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LIQUEFACTION OF KUKERSITE CONCENTRATE AT 330-370 °C IN SUPERCRITICAL SOLVENTS

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The action of lower aliphatic and aromatic hydrocarbons and their mixtures with water on kukersite conversion to liquid products in autoclaves was studied. The effect of methanol or formate as hydrogen donor and zinc dust on the yield and composition of liquid products obtained was investigated as well. The amounts of organic matter dissolved by individual solvents only slightly differed, but the exchange of the part of solvent for the same amount of water in all cases resulted in increasing the oil yield. The latter is strongly dependent on the temperature, reaction time, type of solvent, and the concentration ratio of solvent to water. Using benzene-water mixtures and varying liquefaction parameters, almost complete conversion of kukersite into liquid product was achieved.

The oils obtained by liquefaction are heavy characterized by a high density and molecular weight and a great content of asphaltenes. Kukersite liquefaction by in situ hydrogen generation, using methanol and zinc-water reaction system, resulted in a considerable decrease in the content of asphaltenes and heteroatoms.

During processing of solid fuels, almost all conversion processes begin with the thermal decomposition of the fuel organic matter (OM). Developing information about the course of decomposition is the key to learning fossil fuel chemistry. During low-temperature thermal decomposition (retorting in Fischer assay) of oil shales the main product is a liquid - oil - whose main yield is up to 70 %, on shale OM basis. The mechanism of oil formation has been the subject of many research projects [1, 2]. They are all of the opinion that this process occurs in three stages:

- (1) Formation of oil molecules
- (2) Separation of oil from the solid residue (and vaporization)

(3) Polymerization and condensation of oil accompanied by the formation of coke

The yield and composition of oil depend on how it passes these three stages of transformation and migration, i.e. on the applied decomposition method. In our laboratory, the following methods have been used: retorting, hydrogenation [3], thermal solubilization in low-boiling [4] and high-boiling [5] solvents, and even in water suspension [7] under relatively mild conditions (low temperatures). Our aim was to obtain as high yields of primary oil as possible (the conditions used are given in Table 1). We have examined the effect of single parameters on the stage of oil formation.

Table 1. Parameters of Oil Shale Thermal Decomposition under Laboratory Conditions

Indices	Retorting	Hydrogenation	Liquefaction		
			250-330	380-420	370-400
Temperature, °C	300-550	370-400	250-330	380-420	370-400
Pressure, MPa	0.1	10-20	5-10	3-5	22-30
Duration, h	1.5	1-3	8-60	0.5-2	1-3
Solvent	No solvent	Benzene, toluene	Benzene and other low-boiling	High-boiling distillate of oil	Water solutions of formiate and alkali

The primary decomposition of OM macromolecules is and remains the most mysterious and less studied stage of oil formation. The majority of prior research projects presume this stage to begin with the formation of high-molecular-weight thermobitumen. The presence of solvents, especially of low-boiling ones (benzene, alcohols, tetrahydrofuran), accelerates bituminization processes occurring at temperatures lower than those of active organic matter decomposition (340-360 °C) [8]. In that case temperature, pressure, and solvent density have to exceed corresponding critical parameters. Larger amounts of solvents (and higher pressures) accelerate the solubilization. It is hypothesized that solvents acquire extra destructive properties under critical conditions [9]. Water as a solvent has a very low activity at temperatures below the critical temperature (374 °C).

The next stage is the separation of oil from the solid residue. Upon retorting, this process occurs only after decomposition of the primary bitumen accompanied by the formation of coke, gas and oil. Under sufficient oil vapor pressure the latter are evacuated in the vapor phase. That is why retorting always yields less oil than solubilization. In the latter case, oil separates from the solid residue in its original form. That is the main difference between the methods of retorting and solubilization.

Supercritical solvents are taken for gases, but, due to a high phase density ($\sim 300 \text{ kg/m}^3$), even high-molecular-weight compounds dissolve in them. Mass transfer occurs very rapidly because of lowered viscosity of gas-like solvents.

