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LIQUEFACTION OF ESTONIAN OIL SHALE KEROGEN IN SUB- AND SUPERCRITICAL ETHER MEDIUM

1. EFFECT OF ETHER TYPE ON THE YIELD AND CHARACTER OF DECOMPOSITION PRODUCTS

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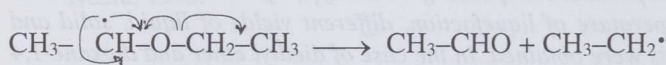
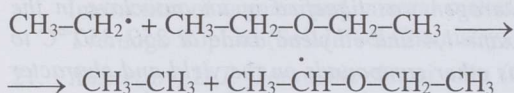
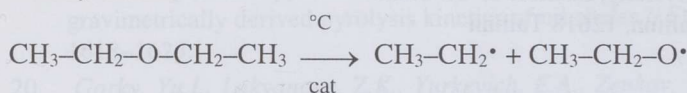
Estonian oil shale kukersite kerogen was liquefied in an autoclave in the presence of diethyl ether, dioxane-1,4 and ethylene oxide at 250–350 °C to investigate the effect of various ether compounds on the yield and character of decomposition products. Depending on the type of ether used as a solvent and on the temperature of liquefaction, different yields of liquid, solid and gaseous products were obtained. In the case of diethyl ether and dioxane-1,4 the products are comparable with those when benzene, n-hexane, ethanol and other conventional solvents were used at the same temperature. As an exception, ethylene oxide gave very high yield of the benzene-soluble product. At 350 °C kerogen was completely converted into liquid benzene-soluble and gaseous products, and no coke was formed. The yield of the liquid benzene-soluble product surpassed 100 %, on kerogen basis, demonstrating that on kerogen liquefaction diethyl ether, dioxane-1,4 and ethylene oxide realize not only their solvolytical but thermochemical potential as well evoking kerogen alkylation and oxyalkylation. On kerogen liquefaction in the ether medium liquid and gaseous products chemically less or more modified depending on the extent of bilateral reactions between kerogen and solvent may be obtained.

Ethers, commonly not used at high-temperature liquefaction processes of solid fuels are comparatively unreactive compounds compared with hydrocarbons, alcohols and other organic solvents. Ethers decompose on pyrolysis, and decomposition may occur even at lower temperatures when transferred into extreme conditions – supercritical state and close contact with reactive substances like kerogen. Free radicals formed may initiate various chemical reactions. Experiments have demonstrated that ether linkages present in coal itself or in the solvent added cleave when the coal is solubilized by thermolysis in oxygenates and α -olefin epoxides, and a high yield of alkylated and acylated products soluble in conventional solvents are obtained [1–3]. Long-term liquefaction of kukersite oil shale in autoclave at

250–300 °C using tetrahydrofuran resulted in a high decomposition degree of both kerogen and the solvent, the latter being decomposed into carbon oxide and *n*-propane [4].

Thus, during solvent liquefaction of kerogen both kerogen and the solvent may be submitted to pyrolytical decomposition. On co-pyrolysis of kerogen and ethers simultaneous rupture of ether (C–O) and other (C–C, C–H) similar bonds present in kerogen as well as in ether occur, and free radicals are formed whose character and composition of their interaction products depend on the type of ether used. Diethyl ether, dioxane-1,4 and ethylene oxide used as solvents in this work may decompose at autoclaving conditions along the pathways described by Equations (1)–(3) as follows:

Diethyl Ether

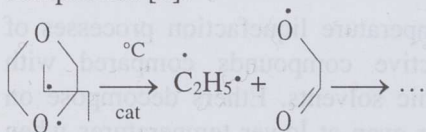


where *R* – alkyl radical.

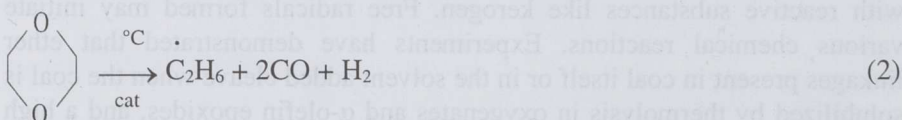
Thus, both alkylation and alkoxylation reactions of kerogen may be initiated by its liquefaction with diethyl ether.

