Application of Microwave Radiation at Coal Treatment Processes

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Summary

This article presents a new approach to evaluation of coal with implementation microwave extraction of powders. Coal is the most abundant hydrocarbon resource on earth; therefore coal structure should be well understood for its effective utilization. Coal is a heterogeneous aggregate formed of cross-linked molecular network organic components. Coal is also considered as an organic polymeric material, with some inorganic impurities. The study of coal structure presents numerous problems due to heterogeneity, non-crystalline and insolubility. The sample of brown coal was from Handlová locality in Slovakia. The microwave extraction of Handlová brown coal was realised in microwave oven with using non-polar solvent dichloromethane. The advantage of using microwave-assisted extraction for the coal sample is the reduction of extraction time. The optimized conditions can be applied for extraction with good recoveries and reproducibility. Microwave technology uses electromagnetic waves that pass through material and cause its molecules to oscillate, generating heat. In a microwave oven, the average temperature of the solvent can be at a significantly higher temperature than the atmospheric boiling point. This is due to the fact that the microwave power is dissipated over the whole volume of the solvent. The coal sample after microwave-assisted extraction was analysed by SEM/EDX, thermal analyses. TG and DTG curves confirmed the major mass loss in the coal sample after the extraction (55.9 %). This is related to the major content of the organic phase. It is not possible clearly specify the mechanism of aggregation of grains. In this process, there is a significant impact of particles of nano size. The identification of dichloromethane extract of brown coal after the microwave assisted extraction by GC-MS method confirmed the presence of various kinds of organic compounds. The existence of polycyclic aromatic hydrocarbons (PAHs) was found.

Keywords: microwave, extraction, coal, dichloromethane

Introduction

The effect of microwave radiation on raw materials has been investigated in many applications. Potential areas for utilisation have included pre-treatment, drying, extraction, desulphurisation of coal, thermally assisted liberation of minerals and rocks from gangue and various technological [1-6]. The microwave heating has been applied to the extraction of organic contaminants such as polycyclic aromatic hydrocarbons, pesticides, polychlorobiphenyls, herbicides, phenols, neutral and basic priority pollutants in various matrices such as sediments, soils, coal or atmospheric particles. According to Letellier [7], the focused microwave assisted extraction at atmospheric pressure is fast and uses with low quantities of solvent as for microwave assisted extraction in closed vessel. The working process at atmospheric pressure is safe. The most common solvents used for the MAE of PAHs from the solid samples are acetone-hexane, dichloromethane, methanol, and methanol-toluene. However, the selection of solvent to extract analyses has to take into consideration the technique which will be used in the final determination. Most solvents or solvent mixtures used for PAHs extraction appear to be perfectly suited for the gas chromatography [8-11]. The attention of pyrolysis processes and flotation of energetic raw materials are currently devotes a considerable amount of research groups [12-15].

Material and Methods

The experiments were realized with the samples of the Slovak brown coal from Handlová (West Slovakia) after the hydrocyclone washing [16]. The chemical analysis of studied samples is in Table 1.

CHN analysis was realized using elementary analyser Carlo Erba Model 1106 equipped with the microprocessor and recorder. Helium (purity 99.998%) was used as the carrier gas, oxygen (99.999 %) was used as the oxidative agent and argon created an inert atmosphere during measurement. The chromatographic column was filled with the Porapak QS with the granularity 80-100 mesh. The cyclohexanone–dinitrophenylhydrazone (content of N = 20.14%, C = 51.79% and H = 5.07%) was used as the standard material.

The studied sample was pretreated in the mill and then the sample of under 0.5mm granularity was activated by the grinding using the planetary mill Pulverisette 6 (Fritsch, Germany) in the air atmosphere at the following conditions: granularity of input -0.5mm, mass of sample – 20g, grinding speed - 400 rev/min, time of grinding 20 minutes. SEM/EDX analysis was carried out at the Institute of The-

Tab. 1 Chemical analysis of brown coal (Handlová) after the hydrocyclone washing

Tab. 1 Analiza chemiczna węgla brunatnego (Handlová) po wzbogacaniu w hydrocyklonie

Sample	W^a [%]	A^d [%]	C [%]	H [%]	N [%]
Coal	7.55	9.01	74.86	4.93	0.6

Tab. 2 Content of elements in the coal sample after the microwave-assisted extraction in dichloromethane

Tab. 2 Zawartość pierwiastków w próbce węgla po ekstrakcji mikrofalami w dichlorometanie

