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Supercritical fluid extraction of coal

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ABSTRACT

Supercritical carbon dioxide extraction as a promising way to analysis of coalfields deposits and chose the way for their primary processing. Eight samples of different coals from Primorye region have been extracted by supercritical carbon dioxide. Extractive capacity for supercritical CO_2 were studied in dependence from the temperature, pressure and the addition of co-solvents. Seven samples were brown coal and one was rock coal. It has been experimentally shown that the addition of co-solvents can significantly increase the degree and rate of extraction. Analysis of the extracts revealed that despite the fact that some of the substances in all coals were identical nonetheless all extracts were unique. Results of extracts analysis may be used to identify coalfields and for evaluation their prospects for the supercritical extraction. It was shown that most of Primorye Region's coalfields valuable for industry to purify a compound – Melicopidine (according to the literature melicopidine has antitumor, immunomodulatory and antioxidant activity).

Keywords: coal, brown coal, supercritical carbon dioxide extraction, SC-CO_2, co-solvents, melicopidine.

INTRODUCTION

Over the past three decades significant achievements in the area of supercritical fluid technology have pushed the extraction of natural plant materials using supercritical carbon dioxide (SC-CO_2) to become a mainstream unit operation. Carbon dioxide gas is mostly used as solvent for supercritical fluid extraction. However, just a few publications where its used for supercritical extraction of coal at present day[1, 2]. The main goal of the authors in the first article on this subject was to study an opportunity to use this method for separation of co-products of coal.
For better extraction authors propose to increase the pressure of the process and to grind coal to a powder[3]. Naphthalene, fluorine, and phenanthrene were the main obtained and established substances in this experiment. More polar compounds was prepared by adding a polar co-solvent.

Chlaobing et al [4] investigated the SC-CO_2 and its mixture with methanol extraction from coal tar contaminated soil containing more than 0.1% of polycyclic aromatic hydrocarbons. An interesting area of application of SC-CO_2 is a removal of sulfur and perchlorethylene from coal[5]. The original design flow apparatus for dissolving of anthracene, phenanthrene and carbazole supercritical extraction eliminated the appearance of the so-called dead areas and compression of the extracted material has been proposed[6]. The same authors have shown the selective removal of up to 82% of phenanthrene in the composition of the resulting crystalline extract [7]. Analysis of experimental results for supercritical extraction showed that CO_2 in the supercritical state has a high selectivity for preferential dissolution of bitumen hydrocarbons from raw materials of coal and methane naphthenic fractions of hydrocarbons[8].

In this article we analyzed different conditions for extraction of brown coal in supercritical conditions. Eight different coal samples of PrimorskyKrai were used. It has been experimentally shown that the most effective extraction process with the large values of temperature and pressure of 70 °C and 51.7 MPa, respectively. It was found that addition of chloroform and ethanol as a co-solvent can significantly increase the yield of the extract. The maximum yields observed in the extraction stage with the addition of chloroform.

It was shown that all coals were unique by its composition (according ESI-MS). Most of the extracts was found valuable for industry stuff – Melicopidine (according to the literature it has antitumor, immunomodulatory and antioxidant activity).

2. Geological setting and sampling

Two major epochs of coal generation are known in Primorye: Early Cretaceous and Paleogene. In addition, some lignite occurrences occur in the Neogene basins. For this study, one sample of the Early Cretaceous coal from the Lipovtsy deposit, six samplesof the Paleogene lignite from the Nezhino, Pavlovka, Rakovka, Vanchino, and Tadusha (Voznovo and Suvorovo Formations) deposits, and one sample of the Neogene lignite from the Siniy Utes occurrence have been collected (Table 1).

Table 1 - Ages and areas of coal samples

№	Samplecod	Coalfields	Age	Coaltype	Mass, g
1	1315	Sinii Utes brown coal Formation	Paleogene-Neogene	browncoal	363.5
2	1318	Nezhinsky Brown Coalfield of PrimorskyKrai	Paleogene Or Paleogene-Neogene	browncoal	427.5
3	1319	Pavlovskoe BrownCoalfield	Paleogene	browncoal	177.2
4	1321	Lipovetsk Coalfield of PrimorskyKrai	LowerCretaceous	coal	323.7
5	1322	Тадушинское	Paleogene	browncoal	149.7
6	1323	VoznovobrowncoalFormation	Paleogene	browncoal	655.0
7	1324	Rakovskoe brown coal deposit of PrimorskyKrai	Paleogene	browncoal	1948.1
8	049/10	Vanchinskoe Brown Coalfield of PrimorskyKrai	Paleogene	browncoal	64.0

3. Experimental and analytical procedures

3.1. Sample preparation

Seven samples of a brown coal and rock coal were collected in Primorye region (Russia) Table 1. Before the experiment analysis procedures, all coal samples were ground, sieved through a 400-screen mesh and dried under room temperature for 48h.