Dioxane-1,4

Destruction of dioxane-1,4 proceeds typically to other cyclic ethers resulting in decyclization. As a result of primary homolytical cleavage of C–O bond in the molecule of dioxane-1,4 active hydrogen and fragments of radical character are formed. Their further transformation via a complex of concurrent and consecutive reactions yields ethane, ethylene and other compounds [5].



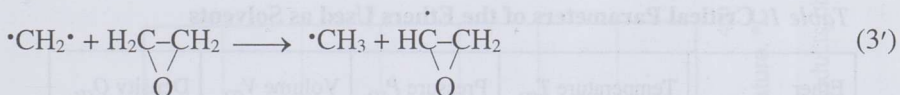
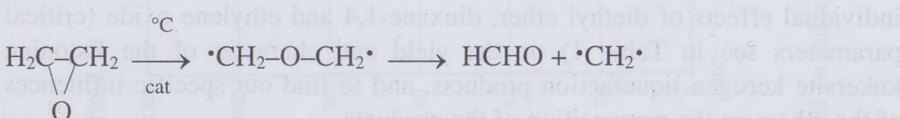
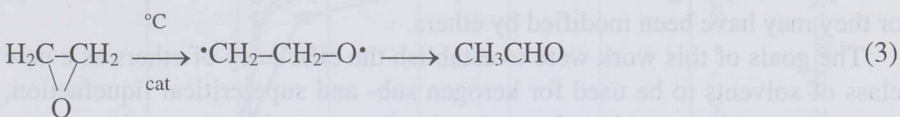
One of the final results of dioxane-1,4 decomposition may be expressed as:



Synthesis gas obtained is widely used in chemical practice [6].

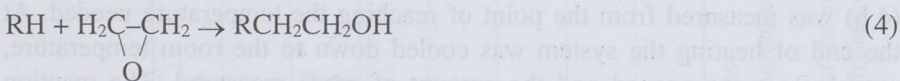
Ethylene Oxide

Pyrolysis of ethylene oxide is believed to occur similarly to other ethers through free-radical mechanism, the character of radicals and the composition of final products depending on which one of the chemical bonds in the ethylene oxide molecule – C–O (3) or C–C (3') – is ruptured.

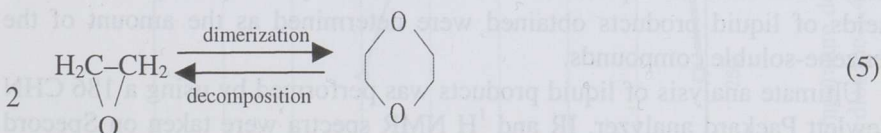


Biradicals as primary ones exist for a very short time forming more resistant metastable radicals. The biradical of dimethylene oxide evokes the reactions of methylation and dehydrogenation. It is believed that simultaneously to isomerization of ethylene oxide into acetic aldehyde (Reaction (3)) also free radicals are formed, initiating subsequent chain reaction of decomposition of acetic aldehyde and formation of cyclic acetal. Depending on the pyrolysis conditions various compounds – CH₃CHO, HCHO, CH₄, CO, CH₂=CH₂, HC≡CH, H₂, C₄H₈, C₆H₆, CH₂=C=O and other final products of ethylene oxide decomposition are formed.

Ethylene oxide, having its cycle stressed, unlike other ethers at subpyrolysis conditions easily reacts with many compounds having a labile hydrogen atom:



Noteworthy interesting is the ability of ethylene oxide and dioxane-1,4 for bilateral transitions:



Thus, on liquefaction of solid fuels in the ether medium, the process efficiency and product composition depend on whether the ether used as the solvent is stable or decomposes in thermolysis conditions applied, and whether one or both of energetically close C–C or C–O bonds (bonds energies 81 and 88 kcal/mole, respectively) are ruptured. The alkylated, alkoxyated, hydrogenated and other products may originate from fuel only, or they may have been modified by ethers.

The goals of this work were to establish the efficiency of ethers as a new class of solvents to be used for kerogen sub- and supercritical liquefaction, to compare them with other already known solvents, to investigate individual effects of diethyl ether, dioxane-1,4 and ethylene oxide (critical parameters see in Table 1) on the yield and character of the Estonian kukersite kerogen liquefaction products, and to find out specific influences of the ethers on the composition of the products.

