>3.7</td>
<td>[41]</td>
</tr>
<tr>
<td>Malaysia</td>
<td>Mirti mine</td>
<td>13.01</td>
<td>55.62</td>
<td>5.3</td>
<td>1.92</td>
<td>24.1</td>
<td>0.65</td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>Spain</td>
<td>Moquemenca</td>
<td></td>
<td></td>
<td>66.4</td>
<td>5.8</td>
<td>1.6</td>
<td></td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>Portugal</td>
<td>Rio Minor Basin</td>
<td></td>
<td></td>
<td>61.27</td>
<td>4.95</td>
<td>0.85</td>
<td>30.86</td>
<td>2.73</td>
<td>[68]</td>
</tr>
<tr>
<td>Turkey</td>
<td>Elbjistan</td>
<td>14.28</td>
<td>41.55</td>
<td>66.0</td>
<td>4.9</td>
<td>1.6</td>
<td>25.5</td>
<td>2.0</td>
<td>[77]</td>
</tr>
<tr>
<td>USA</td>
<td>Knife River</td>
<td></td>
<td></td>
<td>62.23</td>
<td>4.23</td>
<td>0.95</td>
<td>31.3</td>
<td>1.28</td>
<td>[78]</td>
</tr>
</tbody>
</table>

daf – dry ash free (if not noticed, db is valid), daf – dry basis, diff. – by difference

References