Elements	C	O	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
Wt [%]	78.43	17.06	0.19	0.06	0.67	1.42	0.05	1.15	0.08	0.23	0.07	0.59
At [%)]	84.37	13.78	0.11	0.03	0.32	0.65	0.02	0.46	0.03	0.07	0.02	0.14

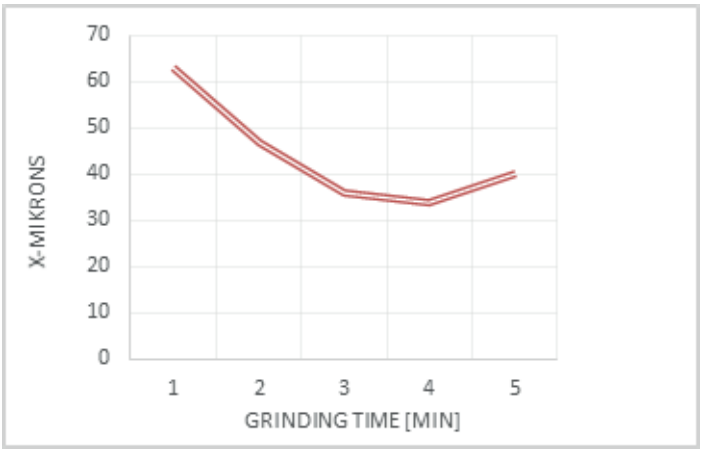

Fig. 1 Dependency of granularity x-fraction of studied coal sample vs. activation grinding time

Rys. 1 Zależność ziarnistości frakcji x badanej próbki węgla w zależności od czasu aktywacji w procesie rozdrabniania

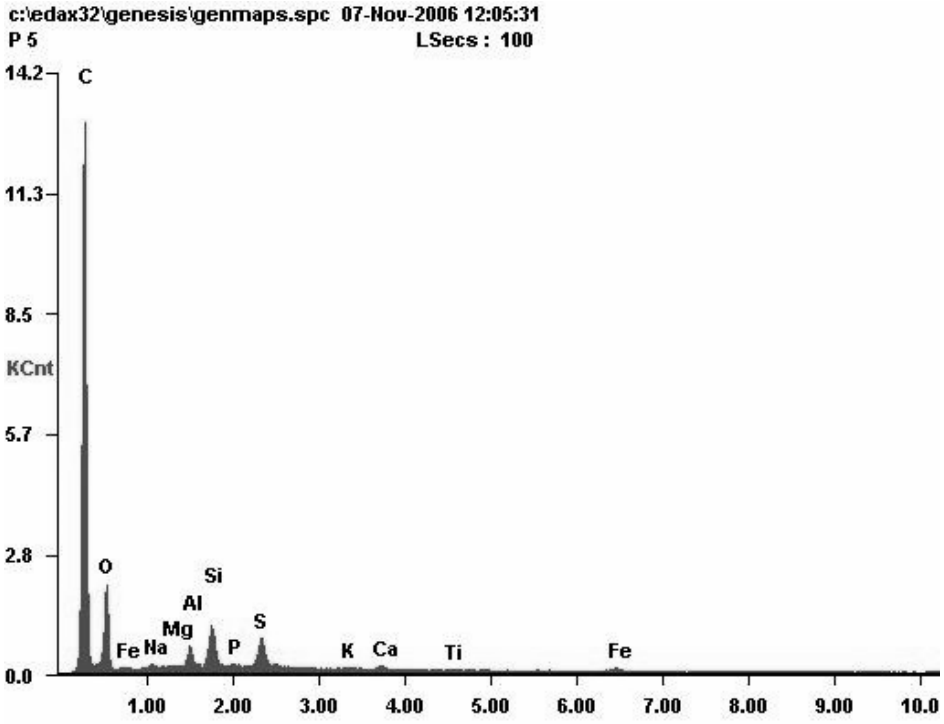

Fig. 2 EDX spectrum of physically treated brown coal sample after the microwave-assisted extraction in dichloromethane

Rys. 2 EDX spektrum przetworzonej próbki węgla brunatnego po mikrofalowej ekstrakcji w dichlorometanie

oretical and Physical Chemistry - Braunschweig, Germany. It was used JSM - 6400 Scanning microscope (JEOL LTD., Tokyo Japan) combined with the Microanalysis System Software, EDAX Genesis V2.50.

The thermal analyses TG, DTG were carried out at temperature up to 1000°C in air at a multimodular thermal analyser Setaram Setsys 1200 (firm SETARAM) with two replaceable heads under the conditions: sample weight 10 - 20mg, heating rate 10°C.min^{-1}, Al_2O_3 crucible.

