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# Effect of the mechanochemical activation for the extraction of diterpenes from the brown coal

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**Abstract**

The paper presents the influence of mechanochemical activation of the Slovak brown coal to make the organic structure of coal accessible for the extraction agent. It was proved that mechanical activation of optimally ground coal sample (20 min) produced ultra-fine and nano-particles with specific surface of 3.79 $m^2/g$. The distribution density curves show two maxima at 6.5 μm and 42 nm, respectively. The identification of 16β(H)-kaurane in the coal extract was performed after the low-temperature supercritical fluid extraction of the coal powders with and without modifier. GC–MS chromatograms present the favourable effect of the modifier. It is well known, that the kaurane derivatives display biological activity.

*Keywords:* Slovak brown coal; Mechanical activation; Ultra-fine and nano-particles; Low-temperature Supercritical Fluid Extraction; Kaurane

## 1. Introduction

The coal reserves are important non-renewable energy sources in the world [1]. The largest deposits of coal in the Slovak Republic are in the Nováky, Záhorie, Cígel' and Handlová regions. The coal material research brings new opportunities for the priority position of coal in the preparation of carbon nano-products (like carbon nanotubes) and some pharmaceutical precursors [2]. The Slovak brown coal contains unusual organic compounds such as podocarpanes, azulenes and kaurane diterpenes [3].

There are several methods for extraction of coal such as Soxhlet Extraction [4], Microwave-Assisted Extraction [5] and Supercritical Fluid Extraction (SFE) [6]. SFE process of coal was studied intensively with many supercritical organic solvents (tetraline, toulene) [7]. In this paper, we have studied SFE using $CO_2$ as primary solvent, because this pure solvent has low critical parameters and $CO_2$ is non-toxic as compared to other organic solvents used in coal treatment.

The large amount of extractable organic material is trapped in the coal polymeric matrix [6]. The pure $CO_2$ cannot often extract matrix fixed compounds and it is not able to extract all analytes [8]. The addition of modifiers to the nonpolar $CO_2$ enhances the extraction efficiency [9]. The modifier with different physical and chemical properties can break the analyte–matrix interactions like Van der Waals forces, electron–acceptor electron–donor interactions and hydrogen bondings. Moreover, their dipole moment or their Brønsted acidity, or basicity are useful properties to disrupt the analyte–matrix interactions [10–13]. Additionally, modifiers can alter the matrix by swelling, facilitating the fluid to access interstitial pores and allow the transport of the analytes to the surface of the matrix [14,15].

It is well known from the literature [16] that the extraction process of rare organic substances is more efficient in the case of granularity of the coal powders under 10 μm. The mechanical activation of coal powders causes structural changes of the coal organic structure [17]. The deformation of organic structure by activation grinding can lead to the accessing of extraction agents [18]. The process of mechanical activation of coal, excitation of organic structure and accessing of extraction agents is important for intensified extraction of humic acids by alkaline leaching with the biological properties of the humic products [2].

In this work we studied the mechanical activation of brown coal for special purposes—making the organic structure for the

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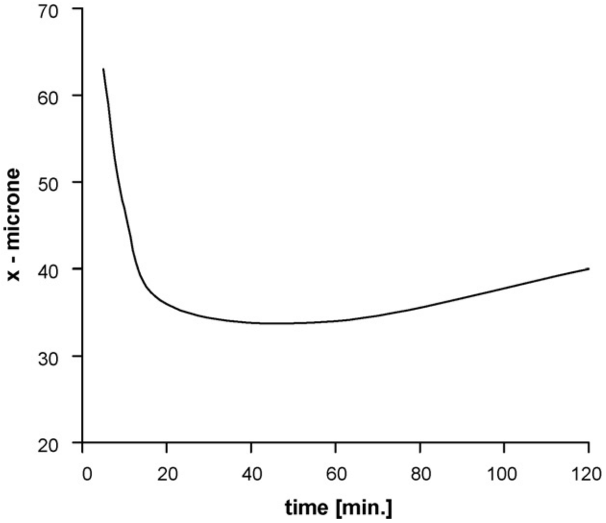

Fig. 1. Dependence of the granularity of x-fraction on the activation grinding time from 5 to 120 min at 400 rpm.

extraction of tetracyclic diterpanes with the identification of kaurane derivate with various biological activity [19,20].

