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

2. COMPOSITION OF LIQUID PRODUCTS

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Liquid benzene-soluble products of kukersite kerogen liquefaction in the medium of diethyl ether, dioxane-1,4 and ethylene oxide were separated into asphaltenes, malthenes, phenols, aliphatic and aromatic hydrocarbons, water-soluble neutral oxygen and high-polar compounds. High-molecular compounds separated were submitted to additional pyrolysis to investigate the composition of secondary compounds. Total products, fractions separated from them and pyrolyzates were analyzed by IR spectroscopy and gas chromatography to investigate the effect of various ethers on their chemical modification. The most characteristic similarities and differences between primary and secondary products of liquefaction were established. It was concluded that the final liquid products were formed as a result of thermal decomposition of previously oxyalkylated intermediates, those being different whether ethylene oxide, dioxane-1,4 or diethyl ether were used as liquefaction medium.

In [1] the effect of ether type at kukersite kerogen liquefaction in an autoclave in the medium of diethyl ether, dioxane-1,4 and ethylene oxide at 250–350 °C on the yield and character of decomposition products was investigated. It was demonstrated that during kerogen liquefaction processes ethers may act as high-effective solvents realizing not only their solvolytical but also thermochemical potential evoking kerogen alkylation and oxyalkylation. Ethylene oxide was chemically active towards kerogen at low temperatures already yielding a specific benzene-soluble product. As a result of ether decomposition at 350 °C and incorporation of the fragments into kerogen decomposition product, the yield of the benzene-soluble product in this case surpassed 100 %, kerogen basis.

The aim of this study was:

- to explain in which manner ether type influences the chemical group and individual component composition of the benzene-soluble liquid product formed at kerogen liquefaction, and

- to establish the main similarities and differences between the products to estimate the prospective for using ethers as a new class of high-temperature liquefiers on oil shale processing instead of known ones.

Experimental

Total benzene-soluble liquid products (TBSLP) obtained on kukersite kerogen liquefaction at 350 °C in the medium of diethyl ether, dioxane-1,4 and ethylene oxide as described in [1] (in different yields, mostly 106–142 %, kerogen basis) were submitted to solvent extraction, and as a result the following narrow fractions were obtained:

- **Water-soluble compounds** separated from TBSLP by extraction with slightly pre-heated distilled water.
- **Asphaltenes** extracted with trichloromethane solution and thereafter precipitated using *n*-hexane.
- **Malthenes** separated as hexane-solubles at asphaltene sedimentation.
- **Phenols** separated from TBSLP by consecutive extraction with 10-% sodium hydroxide, 10-% hydrochloric acid and diethyl ether.

Dephenolated TBSLP were separated into compound groups by preparative thin-layer chromatography (TLC). Plates 24 × 24 cm coated with a 2-mm silica gel (40 μm) layer were used. 500-mg samples were analyzed using *n*-hexane as the eluent. Five fractions of different polarity were obtained: aliphatic hydrocarbons, monocyclic alkylarenes, polycyclic (alkyl)arenes, neutral heteroatomic compounds and high-polar compounds (HPC).

Infrared spectroscopy (*Specord 75 IR*) was used to characterize the content of functional groups in samples.

Gas chromatography on a *Chrom 4* analyzer with temperature programming and columns of different polarity was used to determine individual compounds present in volatile compounds of preparatively separated TBSLP fractions. Secondary pyrolysis of asphaltenes and HPC weighted into Pyrex tubes was carried out in a micropyrolysis apparatus at 450 °C.

Results and Discussion

Fractionation

The main products obtained at kukersite kerogen liquefaction in a chemically active or inert medium – benzene-soluble compounds (98–145 %, kerogen basis) – were separated into seven fractions of different polarity by solvent extraction and preparative adsorption chromatography. The list of fractions obtained is given in Table 1.

Table 1. Group Composition of Benzene-Soluble Products, mass%

Compound group	Content in benzene-solubles obtained on kerogen liquefaction in various solvents			
	Diethyl ether	Dioxane-1,4	Ethylene oxide	Carbon dioxide [2]
Asphaltenes	49	54	48	49
Phenols	3	2	3	—
Malthenes	48	44	49	51
Including:				
Non-aromatic hydrocarbons	2	4	3	6
Aromatic hydrocarbons	4	5	4	7
Neutral oxygen compounds	6	5	8	8
High-polar compounds	36	30	34	30

The table includes also comparative data about the composition of fractions obtained from benzene-soluble compounds of kerogen liquefaction in chemically inert carbon dioxide and separated by the same methods. One can see that at kukersite kerogen liquefaction in diethyl ether, ethylene oxide and carbon dioxide, asphaltenes and malthenes were formed in almost equal quantities – 48–49 and 48–51 %. At liquefaction in dioxane-1,4 the highest yield of asphaltenes (54 %) and the lowest of malthenes (44 %) was observed. Malthenes have the highest concentration of high-polar compounds (up to 75 %) and contain 30–36 % total benzene-soluble compounds not depending on which of the solvents was used. The content of phenols is very low – 2-3 % only as compared with that in kukersite semicoking oil (20–25 %).