The microwave-assisted extraction of the coal sample was realized in the microwave Whirpool at the power 500W and frequency 2.45 GHz. The extraction was realized in the non-polar solvent of dichloromethane at the boiling point 40°C (it increases in microwave oven to 55°C) for the period of 20 minutes. The boiling point of solvent in the microwave was measured using the contactless thermometer Raytek MX4.

GC-MS analyses were realised in National Water Reference Laboratory for Slovakia in Bratislava. The chromatographic analyses were performed using Agilent 6890 gas chromatograph coupled to Agilent 5973 mass spectrometric detector (USA). Capillary GC analysis was performed on a 30m x 250µm I.D.; 0.25 µm df HP-5MS cfgolumn (Agilent Technilogies). Helium was used as a carrier gas. The MSD was used in the scan mode (m/z 40-550) for all samples. Mobile phase was methanol and water Milli-Q. The identification of compounds was performed using mass spectrum libraries Wiley 7n and NIST02, respectively.

Experimental Results

The activation grinding of brown coal in the mill causes significant structural changes in the surface of ultra-fine active powders, which depends on the intensity of the grinding, i.e. grinding time and speed of grinding mill. On the curve depending on the granularity of time grinding (400 rev/min) we can see that in the first phase of the active melting there is a significant decrease in the size of the grains of the active powders (Fig. 1).

When the intensity of the grinding at higher levels of the mill increases, the effective phase of melting will be reduced to 20 minutes. It is the optimum time of grinding. After this time there is a aggregation of grains, which confirms the stagnation of granularity values on the curve.

Our attention was aimed at the study of microwave-assisted extraction of brown coal in dichloromethane at its boiling point, within the period of 20 minutes. Its boiling point is 40°C but it increases in the microwave oven to 55°C. The content of elements in the coal sample after extraction is in Table 2.

Fig. 2 shows the quantity of physically treated brown coal sample after the microwave-assisted extraction in dichloromethane.

Fig. 3 shows the micrograph of mechanically activated coal powders after the grinding time of 20 minutes at conditions of grain agglomeration after the extraction in dichloromethane. The mechanism of aggregation of ultra-fine grains cannot be definitely specified. However, there is, a significant impact of particles of nano size that participate in this process.

TG and DTG curves of physically treated brown coal prepared by the microwave-assisted extraction in dichloromethane we can observed on Figure 4. The mass loss of the coal sample before extraction is 54.5% but in the coal sample after the extraction it is higher 55.9% (Tab. 3). It corresponds to the major content of the organic phase. The temperature of the maximum oxidation speed in the coal sample after the extraction is higher in comparison with the coal sample before extraction. These temperatures show higher content of aromatic hydrocarbons, it means better structural composition.

Figure 5 shows the representative GC-MS chromatogram of coal extract after the microwave extraction in dichloromethane for 20 minutes. The following organic compounds were identified by GC-MS method: naphthalene and its derivates with carbon number 12, 13, 15

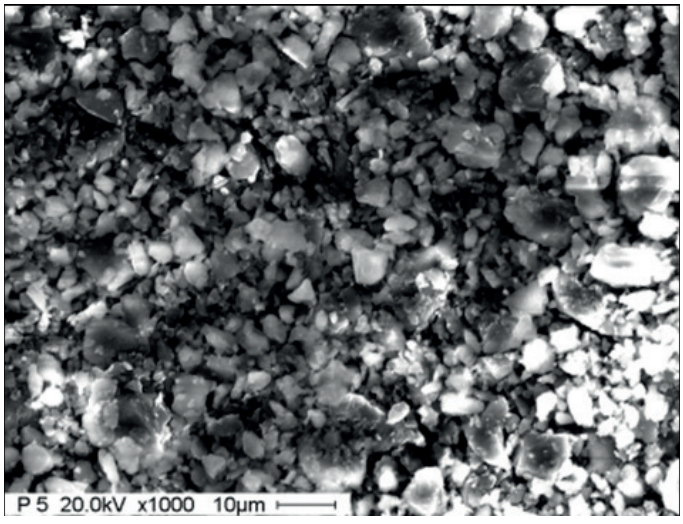

Fig. 3 The micrograph of physically treated brown coal sample after the microwave-assisted extraction in dichloromethane

Rys. 3 Mikrograf przetworzonej próbki węgla brunatnego po mikrofalowej ekstrakcji w dichlorometanie