## 2. Materials and methods

The experiments were carried out with the samples of the Slovak brown coal from the Handlová region after the hydrocyclone washing [21], with the elementary analysis: $A^d$(Ash) = 7.70 wt%, $W^a$ = 12.26 wt%, $C^d$ = 61.6%, $H^d$ = 5.6%, $N^d$ = 0.7%, $S^d$ = 1.2%, $O^d$ = 23.2%.

The coal sample was activated by the high effective grinding using the planetary mill Molinex, type PE 075 (Netzsch, Germany) in the air atmosphere under the following conditions: mass of the coal sample, 20 g; grinding time 5–120 min, grinding speed 400 rpm, 500 ml grinding volume, glass balls Ø2 mm (685 g of the glass balls).

The surface characteristics of the mechanically activated samples were measured by the BET method using Micrometrics Gemini 2360 apparatus ($S_{Ax}$ – specific surface area of the mechanically activated sample at the grinding time – $x$ min). Granulometric characteristics (granularity 0.9–180 μm) of these samples were measured using the Sympatec Helos (Rodos SR) apparatus under wet conditions in order to eliminate aggregation during the measurement ($D_{mx}$ – maximum of the distribution density curve of the mechanically activated sample at the grinding time – $x$ min).

Table 1
Dependence of specific surface area and granularity of the mechanically activated coal sample on the grinding time at 400 rpm

| Time of grinding (min) | 5 | 10 | 20 | 60 | 120 |
|---|---|---|---|---|---|
| Specific area ($m^2$/g) | 3.30 | 3.59 | 3.79 | 5.54 | 5.58 |
| *$D_m$ (μm) | 10–20 | 15 | 6.5 | 4.5 | 5.5 |

* Granularity at the maximum of distribution density curve.

The granulometric analysis for sub-micro and nano-particles (granularity 1 nm–1 μm) was carried out with dynamic laser radiation dispersion using the ALV detection equipment (Germany), with ALV 5000 correlator. The experimental equipment consisted of an argon laser Spectra Physics Stabilite 2017–0.4 S (USA), working within the wave lenght of 514.5 nm at the output of 400 mW. The data were analysed using the CCNTIN method and ALV 800 transputer. The micrographs of ultra-fine particles of the coal samples were performed by the SEM microscopy (TESLA BS 340).

Low-temperature supercritical fluid extractions (LSFE) with $CO_2$ of the mechanically activated coal samples were carried out using an instrument made by SEKO-K (Brno, Czech Republic) at the Department of Analytical Chemistry, University of Pardubice, Czech Republic. The length of the stainless steel extraction vessel was 68 mm and its inner diameter was 12 mm. Extraction was performed in the dynamic mode, which followed after the 15-min static step under the following conditions: mass of the sample, 1 g; $p$ = 30 MPa; $T$ = 363 K; extraction time, 90 min, modificator, acetone/tetrahydrofurane (AC/THF, 2:8). For the extraction process the optimally ground coal sample was selected (grinding time, 20 min, speed; 400 rpm.)

Extracts were analysed by the GC–MS Hewlett-Packard P-1800 equipment under the following conditions: capillary column, HP, 5 (30 m × 0.25 mm), carrier gas was helium; temperature program, 80 °C (kept 5 min) to 280 °C (kept 10 min); scan speed, 20 °C/min; ion source temperature, 250 °C; detector, 280 °C; electron energy, 70 eV; scan 10–425 $m/z$. The temperature program and the chromatographic column have sufficient separation capacity for the identification of terpenoids. Because of the lack of suitable reference compounds, the identification of chromatographic peaks was based on the comparison with the mass spectra from the NIST library or/and literature data.