Comparison of carbon dioxide liquefaction results with other data of Table 1 shows that the composition of all TBSLP is rather similar by the asphaltenes-to-malthenes ratio and by the content of high-polar compounds, but differs by the content of less- and non-polar fractions, the latter being higher in TBSLP from carbon dioxide liquefaction. These data reveal an interesting tendency that with increasing the polarity of the compound group, its content becomes closer in all TBSLP and, *vice versa*, the lower the polarity of the fraction separated, the greater the deviations between its content in TBSLP obtained at liquefaction with various solvents.

The fractions studied are formed as a result of a complex of various simultaneous and consecutive chemical reactions initiated by the temperature chosen for kerogen liquefaction and influenced by the ethers used in this work. Kerogen debituminization, thermal degradation of thermobitumen (oil and gas formation), alkylation and/or oxyalkylation of kerogen-derived decomposition fragments by ethers, and other reactions have taken place. The products obtained at liquefaction in carbon dioxide have formed in a chemically inactive but physically more destructive atmosphere of strongly overcritical inert gas causing much deeper cracking of kerogen. Examining the

data of Table 1 one can further expect that both asphaltenes and malthenes might have been submitted to the alkylation and oxyalkylation reactions with ether fragments. And, last but not least, everyone can see that the sum of asphaltenes and high-polar compounds not examinable by gas chromatography makes 79–85 % of TBSLP.

These are the reasons why asphaltenes and polar malthenes after previous IR spectroscopic investigation were additionally submitted to the secondary thermal fragmentation by pyrolysis.

Additional Pyrolysis of Asphaltenes and Polar Malthenes

The yields of liquid, gaseous and solid products obtained at additional pyrolysis of asphaltenes and polar malthenes separated from TBSLP formed in the medium of various solvents is presented in Table 2. Chemical group composition of some selected liquid products of pyrolysis is given in Table 3.

Table 2. The Yield of Pyrolysis Products, wt. %

No.	Medium	Temperature, °C, of pyrolysis of object formation	Products		
			Liquid	Gaseous	Solid
Polar malthenes					
1.	Carbon dioxide	350	50.8	33.9	15.3
2.	Diethyl ether		52.9	26.5	20.6
3.	Dioxane-1,4		63.9	30.7	5.4
4.	Ethylene oxide		58.8	16.8	24.4
5.	Ethylene oxide	330	61.2	10.0	28.8
Asphaltenes					
6.	Carbon dioxide	350	73.4	11.0	15.6
7.	Diethyl ether		32.8	11.2	56.0
8.	Dioxane-1,4		21.1	7.5	71.4
9.	Ethylene oxide		52.0	12.7	35.3
Solid residues					
10.	Carbon dioxide	330	42.7	5.4	51.9
11.	Ethylene oxide		23.7	4.9	71.4

Table 3. TLC Characterization of Some Liquid Products Formed at Pyrolysis

TLC fractions	Liquid product number (see Table 2)			
	2.	6.	10.	11.
Aliphatic hydrocarbons	17.7	8.6	4.9	12.8
Monocyclic (alkyl) arenes	2.0	0.7	1.4	2.2
Polycyclic (alkyl) arenes	12.0	9.1	3.1	1.0
Neutral heteroatomic compounds	21.5	11.4	7.7	68.2
Polar malthenes	46.7	72.2	82.9	15.8

At pyrolysis, polar malthenes yield always more liquid products (50.8–63.9 %) than by-products gas and solid residue formed simultaneously. Among the latter the gas yield usually exceeds that of the solid residue, except for HPC formed in the medium of ethylene oxide at 330–350 °C giving on pyrolysis more solid residue and less gas. Asphaltenes give significantly less gas than HPC on pyrolysis.

The yield of liquid and solid products obtained varies in large limits being dependent on chemical atmosphere of their formation – asphaltenes formed in the medium of ethylene oxide and carbon dioxide yield much liquid (52.0 and 73.4 %, respectively) and less solid (35.3 and 15.6 %) products while those formed in dioxane-1,4 and diethyl ether give, on the contrary, more solid (71.4 and 56.0 %, respectively) and less liquid final products (21.1 and 32.8 %). Solid residues yield on pyrolysis less gas (4.9–5.4 % only) than HPC and asphaltenes, the yield of the liquid product being lower than that of the solid one. Depending on the extent of thermal or thermochemical modification, solid residues pre-treated in an inert (carbon dioxide) or in a chemically active (ethylene oxide) atmosphere give quite different yields of liquid and solid products (see Table 1).

The results of TLC analysis (see Table 3) show that the secondary liquid products obtained at additional pyrolysis of HPC, asphaltenes and solid residues formed in the first stage of thermolytical liquefaction consist of the same chemical groups of compounds as the primary ones (aliphatic and aromatic hydrocarbons, neutral oxygen compounds and polar malthenes, see Table 1), but the mutual ratios between similar compound groups of primary and secondary origin and between the latter ones themselves are different.

