

LIQUEFACTION OF OIL SHALES IN DIFFERENT SOLVENTS AND REAGENTS

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ABSTRACT

In order to obtain liquid product in higher yield, oil shales from different regions of the USSR and other countries (organic content 20-90%) were liquefied. Supercritical gas extraction (SGE) was carried out at 573 - 673K in low boiling solvents (hydrocarbons, alcohols) and their mixtures with water, as well as in the presence of a series of reagents. Almost complete conversion of organic matter was achieved by using binary water-containing solvents, as well as CO_2 . On liquefaction with binary solvents, especially with azeotropes, a synergistic effect of solvents was observed with respect to extract yield. This effect depends upon the temperature of extraction and the nature of kerogen of shale. The synergistic effect may be accounted for a specific behaviour of azeotropes under critical and supercritical conditions. The shales whose mineral part contains aluminosilicates, dehydrate alcohols C_2 - C_3 into olefins, which further polymerize into branched-chain hydrocarbons. Isopropyl alcohol is more amient to the reactions of dehydration, dehydrogenation and polymerization, yielding highly-branched aliphatic carbonyl-containing compounds.

By liquefaction of the organic matter of kukersite with ammonia obtained from $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_2)_2\text{CO}$, as well as in pure NH_3 , incorporation of nitrogen into the conversion products has been established. Nitrogen (up to 6-7%) is introduced into both the solid and liquid products. By ammonolysis of oil shales, products with a desired functional group can be obtained. The oils may be used as a raw material for the chemical industry.

INTRODUCTION

At present SGE is often used as a method for liquefying the organic matter of geopolymers and for investigating their

composition. This method may also be applied to the synthesis of commercial products with certain functional groups. In both cases, the yield and composition of the products formed are determined by the specific properties of solvent and kerogen, as well as the conditions of conversion used. SGE in different solvents affords, in the presence of chemical reagents and under optimum reaction conditions, high yields of extracts whose composition reflects that of kerogens from a geochemical viewpoint and suggests its use as a technological raw material.

EXPERIMENTAL

SGE of oil shales was carried out in 22 cm³ rocking autoclaves which were charged with powdered shale and reagent. The reaction time was measured from the point of reaching the reaction temperature. At the end of heating the system was cooled down to room temperature and the autoclave was opened. The total reaction product was diluted with benzene, the liquid and solid products were separated by filtration. Benzene was removed by rotary evaporation. Extract yield is determined as the amount of benzene-soluble compounds.

Ultimate analysis of the extracts was performed by using a 186 CHN Hewlett Packard analyzer, i.r. and ¹H n.m.r. spectra were taken on a Specord 75 IR and Tesla BS 567 (100 MHz) spectrometers. For the extracts obtained specific gravity and molecular mass by vapor-phase osmometry were determined. The extracts were separated into groups of compounds by thin-layer chromatography (TLC) on silica gel. The TLC fractions were analysed by gas chromatography in columns of different polarity with temperature programming.

RESULTS AND DISCUSSION

In Table 1 the characteristics of the oil shales and shale-like fuels under study, as well as the yields of extract in some solvents are presented. It can be seen that the extract yield is determined by the specific features of solvent (stability at the reaction temperature, reactivity with respect to kerogen, H-donor properties). In inert solvent (benzene-water) the extract yield depends on the type of kerogen and increases with increasing H/C ratio. No dependence between the extract yield and organic content of kerogen is observed. It has been established that in alcohol medium alcohol itself is resolved

into secondary reaction products, almost 50% of which being light gases. The dehydration products of alcohols C_2-C_3 are subjected to autopolymerization catalysed with aluminosilicates present in the mineral part of some shales. As a result, the extract yield is very high.

The results obtained by liquefaction of organic-poor oil shales from the South Khatar and West Kultak deposits characterize well the behaviour of low boiling alcohols in the SGE process. Both the shales are characterized by a relatively high alumina content in the mineral part, viz. 9.2 and 6.7%, respectively. These oil shales afford extract in very high yields (in proper conditions more than 100% on organic matter), especially on liquefaction in isopropanol-water. In SGE in methanol and ethanol under the same experimental conditions no such high extract yields were obtained.

