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A COMPARATIVE STUDY OF NON-AROMATIC HYDROCARBONS FROM KUKERSITE AND DICTYONEMA SHALE SEMICOKING OILS

Abstract

Non-aromatic hydrocarbon fractions contained in the semicoking oil of two Estonian oil shales, kukersite and dictyonema shale, have been investigated using a combined chromatography-mass spectrometry technique. It has been established that the oils investigated are quite similar with respect to the qualitative composition of their hydrocarbon components, but rather different from a quantitative aspect. Alongside of *n*-alkanes and *n*-1-alkenes, which are typical for shale oils, several series of *n*-alkenes with a different position of double bond (specifically *n*-5-alkanes), dienes, isoprenoic alkanes, alkyl derivatives of cyclohexane, cyclohexene, cyclopentene and decahydronaphthalene have been detected. There is a good probability that some unusual cyclic hydrocarbons of the cyclododecane and cyclohexadecane series have been identified.

Introduction

A considerable amount of work has been performed on shale oils obtained by processing two principal oil shales of Estonia, kukersite and dictyonema shale. However, methods employed for elucidating chemical composition of these oils were often lacking in accuracy, and a comparative characterization of the oils was difficult due to differences in analytical procedures used. The objective of the present work was to obtain comparative data on the composition of kukersite and dictyonema shale oils prepared under identical conditions using a combined chromatography-mass spectrometry method.

Experimental

The oils investigated were obtained according to the Fischer Assay procedure, and, after extraction of phenols from the raw oils, the non-aromatic hydrocarbon fraction was separated by means of thin layer chromatography on silica gel, using *n*-hexane as an eluent. The yield of these fractions was 15.3% and 16.3% of the total oil produced by thermal treatment of kukersite and dictyonema shale, respectively.

Compositions of the produced fractions have been investigated using a Hitachi M-80B gas chromatographic-mass spectrometric system which has an Heliflex capillary column 30 m × 0.32 mm with bonded polydimethylsiloxane RSL-150. Additionally, an Hewlett Packard 5971A chromatomass system with a fused silica capillary column (also 30 m × 0.32 mm) DB-5 has been used. Identification of the