Though the most part of both primary and secondary malthenes consists of HPC and neutral heteroatomic compounds, the concentration of aliphatic compounds is higher and that of aromatic ones lower in the secondary products. Asphaltenes yield on pyrolysis much HPC (72.2 %), while the pyrolysis process of HPC is characterized by high recovery of HPC themselves (46.7 %). It seems that a great deal of HPC, partly formed as a result of decomposition of asphaltenes during BSLP formation, is stable and does not change during the secondary stage of pyrolysis, or is only slightly modified so maintaining their identity as HPC on TLC separation procedures.

The solid residues obtained, in fact, as thermochemically modified kerogens, were on further pyrolysis transformed into solid, liquid and gaseous products whose characteristics and redistribution regularities between different phases depend on the depth of thermochemical modification of the kerogen in the first stage of liquefaction. Obtained in inert (carbon dioxide) and reactive (ethylene oxide) medium solid remnants (positions 10. and 11. in Table 2) give liquid products quite different by composition. The first one consists mainly of HPC (82.9 %) while the other one – of neutral heteroatomic compounds (68.2 %), containing only 15.8 % HPC, but over twice more aliphatic hydrocarbons.

The data obtained demonstrate that previously thermally processed or chemically restructured remnants of kerogen still possess a considerable potential for oil and gas formation to be processed under other conditions. That is why solid residues separated after kerogen liquefaction (incl. positions 10. and 11. in Table 2) should be classified as chars but not as semi-coke. The most effective methods for utilization of such substances have to be worked out.

Some experiments of chemical modification of coals with their simultaneous liquefaction (e.g. alkylation with alcohols) have been carried out with the aim to increase coal solubility and liquid product yield [2–7]. It was found that the total liquid product yield increased as a result of consumption of alkylating reagent – alcohol (the higher the alkylation efficiency and the higher the alcohol consumption, the higher the liquid product yield). However, it was not clearly stated in which stage of liquefaction the alkylation process occurred, and which were the shares of alcohol and kerogen in the extra-yield of liquid product, because, actually, – not only the initial coal but the solid remnants of its decomposition (char fragments) and coal-derived liquid product itself were the potential consumers of alcohol as alkylating reagent available during the whole liquefaction process.

Thus, on *in situ* alkylation and oxyalkylation of solid fuels in alcohols and ethers the mechanism of their chemical modification and the composition of final products, in any individual case, are determined by the differences in stability of high-molecular organic matter of solid fuel modified and of the solvent used at the processing temperature.

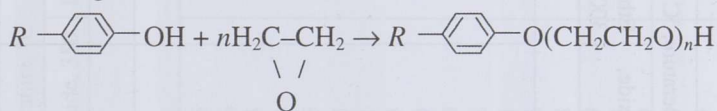
The influence of the temperature can be different:

- it can be too low for solvent decomposition but high enough for rapid destruction of fuel organic matter so contributing to conventional thermal dissolution in thermochemically stable solvent medium
- or, *contra versa*, it can be high enough for total decomposition of the solvent but not sufficient for rapid destruction of fuel organic matter so evoking its chemical modification before subjection to further decomposition
- or, the temperature can be high enough to initiate thermal decomposition of both the fuel organic matter and the solvent as it has usually been chosen to carry out *in situ* chemical modification of various substances.

In the latter case, one never can expect decomposition of both the organic matter modified chemically and the solvent used as chemical modifier to start at the same moment and proceed simultaneously. Always one of them will dominate in the process developing causing either modification of organic matter prior to its decomposition or chemical derivation of decomposition products after organic substance decomposition. The extent and depth of various chemical transformations, as well as the yield and composition of the products obtained and solvent recovery, depend on process duration.

The character of a complex of probable consecutive and concurrent reactions occurring with the substance modified, with the modifier, and between them during limited by time liquefaction processes in the medium of labil solvents depends on process duration. (The reactions taking place are thermal decomposition of both the solvent and the organic substance, modification of the organic matter, thermal decomposition of the modified substance, modification of liquid products formed at organic substance decomposition, modification of char, thermal decomposition of modified char, etc.)

In our experiments, as already established in [1] by material balances of kerogen liquefaction in the medium of ethylene oxide, the chemical modification of kerogen (oxyethylation) occurred prior to its thermal decomposition, and liquid components – asphaltenes, HPC, narrow fractions of hydrocarbons and neutral compounds, gas and char were formed during further decomposition of oxyethylated kerogen. Liquefaction of kerogen in the medium of diethyl ether and dioxane-1,4 proceeded analogously to the process in alcohols, i.e. possible pathways differ from the ethylene oxide process described above. Great reactivity of the three-member cyclic ether – ethylene oxide – is attributed to its highly strained structure. The carbon-oxygen bond in the epoxide ring can be easily ruptured under acidic, basic and even neutral conditions. Such behaviour differs markedly from that of aliphatic, alicyclic or larger cyclic ethers, which are neither readily hydrolyzed by alkali nor susceptible to attacks by anions. One of the possible gates to incorporate into kerogen structure is as follows:



Once incorporated, ethylene oxide chains $-(\text{CH}_2-\text{CH}_2-\text{O})_n$ are mostly disproportionated between TBSP and gaseous compounds during later stages of liquefaction. The part strongly attached to the char structure could be removed as an abundance of neutral oxygen compounds only at additional pyrolysis of the char.