Secondary reactions of polymerization and condensation of the primary thermobitumen, and of the oil formed from it, occur in different ways depending on the method used (see Table 1). In our opinion almost the total amount of retort oil is of secondary origin, formed during cracking of primary products (monomolecular reaction). Dilution in supercritical solvents is carried out at relatively low temperatures when no cracking takes place. Polymerization and condensation are bimolecular reactions which decelerate with diminishing concentrations of reacting compounds. In the case of solubilization, the formed products are diluted in the solvents and, because of that, they contact and interact passively. In the case of liquefaction in a supercritical solvent, the latter and the products occur mainly in the liquid phase, the density of which may reach $\sim 800 \text{ kg/m}^3$. In the case of equal amounts of solvents, the concentration of liquefaction products in the supercritical phase is 2-3 times lower as compared to that in the liquid phase with high-boiling solvents. The rates of secondary reactions occurring in both states differ, correspondingly, too.

As stated in [5, 6], the oil liquefied in a supercritical solvent contains only a few reactive compounds - olefins, phenols, polycyclic aromatic hydrocarbons - as they are mostly abreacted in secondary reactions. The course of these reactions is conditioned not only by elevated concentrations of liquefaction products in the liquid phase but even more by the use of a retort oil fraction as a solvent (without hydrogenation) which is certainly more active as the primary product of liquefaction.

Several factors influence the run of hydrogenation processes (see Table 1), the composition of the initial fuel being the primary one. Conversion in the aqueous medium occurs with the participation of water molecules in destructive reactions, and a lot of coke and gas is formed.

As stated above, the largest amount of oil shale organic matter can be obtained as oil using the method of supercritical extraction. Secondary reactions of decomposition and condensation of formed products are avoided if the processing temperature is low and chemically inert solvent has a high ability for dissolution. High yield and primarity make this oil a suitable object to investigate the structure of the shale initial organic matter. The method has some disadvantages - the process is time-consuming and the pressure has to be kept high. Liquefaction tests at 330 °C have shown that high yields of oil are obtained only after 24 hour of treatment since the solubilization occurs very slowly [4]. A mechanism to describe gaseous extraction is proposed and it is based on the physical characteristics of the process [8].

Since it is known that an active separation of primary thermobitumen begins at 340-360 °C, the transformations occurring in this interval make up the topics of our present study. Special attention has been paid to the action of solvent mixtures and of various admixtures added to the basic solvent.

Use of Individual and Binary Solvents

The experiments were carried out in 20 ml rotating autoclaves. The ratio of kukersite : solvent was kept constant in all cases: 2 g of kukersite concentrate containing 90 % organic matter in 6 g of solvent. To determine the gas yield, autoclave was weighed before and after its opening. The oil was washed out with benzene - i.e. the liquefaction product was the part soluble in benzene. Individual compounds or their mixtures with water were used as solvents. As seen from Table 2, replacement of a part of the solvent with an equivalent amount of water always increased the oil yield. Moreover, using mixtures of solvent and water allows the use of milder reaction conditions and no H₂ addition is needed [10].

Table 2. Oil and Gas Yields with Liquefaction, wt % (340 °C, 4 h)

Solvent	Pure solvent		Solvent + water (1 : 1)	
	Oil	Gas	Oil	Gas
Hexane	24.1	3.5	33.1	4.9
Cyclohexane	25.9	3.2	31.5	3.4
Toluene	25.9	2.1	30.7	3.4
Benzene	28.7	4.9	46.4	4.8
Methanol	34.8	5.0	40.2	3.8
Water	35.5	5.5	35.5	5.5

Pure hydrocarbon solvents liquefy comparable amounts of OM (25-28 %); methanol and water as the sources of hydrogen reveal a higher destructive activity. In the medium of hydrocarbon solvents only a little gas is formed - up to 5 % from the OM. In the case of liquefaction in methanol, the gas yield is the same. Liquefaction of brown coal and coal in methanol always yielded low amounts of gas [11, 12]. When half of the solvent was replaced by water, the oil yield increased by 5-9 %, and even by 17 % when using benzene.

We have used benzene, water, and their mixture as the most interesting solvents to study the dependence between oil yield and temperature (Fig. 1).

