

<https://doi.org/10.3176/oil.2000.3.03>

SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF ESTONIAN OIL SHALE

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*Results on the application of supercritical carbon dioxide extraction (SFE) at different temperatures are presented, and comparison with classical Soxhlet chloroform extracts is made. Pure carbon dioxide extracted preferably *n*-alkanes, whereas modifying of the fluid with methanol intensified the extraction of more polar compounds and increased as a result total yield of extract. Increasing of SFE temperature had the same influence on the yield of extract, however, already at 200 °C partial heterolytic cracking of the kerogen of kukersite started. The similarity of composition and relative distribution of *n*-alkanes, *n*-alkanones-2, *n*-alkylbenzenes and *n*-alkylcyclohexanes in both SFE and Soxhlet extracts of kukersite was observed.*

Introduction

The composition of extractable organic matter (OM) of oil shales is the source of geochemical information about the biogenic precursors of OM and transformation of the latter in the Earth's crust. Solid-liquid Soxhlet extraction using different solvents and mixtures of them is a routine method of oil shale extraction. Among new extraction techniques developed over recent years supercritical fluid extraction (SFE) offers considerable advantages regarding expenditures of time and hazardous solvents. Due to the capacity of supercritical fluid to penetrate into porous media, SFE has been suggested as an ideal method for the recovery of encapsulated or included components in environmental samples. Supercritical carbon dioxide seems to be the fluid preferably used for extraction of natural objects: soils [1], rocks [2], and oil shales [3, 4].

Total yields of carbon dioxide extracts depend in great extent on the nature of inorganic matrix and are lower for oil shales with high clay mineral content [5]. Pure carbon dioxide extracts from oil shales predominantly *n*-alkanes,

whereas modification of the fluid with methanol increases its extraction power, and branched alkanes and polycyclic hydrocarbons (steranes and triterpanes) are extracted more completely [6]. The yields of SFE extracts from studied oil shales did not reach the yields obtained using the Soxhlet extraction. Despite of that, the geochemical parameters calculated on the basis of composition of *n*-alkanes and isoprenoids were similar in both extracts as well as the stereoisomeric composition of polycyclic biomarkers (steranes and triterpanes) [5, 6]. The latter deserves attention as useful in correlation studies of oils and oil source rocks because SFE extraction of polycyclic biomarkers from the rock does not need special sample preparation. Combination with high temperatures for extraction helps to release the trapped components and increase the yield.

To estimate the correlation between compositions of different compound classes of extractable OM of Estonian oil shale kukersite isolated by conventional Soxhlet extraction and SFE the present study has been carried out.

Experimental

The sample of Middle Ordovician oil shale kukersite was taken from the commercial B-layer of the *Sompa* mine, Estonia. Crushed and powdered oil shale was extracted exhaustively in the Soxhlet apparatus with chloroform and, after treatment with hydrochloric acid, with benzene/methanol (3 : 1) mixture. From the extracts obtained neutral compounds were isolated and, using thin layer chromatography (TLC), separated into four fractions: (1) saturated hydrocarbons, (2) aromatic hydrocarbons, (3) neutral heteroatomic compounds, (4) polar compounds.

SFE with carbon dioxide and modified carbon dioxide was performed on a self-made extractor (an HHP 4001 high-pressure pump, Laboratorni Pistoje, Czechoslovakia, and old chromatograph oven as a thermostat) that was able to run at temperatures up to 250 °C and pressures up to 45 MPa.

The pump was operated in the constant pressure to supply fluid through the stainless steel tubing (including a preheating coil placed inside the oven). The dynamic extraction of oil shale was performed using a 10-ml extraction cell with 20-mm frits on either end. For the pressure release, a frit restrictor was used for CO₂ to achieve a fluid flow rate of 0.5 to 1.5 ml/min. The extract was collected from the restrictor or outlet tubing into vial containing 2 ml of hexane. The extraction time varied up to 3 h. The solvent extracts of hexane were carefully evaporated to constant weight to determine the gravimetric yields.

Carbon dioxide, grade 4.6 (99.996 %) was from *Eesti* AGA.