Infrared Spectroscopic Studies of TBSP and Separated Fractions

TBSP and separated from them asphaltenes, HPC, water-soluble compounds, phenols and pyrolyzates of asphaltenes, HPC and solid residues (chars) were characterized by IR spectroscopy. Reduced optical densities were calculated from the absorption maximums that characterize the relative content of specific functional groups [8]. The data in Tables 3–7 show that the spectra of liquid products obtained in the medium of ethylene oxide as well as in the medium of diethyl ether and dioxane-1,4 are characterized by a variety of oxygen compounds and by elevated content of C–O (920, 1050, 1120, 1250, 1290, 1350, 1720 cm^{-1}), C=O (1700 cm^{-1}) and OH (3400 cm^{-1}) vibrations corresponding to various oxygen compounds.

Table 4. IR-Spectroscopic Characterization of TBSLP Obtained on Kerogen Liquefaction in the Medium of Various Solvents at Different Temperatures

Frequency, cm^{-1} , and corresponding functional group		Liquefaction medium and temperature, $^{\circ}\text{C}$						
		Carbon dioxide, 350	Ethylene oxide, 350	Ethylene oxide, 300	Dioxane-1,4, 350	Dioxane-1,4, 330	Diethyl ether, 350	Diethyl ether, 330
Reduced optical densities								
720	$(\text{CH}_2)_n$	0.22	0.24	0.03	0.21	0.10	0.19	0.20
745		0.25	0.30	0.06	0.21	0.07	0.23	0.17
770	CH_{ar}	0.18	0.29	0.06	0.20	0.03	0.21	0.19
815		0.29	0.32	0.15	0.18	0.10	0.26	0.17
880		0.14	0.30	0.31	0.25	0.17	0.27	0.17
920		0.12	0.26	0.37	0.21	0.17	0.21	0.20
1050		0.49	0.73	1.07	0.57	0.84	0.51	0.54
1120		0.58	0.88	1.25	0.77	0.72	0.73	0.85
1250	C-O	0.67	0.77	0.75	0.70	0.64	0.74	0.76
1290		0.65	0.73	0.69	0.68	0.62	0.71	0.71
1350		0.69	0.74	0.78	0.67	0.78	0.71	0.71
1380	CH_3	0.80	0.86	0.77	0.78	0.78	0.83	0.85
1600	$(\text{C}=\text{C})_{ar}$	0.88	0.81	0.54	0.77	0.86	0.79	0.76
1700	C=O	0.55	0.81	0.69	0.75	0.86	0.78	0.86
1720		0.26	0.70	0.72	0.77	0.70	0.59	0.66
2850	C-O	1.02	0.77	1.14	1.03	1.16	0.91	0.78
2930	CH_2	1.11	0.76	1.28	1.16	1.38	0.94	1.05
2960	CH_3	0.96	0.69	1.03	0.96	1.04	0.87	0.98
3020		0.16	0.14	0.03	0.08	0.09	0.11	0.12
3060	CH_{ar}	0.08	0.01	0.02	0.04	0.04	0.07	0.07
3400	OH	0.69	0.59	1.02	0.67	0.96	0.50	0.58

Table 5. IR-Spectroscopic Characterization of Asphaltenes and Polar Malthenes Separated From TBSP

Frequency, cm ⁻¹ , and corresponding functional group	Liquefaction medium and temperature, °C					
	Diethyl ether, 350	Ethylene oxide, 350	Dioxane-1,4, 350	Diethyl ether, 350	Ethylene oxide, 350	Dioxane-1,4, 350
	Asphaltenes					
	Reduced optical densities					
720	0.16	0.05	0.18	0.15	0.10	0.17
745	0.11	0.06	0.21	0.22	0.11	0.20
770	0.20	0.13	0.19	0.30	0.15	0.19
815	0.20	0.13	0.15	0.26	0.14	0.13
880	0.25	0.15	0.24	0.26	0.18	0.11
920	0.24	0.13	0.01	0.15	0.13	0.09
1050	0.65	0.71	0.76	0.81	0.50	0.65
1120	0.78	0.85	0.85	0.63	0.67	0.80
1250	0.64	0.59	0.67	0.59	0.62	0.57
1290	0.63	0.60	0.66	0.63	0.50	0.60
1350	0.66	0.48	0.69	0.56	0.38	0.42
1380	0.75	0.71	0.76	0.93	0.82	0.80
1600	0.81	0.65	0.85	0.74	0.59	0.79
1700	0.63	0.48	0.64	0.74	0.56	0.61
1720	0.44	0.50	0.49	0	0.19	0.27
2850	1.05	1.18	1.34	0.81	0.67	0.99
2930	1.25	1.69	1.51	1.11	1.31	1.18
2960	0.94	1.19	1.31	0.93	1.04	1.19
3020	0.06	0.03	0.06	0.11	0.03	0.07
3060	0.08	0.05	0.12	0.07	0.04	0.05
3400	0.36	0.63	0.78	0.67	0.79	0.83

