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Mild Supercritical-Gas Extraction from Low-Rank Coals: Separation, Spectroscopy, and Composition of Alkane Products

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ABSTRACT

In the separation by silica-gel chromatography of the total-alkane fractions of supercritical-gas (SCG) extracts of Turkish lignites, and in the subsequent 5Å-molecular-sieve adsorption to yield the branched/cyclic alkane subfraction, progress may be monitored by gas-liquid chromatography (GLC) and ^1H nuclear-magnetic-resonance (NMR) spectroscopy. Saturated aliphatic hydrocarbons identified by gas chromatography/mass spectrometry from one lignite include normals n-C_{13} to n-C_{33} inclusive, acyclic isoprenoids C_{18}, C_{19}, and C_{20}, and two C_{31} pentacyclic (triterpane) and one (C_{15}) dicyclic cycloalkanes. The distributions of n-alkanes depend more on extraction conditions than do the distributions of acyclic isoprenoids and cycloalkanes. Overall, batchwise SCG extraction of low-rank coals with toluene or tetrahydrofuran at about 350°C appears to cause little thermolysis and can yield relatively large quantities of paraffinic hydrocarbons, representative of the original coals, and useful as geochemical markers.

INTRODUCTION

Organic Matter in Coals

Coals, lignites and related materials have elemental compositions dominated by carbon, hydrogen and oxygen, together with smaller percentages of a wide range of elements. Most coals are formed under non-marine conditions, while the majority of acknowledged source beds for liquid hydrocarbon generation were deposited in marine environments and contain organic matter from aquatic lower plants and bacteria, especially phytoplankton. Differences in chlorophyll content, for example, between lower and higher plants may be expected to give rise to differences in phytol and thus to the saturated isoprenoid hydrocarbons derived from coal and petroleum.

While the chemical structure of the organic part of the original fossil fuels is complex, there is appreciable evidence for the presence of aromatic and polycyclic aliphatic rings and, more recently, of alkyl side chains. Most processes for conversion of solid fuels to liquid fuels may be roughly classified as direct hydrogenation, complete hydrogenation followed by synthesis, partial pyrolysis (with or without appreciable hydrogenation), or solvent extraction.

SCG Extraction of Coals

Among the more recent variants of the partial pyrolysis approaches to coal liquefaction by solution in specific solvents, extraction by low-molecular-weight solvents compressed into the supercritical state is a promising development. Indeed, solvent extraction of coals and other carbonaceous materials with a compressed gas having its critical temperature close to the extraction temperature can potentially provide an alternative economic process to pyrolysis for obtaining chemicals and liquid fuels (1,2). Near the critical temperature of the gas, the concentration of solute markedly increases with pressure. Moreover, the dissolved material can be removed more readily from the residue than with liquid solvents and may be precipitated by reduction of the solvent gas pressure (3). Thus, at temperatures as low as 350°C, the presence of a supercritical gas (SCG) can vapourise coal liquids which would otherwise either not distil or do so with appreciable decomposition;

for example, with toluene as solvent (largely recoverable), 25% or more of the original coal can be extracted and/or liquified (4).

Structures of the aromatic material obtained in high yield by such SCG extraction of coals (5,6) have been taken as evidence as to the primary (7) structure of coal. Crucial to this argument is the proposal that the extraction conditions are generally so mild that the material released suffers little or no further thermolysis (4,8). SCG extraction is believed to allow material of high molecular weight to be released from the coal matrix by the breaking of heteroatom or alkyl-group bridges between the substituted aromatic polynuclear entities or 'clusters' which are joined in the original structure (5,6). These high-molecular-weight compounds, which are too involatile to distil (and in any case would decompose first), are dissolved from the coal pores by the action of the SCG and so are thought to be representative of the structural types present in the coal (5,6).

Since the nature of the original aromatic material is, of course, unknown, evidence must be adduced from the saturated hydrocarbons produced by the extraction/liquefaction of the coal (9); although most of these alkanes may have been entrapped, some will be liberated by bond breakage. The chemical reactions undergone by these coal alkanes during maturation are comparable with those observed for the alkanes of other sediments and so are better understood (9) than for the aromatics. Thus, a knowledge of the detailed composition of the alkane hydrocarbons both provides convincing evidence of the mildness of the SCG extraction process (in the sense of minimizing pyrolysis) and also is potentially a rich source of organic geochemical information about the original fossil fuel. While some SCG processes continuously recycle the solvent and some incorporate hydrogenation of unsaturateds, we are concerned here with a static process without appreciable accompanying hydrogenation (other than that by free radicals generated by coal thermolysis).