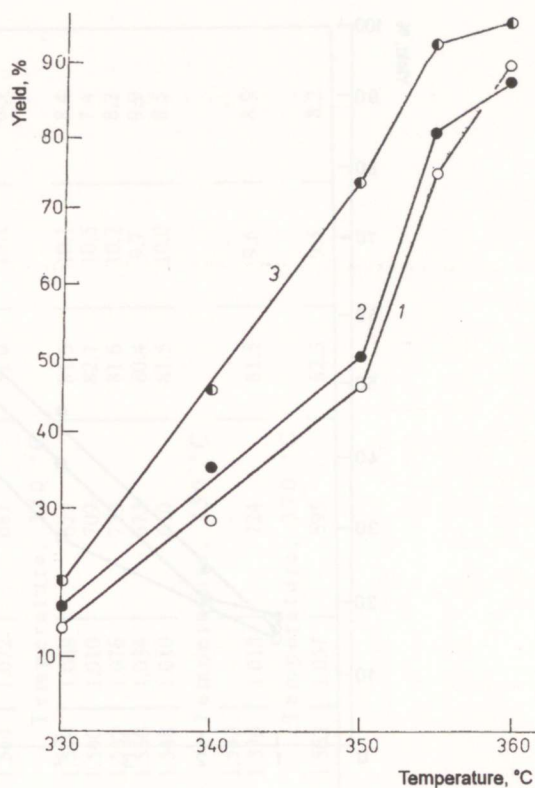


Fig. 1. The dependence of oil yield on the temperature under conditions of supercritical extraction. Liquefaction in benzene (1), water (2), and their mixture (3) after 4 hours

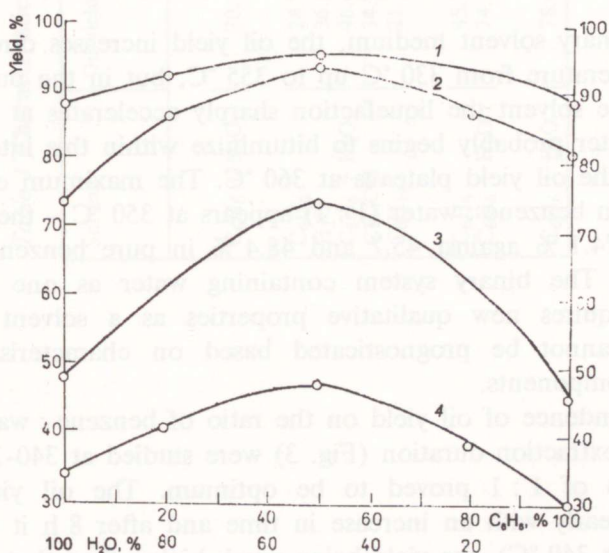


Fig. 2. The dependence of oil yield on the composition of the benzene-water binary system (4 hrs): 1 - 360 °C, 2 - 355 °C, 3 - 350 °C, 4 - 340 °C

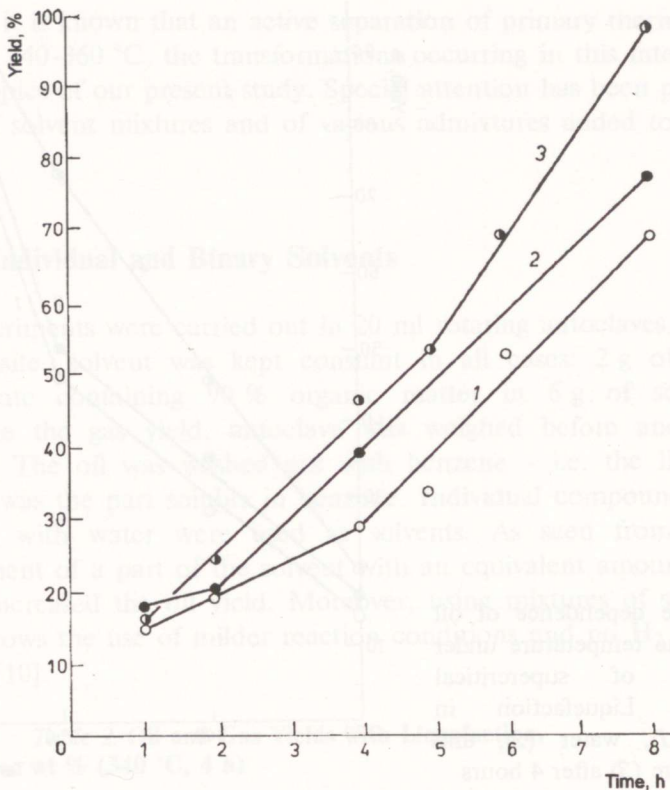


Fig. 3. The yield of extracted oil vs. time at 340 °C (for notations see Fig. 1)