Table 6. IR-Spectroscopic Characterization of Water-Soluble Compounds and Phenols Separated from TBSLP

Frequency, cm^{-1} , and corresponding functional group	Liquefaction medium and temperature, $^{\circ}\text{C}$			
	Diethyl ether, 350	Carbon dioxide, 350	Ethylene oxide, 200	Diethyl ether 350
	Water-soluble compounds			
	Reduced optical densities			
720	0.30	0.48	0.03	0.46
745	0.32	0.47	0	0.49
770	0.27	0.39	0	0.47
815	0.30	0.49	0.33	0.41
880	0.37	0.44	0.64	0.53
920	0.49	0.44	0.77	0.57
1050	0.73	0.66	1.42	0.62
1120	0.90	0.84	0.49	0.81
1250	0.96	0.91	0.89	0.95
1290	0.90	0.91	0.77	0.92
1350	0.83	0.90	0.99	0.85
1380	0.93	0.93	0.72	0.94
1600	0.79	0.92	1.04	0.85
1700	1.04	1.01	0.12	1.10
1720	0.94	0.11	0.61	0.05
2850	1.05	0.40	1.06	0.46
2930	0.55	0.34	0.99	0.47
2960	0.54	0.32	0.96	0.41
3020	0.04	0.10	0	0.05
3060	0.02	0.07	0	0.05
3400	0.67	0.81	1.38	0.87

Table 7. IR-Spectroscopic Characterization of the Pyrolysates of Asphaltenes, Polar Malthenes and Secondary Polar Malthenes Formed on Additional Liquefaction at 350 °C of Solid Residues Obtained at 330 °C in the Medium of Carbon Dioxide and Separated as Upper Layer (Neutral Oxygen-Containing Compounds) and Lower Layer (Usual Polar Malthenes)

Frequency, cm ⁻¹ , and corresponding functional group	Liquefaction medium and temperature, °C							Carbon dioxide, 330	
	Diethyl ether, 350		Ethylene oxide, 350		Diethyl ether, 350		Ethylene oxide, 330		
	Asphaltenes		Polar malthenes		Secondary polar malthenes		Secondary polar malthenes		
	Reduced optical densities								
720	(CH ₂) _n	0.16	0.19	0.09	0.22	0.27	0.17	0.16	
745		0.21	0.30	0.18	0.35	0.14	0.36	0.14	
770	CH _{ar}	0.24	0.25	0.24	0.29	0.10	0.22	0.05	
815		0.33	0.30	0.30	0.34	0.05	0.25	0.16	
880		0.20	0.25	0.18	0.30	0.04	0.22	0.02	
920		0.21	0.22	0.18	0.28	0.04	0.31	0	
1050		0.60	0.48	0.86	0.54	0.42	0.61	0.37	
1120	C-O	0.97	0.77	0.86	0.80	0.59	0.93	0.56	
1250		0.61	0.67	0.65	0.74	0.52	0.69	0.53	
1290		0.66	0.66	0.67	0.77	0.49	0.84	0.70	
1350		0.69	0.64	0.68	0.72	0.52	0.57	0.58	
1380	CH ₃	0.92	0.82	0.91	0.91	0.66	0.90	0.74	
1600	(C=C) _{ar}	0.77	0.78	0.74	0.84	0.64	0.57	0.93	
1700	C=O	0.67	0.61	0.76	0.92	0.66	0.71	0.51	
1720		0.49	0.41	0.65	0.81	0.46	0.82	0	
2850	C-O	0.87	0.78	0.86	0.77	1.24	0.79	1.21	
2930	CH ₂	1.07	0.99	1.14	0.82	1.34	1.27	1.62	
2960	CH ₃	0.90	0.90	0.93	0.74	1.00	1.14	1.07	
3020		0.11	0.12	0.11	0.16	0.05	0.18	0.05	
3060	CH _{ar}	0.07	0.12	0.12	0.16	0.04	0.10	0.02	
3400	OH	0.65	0.60	0.67	0.70	0.84	0.40	1.41	

Introduction of alkyl groups into the kerogen liquefaction products manifests itself in an increase in intensity of the bonds at 2960 and 2930 cm^{-1} and in a decrease in relative intensities of the bonds at 3060 and 3020 cm^{-1} . Oxyalkylation – the introduction of oxyalkyl groups into the liquefaction product composition – manifests itself particularly in an increase in intensity of the bonds at 1350, 1290 and 1250 cm^{-1} considered to be the fingerprints of oxyalkyl groups, but also in a decrease in relative intensity of the bonds at 3400 cm^{-1} on account of alkylation of hydroxyl groups.