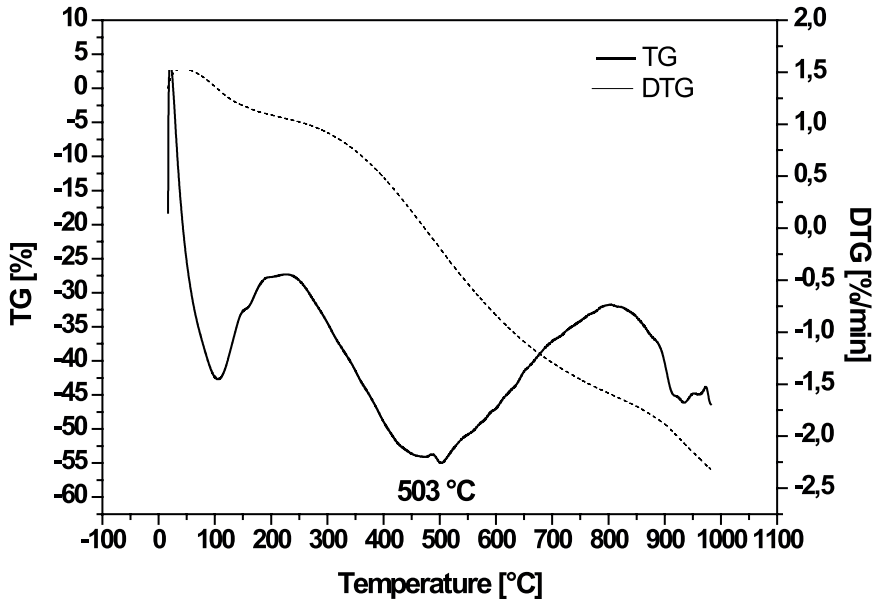

Fig. 4 TG and DTG curves of physically treated brown coal prepared by the microwave-assisted extraction in dichloromethane

Rys. 4 Krzywe TG I DTG przetworzonej próbki węgla brunatnego pochodzącej z mikrofalowej ekstrakcji w dichlorometanie

Tab. 3 Characteristics of the coal sample by thermal analysis

Tab. 3 Charakterystyka próbek węgla uzyskana w wyniku analizy termicznej

Samples	Δm [%]	T_{max} – DTG [°C]	R^2	E_a [kJ.mol^{-1}]
Coal sample before MAE	54.5	454	0.9965	33.4
Coal sample after MAE	55.9	503	0.9979	31.1

R^2 = correlation factor, Ea = activation energy

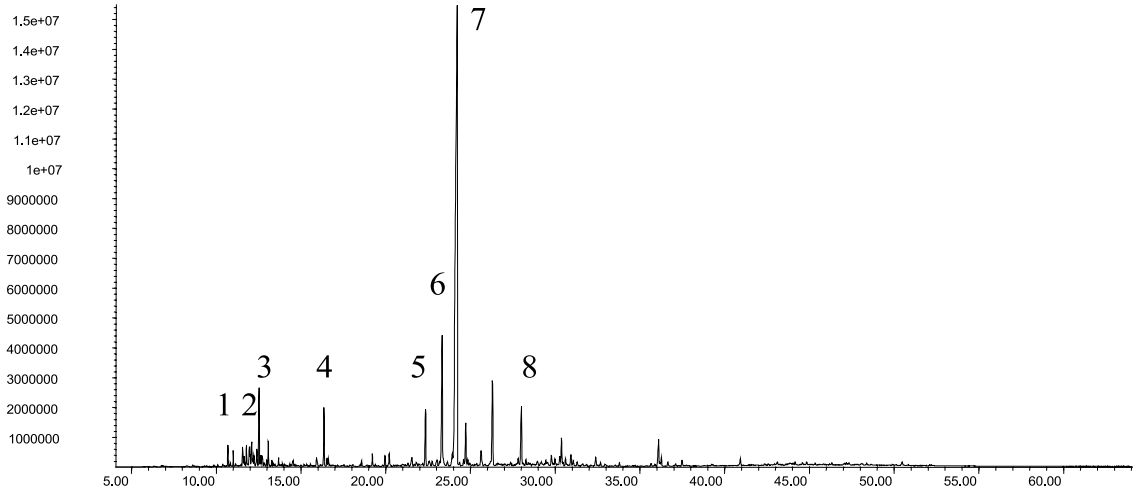

Fig. 5 Typical GC chromatogram of dichloromethane extract of the physically treated brown coal prepared by the microwave –assisted extraction, extraction time 20 min