In the binary solvent medium, the oil yield increases directly with a rise in temperature from 330 °C up to 355 °C, but in the pure water or pure benzene solvent the liquefaction sharply accelerates at 350-355 °C. Organic matter probably begins to bituminize within this interval. In all three cases the oil yield plateaus at 360 °C. The maximum effect of the binary system benzene : water (1 : 1) appears at 350 °C - the oil yield is as high as 74.1 % against 45.7 and 48.4 % in pure benzene or water, respectively. The binary system containing water as one component probably acquires new qualitative properties as a solvent and these properties cannot be prognosticated based on characteristics of the individual components.

The dependence of oil yield on the ratio of benzene : water (Fig. 2) and on the extraction duration (Fig. 3) were studied at 340-360 °C. The solvent ratio of 1 : 1 proved to be optimum. The oil yield initially increases linearly with an increase in time and after 8 h it reaches the maximum (at 340 °C), the yield being much higher than that of retorting (65 %). Consequently, varying the temperature and time of liquefaction, one can obtain oil yield as high as desired, but the result seems highly dependent on the solvent properties.

Table 3. Characteristics of Liquid Product of Kerogen Extraction

Solvent	Oil yield, %	n_D^{20}	d_4^{20}	Molecular mass	Elemental composition %										
					C	H	O + N + S								
C ₆ H ₆ + H ₂ O	20.1	1.544	1.072	681	81.0	10.1	8.9								
								Temperature, 330 °C							
C ₆ H ₆ H ₂ O C ₆ H ₆ + H ₂ O CH ₃ OH C ₆ H ₁₄	28.7 36.5 46.4 34.8 21.1	1.549 1.540 1.532 1.550 1.548	1.068 1.010 1.076 1.034 1.010	625 709 773 672 610	81.5 82.1 81.6 80.4 81.5	10.1 10.5 10.2 9.7 10.0	8.4 7.4 8.2 9.9 8.5								
								Temperature, 340 °C							
								C ₆ H ₆ C ₆ H ₆ + H ₂ O	45.7 74.1	1.543 1.536	- 1.018	724	- 81.5	- 9.6	- 8.9
								C ₆ H ₆ + H ₂ O	78.6	1.562	1.057	595	82.3	9.5	8.2
Temperature, 370 °C															