TLC fractions of neutral compounds, methyl esters of organic acids and SFE extracts were analysed using capillary gas chromatography (GC)

(Chrom 5, Czechoslovakia) and gas chromatography mass spectrometer (GC-MS) (Hitachi 80B system, Japan). Different homologous series were identified using selected ion monitoring (SIM). Key ions to identify homologues were: $m/z = 71$ – *n*-alkanes, $m/z = 83$ – cyclohexanes, $m/z = 92$ – alkylbenzenes, $m/z = 58$ – *n*-alkanones-2.

Carbon isotope ratios were measured relative to the PDB standard (Finnegan MAT Delta E mass spectrometer).

Results and Discussion

First of all it must be mentioned that Soxhlet extraction and supercritical fluid extraction with carbon dioxide even with modifiers and at higher temperatures leave most of kerogen matrix untouched and bring out the soluble matter trapped in the shale matrix. The sample of Estonian oil shale appeared relatively deficient in soluble organic matter with yields on the level of 1 mg/g at 1 h of extraction time. Longer extraction time and/or increased temperature both increased the yield substantially (Fig. 1). However, even 2-h extraction with CO₂ at 150 °C was not exhaustive. The temperature for exhaustive extraction will depend on both the molecular characteristics of the analytes and the geochemical characteristics of the sample matrix.

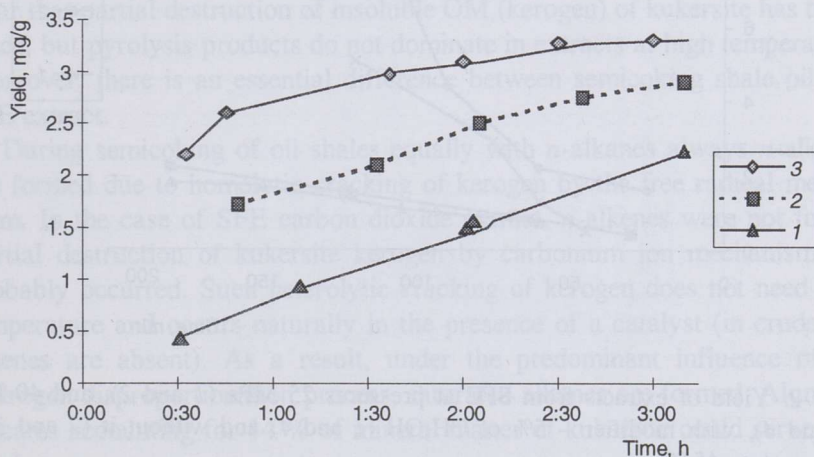


Fig. 1. Yields of extracts from SFE with pure carbon dioxide at different temperatures (1 – 45 °C; 2 – 100 °C; 3 – 150 °C) and pressure 40 Mpa

Variations in the extraction conditions (pressure, temperature) seem to result in both quantitative and qualitative differences for extracted samples. This supports the possibility of strong interaction of the soluble part with matrix components (both organic and inorganic). High-temperature

supercritical fluid extraction needs to be applied with care, and always compared with Soxhlet extraction, since the recovered hydrocarbons could be derived from different compartments within the sample matrix.

Estonian oil shale having predominantly the carbonate mineral matrix (70.8 rel.%) gave very similar yields of Soxhlet and carbon dioxide SFE extracts (1.6 and 1.8 mg/g oil shale [5]). Modifying of carbon dioxide with methanol increased the yield of extract several times (Fig. 2). This is possibly indicative of the co-extraction of compounds conventionally extractable separately with chloroform and, after treatment with hydrochloric acid, with benzene/methanol mixture. Really, by the composition and relative distribution of *n*-alkanes pure carbon dioxide extract of kukersite (Fig. 2,1) may be identified as its chloroform extract, and carbon dioxide/methanol extract is similar to the sum of chloroform and benzene/methanol extract (Fig. 2,2). This shows relatively weak interaction between mineral matrix and soluble part of organic matter for kukersite.