Table 1. Critical Parameters of the Ethers Used as Solvents

Ether	Temperature T_{cr} , °C	Pressure P_{cr} , at	Volume V_{cr} , cm ³ /mol	Density ρ_{cr} , g/cm ³
Diethyl ether	193.6	35.9	280	0.264
Dioxane-1,4	313.9	51.4	238	0.370
Ethylene oxide	195.9	71.0	140	0.300

Experimental

Liquefaction of kukersite kerogen (characterization see in Table 2) was carried out in 22 cm³ rocking autoclaves, which were charged with powdered kukersite kerogen concentrate (organic content 92.4 %) and ether as solvent.

Kerogen to solvent ratio was 1 : 3 (2 g : 6 g) in all the experiments. The experiments were conducted at 250, 300, 330 and 350 °C. The reaction time (4 h) was measured from the point of reaching the temperature needed. At the end of heating the system was cooled down to the room temperature, autoclaves were opened and the amount of gases measured. The reaction products remaining in the autoclave were diluted with benzene and the liquid products were separated from solid ones by filtration. Benzene and the solvent used on liquefaction were removed by rotary evaporation. The yields of liquid products obtained were determined as the amount of the benzene-soluble compounds.

Ultimate analysis of liquid products was performed by using a 186 CHN Hewlett Packard analyzer, IR and ¹H NMR spectra were taken on Specord 75 IR and Tesla BS 567 (100 MHz) spectrometers.

The composition of the total converted and filtrated benzene-soluble matter was investigated using scanning electronmicroscopy (Tesla BS 300).