EXPERIMENTAL

Materials and Mode of Extraction

Supercritical toluene or tetrahydrofuran (THF) extracts of three Turkish lignites covering a range of coal rank, prepared as described in references (10,11), were supplied by Prof. Aral Olcay (Ankara University). The batchwise SCG extraction procedure was as follows: a 30 g sample of each lignite (250 BS mesh) was heated for 30 minutes with 200 g solvent at temperatures between 340 and 400°C and pressures between 3 and 17 MPa in a 1-litre autoclave. Yields of solvent-free extract were between 14 and 25 wt% of the dry ash-free coals.

A fourth sample, Montan wax from a Turkish lignite, provided a control, in that alkanes could be extracted straightforwardly by Soxhlet over one day (at the temperature of the boiling solvent) with little or no pyrolysis. Sources and extraction yields are summarised in Table 1.

Separation of the Extracts

Total-alkane fractions of the extracts were separated by chromatography on silica gel of the fraction soluble in n-hexane (4,10) or n-pentane (12). One-gram portions dissolved in 2 cm^3 n-hexane were eluted with distilled n-hexane (flow rate of 0.05 cm^3/s) through a 1 m x 30 mm I.D. glass chromatographic column containing distilled n-hexane and 140 g of silica gel (60-120 mesh, dehydrated at 150°C for 5 h). UV (30 000 - 45 000 cm^{-1}) and, particularly, ^1H NMR (range 3-9 ppm downfield from TMS) spectra characteristic of unsaturated hydrocarbons enabled termination of elution of saturates (collected in 10 cm^3 fractions) through the column to be detected.

Further separation of a branched/cyclic alkane subfraction from some of these total-alkane fractions was effected by adsorption on 5Å molecular sieve. This was preferred to urea adduction, since effective separation (monitored by GLC and by 100 and 220 MHz

TABLE 1

Sources, Extraction Conditions and Yields of Alkanes

Coal (Turkish)	% Carbon of coal (dry ash-free)[b]	SCG extraction conditions			Total extract	Total alkane fraction	n-alkanes
		Solvent	Temperature °C	Pressure MPa	wt% of coal	wt% of coal	wt% of coal
Elbistan	58.9	Toluene	340	8	14.0	0.7	0.45
Elbistan	58.9	Toluene	400	16	24.1	2.0	0.8
Elbistan	58.9	THF	400	10	23.0	2.2	1.1
Seyitomer	65.3	Toluene	340	8	16.0	0.7	0.5
Tuncbilek	74.5	Toluene	400	16	23.1	2.0	ND[d]
Demirciköy[a] (Montan wax)	58.8	-	-	-	8.5[c]	0.05	IS[e]

[a] Soxhlet extraction for one day with 80:20 benzene/isopropanol (8.5% yield) 77°C