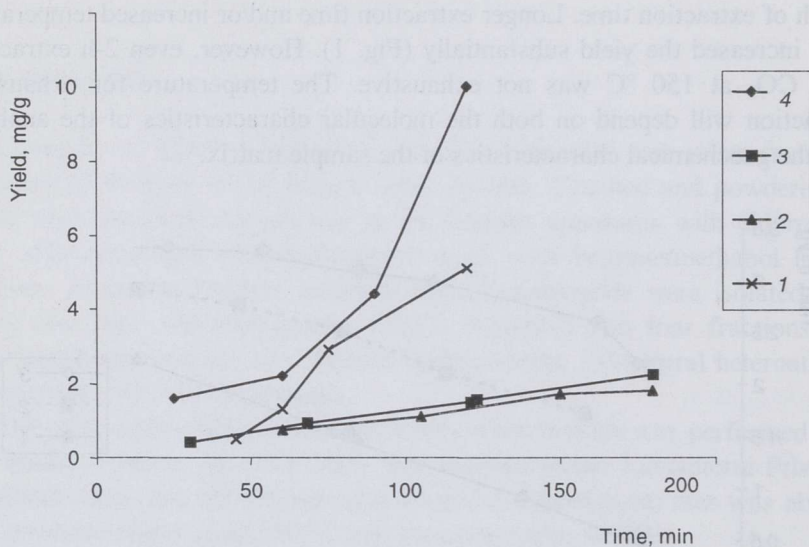


Fig. 2. Yield of extracts from SFE at pressures 25 MPa (1 and 2), and 40 MPa (3 and 4), with modifier – 5% of CH₃OH (1 and 4) and without it (2 and 3) at temperature 45 °C

Such geochemical parameters as carbon predominance index (CPI) and pristan-to-phytane ratio are comparable for the named pairs of extracts (the Table). However, other isoprenoid coefficients show that pure carbon dioxide extracts predominantly *n*-alkanes and modifying of it with methanol intensifies extraction of isoprenoid alkanes and the ratios of pristane and phytane to nearest homologues of *n*-alkanes (C₁₇ and C₁₈) increase (the Table).

Geochemical Parameters on the Basis of Extract Composition and Carbon Isotope Composition Data

Parameter	Extraction conditions			
	SFE, CO ₂	Soxhlet, chloroform	SFE, CO ₂ + MeOH	Soxhlet, chloroform + B/M
CPI of <i>n</i> -alkanes	1.44	1.52	1.42	1.33
Pristane/phytane	1.25	1.12	1.25	1.23
Pristane/ <i>n</i> -C ₁₇	0.20	0.34	0.52	0.84
Phytane/ <i>n</i> -C ₁₈	0.27	0.48	0.59	0.58
(Pristane + phytane)/(<i>n</i> -C ₁₇ + <i>n</i> -C ₁₈)	0.22	0.39	0.56	0.72
< <i>n</i> -C ₁₇ /> <i>n</i> -C ₁₇	0.97	0.81	0.30	0.37
δ ¹³ C _{PDDB} ‰	-31.7	-31.8	-31.5	-31.2

As it was shown (Fig. 1), the increase in the extraction temperature results in increasing the extract yield, which can be explained either by increasing solubility of extractable compounds or by the possibility that the compounds are released due to thermally induced structural changes in the matrix. However, by GC data the composition of extract obtained already at 200 °C is enriched with low-molecular *n*-alkanes and becomes similar to the composition of semicoking oil of kukersite (Fig. 2,3). From this it becomes clear that partial destruction of insoluble OM (kerogen) of kukersite has taken place, but pyrolysis products do not dominate in extracts at high temperature. Moreover, there is an essential difference between semicoking shale oil and SFE extract.