## 3. Results and discussion

### 3.1. Surface structural changes and granularity

The surface structural changes and granularity of the ultra-fine coal powders depend on the genesis of the activated coal [18]. Fig. 1 shows the dependence of granularity of the ultra-

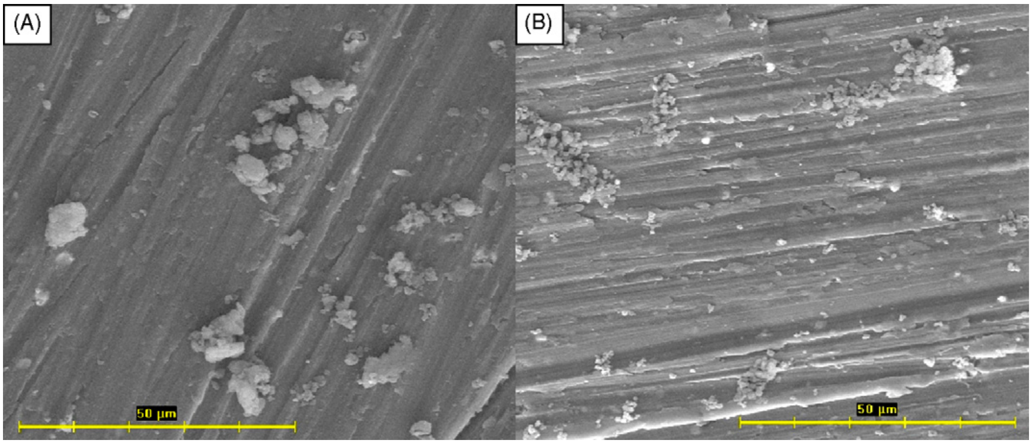

Fig. 2. The micrographs of ultra-fine particles of the Slovak brown coal after the mechanical grinding, taken from the screening electronic microscope at the magnitude of 2000 times: (A) 400 rpm, 20 min; (B) 400 rpm, 60 min.

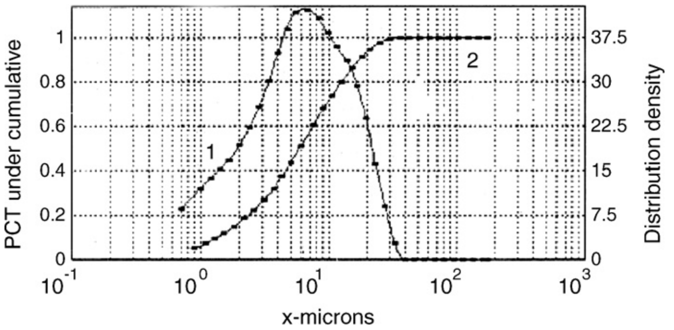

Fig. 3. The particle size analysis of the Slovak brown coal after the mechanical activation (400 rpm, 20 min): (1) $D_m$, distribution density curve and (2) cumulative curve.

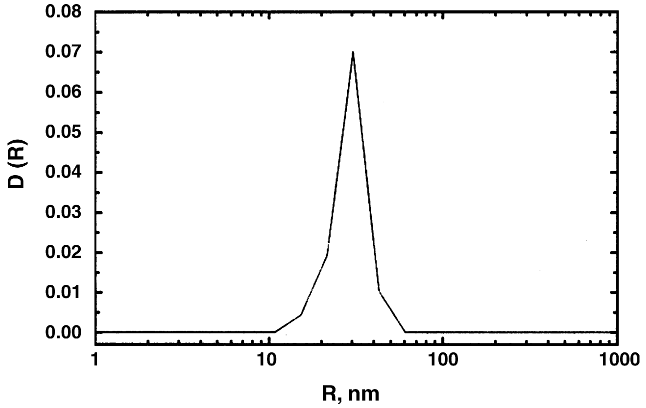

Fig. 4. Weight distribution of the coal nano-particles with radius *R* vs. after the mechanical activation (400 rpm, 20 min).

fine coal powders on the time of the mechanical activation. It is clear from the Fig. 1, that in the stage of effective grinding (the grinding time is below 20 min) there is a strong decrease of granularity of the mechanically activated coal powders within the range of 64–35 μm.

The experimental structural results (see Table 1) confirm that the long-time grinding gives the highest increase of the specific surface at the extreme time of 120 min. The biggest increase of $S_A$ is observed between 20 and 60 min ($S_{A60} - S_{A20} = 1.75\ m^2/g$). Fig. 2 displays the micro-shots of these mechanically activated coal powders, e.g. the optimally ground sample at 20 and 60 min, respectively. The microscopic study of these mechanically activated coal samples confirms that the extending grinding time after the optimally grinding condition (20 min) can lead to the agglomeration of the ultra-fine particles.