[b] Based on more representative samples than those reported in Reference 12

[c] Montan wax

[d] Not determined

[e] Insufficient sample

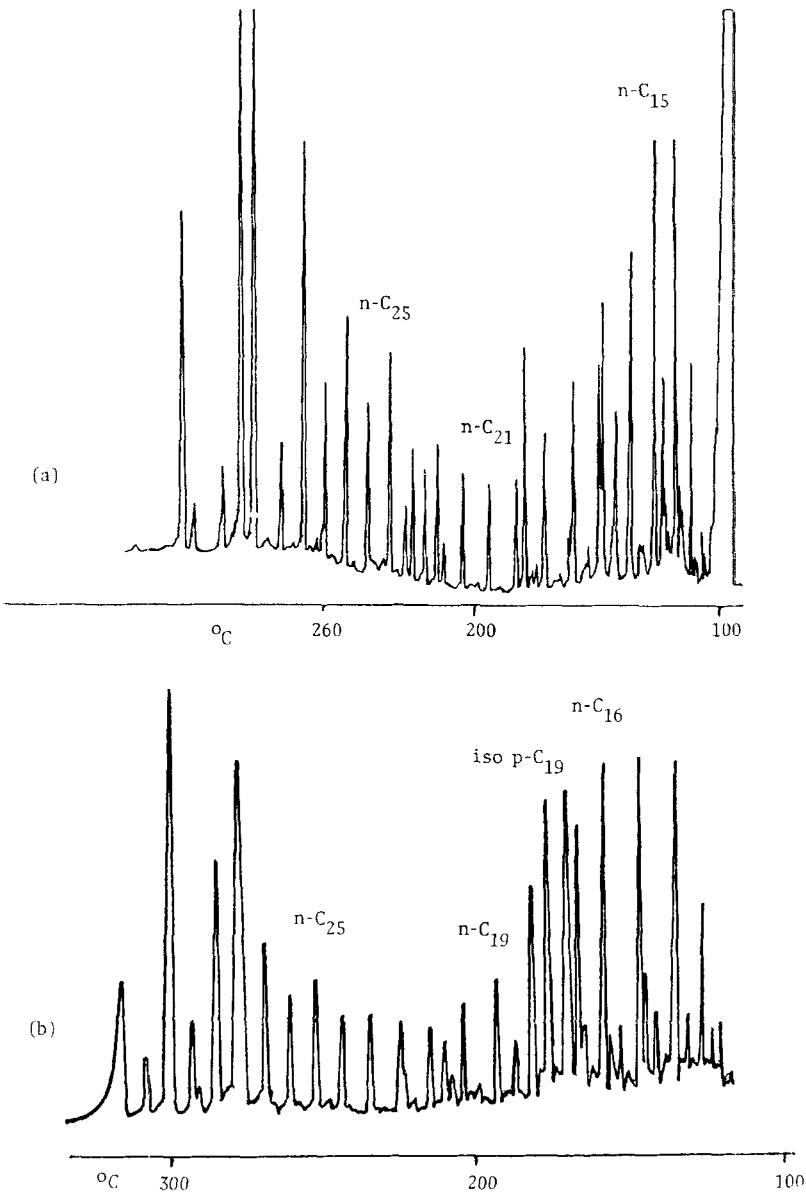

FIGURE 1. Demirciköy (Turkey) lignite (wax) total-alkane fraction: comparison of gas liquid chromatograms recorded with (a) 50 m x 0.25 mm glass WCOT capillary column; and (b) 4 m x 0.25 mm glass column packed with 30% eutectic on Chromsorb W.

^{1}H NMR) could be achieved in a single stage for a small quantity (0.5 g) of alkane fraction.

Analyses of the Alkane Fractions

Alkane fractions were analysed by gas chromatography (GC) with packed and capillary columns (4) and by combined GC/mass-spectrometry (MS). All samples were examined by GC: typically, on a preparative Pye 105 instrument with a flame-ionization detector, 300°C injection temperature and nitrogen carrier gas. The 4 m x 5 mm I.D. glass column was packed with 30% eutectic salt (54.5 wt% KNO_3, 27.3 wt% $LiNO_3$ and 18.2 wt% $NaNO_3$ (from Analabs) (13)) supported on Chromosorb W. The flow rate was 46 mm/min, and the temperature was programmed at 8°C/min over 100-350°C; the resolution was about 10^4 theoretical plates. Furthermore, with the same Pye 105/FID instrument the Demirciköy Montan-wax and Elbistan lignite branched/cyclic alkanes were also examined on a 25 m x 0.3 mm I.D. glass WCOT capillary column coated with OV-1, temperature programmed at 2.5°C/min over 100-260°C (Montan wax, Fig. 1).

Limited GC/MS component identification was undertaken for some of the alkane fractions. For the branched/cyclic fractions of Elbistan lignite extracts at the various conditions, mass spectra were recorded for compounds that emerged from the described WCOT capillary column coupled to a Finnigan 4000 mass spectrometer. Fragmentograms were either computer-reconstructed GC traces from the total ion current (TIC) or amplified current from a selected ion present from one or more compounds. GC/MS identification of alkanes from the Soxhlet extracts of Montan-wax (from Demirciköy lignite) was carried out on a 70 eV AEI MS50 mass spectrometer with both the OV-1 and eutectic packed columns described above.

RESULTS AND DISCUSSION

SCG extraction, as we have noted previously (12), releases a much larger proportion of alkanes (of all types) than conventional solvent extraction of humic coals (which do not contain Montan wax); extraction of the less common sapropelic coals yields Montan wax, which contains a large proportion of alkanes. Thus, alkanes SCG-extracted from humic coals are potential indicators of extraction conditions.