Chromatographic and spectroscopic analysis of the isopropanol extracts showed them to contain mainly the products of conversion of the starting alcohol. The concentration of non-aromatic branched-chain hydrocarbons C_{12} , C_{15} and C_{18} was high (36-59%). The oxygen and high-polar compounds (16-25%) are high-molecular compounds with branched carbonyl-containing chains. In addition, ether groups in these compounds were identified. It is difficult to determine the contribution of organic matter to the yield and composition of extract. Isopropanol was shown to be the most reactive alcohol in the reactions of dehydrogenation, dehydration and polymerization. On SGE of the shales, which are characterized by a low organic content and the presence of alumina in the mineral part, the very high yield of liquid product is due only to the conversion products of alcohol. The presence of these products makes it more difficult to elucidate the mechanism of liquefaction of organic poor-oil shales.

In binary solvents (benzene-water, Table 1.) a synergistic effect with respect to extract yield is observed. To investigate this phenomenon, the organic matter concentrates from three different oil shales were subjected to liquefaction, viz. Kukersite shale, Sysola and Krassava shales.

Investigations demonstrated that the value of the synergistic effect depends on the extraction temperature. Also, depending upon the kerogen structure, this effect may be observed within a certain benzene-water ratio range. In the beginning of liquefaction kerogen from the oxidized Sysola and Krassava oil shales affords in situ an additional amount of water which

Table 1. Yield of extracts (wt.-% on organic matter) from the fossil fuels of different deposits
 SGE conditions: 623K, 4h, fuel-solvent ratio 1:1.5 and 1:10*

Fossil fuel, deposit	Organic content, %	H:C	N	O+S	Extract yield on organic matter by liquefaction with extragents			
					Benzene	Benzene-Water	Etha-nol	Iso-panol
Shale, Chagansk, Russian SFSR	56.7	1.57	1.0	28.3	53.8	48.6	87.5	92.6
Shale Kenderlyk, Kazakh SSR	48.4	1.25	1.8	18.3	5.3	8.8	50.7	67.8
Menilitic shale, the Carpathians, Ukrainian SSR	19.9	1.20	1.0	31.0	9.3	8.3	69.4	62.0
Kukersite, Estonian SSR	47.6	1.45	0.6	11.6	51.2	50.0	78.3	96.2
Shale, Borov Dol, Bulgaria	22.0	1.86	2.2	26.4	26.5	12.5	69.2	72.5
Shale, Green River, USA	29.2	1.74	1.9	17.5	68.8	52.0	96.2	78.4
Balkhashite, Kazakh SSR	94.0	1.70	0.7	12.5	63.8	60.0	89.6	95.5
Boghead, Borov Dol, Bulgaria	48.3	1.46	2.4	23.1	34.1	24.9	84.3	98.7
Liptobiolith, Lipovetski, Russian SFSR	43.7	1.13	---	11.6	17.9	5.5	48.4	37.1
Liptobiolith, Tkibuli, Georgian SSR	84.8	1.23	1.7	10.9	16.4	---	52.3	58.7
Shale, Krassava, Bulgaria	45.9	1.51	1.0	23.8	33.8	20.4	53.6	43.3
Shale, Sysola, Komi ASSR	24.3	1.36	1.7	25.7	36.7	8.1	73.1	74.8
Shale, South Khatar, Uzbek SSR*	13.7	1.23	2.0	22.1	10.0	40.0	90.0	160.0
Shale, West Kultak, Uzbek SSR*	5.0	1.20	1.9	26.8	40.0	16.0	80.0	85.0

shifts the synergistic effect towards the higher benzene content (Table 2. and Fig.1.).

Table 2. Yield of extract from enriched shales at 623K in individual and binary solvents.

