

INVESTIGATIONS ON THE STRUCTURE AND COMPOSITION OF OIL SHALE FOR UTILIZATION AS ENERGY AND CHEMICAL SOURCES

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ABSTRACT

As a result of prolonged investigations on oil shale by extraction, oxidative (KMnO₄ and HNO₃) and thermo-destructive methods, on the bitumen and kerogen, the possibility of their use as crude oil and chemical source is consolidated.

The results from oxidative and thermal destructive treatments show that about 40% of macromolecular kerogen is built of fragments, with high molecular weight and consisted of two types of structures. The first type of structures are of higher molecular weight and are dominantly built of aliphatic moieties. The second type of structures are aromatic and are located at peripheral parts of the macromolecules. Around 20% of the organic substance of the kerogen is contained in straight carbon chains with length of 33 carbon atoms. These chains connect different groups and promotes net-like structures. The content of the side chains in the macromolecule of the kerogen is low (~ 1% in the organic substance). Their length is from 9 to 24 carbon atoms. The presence of benzene and naphthalene structures is proved, and the benzene compounds are dominant

The analysis of the products from the thermal treatment in the presence of water vapor shows paraffin chains and saturated cyclic compounds with different chain lengths of the substitutes. This treatment resulted in a product which has 50% volatile products and 30% oil. Fractionation of the oil showed that 78.43 % of it are neutral components.

The composition of the products from oxidative treatment with potassium permanganate in alkaline medium contain mono-, di- carboxylic and poly-functional acids. The presence of the bonded and net-like units with chain length up to 25 carbon atoms and side chains from 9 to 24 carbon atoms is identified.

Key words: oil shale, extraction, oxidation, pyrolysis

1. INTRODUCTION

Even though there are considerable amounts of oil and gas resources in the world, rapid increase of the price of these fuels in the last years has caused concern and have a negative influence on the economy and stability in the world. Therefore, like 1970's, once again the attention of scientists and the governments are concentrated on the development of oil substitutes. Possibilities of using these substitutes as chemical materials will no doubt help the economics of the alternative sources. A prospective source for liquid and gaseous fuels and chemical materials are oil shales, especially those from the sapropelic and humous-sapropelic types. Oils shales are natural materials derived mainly from plant debris and algae, and can be used for different purposes [G. Angelova et al., 1983]. Both organic and inorganic parts of oil shales are of some interest for practical utilization.

The oil shales are complicated native sources. Both organic and inorganic components represent a definite practical interest. The kerogen is the main part of organic substance, which is insoluble in usual organic solvents. The study of the kerogen is difficulty due to its macromolecular structure, heterogeneity of the building fragments, as well as to the very intimate connection with mineral matter. According to the complicated structure of oil shales the soluble part in organic solvents and insoluble part (kerogen) are studied. In order to realize this purpose the following investigation are carried out:

- Investigation of the composition of acids, contained in the extractable compounds which are separated before and after selective dissolving of the mineral components and the acids connected with kerogen with ester bonds.
- Selection of the suitable chemical and pyrolysis methods and conditions for obtaining fuel and chemical products from the macromolecules of kerogen.

2. EXPERIMENTAL

The proximate and ultimate analysis of the oil shale investigated is presented in Table 1.

Table 1. Proximate and ultimate analysis of oil shale.

Proximate analysis wt. %					Ultimate analysis wt.%, daf						
Moisture	Ash _{db}	CO ₂	V _{daf}	OM	C	H	N	S _t	S _{pyr.}	H/C	Q(KJ/kg)
0.41	59.00	16.38	80.50	24.62	75.80	8.70	1.90	1.72	0.80	1.38	10270(KJ/kg)

db- dry basis; daf- ash-free; S_t-total sulfur; S_{pyr.}-pyritic sulfur

The separation of the neutral part of the swelling oil is performed according to the procedure of Sawatski(Sawatski et al.,1976) at atmosphere pressure in glass column.

Neutral oil is separated in column, filled with Al₂O₃ and silica gel. The first three fractions are separated using hexane, CH₂Cl₂, and CHCl₃ and CH₃OH.

The mixture of methylesters of the acids is separated on capillary column on chromatograph Pye Unicam. The column is 50 m long and coated with stationary phase OV-17.

Gas chromatographic (GC) analyses of the pentane eluate from silica gel column were performed on Pye Unicam gas chromatograph. A capillary column 25 m VVCOT as a stationary phase is used. The GC oven temperature was programmed from 90 to 280°C at a heating rate of 6°C/min.