During semicoking of oil shales equally with *n*-alkanes always *n*-alkenes are formed due to homolytic cracking of kerogen by the free radical mechanism. In the case of SFE carbon dioxide extract, *n*-alkenes were not found. Partial destruction of kukersite kerogen by carbonium ion mechanism has probably occurred. Such heterolytic cracking of kerogen does not need high temperature and occurs naturally in the presence of a catalyst (in crude oils alkenes are absent). As a result, under the predominant influence of the hydrogen disproportionation process, saturated alkanes are formed. Alumino-silicates accounting for 14 % of mineral matter of kukersite could serve as a catalyst.

n-Alkanes isolated from kukersite by conventional Soxhlet extraction as well as by SFE have one trait in common, namely strong odd/even predominance in their relative distribution (carbon predominance index (CPI) >1) which is characteristic of biogenic *n*-alkanes and is being preserved in immature OM. Odd/even predominance is characteristic of the composition of *n*-alkylbenzenes and *n*-alkylcyclohexanes ("odd" alkyl substituents) and *n*-alkanones-2, too (Figs 3 and 4).

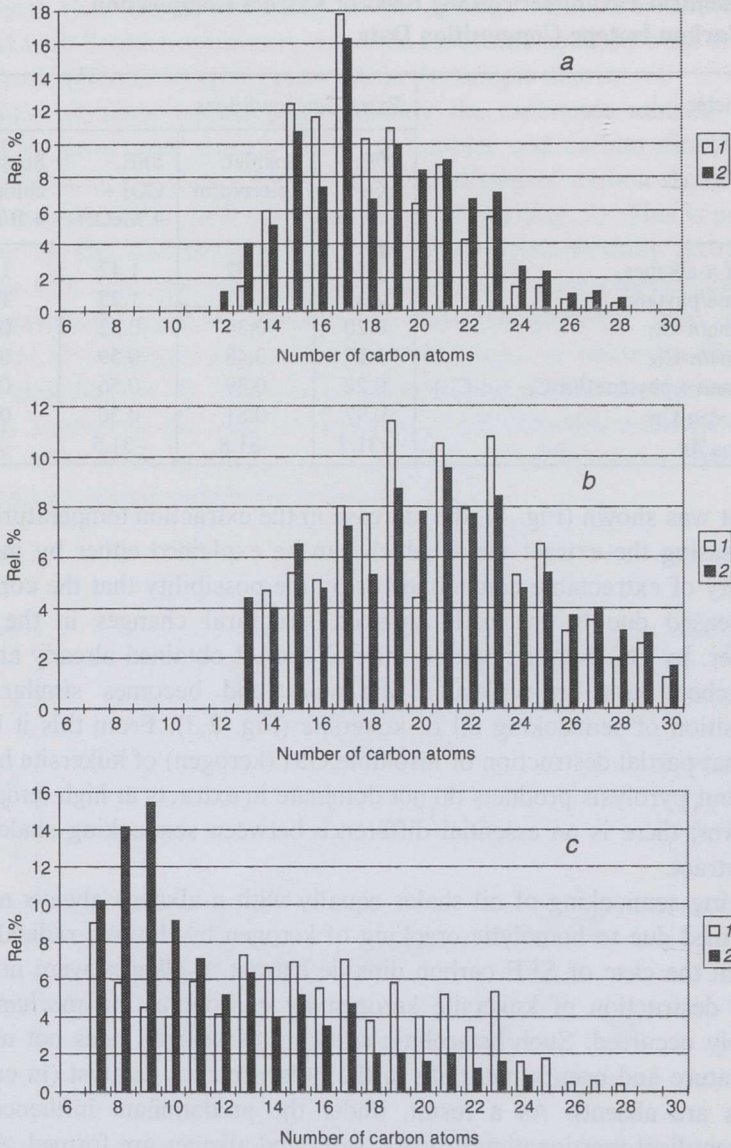


Fig. 3. Relative distribution of *n*-alkanes in: *a* – SFE with carbon dioxide and Soxhlet chloroform extracts; *b* – SFE with carbon dioxide/methanol and Soxhlet chloroform + benzene/methanol extracts; *c* – SFE with carbon dioxide at 200 °C and semicoking oil (1 – SFE extract, 2 – Soxhlet extract)