Table 4. Characterization of Supercritical Extraction Oil by IR-Spectrum

Solvent	Frequency, cm^{-1}													
	720	745	815	880	1380	1600	1700	2930	2960	3020	3055	3400	2930/ 2960	3050/ 2930
$\text{C}_6\text{H}_6 + \text{H}_2\text{O}$	Temperature 330 °C													
	0.20	0.13	0.32	0.04	0.82	0.91	1.02	0.77	0.70	0.11	0.03	0.74	1.11	0.04
C_6H_6 H_2O $\text{C}_6\text{H}_6 + \text{H}_2\text{O}$ CH_3OH C_6H_{14}	Temperature 340 °C													
	0.15	0.10	0.27	0.05	0.71	0.80	0.73	0.59	0.52	0.09	0.05	0.62	1.13	0.08
	0.26	0.17	0.33	0.05	0.84	0.95	0.95	0.78	0.57	0.09	0.05	0.86	1.36	0.07
	0.23	0.16	0.30	0.11	0.82	0.92	0.91	0.73	0.62	0.10	0.04	0.73	1.18	0.05
	0.16	0.12	0.18	0.08	0.80	0.83	0.88	0.91	0.81	0.16	0.07	0.63	1.12	0.08
$\text{C}_6\text{H}_6 + \text{H}_2\text{O}$; asphaltenes $\text{C}_6\text{H}_6 + \text{H}_2\text{O}$; malthenes	0.21	0.12	0.32	0.07	0.78	0.88	0.81	0.85	0.74	0.12	0.05	0.69	1.16	0.06
	0.13	0.36	0.43	0.08	0.83	0.98	0.77	1.15	0.94	0.09	0.06	0.91	1.22	0.05
	0.12	0.22	0.26	0.10	0.67	0.74	1.00	1.19	1.07	0.22	0.12	0.70	1.12	0.10
$\text{C}_6\text{H}_6 + \text{H}_2\text{O}$ $\text{H}_2\text{O} + \text{HCOONa} + \text{Zn}$ C_6H_6 ; asphaltenes $\text{C}_6\text{H}_6 + \text{HCOONa} +$ $\text{H}_2\text{O} + \text{Zn}$; asphaltenes	Temperature, 350 °C													
	0.30	0.22	0.46	0.13	0.84	0.98	0.94	1.10	0.64	0.10	0.06	0.85	1.72	0.05
	0.27	0.16	0.73	0.05	0.77	0.63	0.91	1.11	0.95	0.19	0.08	0.61	1.17	0.07
	0.24	0.18	0.38	0.12	0.76	0.94	0.56	1.13	0.83	0.02	0.01	0.56	1.36	0.01
	0.22	0.14	0.18	0.06	0.73	0.80	0.78	1.39	1.18	0.18	0.12	0.65	1.18	0.08
$\text{C}_6\text{H}_6 + \text{H}_2\text{O}$	Temperature 370 °C													
	0.33	0.31	0.45	0.22	0.84	0.95	0.87	0.70	0.58	0.10	0.07	0.78	1.21	0.10
Retort oil	Temperature up to 525 °C													
	0.21	0.42	0.30	0.11	0.73	0.87	0.56	1.20	1.08	0.19	0.11	0.71	1.11	0.09

Characterization of Liquefaction Oils

The data given in Table 3 demonstrate that liquefaction oils obtained in the medium of different solvents have similar physical and chemical properties. Even the oil obtained in methanol presents no exception.

Oil yield increases with an increase in the temperature, and changes in composition are negligible. Oils are characterized by high density and molecular mass. Asphaltenes were separated through solution in chloroform and consequent precipitation with *n*-hexane. 53-58 % of the oils are compounds soluble in *n*-hexane, and the asphaltene content is smaller.

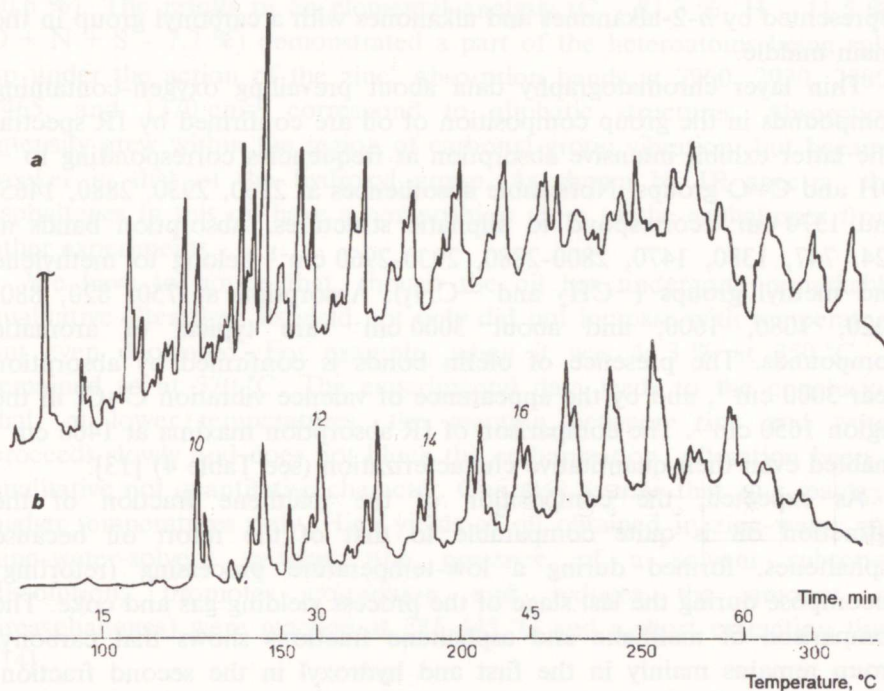


Fig. 4. Chromatograms of (a) total oil extracted with water, and (b) ketone fraction at 360 °C. The numbers identify the number of C atoms in the ketone molecule.