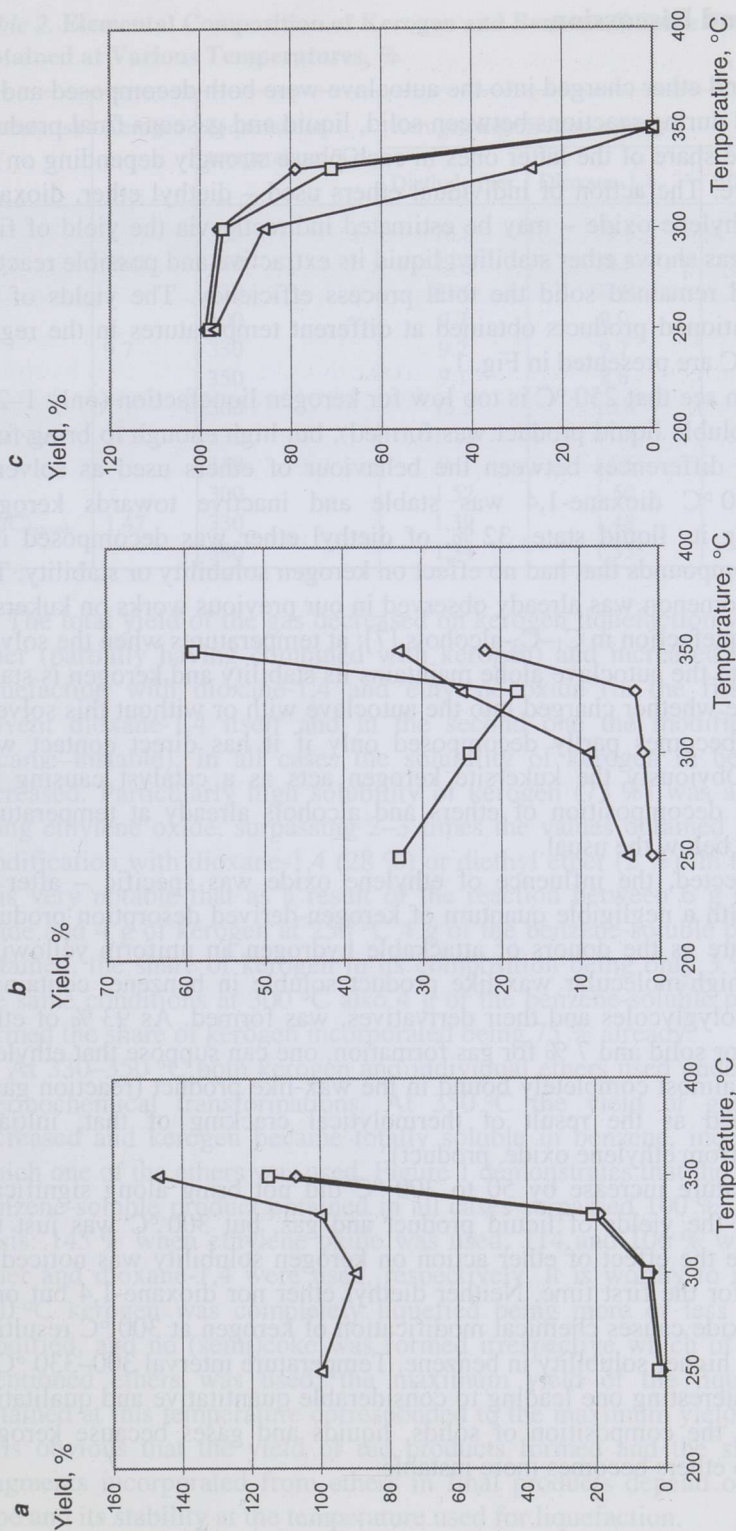


Fig. 1. Temperature dependence of the yields of liquid (a) gaseous (b), and solid (c) products obtained on kukersite kerogen liquefaction in diethyl ether (△), dioxane-1,4 (◇) and ethylene oxide (□) medium

Results and Discussion

Kerogen and ether charged into the autoclave were both decomposed and re-distributed during reactions between solid, liquid and gaseous final products formed, the share of the latter ones in each phase strongly depending on the temperature. The action of individual ethers used – diethyl ether, dioxane-1,4 and ethylene oxide – may be estimated indirectly via the yield of final products: gas shows ether stability, liquid its extractive and possible reactive ability and remained solid the total process efficiency. The yields of the above-mentioned products obtained at different temperatures in the region 250–350 °C are presented in Fig. 1.

One can see that 250 °C is too low for kerogen liquefaction (only 1–2 % benzene-soluble liquid product was formed), but high enough to bring forth significant differences between the behaviour of ethers used as solvents. Below 250 °C dioxane-1,4 was stable and inactive towards kerogen, maintaining its liquid state. 32 %, of diethyl ether was decomposed into gaseous compounds that had no effect on kerogen solubility or stability. The same phenomenon was already observed in our previous works on kukersite kerogen liquefaction in C₁–C₃-alcohols [7]: at temperatures when the solvent charged into the autoclave alone maintains its stability and kerogen is stable irrespective whether charged into the autoclave with or without this solvent, a solvent becomes partly decomposed only if it has direct contact with kerogen. Obviously the kukersite kerogen acts as a catalyst causing the pyrolytical decomposition of ethers and alcohols already at temperatures 50–100 °C below the usual.

As expected, the influence of ethylene oxide was specific – after its reaction with a negligible quantum of kerogen-derived desorption products and moisture as the donors of attackable hydrogen an uniform yellowish-brownish high-molecular wax-like product soluble in benzene, containing probably polyglycoles and their derivatives, was formed. As 93 % of ether was used for solid and 7 % for gas formation, one can suppose that ethylene oxide was almost completely bound in the wax-like product (reaction gases were formed as the result of thermolytical cracking of that, initially originated from ethylene oxide, product).

Temperature increase by 50 to 300 °C did not bring along significant changes in the yields of liquid product and gas, but 300 °C was just the temperature the effect of ether action on kerogen solubility was noticed in this work for the first time. Neither diethyl ether nor dioxane-1,4 but only ethylene oxide causes chemical modification of kerogen at 300 °C resulting in its 10 % higher solubility in benzene. Temperature interval 300–330 °C is the most interesting one leading to considerable quantitative and qualitative changes in the composition of solids, liquids and gases because kerogen similarly to ethers becomes more instable.

Table 2. Elemental Composition of Kerogen and Benzene-Soluble Products Obtained at Various Temperatures, %

Element(s)	Kerogen	Liquefaction temperature, °C	Kerogen liquefaction medium		
			Diethyl ether	Dioxane-1,4	Ethylene oxide
C	79.0	300	76.8	79.3	67.7
		330	79.7	78.5	67.1
		350	81.6	77.9	66.7
H	9.7	300	9.7	9.9	8.5
		330	9.2	9.7	7.9
		350	9.1	8.6	7.5
O+(N+S)	11.3	300	13.5	10.8	23.8
		330	11.1	11.8	25.0
		350	9.3	13.5	25.8
(H/C) _{atomic}	1.47	300	1.52	1.50	1.51
		330	1.39	1.48	1.41
		350	1.34	1.33	1.35