3.2. Screening and analytical procedures of supercritical carbon dioxide extraction

To study the SFE-CO_2 extraction conditions was used a sample with the highest weight – 1324. Rakovskoe brown coal deposit sample were used to prepare 90probe of 20 grams. The influence on the efficiency of SFE-CO_2 of three experimental factors – operating pressure, temperature and co-solvent, and their combinations was studied. A multilevel factorial design of the response surface methodology (RSM) was employed using OriginPro 8 SR0 software to determine the influence of the operating parameters and their interactions on the yield of total extract. Operating pressure was varied at four levels, 68.95, 172.37, 206.84, 344.74, 413.69 and 517.11 bar, operating temperature was varied at three levels 33, 40, 50, 60 and 70 ˚C, flow of SFE-CO_2 was 0.22 kg/h and extraction time was used as a end point 3 hour. As a co-solvents were used EtOH and CCl_4. At the each temperature within the each co-solvent pressure were changed step by step way, extract were collected and calculated. A total of 90 experimental runs were carried out and the response of coal extract was obtained.

3.2. Supercritical carbon dioxide extraction

For the coal deposits analysis 3 sample 20 g. of each coalfield were prepared. They were extracted with supercritical CO_2 in three step conditions: a pure carbon dioxide, 5% co-solvent chloroform and the third 5% of co-solvent ethanol extraction. The extraction time for each step was 60 min, pressure 517.11 Bar, temperature of 70 °C, CO_2 flow 0.22 kg/h. Extracts were dried to a constant weight under vacuum at 60 °C for 8h. Then extracts were diluted into 1000 times and analyzed by ESI MS analysis.

3.3. ESI MS analysis

The ESI MS/MS were recorded on an Agilent 6510 Q-TOF LC/MS mass spectrometer. The mass spectrometer was equipped with a Dual-Spray ESI ionization source. Ionization parameters were optimized as: a capillary voltage of ±3.5 kV, nebulization with nitrogen at 2 bar, and dry gas flow of 5 L/min at a temperature of 325 C, fragmentor voltage of 300 V, 330 V and 350 V in negative and positive ion mode, respectively. MS/MS spectra were recorded in auto-MS/MS mode. The mass spectrometer was calibrated using the ESI-L Low Concentration Tuning Mix (Agilent Technologies, USA). High resolution LC-MS analysis was performed using addition of Reference Mix (Agilent Technologies, USA) through a reference sprayer in Dual-Spray ESI ionization source. The instrument was operated using the program MassHunter Data Acquisition. Data were analyzed using the MassHunter Qualitative Analysis and MassHunter Quantitative Analysis Software (ver.02.00, Agilent Technologies, USA).

3.4. Raman spectrometry

Raman spectrometry was conducted on Morphologi G3-ID (Malvern, London, Great Britain) with RamanRxn1 (Kaiser Optical Systems Inc., Ann Arbor, USA)

RESULTS AND DISCUSSION

Screening of most effective condition for the supercritical extraction was conducted at first. Extractive capacity of supercritical CO_2 were studied in dependence of the temperature, pressure and the addition of co-solvents. Multi level graphs were plotted for CO_2 only extraction (Fig. 1 A), for supercritical extraction with co-solvent ethanol (Fig. 1 B) and co-solvent CCl_4 (Fig. 1 C).It was shown that pressure changes and addition of co-solvent most significantly influence on extraction, while influence of temperature is not so important for this process. Inefficient extraction using an alcohol as a co-solvent can be explained by two factors, the first is that when ethanol used as a co-solvent supercritical state of the system appears at much high pressure, and the second is that substances easy to extracted with ethanol are hide in cells from nonpolar compounds.