n-Alkanes

Even though SCG extraction of coals produces distributions of n-alkanes, C_nH_{2n+2}, which depend on geological origins and which can indicate the severity of the extraction procedure, it has been shown (12) that the commonly used Carbon Preference Index $[CPI$, defined as $\frac{1}{2}\{odd(C_{15}-C_{29})/even(C_{14}-C_{28})+odd(C_{15}-C_{29})/even(C_{16}-C_{30})\}]$ is not a valid indication of coal rank when derived from products of SCG extraction of coals--even at conditions as mild as 350°C. The low content of the lower ($C_{10}-C_{15}$) alkanes (Fig. 2) together with the small concentration of alkenes suggest that any degradation of the alkane fraction at 340°C is slight. (For example, extraction at 400°C shifted the n-alkane distribution to lower carbon numbers (Fig. 2), reduced their odd-over-even predominance (Fig. 2), and generated more significant concentrations of alkenes (10).) The "extra" n-alkanes found in products of SCG extraction at 340°C can hardly have been generated from pyrolysis of fatty acids since such acids suffer very little degradation during SCG extraction at around 350°C (14); the alkanes are either liberated from deep within the pore structure of the coal or are generated by thermolysis of long-chain alkyl structures bonded to the coal matrix. For the wax from Demirciköy lignite, mass spectra patterns (which also resembled those for carbonization products of higher-rank coals) allowed identification of n-alkanes from n-C_{13} to n-C_{33}; furthermore, their distribution differed appreciably from those of the SCG-extracted Elbistan and Seyitomer lignite n-alkanes (Fig. 2, from Ref. 12). Additionally one sees in Fig. 2 that the distributions of n-alkanes in the SCG extracts of the Elbistan and Seyitomer lignites at the same temperature (340°C) are rather similar to each other and mark-

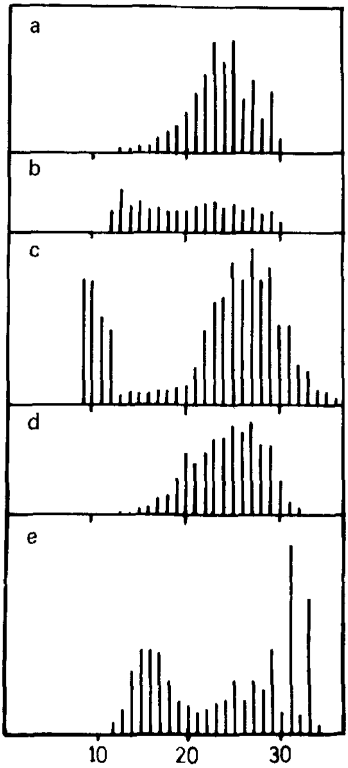

FIGURE 2. Distributions of n-alkanes in paraffinic fractions of coals: (a) Elbistan lignite, SCG extraction with toluene at 340°C(12) (b) Elbistan lignite, SCG extraction with toluene and THF at 400°C(12); (c) Elbistan lignite, Soxhlet extraction; (d) Seyitomer lignite, SCG extraction with toluene at 340°C(12); (e) Wax from Demirciköy lignite, Soxhlet extraction.

edly different from those of the Elbistan soxhlet and 400°C-SCG extractions.

Saturated Acyclic Isoprenoids

With coals of higher rank, saturated acyclic isoprenoids, C_nH_{2n+2}, are generated by SCG extraction in several times the quantity yielded by Soxhlet extraction (12) (although they form a bigger