Since, malthenes are quite similar in their composition, according to IR-spectroscopy data, only one fraction of malthenes was separated into groups using the method of thin layer chromatography (silica gel L 40/100 μm). Over 60 % of malthenes remained on the starting line. The percentage of other compounds was as follows: ketones - 17 %, polycyclic aromatic hydrocarbons - 7 %, monoaromatic compounds - 4 %, and paraffins-olefins - 12 %. Retort oils contain less heteroatomic compounds (59 % together with phenols), but more polycyclic compounds (18-21 %). Liquefaction oil contains more oxygen, sulfur and

nitrogen compared to retort oil, and, correspondingly, more heteroatomic compounds. The use of gas chromatography to analyze the total oil is complicated due to the low volatility of the samples.

The chromatograms (Fig. 4) of the total oil and ketones of one liquefaction test show that their composition is comparable to that of oil and ketones obtained from retorting. Odd-number paraffins and even-number olefins dominate in the liquefaction samples though not so markedly as in the retort oil. Some hydrocarbon fractions contain only small amounts of hexadecane. The content of olefins was somewhat higher than that of extraction oils (at temperatures below 330 °C). Oxygen-containing compounds separated by gas chromatography are represented by *n*-2-alkanones and alkanones with a carbonyl group in the chain middle.

Thin layer chromatography data about prevailing oxygen-containing compounds in the group composition of oil are confirmed by IR spectra. The latter exhibit intensive absorption at frequencies corresponding to —OH and C=O groups. Noticeable absorbences at 2960, 2930, 2880, 1465, and 1370 cm^{-1} correspond to aliphatic structures. Absorption bands at 724, 747, 1380, 1470, 2800–2880, 2930–2960 cm^{-1} belong to methylene and methyl groups ($-\text{CH}_2$ and $-\text{CH}_3$). Absorption at 750, 820, 880, 1020, 1080, 1600, and about 3000 cm^{-1} are typical of aromatic compounds. The presence of olefin bonds is confirmed by absorption near 3000 cm^{-1} , and by the appearance of valence vibration C=C, in the region 1650 cm^{-1} . The comparison of IR absorption maxima at 1460 cm^{-1} enabled even their quantitative characterization (see Table 4) [13].

As expected, the composition of the malthene fraction of the extraction oil is quite comparable to that of the retort oil because asphaltenes, formed during a low-temperature processing (retorting) decompose during the last stage of the process yielding gas and coke. The comparison of malthene and asphaltene fractions shows that carbonyl group remains mainly in the first and hydroxyl in the second fraction. The physical characteristics of the total oils differ only slightly from each other (Table 3), the differences being better observed in IR spectra (Table 4). We have to add that oils extracted with water or with a mixture of solvent-water, contain more —OH and C=O groups as compared to the case when only solvent is used (Table 4).

The Effect of Various Admixtures on the Quantitative and Qualitative Alteration of Oil during Liquefaction

1. Liquefaction in the Presence of Zinc

The reaction between zinc and water, with heating, occurs according to the reaction $\text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2$ [14, 15]. Experiments with

standards demonstrated that hydrogenation takes place as a result of reactive hydrogen being liberated in that manner. All the present experiments used 1.5 g of Zn and usually 6 g of solvent. The oil obtained in the experiments with Zn + H₂O differed significantly from other oils characterized in Table 3. It was lighter ($d_4^{20} = 0.960$, $n_D^{20} = 1.515$), but had a molecular mass as high as other oils - 683.

Chromatographic analysis of the oil demonstrated a differing distribution of paraffins and olefins by the length of the hydrocarbon chain. This was very likely caused by hydration of some part of the olefins. The oil contained somewhat more ketones (26 %), with symmetrical ones prevailing. The content of asphaltenes was remarkably lower (up to 30.6 %). The results of an elemental analysis (C - 81.3 %, H - 11.5 %, O + N + S - 7.2 %) demonstrated a part of the heteroatoms being split up under the action of the zinc. Absorption bands at 2960, 2930, 2880, 1465, and 1370 cm⁻¹ correspond to aliphatic structures. Absorption intensity grew within the region of carbonyl group vibration, but became weaker in that of the hydroxyl group. As shown by IR spectra, the asphaltenes in this oil have a composition close to the asphaltenes from other experiments.