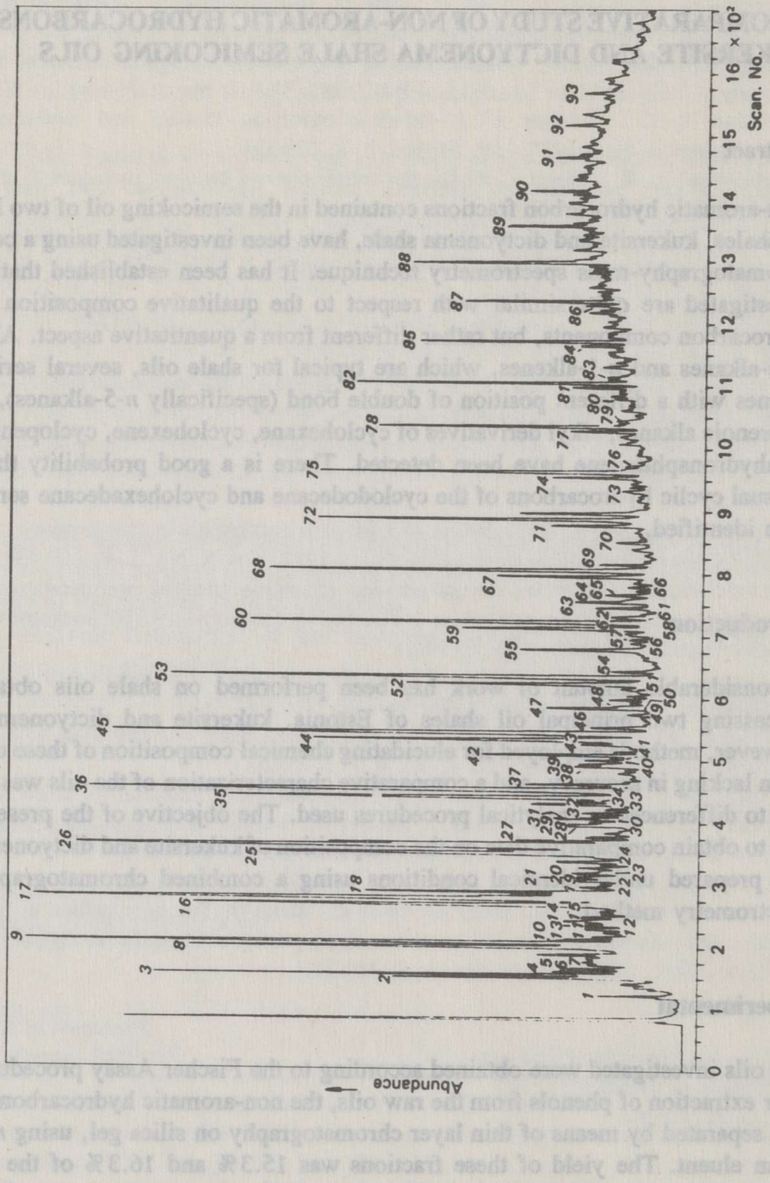
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Fig. 1. Chromatogram of the non-aromatic hydrocarbon fraction of the dictyonema shale semicoking oil (by Hitachi chromatomass system):
1 — *n*-nonane; *2* — *n*-1-decene; *3* — *n*-decane; *4* — alkylcyclohexene C_{10}; *5* — 2,6-dimethyl-nonane; *6* — butylcyclohexane; *7* — pentyl-cyclopentene; *8* — *n*-1-undecene; *9* — *n*-undecane; *10* — *n*-4-undecene; *11* — 2,6-dimethyl-decane; *12* — pentylcyclohexane and *n*-2,4-undecadiene; *13* — hexylcyclopentene; *14* — 2-methyl-2,4-decadiene; *15* — isoalkene C_{12}; *16* — *n*-1-dodecene; *17* — *n*-dodecane; *18* — 2,6-dimethyl-undecane; *19* — isoalkene C_{13}; *20* — hexylcyclohexane and *n*-2,4-dodecadiene; *21* — heptyl-cyclopentene; *22* — isoalkene C_{13}; *23* — isoalkane C_{13}; *24* — 2,6,10-trimethylundecane; *25* — *n*-1-tridecene; *26* — *n*-tridecane; *27* — *n*-6-tridecene; *28* — heptyl-cyclohexane; *29* — *n*-2,4-tridecadiene; *30* — octyl-cyclopentene; *31* — heptylcyclohexene; *32* — 2-methyl-1-tridecene; *33* — 2,6,10-trimethyl-dodecane; *34* — alkene C_{14}; *35* — *n*-1-tetradecene; *36* — *n*-tetradecane; *37* — *n*-5-tetradecene; *38* — octyl-cyclohexane; *39* — nonyl-cyclopentene; *40* — 2,6,10-trimethyl-tridecane; *41* — octyl-cyclohexene; *42* — isoalkane C_{15}; *43* — alkene C_{15}; *44* — *n*-1-pentadecene; *45* — *n*-pentadecane; *46* — *n*-5-pentadecene; *47* — nonyl-cyclohexane; *48* — decyl-cyclopentene; *49* — nonyl-cyclohexene; *50* — alkane C_{16}; *51* — alkene C_{16}; *52* — *n*-1-hexadecene; *53* — *n*-hexadecane; *54* — *n*-5-hexadecene; *55* — decyl-cyclohexane; *56* — 2,6,10-trimethyl-pentadecane; *57* — alkylcyclohexene C_{16}; *58* — alkene C_{17}; *59* — *n*-1-heptadecene; *60* — *n*-heptadecane; *61* — 2,6,10,14-tetramethyl-pentadecane; *62* — *n*-5-heptadecene; *63* — isoalkene C_{19}; *64* — isoalkane C_{19}; *65* — undecyl-cyclohexane; *66* — alkylcyclohexene C_{17}; *67* — *n*-1-octadecene; *68* — *n*-octadecane; *69* — *n*-(5 and/or 6)-octadecene and 2,6,10,14-tetramethyl-hexadecane; *70* — alkylcyclohexane C_{18}; *71* — *n*-1-nonadecene; *72* — *n*-nonadecane; *73* — alkylcyclohexane C_{19}; *74* — *n*-alkene C_{20}; *75* — *n*-alkane C_{20}; *76* — isoalkene C_{20}; *77* — *n*-alkene C_{21}; *78* — *n*-alkane C_{21}; *79* — isoalkene C_{21}; *80* — alkylcyclohexane C_{21}; *81* — *n*-alkene C_{22}; *82* — *n*-alkane C_{22}; *83* — isoalkene C_{22}; *84* — *n*-alkene C_{23}; *85* — *n*-alkane C_{23}; *86* — *n*-alkene C_{24}; *87* — *n*-alkane C_{24}; *88* — *n*-alkane C_{25}; *89* — *n*-alkane C_{26}; *90* — *n*-alkane C_{27}; *91* — *n*-alkane C_{28}; *92* — *n*-alkane C_{29}; *93* — *n*-alkane C_{30}