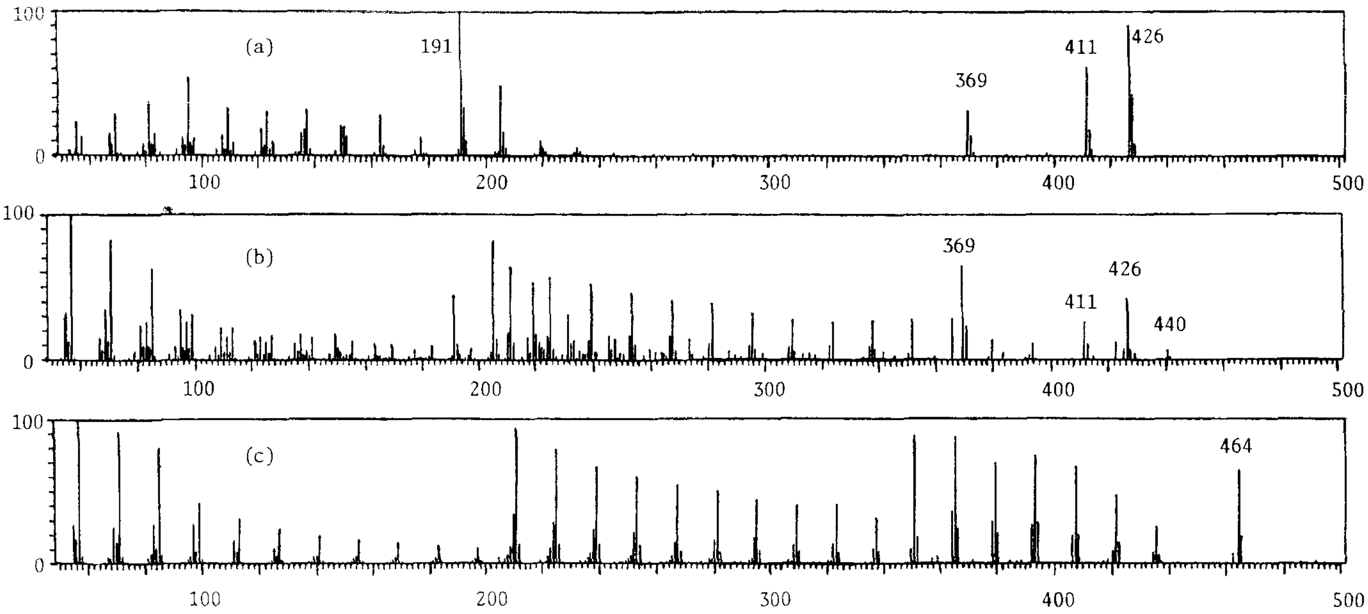

FIGURE 3. Demirciköy (Turkey) lignite (wax) total-alkane: mass spectra of three of the TIC GC (eutectic packed column) peaks, attributed to (a) 17αH $C_{31}H_{54}$; (b) n-$C_{30}H_{62}$, 17βH pentacyclic triterpane $C_{31}H_{54}$; and (c) n-$C_{33}H_{68}$.

percentage of the total alkanes obtained with Soxhlet extraction). At least three (C_{18}, C_{19} and C_{20}) were identified from retention data and mass spectra of the wax sample from the Demirciköy lignite (Fig. 3) and six (C_{14}, C_{15}, C_{16}, C_{18}, C_{19} and C_{20}, with four of these confirmed by MS) in all three Elbistan lignite extracts described in Table 1. Only GC retention data were used to identify the various acyclic isoprenoids in theSeyitomer (C_{15}, C_{16}, C_{18}, C_{19}, and C_{20}) and Tuncbilek (C_{13}, C_{14}, C_{15}, C_{18}, C_{19}, and C_{20}) SCG extracts.

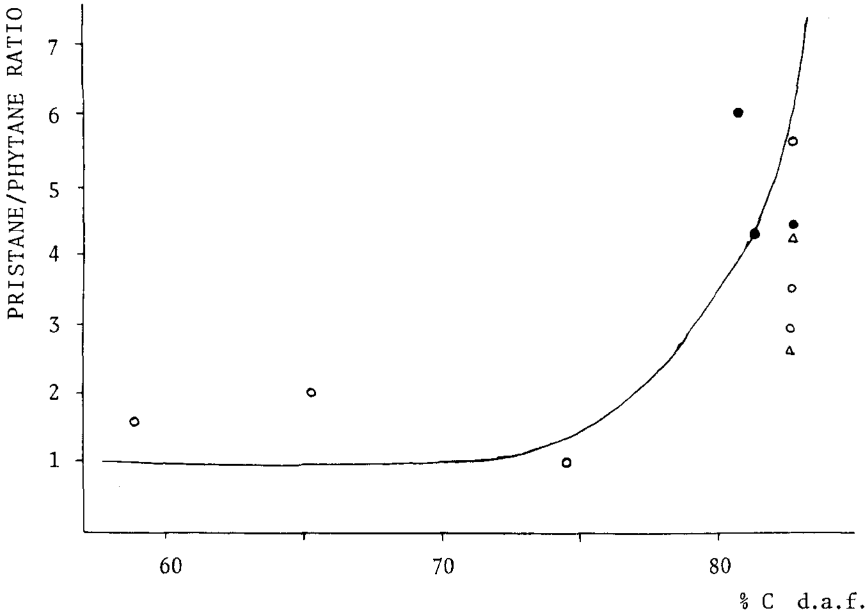

FIGURE 4. Graph against carbon content (d.a.f. basis) of ratio of pristane to phytane in toluene SCG extracts (o), low-temperature tars (•), and Soxhlet extracts (12) (Δ); coals were from Britain, Turkey and U.S.A. The line is that determined by Brooks et al (16) from Soxhlet extracts of many Australian coals (above 85%C, their Pr/Ph ratio decreases owing to the increase in phytane concentration).