We have to notice that, though the oil has undergone remarkable qualitative alteration, its yield not only did not increase with temperature but even decreased. For example, when it was 44.3 % at 350 °C, it remained so at 370 °C. The experimental data leads to the conclusion that, at lower temperatures, the reaction between zinc and water proceeds slowly and does not block the carbonization. Alteration bears a qualitative not quantitative character. One may assume that zinc reacts at higher temperatures only. High yields of oil obtained in zinc-water and zinc-water-solvent systems (the presence of a solvent subserves dissolution, promotes conversion and reduces the amount of preasphaltenes) were reached at 385-445 °C and a short extraction time [14].

2. Liquefaction in the Presence of Hydrogen Donors

The general mechanism of this process consists of a stabilization of the produced radicals during thermal decomposition by hydrogen atoms of the donor substances. The efficiency of a donor depends on how easy hydrogen atoms are to obtain, and even more on the molecules chemical structure [16].

Methanol and sodium formiate were used as donors. H-donor ability of these compounds are well known [12, 14]. With liquefaction, in the presence of methanol, carbon-carbon and ether bonds undergo splitting, and aromatic nuclei undergo alkylation and hydrogenation. Methanol decomposes as follows: $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2$. The reaction continues in

the presence of water in the reaction vessel: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, and additional amounts of hydrogen are formed (which can also be used for hydrogenation). The addition of methanol accelerates liquefaction and elevates the hydrogen content of the liquid product through hydration of some functional groups. The oil is characterized in Table 3. The oil yield may be increased from 34.8 up to 40.2 % by replacing half of methanol with water. Catalysts are usually used for methanol decomposition (metals and their oxides). Our experiment without a catalyst has given a satisfactory result.

Sodium formiat reacts with water as follows: $\text{HCOONa} + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{H}_2$. The oil yield (wt. %) at 350 °C and 25-percent water solution of sodium formiat, had the following values:

$\text{H}_2\text{O} + \text{HCOONa}$	60.8
$\text{Zn} + \text{H}_2\text{O} + \text{HCOONa}$	40.3
$\text{C}_6\text{H}_6 + \text{Zn} + \text{H}_2\text{O} + \text{HCOONa}$	42.3
$\text{C}_6\text{H}_6 + \text{H}_2\text{O} + \text{HCOONa}$	51.3

One can see that the presence of zinc reduces the degree of liquefaction. We have to add that when studying the structure of kerogen, using the distillation method, the oil yield was always lower with zinc dust (at atmospheric pressure) as compared with the results of experiments without zinc dust. Further investigations are needed to find out the reasons for low yields in the benzene-water-formiat system.

Discussion

The most interesting phenomenon observed during these studies was the elevated solubilization (destructive) action of binary systems in oil shale organic matter. Equal weights of water and individual low-boiling hydrocarbons used separately do not decompose organic matter as intensively as the same components used in mixtures. Synergistic effect of mixtures of these components has been established. This effect was observed at temperatures below 360 °C, under conditions where water, if used in sufficient amounts, still exists partly in the liquid phase ($t_{\text{critical}} = 374 \text{ °C}$) but all organic solvents used in the experiments are already in the supercritical phase. The values for the density of saturated water vapor in our experiments at temperatures of 340 °C and 370 °C were 93 and 147 kg/m³, respectively. Consequently, the quantity of water in the liquid phase was different, one may conclude that the quantity of the liquid phase had no effect on experiment results.

The degree of solvent efficiency varies over a very wide range. The highest yields of oil were obtained when using benzene. Benzene dissolves in water better than other solvents (*n*-hexane - 0.013, toluene -

0.22, benzene - 1.00 mg/ml at 20 °C) [17, 18], and benzene can be separated from the hydrocarbon mixture by using extraction with superheated water. The elevated decomposing action of the benzene-water mixture is probably caused not only by the chemical properties of benzene but more aptly by its elevated concentration in water as compared to other hydrocarbons.

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