GC-MS analyses of eluates from silica gel and Al₂O₃ column were performed on a gas chromatograph directly coupled to the Jeol-D 300 mass spectrometer. A capillary columns with OV-17 and OV-101 stationary phases were used.

The oxidation with 57% HNO₃ was performed in stationary reactor at 105°C for 3 hours. The sample was heated from room temperature to the final heat treatment temperature for 60 min.

The IR spectra are obtained on Bruker IFS 113V and NMR spectra were obtained on Bruker MSL 200 spectrometer.

3. RESULTS AND DISCUSSION

3.1. A study of the kerogen bond with bitumens and mineral components.

3.1.1. Investigation of acids, contained in extractable substances.

The investigations on the demineralization of oil shale show the presence of strong bond between organic matter and inorganic substances, namely between the three basic components: bitumens, kerogen and mineral components. The separation of the kerogen requires the destruction of this bond. This bond is probably complicated and multiform. We have investigated the role of acids in this bond. We supposed that the acids have had a considerable influence upon the realization of this bonding on the grounds of the fact that it is considered that the acids are the initial precursors for the formation of the organic matter of sapropelics including oil shales [Razvigorova et al.,1988]. The kerogen is obtained by demineralization of the oil shale and the bitumens are removed after each demineralization step according the scheme, presented in Figure 1. This scheme allows to elucidate the influence of the removing of the different mineral components (carbonates and silicates aluminum) on the yield of bitumens and the acids in the bitumens. Bitumen I contains free extracted substances and Bitumen II, III and IV contain substances removed by the

subsequent acid treatment. The content of the free extracted components are highest (5.1%). The consecutive demineralization resulted in 5.5% extracted bitumens. The bigger part of bitumens is retained from carbonic mineral matrix. The necessity of carrying out deep demineralization for extraction of all bitumens to separate the kerogen confirms the presence of strong bonding between organic and inorganic parts in oil shale.

The content of free and bonded acids in bitumens is determined as follows: free acids are separated from the CHCl_3 solutions of the bitumens after treatment with 1 M solution of NaHCO_3 ; the acids, which are in the form of salts, are separated after treatment of bitumens with 6 M HCl , and extraction with 1 M NaHCO_3 ; the acids in the form of esters, are separated after saponification of the extracts with 6 % alcoholic solution of KOH .

All these types of acids bonded to the kerogen matrix are investigated by GC and GC-MS spectroscopy. The composition is presented in Table 2. n-Monocarboxylic and di-carboxylic acids are identified in all fractions. The presence of di-carboxylic acids with more than 12 carbon atoms is considered as indication of microbiological processes in alteration.

Table 2. Composition of the in-identified acids in bitumens.

Acids	$n\text{C}_n\text{H}_{2n}\text{O}_2$	$n-\alpha,\omega-\text{C}_n\text{H}_{2n-2}\text{O}_4$
Free acids	n=12-26 $n_{\text{max.}}=22$	n=12-18 $n_{\text{max.}}=16$
Like salts	n=12-26 $n_{\text{max.}}=16,18$	n=12-18 $n_{\text{max.}}=16$
Like esters	n=16,18,22 $n_{\text{max.}}=22$	n=12-20 $n_{\text{max.}}=16$