The total yield of the gas decreased on kerogen liquefaction with diethyl ether (partially having combined with kerogen) and increased on kerogen liquefaction with dioxane-1,4 and ethylene oxide (in the first case the solvent dioxane-1,4 itself and in the second one the modified kerogen became instable). In all cases the solubility of kerogen in benzene was increased. Particularly high solubility of kerogen (73 %) was achieved by using ethylene oxide, surpassing 2–3 times the values obtained on kerogen modification with dioxane-1,4 (28 %) or diethyl ether (2 %). In this context it is very notable that as a result of the reaction between 6 g of ethylene oxide and 4 g of kerogen at 250 °C 4 g of the benzene-soluble product was obtained, the share of kerogen in its composition being only 3 %, while in the same conditions at 300 °C also 4 g of the benzene-soluble product was formed the share of kerogen incorporated being 75 % already.

At 330–350 °C both kerogen and individual ethers used underwent deep thermochemical transformations. At 350 °C the yield of gases steeply increased and kerogen became totally soluble in benzene, independent of which one of the ethers was used. Figure 1 demonstrates that the yield of the benzene-soluble product obtained in all cases surpassed 100 %, on kerogen basis: 145 % when ethylene oxide was used, 114 and 106 % when diethyl ether and dioxane-1,4 were used, respectively. It is worthy to note that at 350 °C kerogen was completely liquefied being more or less chemically modified, and no (semi)coke was formed irrespective which of the above-mentioned ethers was used; the maximum yield of the liquid product obtained at this temperature corresponded to the maximum yield of the gas. It is obvious that the yield of the products formed and the share of the fragments incorporated from ethers in final products depend on the ether type and its stability at the temperature used for liquefaction.

Elemental composition of liquid benzene-soluble products obtained by liquefaction of kukersite kerogen in diethyl ether, dioxane-1,4 and ethylene oxide media at 300, 330 and 350 °C is given in Table 2. Though making far-reaching conclusions on the basis of elemental composition only is unjustified, one can see some obvious regularities referring to the chemical action of ethers on kerogen.

Compared with the elemental composition of initial kerogen, that of liquid products is significantly changed in favour of carbon or oxygen, their share in liquid products being always higher. The atomic H : C ratio decreases nearly proportionally with increasing the liquid product yield and with elevating the liquefaction temperature. In general the elemental composition of liquid products is distorted as compared with that of kerogen when the latter is decomposed incompletely, and usually the higher the yield of liquid product the closer the content of C, H and O in the liquid product and in kerogen.

In this work rather the vice versa tendency was observed, and at maximum yields of liquid products the most distorted H : C relations and O content not typical to the source kerogen were measured indicating that kerogen liquefaction occurred not in an inert but in a chemically active atmosphere. At 350 °C kerogen was totally decomposed. In all cases the liquid product yield surpassed 100 % (on kerogen basis) demonstrating that the compounds containing ether groups are brilliant liquefiers for kerogenous materials. Ethers have both alkylation and oxyalkylation potentials in respect to kerogen but which one of them will be preferably realized depends on the ether type. Diethyl ether could probably be considered to be C-alkylating agent with maximum C content at the maximum liquid product yield, whereas dioxane-1,4 and ethylene oxide represent oxyalkylating agents (with maximum O content at the maximum liquid product yield) not excluding their parallel C-alkylation ability.

Table 3. Assignments of the Bands in the ^1H NMR Spectra of Benzene Extracts

Hydrogen type	ppm	Hydrogen distribution, %			
		Benzene extracts from kerogen liquefaction at 350 °C with			
		carbon dioxide	diethyl ether	dioxane-1,4	ethylene oxide
Aromatic	8.5–6.5	13.8	17.4	16.7	14.8
Olefinic or methylene joined to aromatic ring	6.5–4.5	3.4	4.0	2.3	1.5
CH ₃ , CH ₂ , CH α to an aromatic ring or to O or N atoms	4.5–1.9	29.3	43.2	41.9	42.8
CH ₃ , CH ₂ , CH β or further from aromatic ring or to N, O atoms	1.9–0.5	53.5	35.4	40.1	40.9

The influence of diethyl ether, dioxane-1,4 and ethylene oxide on kukersite kerogen liquefaction process was also investigated by ^1H NMR and infrared spectroscopy. Spectra obtained were compared with each other and with the spectrum of the liquid product obtained on kukersite liquefaction with carbon dioxide. Our previous experiments have shown that CO_2 is one of the most powerful agents among chemically inert solvents yielding a benzene-soluble product (98 %, on kukersite kerogen basis) at 350 °C [8].

