

PROGRESSIVE AND EFFICIENT NON-ENERGY APPLICATIONS OF LIGNITE

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ABSTRACT

Project was aimed at research of non-fuel uses of lignite from the South Moravia Coalfield as a valuable chemical raw material with minimum additional costs in following areas: sorbent technologies, composites lignite-biopolymers, lignite-polymers, radical and photochemical processes on lignite, cost-effective isolation of humic acids. Results proved universal sorption properties of untreated lignite, its high affinity to both inorganic and organic substances. Lignite works as a buffer forcing final pH value to about 5-6. Organic lignite components are leached in negligible amounts, inorganic elements on acceptable level. Results confirm potential of natural lignite for applications in a variety of soil treatment and environment care technologies. Both physical and chemical polyvinylalcohols hydrogels were filled with lignite. Combining lignite and starch granules were formed and their disintegration rate in aqueous environment easily controlled. All prepared lignite-polymer and lignite-biopolymer composites, granules and humic products due to its properties established can be used in sorbent technologies, soil protection and remediation, agriculture.

KEYWORDS: lignite, humic acids, sorbents, composites, South Moravian Coalfield

1. INTRODUCTION

Lignite from the South Moravian Coalfield represents after international classification ECE-UN (1998) ortho-lignite which was named as a soft brown coal in previous classification. It is used also in the South Moravia as a fuel for decades. Simple burning of this raw material is highly inefficient use of valuable matter. Lignite can be used as a versatile and interesting substance in several application fields due to its specific properties and composition. Project was aimed at non-fuel and cost-effective uses of lignite mined in Mikulčice locality in the South Moravia Coalfield in following areas: sorbent technologies, composites lignite-biopolymers, radical and photochemical processes in the presence of lignite, cost-effective isolation of humic acids.

2. RESULTS OF THE PROJECT

1. Sorption properties of metal ions (Pb^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+}) were studied onto lignite and solid humic substances (humins and humic acid) derived

from it by alkali extraction using two procedures (Havelcová et al., 2006; Sýkorová et al., 2007). It was obvious that the two extraction procedures yielded materials with significantly different properties, particularly in their minerals content reflected on both ash content and elemental composition (namely Si, Al, and Fe). The critical point in the separation procedures with greatest impacts on the sorbent composition and properties was clarified. At the standard procedure, NaOH concentration is sufficient for leaching of humic acids and for suppressing of aluminosilicates. On the other hand, the ten times lower alkali concentration at the economical procedure allows dissolution of silicates, aluminates and iron hydrocomplexes. Aluminium and iron are subsequently co-precipitated with silica and humic acids at the acidification step. The efficiency of these sorbents was studied as a function of contact time, solution pH, and metal concentration. The sorption efficiency was higher for humins and lower for humic acids samples than

for the original lignite. The raw lignite demonstrated a good sorption ability promising its highly economical utilization without further chemical treatment. Its sorption capacity, particularly for the toxic metals lead and cadmium, has indicated a high suitability of the South Moravian lignite as an inexpensive and effective material for the removal of heavy metals from wastewaters (Pekař and Klučáková, 2005; Havelcová et al., 2009).

Pure low ash humic acids were isolated from lignite in high yield and in one step only by extraction with organic nitrogen bases. Alkaline leaching must be followed by purifying operations but very high yield can be achieved by repeated extraction. Liquid to pasteous humic products for agriculture application were prepared by mechanical peptization of lignite.

2. The binding of other inorganic and organic compounds to lignite which can be interesting for treatment of waste water from surface finishing technologies were investigated. Results proved universal sorption properties of untreated, natural lignite, its high affinity for fluoride anions (Pekař, 2006) and organic substances particularly phenol, surfactants and dyes (Cechlová et al., 2006). Lignite sorption properties can be further improved by microwave assisted thermal treatment (Pekař et al., 2006).
3. Possible lignite use in soil or natural environment in general involves knowledge on leaching lignite in water or aqueous solutions including lignite effects on pH. Leaching tests in aqueous solutions were made on fresh grinded samples. It was determined that in aqueous environment, lignite works as a buffer forcing final pH value to about 5-6. Leaching experiments showed that although lignite contains a variety of both organic and inorganic components their penetration into aqueous environment is negligible or low. Application of lignite in natural environment should not be risky (Bušinová and Pekař, 2006, 2007; Pekař et al., 2006).
4. Lignite can serve as a soil conditioner and plant nutrition support mainly because of its high contents of humic substances, especially humic acids. We demonstrated that lignite humic acids are comparable to humic acids isolated from different types of soils. Lignite cannot be considered as a true fertilizer but it may serve as a source of organic carbon and positively influence not only the transport of plant nutrients but also the transport of risky elements by immobilizing them in humic (or organic) complexes. Types of lignite activity were demonstrated in pot tests made on carrots, maize and vetch. Control test was realized with a standard NPK dosage, lignite

was supplied by molasses and also by NPK to achieve the same level of basic nutrients (nitrogen, phosphorus and potassium) as in the control. Pot tests demonstrated some positive influence of lignite on yield of various plants when applied with appropriate amount of inorganic fertilizer. The results indicate that lignite really contributes to controlled transport of plant nutrients probably by forming organo-mineral complexes slowly releasing the nutrients in response to their depletion from the soil solution. In most cases lignite also hampered penetration of heavy metals into plants. Metals are immobilized by relatively tight binding to lignite organic matter, especially due to complexation with humic acids.