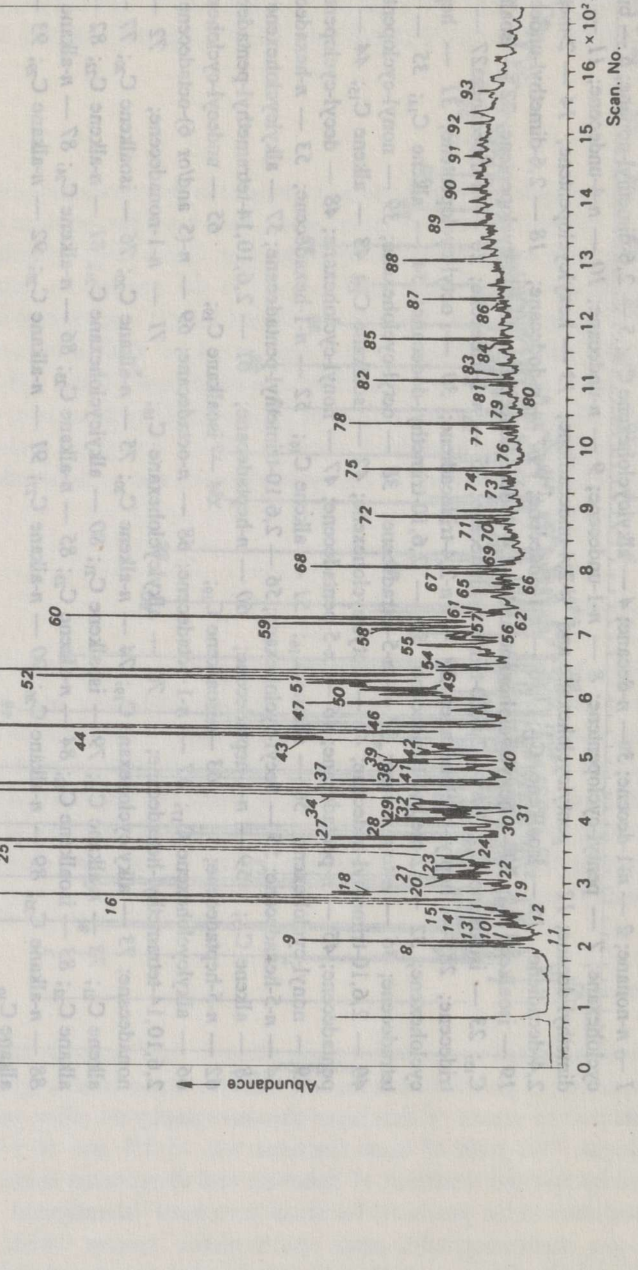

Fig. 2. Chromatogram of the non-aromatic hydrocarbon fraction of the kukersite semicoking oil (by Hitachi chromatomass system). See legend in Fig. 1.

compounds contained in the tested oil fractions has been carried out by using standard compounds and reference library data.