Quantitative calculations basing on ^1H NMR spectra (Table 3) prove the introduction of ether alkyl groups into liquid products – the content of aliphatic α -protons, which absorb in the region between 4.5 and 1.9 is increased in ether-influenced liquid products. Basing on ^1H NMR spectra, alkylation effects of chemically and thermodynamically specific diethyl ether, dioxane-1,4 and ethylene oxide seem to be almost equal (42–43 % of total hydrogen is bond into CH_3 , CH_2 and CH in α -position to an aromatic ring or to oxygen atoms) pointing to the fact that kerogen susceptibility to external functional groups available is not unlimited.

Slightly increased absorption of ether extracts in the region 8.5–6.5 ppm compared with that of CO_2 extract is due to protons belonging to aromatic rings and points to the presence of aromatic structures with electron donor (e.g. OH, OR) and electron acceptor ($>\text{C}=\text{O}$) substituents.

The content of protons belonging to CH_{1-3} groups from β or further position to an aromatic ring (absorption in the region 1.9–0.5 ppm) in ether extracts was found to be significant but lower than in the CO_2 extract.

The absorption in the range 6.5–4.5 ppm points to the presence of some olefinic systems but in low concentration.

Infrared spectra of liquid benzene-soluble products obtained at various temperatures are presented in Fig. 2. One can see that all the spectra contain absorption bands characteristic of kukersite thermal derivation products, whose intensity belongs to various functional groups and is influenced by the temperature and the solvent used. Besides those groups there are also some other absorptions indicating essential differences between ether and carbon dioxide extracts on the one hand and between ether extracts themselves on the other hand.

Absorption bands at 725, 750, 1380, 1460, 2860, 2930 and 2960 cm^{-1} belong to CH_3 -, $-\text{CH}_2-$ and $\text{CH}-$ groups in aliphatic chains. Bands at 745, 770, 820 880, 1020, 1080, 1600 and about 3000 cm^{-1} indicate the presence of aromatic ring systems of different degree of condensation and substitution. The presence of olefinic systems suggested to be present in the liquid product composition in low concentration by ^1H NMR spectroscopy could not be detected in the IR spectra because of the masking effect of aromatic systems.



Fig. 2. Infrared spectra of the liquid products obtained on kukersite kerogen liquefaction in the following solvents: diethyl ether (1) and dioxane-1,4 (2) at 330 °C, ethylene oxide (3) at 300 °C, diethyl ether (4), dioxane-1,4 (5), ethylene oxide (6) and carbon dioxide (7) at 350 °C