Rys. 5 Typowy chromatogram GC ekstraktu dichlorometanu węgla brunatnego poddanego ekstrakcji mikrofalowej, czas ekstrakcji 20 min

Tab. 4 The composition of the Slovak brown coal after the microwave extraction in dichloromethane

Tab. 4 Skład słowackiego węgla brunatnego po mikrofalowej ekstrakcji w dichlorometanie

Peak number	Ion Intensity [m/z]	Formula	Characterization of the compounds
1	174	$C_{13}H_{18}$	1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene
2	156	$C_{12}H_{12}$	2,7-dimethylnaphthalene
3	208	$C_{15}H_{28}$	4a,8-dimethyl-2-isopropylperhydronaphthalene
4	198	$C_{15}H_{18}$	1,6-dimethyl-4-(1-methylethyl)naphthalene
5	272	$C_{20}H_{32}$	(5.alpha.,9.alpha.,10.beta.)kaur-15-ene
6	276	$C_{20}H_{36}$	2-ethyl-2,4,8,8-tetramethylperhydrophenanthrene
7	274	$C_{20}H_{34}$	4b,8,8-trimethyl-2,10a-(2´-methylethano)perhydrophenanthrene
8	234	$C_{18}H_{18}$	1-methyl-7-(1-methylethyl)phenanthrene

(m/z = 156, 174, 198, 208), phenanthrene derivates with carbon number 18 and 20 (m/z = 234, 274, 276). All analysed compounds belong to group of polycyclic aromatic hydrocarbons (Table 4).

Conclusion

The paper described utilization of microwave energy at extraction coal in dichloromethane. Knowledge of the structural parameters can provide the whole vision of the structural changes of coal. The advantages of a microwave heating are decreased extraction time, reduced solvent consumption and improved extraction efficiency. The decrease of solvent waste, solvent release into the environment and human exposure is also important. The presence organic compounds with carbon numbers C12, C13, C15, C20 was confirmed in the extract by GC-MS method. All analysed compounds belong to group of polycyclic aromatic hydrocarbons.

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Zastosowanie promieniowania mikrofalowego w procesach obróbki węgla

W artykule przedstawiono nowe podejście do ewaluacji węgla z użyciem mikrofalowej ekstrakcji proszków. Węgiel jest źródłem węglowodorów najczęściej występującym na Ziemi; z tego powodu struktura węgla powinna być dobrze zrozumiana w celu jego skutecznego wykorzystania. Węgiel jest niejednorodnym kruszywem utworzonym z sieci molekularnych wiązań składników organicznych. Węgiel jest także uważane za organiczny materiał polimerowy zawierający zanieczyszczenia nieorganiczne. Badanie struktury węgla sprawia wiele problemów ze względu na jego różnorodność, nie-krystaliczność i nierozpuszczalność. Próbka węgla brunatnego pochodziła z rejonu Handlová na Słowacji. Ekstrakcja mikrofalowa węgla brunatnego z Handlová została przeprowadzona w piecu mikrofalowym z użyciem apolarnego rozpuszczalnika - dichlorometanu. Zaletą stosowania ekstrakcji mikrofalowej dla próbki węgla jest skrócenie czasu ekstrakcji. Zoptymalizowane warunki mogą być stosowane do ekstrakcji z dobrym wynikiem odzyskiwania i powtarzalności. Technologia mikrofalowa wykorzystuje fale elektromagnetyczne, które przechodzą przez materiał i powodują drgania oscylacyjne jego cząsteczek wytwarzając ciepło. W piecu mikrofalowym, średnia temperatura rozpuszczalnika może być znacznie wyższa niż temperatura wrzenia pod ciśnieniem atmosferycznym. Wynika to z tego, że moc mikrofal jest rozproszona w całej objętości rozpuszczalnika. Próbka węgla po ekstrakcji z użyciem mikrofal została przeanalizowana metodą SEM/EDX, analizą termiczną. Krzywe TG i DTG potwierdzają znaczącą utratę masy w próbce węgla po ekstrakcji (55,9%). Jest to związane z zawartością głównego składnika fazy organicznej. Nie jest możliwe jasne określenie mechanizmu agregacji ziaren. W tym procesie, znaczący wpływ mają cząstki rozmiarów nanometrowych. Identyfikacja ekstraktu dichlorometanu z węgla brunatnego po ekstrakcji mikrofalowej metodą GC-MS potwierdziła obecność różnych rodzajów związków organicznych. Stwierdzono występowanie wielopierścieniowych węglowodorów aromatycznych (WWA).

Słowa kluczowe: mikrofale, wydobycie, węgiel, dichlorometan