The granulometric analysis in the sub-micron range gives new information on granularity of the mechanically activated coal powders. Fig. 3 shows the distribution density ($D_m$, curve 2) of the mass yield of powders versus granularity of the optimally mechanically activated coal powders (time of grinding 20 min). The maximum of the distribution density curve can be reached at the granularity of 6.5 μm with the mass yield of 50%. In the first stage of the effective grinding (time is 5 min) of the coal powders the maximum of the distribution density curve is higher (granularity is 15 μm). The extending of the grinding time of the coal powders from 20 to 120 min causes the decrease of the maximum of the distribution density, $D_{m20}$ from 42 to 37.5% $g^{-1}$ and the maximum of distribution density curve ($D_{m120}$) is placed at lower values (from 6.5 to 5.5 μm, see Table 1).

### *3.2. Distribution of the coal nano-particles*

Fig. 4 illustrates the distribution density curve of the mass yield of nano-particles in the optimally ground coal powder. The curve has its significant maximum at the granularity of 42 nm with 0.07% mass yield. The running of the distribution density curve suggests that the initial phase of the curve occurs at two breaking points (the first one is moderate from 11–16 nm and the second one is more evident from 16 to 26 nm). It is interesting that in the second decreasing part of this curve there is only one similar breaking point from 54 to 66 nm. The mechanism of these phenomena has not been explained yet.

### *3.3. Coal extraction and GC–MS identification of organic compounds*

Fig. 5 shows selected chromatograms of the coal extracts after LSFE with $CO_2$ and LSFE with $CO_2$ + modifier analysed by GC–MS method**.** From the GC–MS chromatograms (Fig. 5, Table 2) the effect of the modifier leads to detection of two new

Table 2
The composition of the Slovak brown coal extracts from LSFE + $CO_2$

| Peak number | Ion intensity (*m/z*) | Formula | Characterization of the compounds |
|---|---|---|---|
| 1 | 153, 168, 183, 198, 235, 250 | $C_{15}H_{18}$ | Azulene 1, 4 dimethyl 7-(1-methyletyl) |
| 2 | 131, 145, 160, 187 | $C_{15}H_{22}$ | Cycloisolongifolene derivate |
| 3 | 185, 241 | $C_{15}H_{15}$ | Acridinone derivate |
| 4 | 123, 137, 163, 191, 233, 262 | $C_{30}H_{50}$ | Unknown |
| 5 | 123, 163, 191, 247, 261, 275 | $C_{20}H_{30}$ | Podocarpane |
| 6 | 123, 149, 163, 189, 231, 259, 274 | $C_{20}H_{34}$ | Derivate of kaurane |
| 7 | 195, 237, 252 | $C_{15}H_{12}N_2O$ | Carbamazepine |
| 8 | 175, 189, 201, 271, 286 | $C_{20}H_{30}O$ | Derivate of totarol |
| 9 | 165, 180, 219 | $C_{15}H_{12}N_2$ | Diphenyl imidazole |
| 10 | 177, 206, 220 | Unknown | Unknown |
| [*]Sheng et al. [22] | 123, 136, 163, 177, 189, 231, 259, 274 | $C_{20}H_{34}$ | Standard 16β(H)-kaurane |

Data from the GC–MS analysis.

[*] Comparison with the standard data from the literature [22].