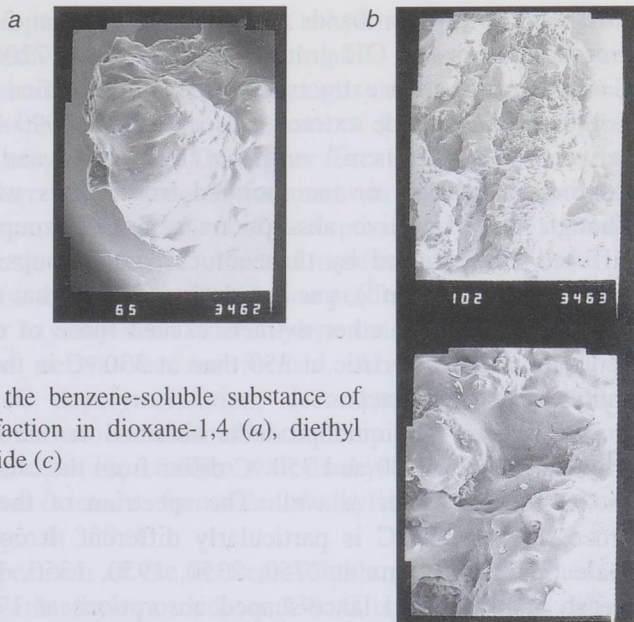
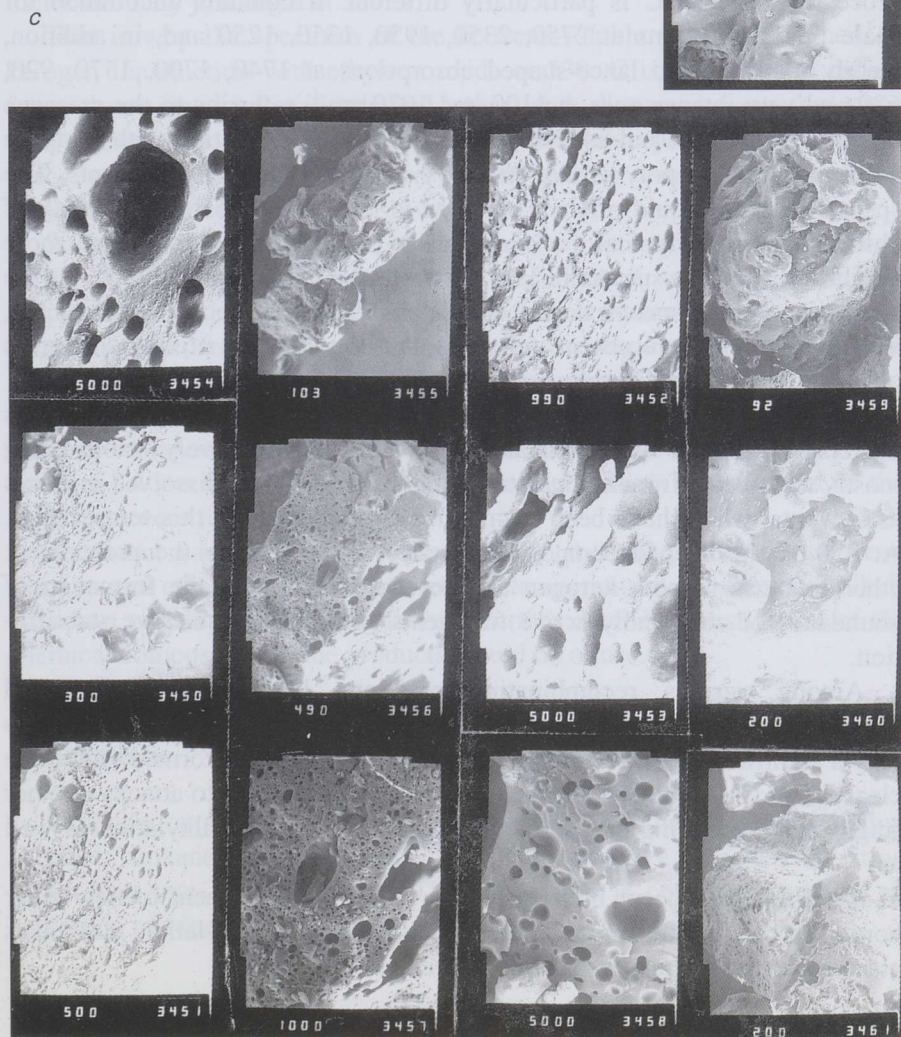


Fig. 3. Photographs of the benzene-soluble substance of kukersite kerogen liquefaction in dioxane-1,4 (a), diethyl ether (b) and ethylene oxide (c)



Broad absorption bands with a maximum at 3450 cm^{-1} indicate the presence of various OH groups. Absorption at 1720 cm^{-1} belonging to the C=O groups in ether extracts is noticeably amplified as compared with that in the carbon dioxide extract. Absorptions at 2990–2970, 2850, 1430 and between $1300\text{--}1100\text{ cm}^{-1}$ originate from C–O and C–O–C groups pre-existing in kerogen or incorporated from ethers when used as solvents. Though the respective absorptions of ether groups are poorly shaped, diffused and eclipsed by those of carbonyl groups in this region (1250 , 1100 , $1040\text{--}1020\text{ cm}^{-1}$), one can notice (Fig. 2) that the intensities of these absorption bands in ether extracts exceed those of carbon dioxide extract being more characteristic at 350 than at $330\text{ }^\circ\text{C}$ in the case of diethyl ether and dioxane-1,4 extracts.