Positive influence of lignite on maize production is evident and statistically significant even in the soil of good quality. To achieve the same yield part of NPK fertilizer can be substituted by cheaper lignite (Pekař et al., 2006).

5. Filling of polymers with solid particles is a well known method to control their properties and performance. Lignite could be used in polymers for two reasons. First, it may serve as a regulator of polymer stability, *i.e.* to control polymer lifetime. Second, lignite may be conducive to the very function of a polymer product. For example, lignite may be a part of mulching foil where it can absorb heat and water and serve also as a soil amendment.

This research was initiated by testing lignite compounding with commercial large scale polymers – polypropylene (PP), polyethylene (PE) and polyvinylchloride (PVC). Lignite was mixed with these polymers in standard laboratory extruders and molten state of polymer at 160 °C in the case of PVC or 200 °C in the case of PE and PP. Lignite filled polymers were subjected to basic tests of mechanical properties and stability analysis by thermogravimetry. Incorporation of higher amounts of lignite into polymer matrix led to tough and more brittle materials. Consequently, when mechanical properties of resulting material should not be too different from the native polymer, lignite filling should be only moderate – at several percents. Regarding polyolefin, lignite-polyolefin composites are more resistant to thermooxidative degradation than native polyolefins, esp. when the lignite contents are above 2 %. The highest protective effect was observed for commercial polymer LDPE type Bralen VA 20-60 (Slovnaft Bratislava), lowest for HDPE type MB62 (Chemopetrol Litvínov) (Bakajová, 2007; Klimovič et al., 2007; Kučerík et al., 2008).

6. Addition of lignite to polymers may also affect their biodegradability. Part of research was

focused on biodegradability of polyurethane (PUR) foams by various microorganisms. Lignite was mixed with polyol component of several commercial TDI (Gumotex Břeclav, a.s.) and MDI (IPI Břeclav) based soft and hard foams. Foams containing lignite in the range 1 % – 5 % were subjected to biodegradability tests and in comparison with unmodified polyurethane foams. Aerobic microorganisms – mixed culture of thermophilic bacteria and pure cultures of mould *Phanerochaete chrysosporium* and yeast *Aureobasidium pullulans* were used for biodegradation experiments. Lignite-modified polyurethane foams were cultivated in the presence of these cultures under permanent shaking during 3-week experiment. In regular intervals growth characteristics, chemical oxygen demand, surface microscopy and some mechanical properties were followed. Preliminary results showed that addition of lignite into polyurethane foam can lead to increased mechanical stability and to higher adsorption of microorganisms on modified foam surface, when compared with reference foam. Regarding adsorption, the most effective was the addition of 1% lignite, which caused about 2x higher amount of cells isolated from foam surface. Better mechanical stability of modified foam was observed after addition of 5 % lignite. Further experiments are needed for better understanding of biodegradation processes and also for testing of degradation products, because in the presence of lignite modified PUR the total biomass amount was substantially decreasing, thus, some potential toxic products were probably formed (Pekař et al., 2006).

7. The activity of natural lignite in radical processes which can be directly related to its applications in polymers comprised part of the project solution. Lignite in the solid state was subjected to heat treatment in the range of 120-180 °C and also to UV irradiation. EPR spectroscopy confirmed that whereas heating generates new and more radicals in lignite, UV irradiation is effectively screened by the lignite and no measurable effect of the irradiation on radical content was detected. Two model radical reactions were studied in the presence of lignite – hydrogen peroxide decomposition in aqueous solution and *t*-butylhydroperoxide (TBHP) decomposition in benzene solution and upon UV irradiation. Hydrogen peroxide at 0.1 mol/dm³ concentration was decomposed in the presence of lignite within about 6 hours and kinetic data indicated a two-step (probably consecutive) decomposition process. Activity of lignite can be attributed to free radical naturally present in its structure and to the action of metals (metal ions) occurring in lignite. The spin-trap EPR technique confirmed generation of radicals by decomposition of TBHP

in the presence of lignite after UV irradiation. Thus, the lignite UV-screening effect can be suppressed in suspensions and lignite could be used, e.g., to accelerate UV decomposition of dissolved pollutants (Majzlík et al., 2007 a,b).