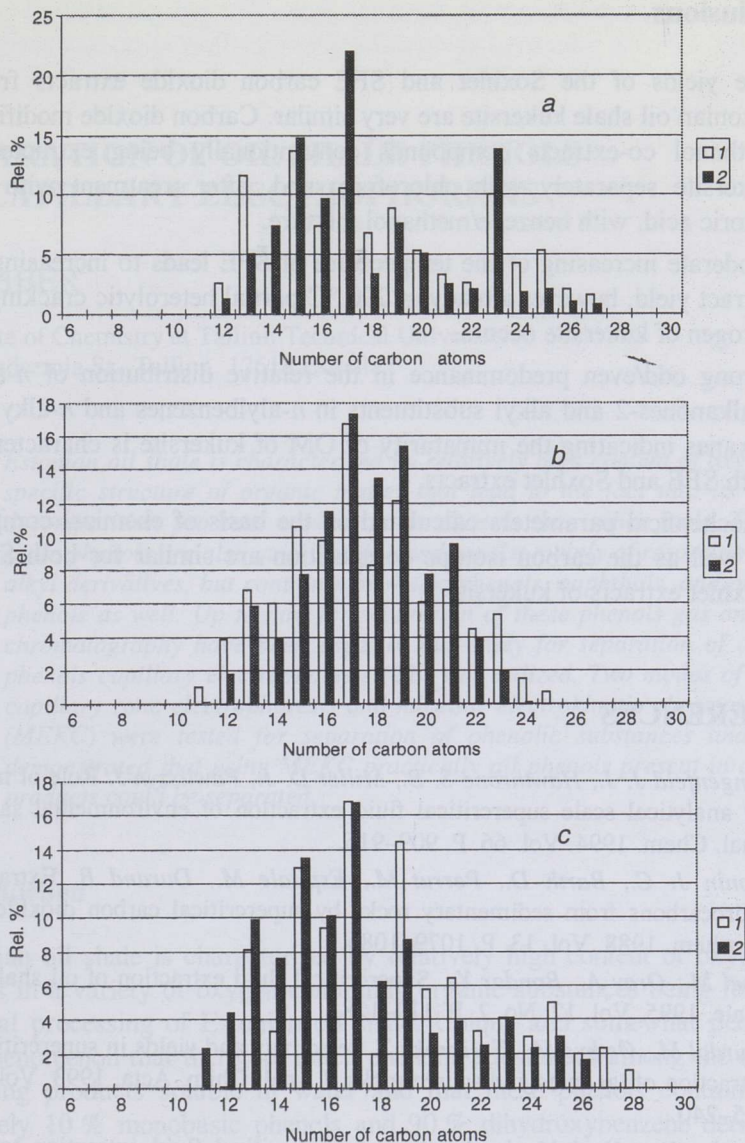


Fig. 4. Relative distribution of: *a* – *n*-alkylbenzenes; *b* – *n*-alkylcyclohexanes; *c* – *n*-alkanones-2 (1 – SFE with carbon dioxide/methanol, 2 – Soxhlet chloroform (*a* and *c*) or benzene/methanol (*b*) extract)

Side by side with the similarity between molecular composition of Soxhlet and SFE extracts of kukersite, the similarity between their carbon isotope composition was observed (Table). $\delta^{13}\text{C}_{\text{PDB}}$ values of SFE pure carbon dioxide and Soxhlet chloroform extracts in which *n*-alkanes predominate are naturally lower than the same values of SFE modified with polar compounds and Soxhlet extracts isolated with more polar solvents.

Conclusions

- The yields of the Soxhlet and SFE carbon dioxide extracts from the Estonian oil shale kukersite are very similar. Carbon dioxide modified with methanol co-extracts compounds conventionally being extracted from kukersite separately with chloroform and, after treatment with hydrochloric acid, with benzene/methanol mixture.
- Moderate increasing of the temperature of SFE leads to increasing of the extract yield, however already at 200 °C partial heterolytic cracking of the kerogen of kukersite occurs.
- Strong odd/even predominance in the relative distribution of *n*-alkanes, *n*-alkanones-2 and alkyl substituents in *n*-allylbenzenes and *n*-alkyl-cyclohexanes indicating the immaturity of OM of kukersite is characteristic of both SFE and Soxhlet extracts.
- Geochemical parameters calculated on the basis of chemical composition as well as the carbon isotope composition are similar for both SFE and Soxhlet extracts of kukersite.

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Presented by J. Kann

Received January 21, 2000