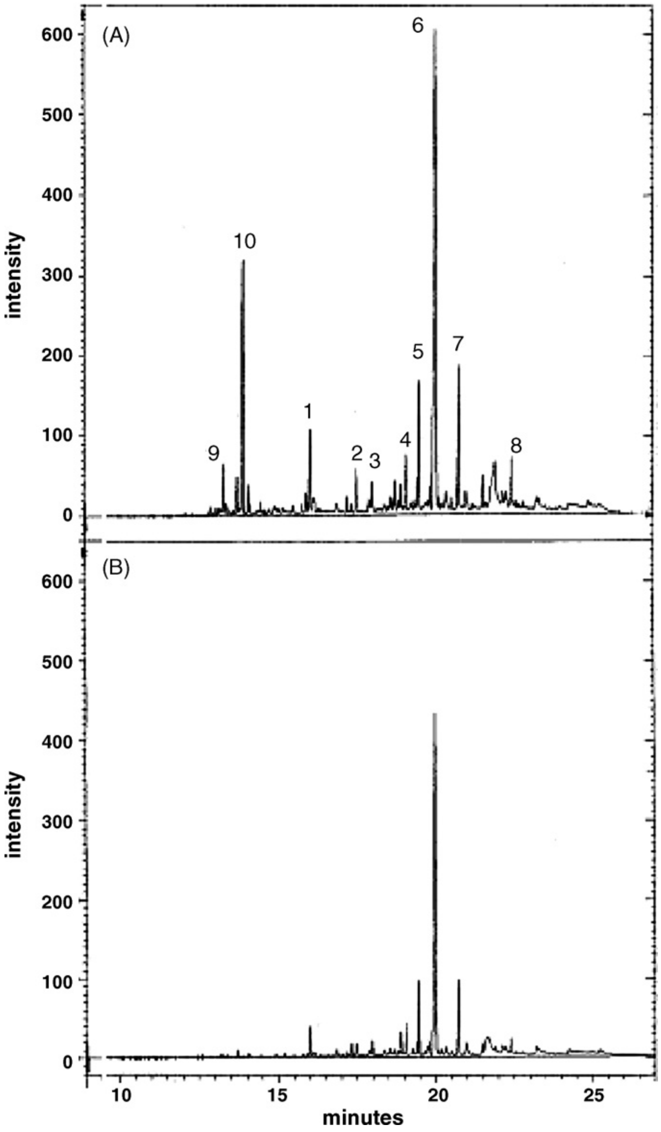

Fig. 5. Typical GC chromatogram of LSFE extracts from the Slovak brown coal powders: (A) LSFE with $CO_2$ + modificator; (B) LSFE with $CO_2$ (the peak numbers presented in Table 2).

intensive peaks 9 (difenyl-imidazole derivate) and 10 (unknown) and as well the increase of relative intensity of chromatographic signals which allows a more accurate interpretation of spectra. The effect of the modifier also shows itself in the extraction of azulenes-$C_{15}$. Table 2 further shows that in the group $C_{15}$ there are N-derivative of carbamazepine (peak 7) and acridinone derivative (peak 3). The coal extract contains also other compounds, such as triterpene-$C_{30}$, which are not interesting from the point of view of biological activity. We also determined biologically active compounds, primarily tetracyclic diterpens $C_{20}$. The peak number 5 (see Table 2 and Fig. 5) is assigned to derivate of $C_{20}$, labeled in Table 2 as podocarpane and the peak number 8 is assigned to the totarol.

Table 2 displays the fragmentation of MS spectra of the indicated organic compounds where the most important are kaurane derivates with most intensive chromatographic peak number 6, which has been compared to Shang [22]. The experimental data of these biologically activated diterpenes [19,20], which were identical to the standard data from the literature [22] clearly show, that the most intensive peak of the extract is 16β(H)-kaurane. The study of the structure of isolated kaurane from the coal extract by $^{13}C$, $^{1}H$ CP, NMR, MS and testing of the biological activity will be the subject of our future experimental research.

## 4. Conclusion

The results of the experiments confirm that the process of mechanical activation of coal (20 min) creates ultra-fine powders of the granularity 6.5 μm with 50% mass yield. The distribution density curve of nano-particles of this optimally ground sample shows, that the maximum of the curve is reached at 42 nm with 0.07% mass yield.

The study of extraction of diterpenes from the coal powders was aimed at the impact of the modifier (acetone/tetrahydrofurane) favourably influencing the process. The evaluation of the results of the GC–MS chromatograms detected the molecules $C_{15}$, $C_{20}$, $C_{30}$. The purpose of the experimental study was the identification of tetracyclic diterpenes especially 16β(H)-kaurane, which is the potential biological activating precursor for pharmaceutical purposes.

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