All the ethers used for pyrolytical decomposition in this work – diethyl ether, dioxane-1,4 and ethylene oxide – without exception produce no radicals longer than C_2 , i.e. only ethyl and oxyethyl radicals, and so kerogen alkylation or oxyalkylation means its ethylation or oxyethylation. The latter process occurs in two parallel ways: by incorporation of new oxyethyl groups *in corpore* and by ethylation of the pre-existent and previously deprotonized hydroxyl groups.

So, being simultaneously attacked by $-\text{CH}_2-\text{CH}_3$ and $-\text{O}-\text{CH}_2-\text{CH}_3$ groups from ether decomposition, ethylation of kerogen $-\text{OH}$ groups (O-alkylation) and oxyethylation of kerogen carbon bond vacancies (C-oxyalkylation) both lead to kerogen alkylation and oxyalkylation, while simultaneous C-alkylation leads to kerogen alkylation only. Reaction with ethylene oxide leads mainly to kerogen oxyalkylation but, because of high reactivity of ethylene oxide, it can evoke O-oxyalkylation as well, and as a result polymers and complex compounds like esters, lactones, carbonates and others are formed. It makes estimation of alkylating and oxyalkylating potentials (separate shares of CH_3-CH_2- and $-\text{O}-\text{CH}_2-\text{CH}_3$ groups of ether origin) of one or another ether almost impossible. In our opinion, oxidative alkylation could be the most successful term to explain the processes of kerogen chemical modification in ether medium, process efficiency depending on the total share of ether constituents introduced into kerogen.

TBSLP obtained at kerogen liquefaction in ether medium are characterized by significantly higher relative content of C–O and C=O functional groups and by lower content of $\text{C}=\text{C}_{ar}$ than those obtained in carbon dioxide. TBSLP obtained in ethylene oxide are characterized by higher values of C–O optical densities calculated for the region of 920–1350 cm^{-1} than those effected by decomposition products of diethyl ether or dioxane-1,4. TBSLP obtained at 350 °C in diethyl ether and in dioxane-1,4 contain more C–O groups than those obtained in the same solvents at 330 °C.

One can also see (Table 2) that the products obtained at lower temperatures usually contain more hydroxyl groups. A particularly high content of hydroxyl groups was observed when ethylene oxide was used at 300 °C, referring to the presence of firstly formed polyols and glycols and their further decomposition at elevating the temperature. The content of CH_2 (720–2930 cm^{-1}) and CH_3 (1380 and 2960 cm^{-1}) groups is variable depending on the extent of addition, substitution, and cracking reactions.

Asphaltenes contain substantially less carbonyl groups and more methylene and methyl groups than TBSLP. When compared to HPC, asphaltenes contain more C–O groups and less OH. Asphaltenes obtained in the medium of ethylene oxide contain less ether and carbonyl groups as well as less methylene groups in long alkyl chains than those obtained in the medium of other ethers. It can be considered the influence of temperature – once formed oxyethylated products were submitted to further thermal degradation.

Water-soluble compounds and phenols are characterized by high content of not only OH but also other oxygen-containing groups, the latter ones not influencing their hydrophilic or slightly acidic properties.

Polyglycols are known to be formed in small amounts in the reaction of ethylene oxide with alkylphenols (5-alkylresorcinols are typical among kukersite thermal decomposition products), and low-molecular-weight poly(ethylene)glycols represent a series of water-soluble polymers.

IR-spectroscopy of liquid products formed at pyrolysis of asphaltenes, HPC and chars demonstrate that most of the typical functional groups have been transferred into the composition of the secondary liquid products, and the pyrolyzates saturated with alkyl and oxyalkyl groups of ether origin are generally characterized by similar functional group compositions and regularities as the primary liquid products and separated from them fractions.

Gas Chromatographic Analysis of Malthenes

Non-polar and neutral fractions of compounds separated from TBSLP and from the pyrolyzates of asphaltenes and HPC – *n*-alkanes, *n*-alkenes, *n*-alkylbenzenes, symmetric alkanones having the carbonyl group in the middle of the carbon chain and 2-alkanones – were characterized by gas chromatographic analysis. The content of individual homologues and the regularities of their distribution inside the respective fraction are presented in Figs 1–3.

Figure 1 demonstrates that the content of aliphatic and aromatic hydrocarbon homologous series in the region C₁₁–C₁₇ almost proportionally increases with increasing the length of hydrocarbon chain despite the type of solvent used for liquefaction. Since C₁₈ the concentration of higher homologues abruptly decreases and diminished concentrations remain on an almost equal level up to the homologue C₂₄. The products obtained in ethylene oxide have highest concentrations of *n*-alkanes and *n*-alkylbenzenes in the middle and in the end of homologous series presented. It is believed [9] that at pyrolysis long hydrocarbon chains split just at the middle and, as ethylene oxide evokes polymerization processes, an increase in the concentration of higher homologues could be expected. Two homologous series of ketones with maximum concentrations at C₁₅–C₁₇ are distributed more evenly, and they show no sharp diminishing tendency towards homologues higher than C₁₇.