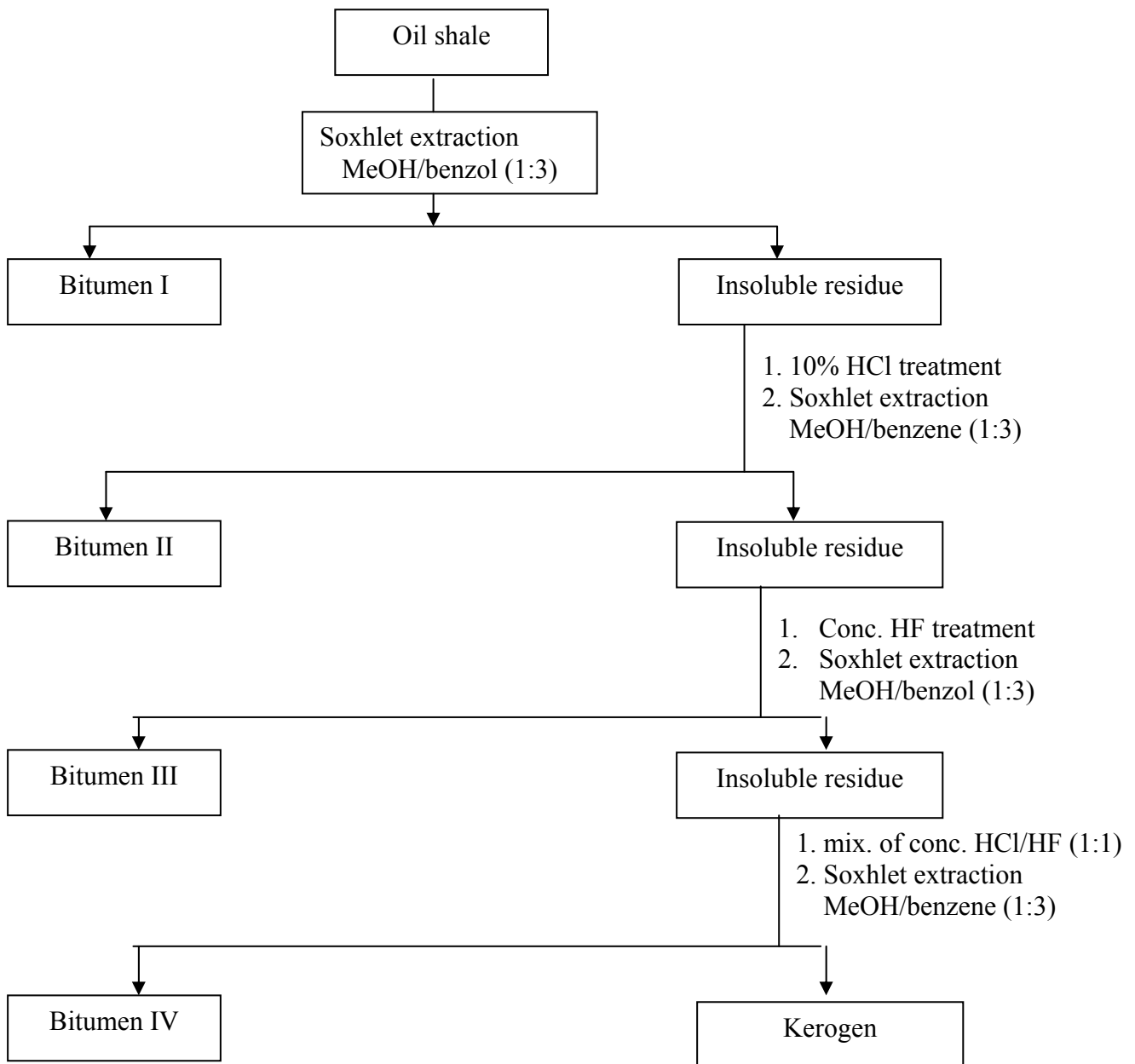


Figure 1. Scheme of the separation of kerogen

3.1.2. Investigation of acids, obtained by alkaline hydrolysis

The kerogen, obtained according to the scheme 1 was subjected to alkaline hydrolysis. The major components found are normal carboxylic, normal α,ω -dicarboxylic and aromatic acids as the content of stearine and palmitate acids are higher. The results are presented in Table 3. The yield of acids is 83 % from all saponificated substances, which shows that the kerogen participated in ester bonds mainly with hydroxyl groups. The qualitative investigation of the carboxyl-, carbonyl and hydroxyl groups shows that the content of the hydroxyl groups is highest: 0.3923, 0.3244 and 1.3170 mgequiv/g, respectively.

Table 3. Composition of identified acids, obtained at alkaline hydrolysis.

Homologous number	Range	Maximum content
$n-C_nH_{2n}O_2$	$C_{11} - C_{20}$	C_{16}, C_{18}
$n-\alpha,\omega-C_nH_{2n-2}O_4$	$C_6 - C_{12}$	C_6
$C_8H_6O_4$	o-phthalic	

On the basis of the results of the acids composition in extractable substances and in the hydrolysis products, as well as the determined content of oxygen functional groups in the kerogen, it is possible to present the following scheme (Figure 2) about the bonding between kerogen, bitumen and mineral matter.

The proximate and ultimate analysis of the kerogen is presented in Table 4.

According to the Van Krevelen diagram (H/C vs O/C), kerogen belongs to type II [Tisso and Velte, 1981]. Type II kerogen is generated from deposits with autochthonic organic matter, obtained from phytoplankton, zooplankton and microorganisms (bacteria), accumulated in redox medium.