Concentrate	Kerogen I content, %	Extract yield, wt-% on org.matter		
		Water	Benzene	Water-benzene(1:1)
Kukersite	93	48	46	74
Sysola shale	76	11	29	26
Krassava shale	82	16	38	11

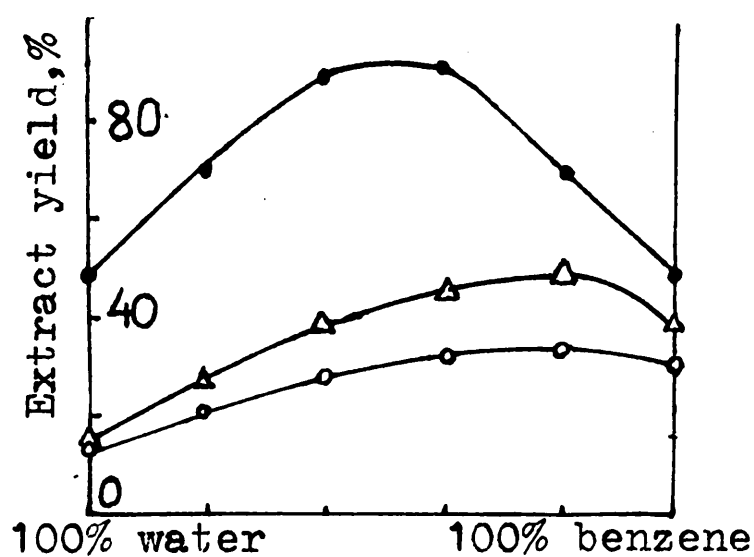


Fig. 1. Extract yield versus benzene-water mixture composition.

- - Kukersite(623K)
- △ - Krassava (610K),
- - Sysola (603K).

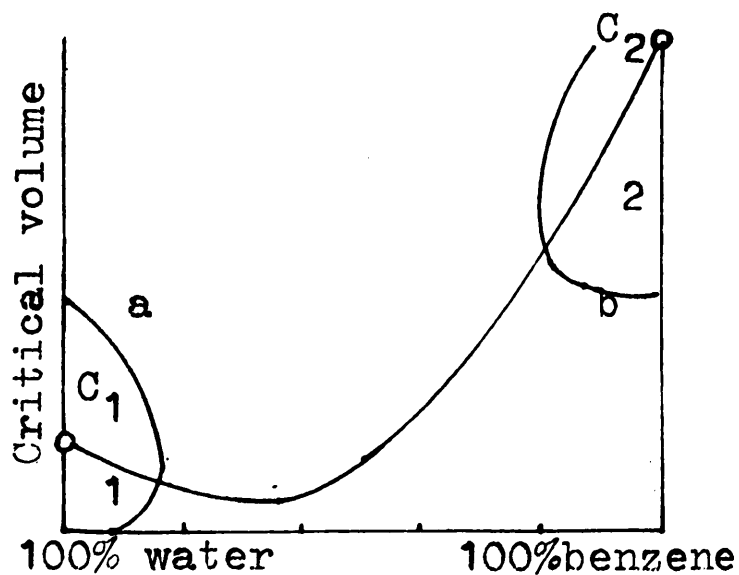


Fig. 2. Critical molar volume of benzene-water mixture versus composition. C_1 -critical point of water: C_2 -critical point of benzene, a, b-isobars -- isotherms; 1 and 2 -- regions of retrograde condensation.

As this effect is observed with heteroazeotropic mixtures, it may be explained and predicted by the specific behaviour of azeotropes in critical and supercritical conditions. This means that by transition of a certain azeotropic extractant into a critical condition, two regions of retrograde condensation ap-

pear. Figure 2 illustrates the existence of such regions for the azeotropic mixture water-benzene. In the first region, the vapor phase will be rich in water and poor in benzene, but in the second region, vice versa, the vapor phase will be rich in benzene and poor in water. It is considered that fuel is easy to liquefy with the dense solvent vapor. In the region of retrograde condensation the density of the solvent vapor decreases, and at the same time, the composition of the liquid and vapor phases changes, too. The oil yield depends on these factors and consequently, the phenomenon of retrograde condensation is reflected on the amount of extract, i.e. on the efficiency of fuels SGE.