Fig. 1. Content and distribution of *n*-alkanes (a), *n*-alkylbenzenes (b), symmetric alkanones (c) and *n*-2-alkanones (d) in the composition of TBSPSLP obtained on kerogen liquefaction in the medium of carbon dioxide (1), diethyl ether (2), dioxane-1,4 (3) and ethylene oxide (4)

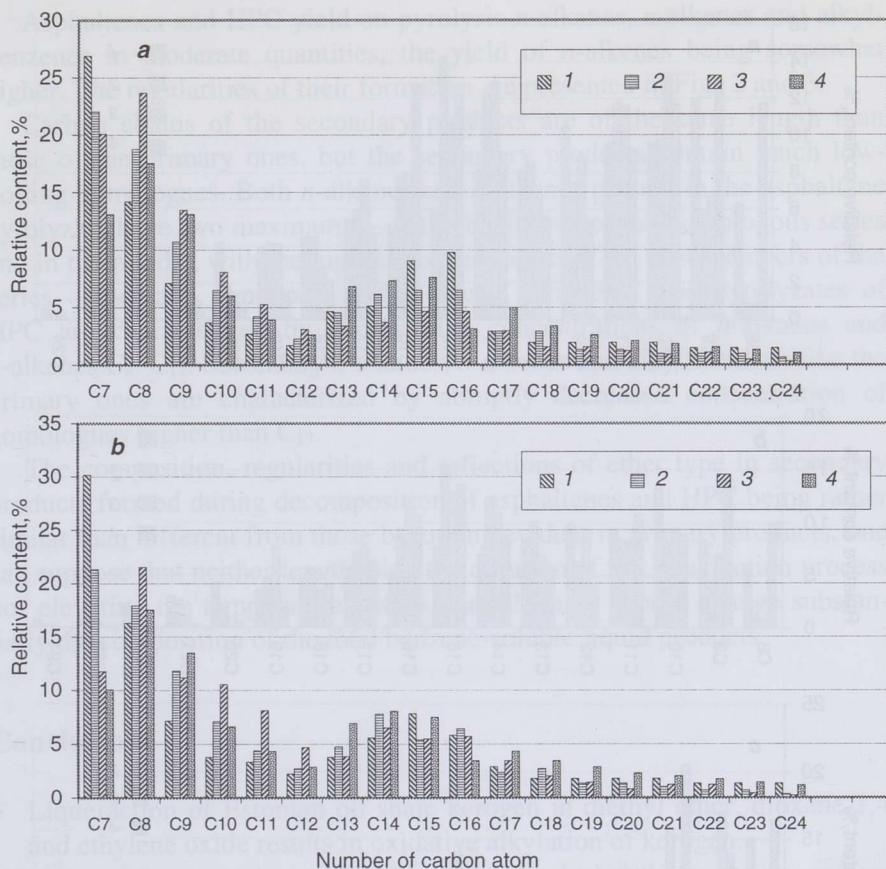


Fig. 2. Content and distribution of secondary *n*-alkanes (a) and *n*-alkenes (b) formed at pyrolysis of asphaltenes separated from TBSLP obtained in the medium of carbon dioxide (1), diethyl ether (2), dioxane-1,4 (3) and ethylene oxide (4)

For kukersite oils, due to the marine origin of kukersite kerogen, the most characteristic compounds contain in carbon skeleton up to 17 carbon atoms. The content of higher homologues of terrigenous origin is usually very low. That is why the region over C₁₇ was chosen to study the influence of ethers and their type. Some significant differences between the action of various ethers were elucidated. The effect of diethyl ether is expressed by formation of *n*-alkanes C₁₈–C₂₃ in practically equal concentrations, by significantly high concentration of alkylbenzene C₂₀, and by visually proportional decrease in the content of both symmetric and *n*-2-alkanones. In the medium of dioxane-1,4, *n*-alkanes and alkylbenzenes C₁₈ and higher were formed in almost equal concentrations, among symmetric alkanones C₁₈ and C₂₁ were formed in maximum amounts. As for 2-alkanones, the longer the alkyl chain, the lower its concentration.