The spectra of liquid products obtained on kerogen liquefaction with ethylene oxide at 330 and $350\text{ }^\circ\text{C}$ differ from the others presented in Fig. 2 and from each other as well. The spectrum of the product obtained on processing at $330\text{ }^\circ\text{C}$ is particularly different. It contains uncommon for shale oils absorptions at 2750, 2350, 1950, 1350, 1250 and, in addition, clearly distinguished lance-shaped absorptions at 1740, 1700, 1370, 920, 680 and very intense ones at 1100 and 1070 cm^{-1} , referring to the presence of various alcohols and esters formed as a result of reaction with ethylene oxide and further polymerization of oxyalkylated kerogen fragments. The spectrum of the liquid product obtained at $350\text{ }^\circ\text{C}$ has lost the majority of absorption bands typical for etoxylation products having become more similar to the other spectra in Fig. 2 than to that obtained at $330\text{ }^\circ\text{C}$. At the same time in both spectra described, the absorptions of epoxy rings at 1265, 915 and 835 cm^{-1} are absent indicating that the addition of ethylene oxide occurs after its decyclization.

Spectroscopic data obtained demonstrate that at $330\text{ }^\circ\text{C}$ the ether bonds in kerogen, diethyl ether and dioxane-1,4 are still relatively stable being mostly transferred from kerogen to the liquid product and dissolved in ethers as solvents, which have been maintained their identity at this temperature. At $350\text{ }^\circ\text{C}$ the deep decomposition process involves also the pre-existent ether linkages in both kerogen and solvent resulting in the formation of abundance of chemically active fragments and their consecutive stabilization.

Among various recombination reactions kerogen alkylation and oxyalkylation reactions initiated by ether decomposition as concurrent ones play a significant role. Kerogen decomposition fragments formed due to the cleavage of C–O and C–C bonds have vacancies available to attacks of ether fragments. Depending on recombination pathways, C-oxyalkylation as well as

O-alkylation may occur both leading to the re-establishment of new ether bonds instead of the initial ones. Simultaneously C-alkylation also takes place lessening the relative share of oxyalkylation.

Liquefaction of kerogen in the presence of ethylene oxide differs from that described above. Ethylene oxide reacts with labile hydrogen in kerogen at early stages of thermolysis already giving high yields of the benzene-soluble product in which composition the share of kerogen is negligible compared with that of ethylene oxide. On further thermolysis with elevating the temperature the share of kerogeneous fragments in the benzene-soluble product formation increases into account of desorption and pyrolysis fragments and so its composition becomes more and more complicated.

At the same time low-molecular oxyethylation products once formed will be submitted to further oxyethylation with ethylene oxide available and as a result polyoxyethylene derivatives are formed. At the final stage of liquefaction at 350 °C depolymerization, decomposition and cracking reactions lead to the formation of smaller and simpler gas and liquid molecules again. On kerogen liquefaction with diethyl ether or dioxane-1,4 chemical interaction and extensive formation of alkylated and oxyalkylated molecules only just begin at 350 °C.

That is why the spectrum of the benzene-soluble product obtained on kerogen liquefaction with ethylene oxide at 330 °C is specific and differs from those obtained with diethyl ether and dioxane-1,4 at the same temperature while the spectra of the benzene-soluble products obtained on kerogen liquefaction at 350 °C are broadly similar whatever of the above mentioned ethers was used as a solvent.

Some additional information concerning the microstructural composition of the benzene-soluble substances may be obtained using electronmicroscopic investigation visualized in Fig. 3. One can see that the benzene-soluble product from kerogen liquefaction in the medium of ethylene oxide is rich in various specific organic, organomineral or mineral formations and ingredients, and 12 varieties in all were found (Fig. 3,c) while soluble in benzene compounds from other experiments where diethyl ether and dioxane-1,4 were used are mostly uniform, and mainly constituents of the same kind were found (Fig. 3,a and b).

To obtain a more thorough understanding about the processes between kerogen and ether compounds at elevated temperatures, the extent of alkylation and oxyalkylation among them, a further detailed investigation of the chemical composition of the products would be of use.

Conclusions

1. Liquefaction of the kukersite kerogen at 350 °C in the medium of diethyl ether, dioxane-1,4 or ethylene oxide is an effective process converting kerogen into liquid and gas. The conversion is complete yielding no carbon residue.

2. Ethers when used as solvents at elevated temperatures on kerogen liquefaction represent chemical agents causing both alkylation and oxyalkylation of kerogen giving extra yields of gas and liquid.
3. The yield and character of the products formed on kerogen liquefaction in ether media as well as their degree of chemical modification depend on ether type and liquefaction temperature. Ethylene oxide evokes chemical reactions with kerogen at early liquefaction stages already, while the chemical potential of diethyl ether and dioxane-1,4 bursts simultaneously with kerogen intensive decomposition.

Acknowledgements

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