Binary solvents of the hydrocarbon-water type, as well as CO_2 , have the best liquefying properties and rapidly decompose kerogen, revealing no chemical action upon it. Using these solvents in different conditions (temperature, time of extraction, solvent-fuel ratio, density of solvent) liquefaction of Kukersite into extract and gas was almost complete - up to 95 and 5 % respectively. High extract yields were achieved the other shales under study (Table 1.). It is notable that the extract yield in the SGE process is higher than that of Fischer assay oil by a factor of 1.5-2.

The high extract yield can also be achieved if liquefaction is carried out with reagents such as HCOONa , Zn , NaOH . By using the hydrogen formed in situ high extract yields have been obtained from the decomposition of HCOONa or the reaction of $\text{Zn} + \text{H}_2\text{O}$ by liquefaction of oil shales abundant in heteroelements. Thus, on conversion of Sysola shale in water, the extract yield was 13% on organic matter, but on addition of NaOH or HCOONa (10 wt.-%), it increased up to 20 and 38% respectively. The efficiency of liquefaction grows with decreasing degree of decomposition of the donor used. The maximum degree of decomposition of formate and urea is achieved without water, as the process is initiated by the water formed from the decomposition of kerogen itself. Urea is decomposed only in the presence of an additional amount of water. The chemical composition of the extracts obtained from the liquefaction of oil shales in inert solvents (hydrocarbons and their mixtures with water) under various conditions depends on the type of shale used. The extracts from Kukersite have a density of 1.01-1.08 g/cm^3 and molecular mass 510-770. The extracts are similar in elemental composition and functional groups content. They contain 42-47% of asphaltenes, the maltenes being similar in group composi-

tion to the semicoking oil. It has been found that the extracts from other oil shales contain no other specific functional groups or hydrocarbon skeletons observed in semicoking oils. All the SGE extracts differ from the latter in the lower degree of transformation. The use of zinc improves the quality of the extract to be used for liquid fuel purposes - zinc binds the oxygen and sulfur of kerogen and decomposes asphaltenes, thus lowering the density of extract.

By liquefaction in the presence of nitrogen containing compounds nitrogen is introduced into the extraction products. Table 3 presents the elemental composition of benzene-soluble extracts from the reaction of Kukersite with some nitrogen-containing compounds.

Table 3. Composition of extracts

Element	Nitrogen donor		
	Ammonia	Urea	Ammonium carbonate
C	78.5	77.7	78.7
H	9.5	10.0	10.4
N	6.2	7.5	6.3
O+S	5.8	4.8	4.6

The yield of the benzene-soluble product depends on the reaction temperature and partial pressure of NH_3 in the system, in the reaction of Kukersite with ammonia at 597K the extract yield was about 50% on organic matter. By the reaction of Kukersite with ammonium hydroxide (29 wt.-% NH_3) in the same conditions the extract yield decreased 5 times, although the nitrogen content in the extract remained the same (5.0%). From this it follows that besides the direct incorporation of ammonia into the oil, it probably splits the weak bonds in the kerogen macromolecule, thus favoring ammonolysis. The main product of Kukersite ammonolysis - the benzene-soluble substance is a viscous oil with a nitrogen content of 3.9 to 6.2%, depending upon the process conditions, and with a molecular mass of 420 - 730. I.r. spectrum (Fig.3) showed the extracts to be long-chain low-branched primary aliphatic amines and amides. The content of such nitrogen-containing compounds is characteristic also of the benzene-soluble extracts obtained by the reaction of Kukersite with the other nitrogen-containing compounds. The am-

monolysis of Kukersite demonstrates that from kerogen long-chained aliphatic amines can be obtained.