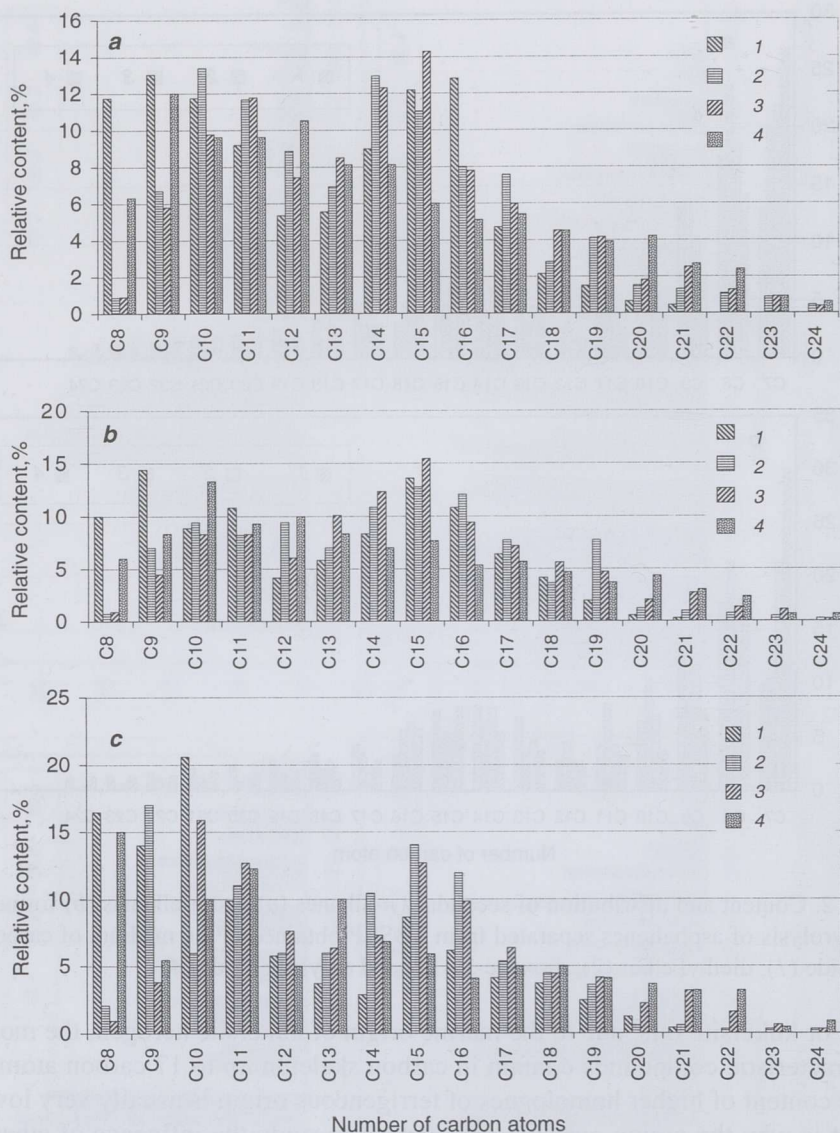


Fig. 3. Content and distribution of secondary *n*-alkanes (a), *n*-alkenes (b) and *n*-alkylbenzenes (c) formed at pyrolysis of polar malthenes separated from TBSLP obtained in the medium of carbon dioxide (1), diethyl ether (2), dioxane-1,4 (3) and ethylene oxide (4)

The effect of ethylene oxide, in comparison with other solvents, is expressed by maximum concentrations of individual *n*-alkanes C₁₉–C₂₄, alkylbenzenes C₁₉ and C₂₃ and by minimum concentrations of symmetric ketones C₁₇ and C₁₉. Among *n*-2-alkanones lower than C₁₇, ethylene oxide caused their absolute maximum at C₁₆ and a significantly elevated concentration of C₁₂ compounds.

Asphaltenes and HPC yield on pyrolysis *n*-alkanes, *n*-alkenes and alkylbenzenes in moderate quantities, the yield of *n*-alkenes being somewhat higher. The regularities of their formation are presented in Figs 2 and 3.

Carbon chains of the secondary products are of the same length than those of the primary ones, but the secondary products contain much low-boiling homologues. Both *n*-alkanes and *n*-alkenes present in the asphaltene pyrolyzate have two maximums – at the beginning of the homologous series and in the middle, with the highest concentration of the first members of the series – *n*-octane, *n*-nonane, and *n*-octene, *n*-nonene. The pyrolyzates of HPC are characterized by evenly high concentrations of *n*-alkanes and *n*-alkenes C₈–C₁₇. Secondary *n*-alkanes, *n*-alkenes and alkylbenzenes like the primary ones are characterized by abruptly decreased concentration of homologues higher than C₁₇.

The composition, regularities and reflections of ether type in secondary products formed during decomposition of asphaltenes and HPC being rather similar than different from those becoming evident in primary products, one can suppose that neither lengthening the duration of the liquefaction process nor elevating the temperature within normal limits should change substantially the composition of the total benzene-soluble liquid products.

Conclusions

- Liquefaction of Estonian oil shale kerogen in diethyl ether, dioxane-1,4 and ethylene oxide results in oxidative alkylation of kerogen.
- Thermal decomposition of previously oxidatively alkylated intermediate (kerogen when ethylene oxide is used, and asphaltenes, high-polar compounds and char when diethyl ether or dioxane-1,4 are used) is a key process of liquid product formation on kukersite kerogen liquefaction in ethers determining the composition of final products.
- The composition and content of primary and secondary compounds obtained at different stages of liquefaction in ether media are rather similar than different. Secondary products are characterized by high content of oxyethylation products.

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