Results and Discussion

Chromatograms of the fractions obtained by a mass-selective detector are presented in Figures 1 and 2, together with peak identifications. Though these fractions are quite similar with respect to their qualitative composition, it is evident that the quantitative composition, specifically that of *n*-alkanes, is rather different. This can be associated with the chemical structure of initial kerogens. Thus, in the kukersite-derived oil, the concentration of aliphatic chains drops sharply after C_{17}. This confirms the important role of photosynthetic marine bioproduction in the origins of this shale [1]. In contrast, the dictyonema shale semi-coking oil *n*-alkane distribution is comparatively uniform when the distribution is based on the chain length. Therefore, a substantial contribution can be attributed to microbial bioproduction (chains C_{18}-C_{25}) during the kerogen formation [2-5].

There is a somewhat lower concentration ratio of *n*-1-alkenes to *n*-alkanes in the dictyonema shale oil than in the kukersite-derived oil. This is probably connected with the effect of aluminosilicates (which are characteristic of the dictyonema shale mineral matter) on the pyrolysis process [6, 7].

Data on the composition of low-boiling (up to C_{11}-C_{12}) compounds of the tested oils are not relevant since a considerable portion of these hydrocarbons is lost in the course of the oil fractionation by thin layer chromatography.

In the present case, the minor components of oils are of greater interest since their presence in these oils was formerly unknown or uncertain.

These minor components include three series of cycloalkyl alkanes: alkyl derivatives of cyclohexane (compounds C_{12}-C_{21} have been identified), alkyl cyclopentenes (C_{10}-C_{15}) and alkyl cyclohexenes (C_{13}-C_{17}). Among these, derivatives of cyclohexane prevail, especially in the range C_{14}-C_{17}. Their concentration is higher in the kukersite semicoking oil. The distribution of cycloalkyl alkanes according to C-number is similar to that of *n*-alkanes. This points to the possibility of the former being cyclization products of straight-chain hydrocarbons present in kerogens and primary oils.

If one considers the regular aliphatic isoprenoids (2,6,10...-methylalkanes), it seems that their concentration in the dictyonema shale processing oil has previously been overestimated. This is due to the overlapping of peaks in the case of ordinary gas chromatographic analysis. From Figure 1 it is evident that only iC_{13}-iC_{15} are present in significant concentrations in this oil. In total, iC_{11}-iC_{20} have been identified. The isoprenoic hydrocarbon content in the kukersite-derived oil is even lower. In neither case has iC_{17} been detected; its absence or a very low concentration is obviously connected with the specific character of thermal decomposition mechanism of the phytyl radicals [8].

It is characteristic of the normal alkenes of the oils investigated that, besides the usual *n*-1-alkenes, there are also *n*-5-alkenes present in considerable quantities (especially *n*-5-tetradecene and *n*-5-pentadecene). There are more compounds of this type in the kukersite semicoking oil than the dictyonema shale pyrolysis product.

In addition to the above-named compounds, some more "exotic" constituents of the oils have been identified, mostly by using the Hewlett Packard chromatomass system. Thus, the presence of a number of dienes (7-methyl-3,4-octadiene; 2-methyl-4,5-nonadiene; *n*-4,6-decadiene; 2-methyl-2,4-decadiene, *n*-2,4-undecadiene; *n*-2,4-dodecadiene; *n*-2,4-tridecadiene) has been established. Also, these oil fractions contain some cyclohexane derivatives with a double bond in the alkyl substituent, such as 1-methyl-4-(1-methylethylidene)-cyclohexane and 1-methyl-4-(1-methylethenyl)-cyclohexane. Besides hydrocarbons of the cyclohexane and cyclopentane series, some more complex cyclic hydrocarbons have been identified with a good probability, for example, 1-methyl-octahydropentalene, 1-ethyl-octahydro-7a-methyl-indene, 2,2-dimethyl-cyclopentyl-cyclohexane, 1,1-(1,2-ethandiyl)*bis*-cyclohexane, 2-methyl-decahydronaphthalene, and 1,5-, 1,6- and 2,6-dimethyl-decahydronaphthalenes.

Some quite unusual cyclic hydrocarbons (cyclododecane, ethylcyclododecane, 1-ethyl-2-methylcyclododecane and cyclohexadecane) seem to be present in the oil, at least judging by the high probability of their identification.

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