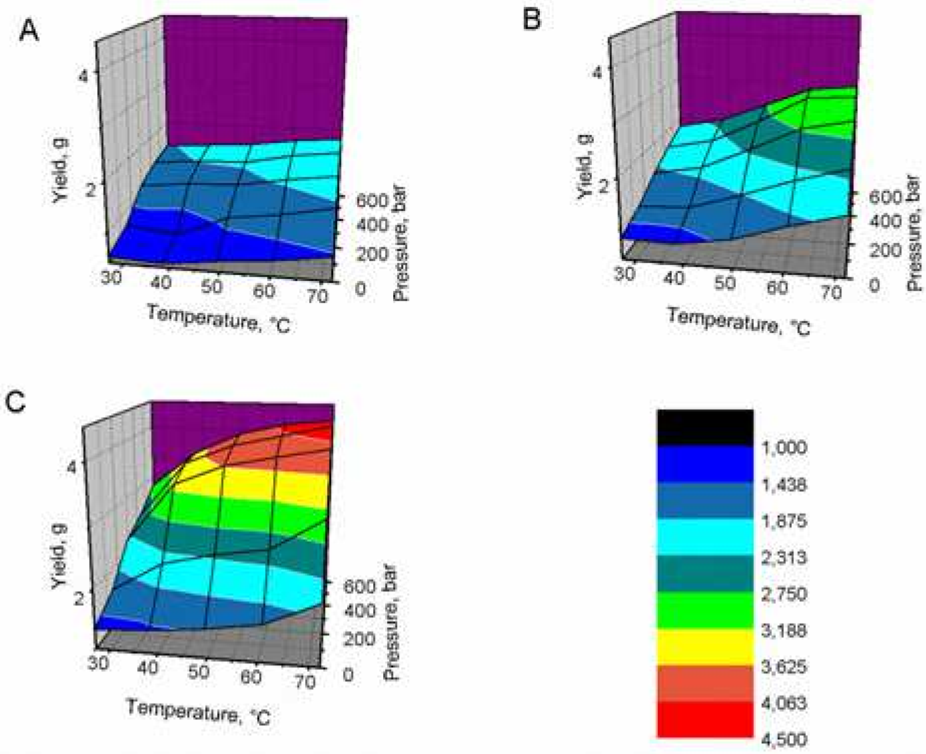

Figure 1 - Multi level graphs of the total extract yield from the brown coal sample. A - CO_2 only extraction; B – supercritical CO_2 extraction with co-solvent ethanol; C- supercritical CO_2 extraction with co-solvent CCl_4

For the further investigation of the coal samples from different deposits three-steps extraction were used. The first step is standard supercritical extraction with the CO2 only on the ESI-MS spectrum this extracts marked as "Sample number.1 +d" in positive mode and "Sample number.1 -d" in negative mode.In this conditions charged compounds of every coals extract differ slightly. From these extracts to reliably determine using ESI-MS, ESI-MS-MS spectra and absorption wavelength was only milicopidine (compound demanded by the chemical industry). It was in all samples of coal but the most enriched by milicopidine sample was 1319 from Pavlovskoe Brown Coalfield of Primorskii Krai. The second stage of extraction using as a co-solvent of chloroform showed no significant qualitative difference samples. However, significantly higher mass yield of substances were observed. This stage's extracts marked as "Sample number.2 +d" in positive mode and "Sample number.2 -d" in negative mode.

The third extraction step, when most of the non-polar compounds have been already removed, and as a co-solvent, ethanol was used, there was a significant increase in diversity of extracts. In addition there was a significant qualitative difference in these extracts yields (Table 2).

Table 2 Total yields of SCF extractions for the different coals sample

Code	MassA, mg	MassB, mg	MassC, mg	Yield , mg	Yield, %
1315	32.7 ± 1.5	131.3 ± 2.8	150.9 ± 3.3	314.8 ± 17.0	1.57 ± 0.03
1318	102.4 ± 3.3	220.8 ± 6.0	104.1 ± 2.9	427.3 ± 21.8	2.14 ± 0.03
1319	78.2 ± 3.3	28.5 ± 1.4	97.9 ± 3.9	204.6 ± 15.3	1,02 ± 0.04
1321	11.6 ± 0.9	62.7 ± 3.9	17.9 ± 1.1	92.3 ± 11.0	0.46 ± 0.06
1322	14.1 ± 0.4	22.8 ± 0.5	12.0 ± 0.4	49.0 ± 2.4	0.25 ± 0.02
1323	24.7 ± 1.4	73.0 ± 3.3	88.8 ± 6.4	186.5 ± 19.2	0.93 ± 0.05
1324	104.5 ± 3.2	158.8 ± 14.2	141.3 ± 11.2	404.6 ± 50.0	2.02 ± 0.06
049/10	15.7 ± 4.0	122.7 ± 33.4	26.2 ± 6.7	164.6 ± 74.6	0.82 ± 0.23

The obtained mass spectra of these extracts would be used for identification and comparison of coal deposits. Greater similarity of the results of these spectra may indicate that once a similar ecosystem in these regions. RAMAN spectroscopy data was not helpful because of the too large signal of the carbon that makes undetectable other signals.

CONCLUSION

Pressure changes and addition of co-solvent possess most significantly influence on extraction, while influence of temperature is not so important for this process. Supercritical extraction of coal is highly selective and could be used for demand in the chemical industry compounds such as milicopidine and may be other. Supercritical carbon dioxide extraction with co-solvent ethanol could be used for characterization of different coalfields and probably could help to understand similarity in ecosystems of different regions in the past.

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