The Pr/Ph ratio between the concentrations of two of these isoprenoids, pristane (C_{19}) and phytane (C_{20}), is shown for the SCG (toluene) extracts of the three lignites (Elbistan, 340°C; Seyitomer, 340°C; and Tuncbilek, 400°C) in Fig. 4 along with that ratio for various tars and other coals (12). The Pr/Ph ratio does not seem to vary much with conditions of extraction of a given coal (Fig. 4); samples of diverse origin extracted in different ways fall close to a line drawn for a range of Soxhlet-extracted Australian coals (16). However, SCG extraction releases smaller amounts of these isoprenoids (but in essentially the same Pr/Ph ratio) than when lignites are subjected to prolonged heating at 300°C for three days in the absence of solvent (15). In general, Pr/Ph ratios for the SCG-extracted lignites (left-hand side of Fig. 4) are in accord with the correlations with age for conventional extracts of other coals found by Brooks et al (16).

Sources other than phytol have been suggested (17) for saturated isoprenoids, particularly terpenoids and sesquiterpenoids. Thus, dycopane and solanesol may be precursors of C_{17} (18), while Spyckerelle (19) has proposed that C_{25} terpenes could lead to C_{21}-C_{25} isoprenoids. However, since C_{17} and C_{21}-C_{25} isoprenoids are all scarce in coal (as confirmed by the described analyses of our Soxhlet and SCG extracts), neither of these possible routes can be important for coals.

Cyclic Alkanes

Detailed examination of the mass spectra from GC peaks of the Elbistan lignite (20) branched/cyclic fractions from all three SCG extractions showed appreciable evidence of triterpanes (six pentacyclics, C_nH_{2n-8}), some of a 5α-sterane (tetracyclic, C_nH_{2n-6}) but little sign of mono-, di- and tricyclic alkanes. From mass spectra of the total-alkane fraction of Demirciköy Montan wax, we also find rather low contents of mono-, di-, tri-, and tetracyclics with specific identification of a C_{15} dicyclic and a C_{24} tetracyclic; two $C_{31}H_{54}$ triterpanes (17αH and 17βH) were also detected [Fig. 3

(a) and (b)]. Since the 17αH C_{31} cyclic alkanes had a peak about as intense as those of n-C_{33} and n-C_{31}, it is thought that they form a relatively high proportion of the source material (∿ 3 ppm), with the 17αH conformation predominating over the 17βH (approximately in the ratio 10:1). For terpane-type cyclic alkanes with 17αH or 17βH configuration the most abundant ions are generally at m/e 191 and (149 + 14n), where n is the number of carbons in the substituent.

Thus, pentacyclic cycloalkanes were observed in both Elbistan lignite and Montan wax, though in considerably smaller amounts than for higher-rank coal-tar carbonization products (20). Much lower proportions of mono-, di- and tri-cyclics (which can result from degradation of pentacyclics) occur in the lignites and wax than in high-yield carbonization derivatives of higher-rank coal (20). These new cycloalkane data, like those for the isoprenoids (16), fit well with the correlations noted by Gallegos (21), i.e., that the 17βH, 21βH hopanes tend to decrease in concentration with age of source while the concentrations of 17αH, 21βH hopanes increase. Hopanes, pentacyclic alkanes, are the most widespread group of geolipids; they are reduced forms of triterpenoid constituents of living organisms and their relative epimer concentrations depend markedly on degree of maturation.

CONCLUSIONS

For extraction of organic matter from lignites, 350°C SCG is more effective (in the sense of involving less cracking and yielding more extract) than Soxhlet, but the additional alkanes do not originate, during SCG extraction, from the fatty acids. The larger recovery for the SCG procedure presumably results from enhanced mass transport of the supercritical fluid (viscosity and diffusivity) and/or some limited solvent (chemical) interaction with the coal.

Whereas distributions of isoprenoids and cycloalkanes are to a fair degree independent of the severity of the extraction process (and are thus particularly valuable as organic geochemical indicators), n-alkanes are sensitive to cracking, so that their distributions depend on the mode of extraction as well as on the origin. Therefore, for low-rank fossil fuels, n-alkanes from the rather gentle SCG extraction at 350°C can form the basis of reliable indications of maturity.

For Montan wax from Demirciköy lignite, combined GC/MS allows identification of 21 n-alkanes, three acyclic isoprenoids and three cycloalkanes; 27 n-alkanes, six acyclic isoprenoids and eight cycloalkanes were identified in Elbistan lignite SCG extracts.

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