8. Lignite was used in grinded or milled form in sorption or agricultural experiments described above. Using dusty or “sandy” lignite in such ecological or agricultural applications is often not “user-friendly” and, moreover, very small particles may have not sufficient stability, e.g. in soil. On the other hand, large particles in size of several centimetres, which are still present in the finest fraction currently produced by mining company, may have very little sorption or plant nutrition support effect over several years before they disintegrate into smaller sizes. Therefore, we are also investigating formation of fine lignite fractions into suitable particles – granules, extrudates, pellets etc. – bonded by suitable and preferably biodegradable biopolymer or polymer. The granules should not only be more convenient for practical applications in natural environments but should also possess controlled disintegration upon an effect of aqueous media.

Laboratory experiments used the lignite fraction that passed 0.2 mm after drying at 105 °C and moisture re-equilibrating at ambient atmospheric conditions. The lignite was mixed with molasses, hydrated lime, water-glass, aqueous acrylic dispersion Sokrat and four starch types as binders, and deionized water by thorough hand-mixing with a metal rod in a plastic container. Prepared mass was either left as such or impressed into a propylene mold with cylindrical holes forming particles of 6 mm diameter and length of 10 mm. In both cases obtained products were dried freely at laboratory conditions, selected samples at 60 °C in a laboratory drier. Resulting particles were subjected to simple tests for their (structure) resistance to water.

The best results regarding the particle structure resistance to water were obtained with the modified starch Solvarin AP. These particles showed no disintegration in water for at least 3 months. Drying at elevated temperature had no appreciable effect on the water resistance. Interestingly, too high amount of the starch decreased the water resistance and generally, the starch amount in the initial mass for particle production should be less than 22-23 %. On the opposite side, granules prepared from molasses had very low resistance to water, they completely disintegrated within the first hour and the higher the molasses contents the faster disintegration. We also simulated industrial production of granules by extrusion using a semipilot scale chopper.

As expected Sokrat binder gave particles with a very good water resistance which, moreover, is not diminished by addition of relatively high amount of molasses. Molasses itself was confirmed to give particles with very low water resistance. Surprisingly, water-glass does not insure sufficient particle stability in water. Particles prepared by the semi-pilot extrusion were subjected also to tests for mechanical properties, particularly abrasion and compression resistance. Abrasion resistance of all samples was good – the loss was usually less than 10 %. The highest resistance was obtained for composite binders (Sokrat or water-glass with molasses) – loss about 5 %, the lowest one for the molasses with the lowest amount of added water – loss 17%. Compression tests resulted in rather scattered outputs due to heterogeneity of lignite and diversity in structural details of particles prepared from the same mass. Molasses at proper amount of water and/or in combination with other binder gives hard particles with highest compression resistance (Bušinová and Pekař, 2007).

3. CONCLUSIONS

Selected results from our research presented in this contribution support versatility of natural lignite for various applications outside the fuel sector (Pekař et al., 2006; Pekař et al., 2007). Due to its complex composition and inherent heterogeneity a precise reproducibility of experimental data is sometimes difficult but on average lignite shows clear trends or effects in all studied applications. Lignite possesses non-negligible activity in the natural state which makes it also a cost-effective material. Its properties can be further improved and made controllable and better reproducible by suitable physical or chemical treatment.

Results that were obtained so far substantiate efforts to apply lignite as an effective agent especially in various environment care and protection technologies. Though the lignite mining in the South Moravia is not landscape-devastating, the lignite can even contribute to landscape cultivation, particularly in countries fighting the problem of low soil quality, arid soils or desertification.

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PROGRESIVNÍ, EKONOMICKY EFEKTIVNÍ NEENERGETICKÉ APLIKACE LIGNITU

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ABSTRAKT:

Projekt byl zaměřen na výzkum ne-energetického využití hnědého uhlí z Jihomoravského lignitového revíru jako hodnotné chemické suroviny s minimálními dalšími náklady v těchto oblastech: sorpční technologie, kompozity hnědé uhlí-polymery a hnědé uhlí-biopolymery, radikálové a fotochemické procesy probíhající za přítomnosti studovaného uhlí, izolace huminových kyselin ekonomicky efektivním způsobem. Výsledky prokázaly univerzálnost původního hnědého uhlí a jeho využití jako sorbentu s vysokou afinitou vůči anorganickým a organickým látkám. Bylo zjištěno, že studované uhlí ve vodném prostředí vykazuje významné pufrací schopnosti s výsledným pH v rozmezí 5-6, že organické komponenty se vyloužily v zanedbatelném množství a anorganické prvky v přijatelném množství. Přídavek studovaného uhlí do kontaminované půdy podporuje její bioremediaci. Výsledky potvrdily možnost aplikací původního hnědého uhlí z JMLR v technologiích ochrany půdy a životního prostředí. Uhlím se daly poměrně snadno plnit fyzikální a chemické polyvinylalkoholové hydrogely. Z uhlí a ze škrobu byly připraveny granule s řízenou dobou rozpadu ve vodném prostředí. Všechny kompozity, granule a huminové látky připravené ze studovaného uhlí mohou být vzhledem ke svým vlastnostem mohou být využity v oblasti sorbentů, ekologie, zemědělství, půdní remediace a ochrany a v zemědělství.