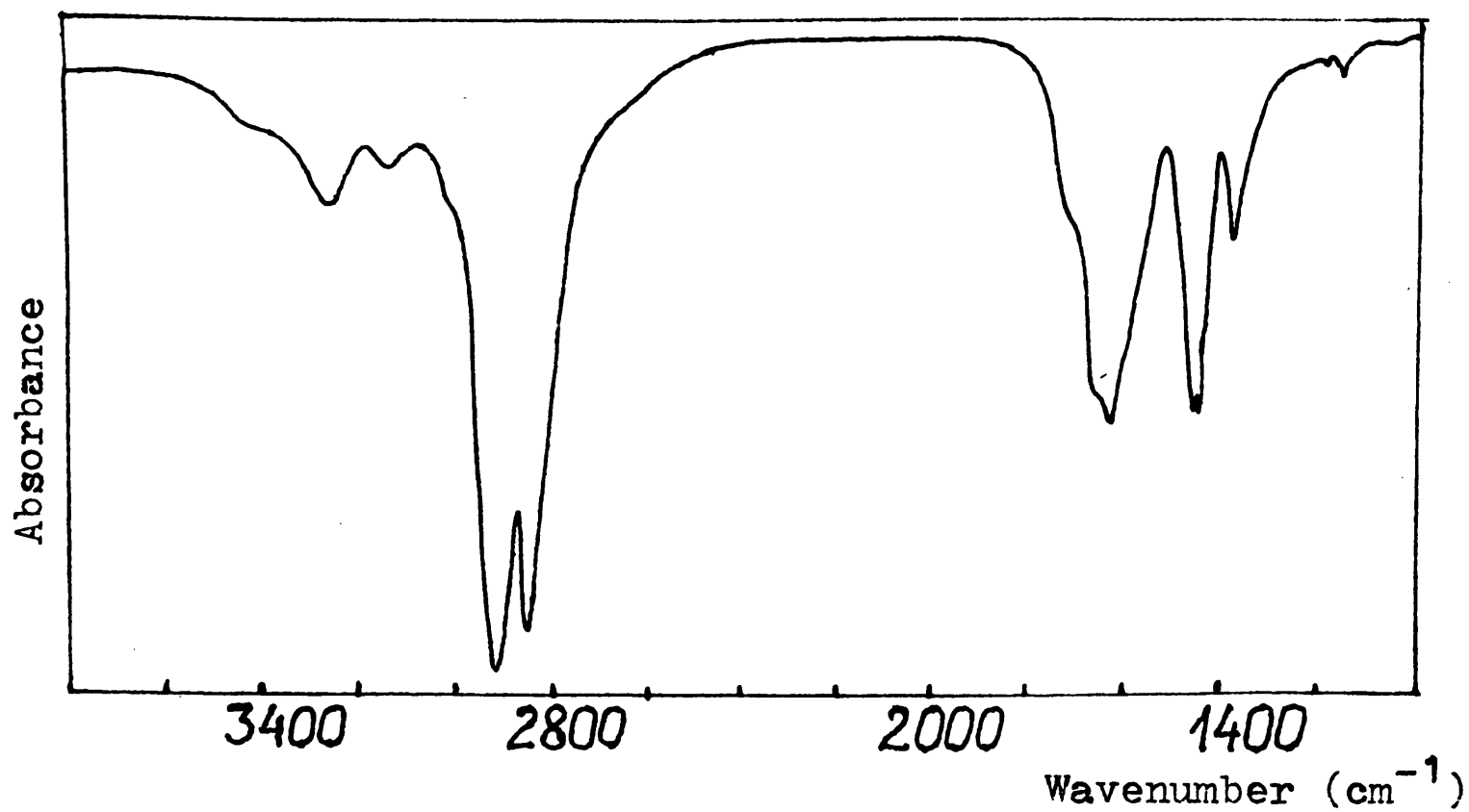


Fig. 3. I.r. spectrum of the benzene-soluble extract from ammonolysis of Kukersite with ammonia.