Table 4. Proximate and ultimate analysis of the kerogen, percentage.

Ash	V_{daf}	S_t	$S_{pyr.}$	C	H	S	$O_{diff.}$	H/C	O/C
8.38	69.04	7.67	3.14	70.89	7.40	1.30	15.88	1.25	0.17

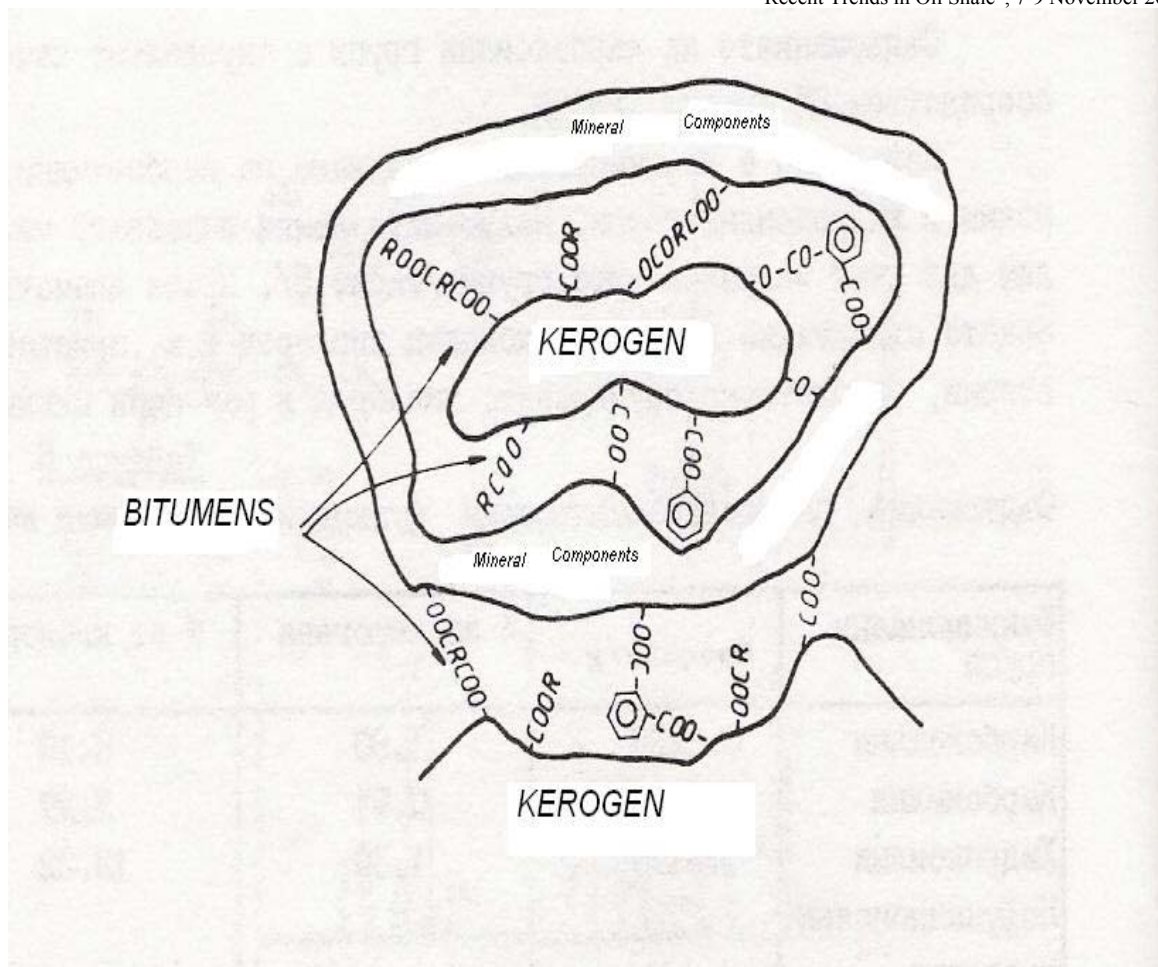


Figure 2. Schematic picture of the participation of the acids at the realization of the bond between mineral components, kerogen and acids.

3.2. Destructive methods of analysis of the kerogen

Due to the insolubility of the kerogen in organic solvents, the study of its structure is complicated. Therefore the use of destructive methods is necessary. In this study, differential approach is used in order to reveal the characteristic structural features. For this purpose the following methods are used: step-wise oxidation with potassium permanganate at ambient temperature, step-wise permanganate oxidation at 90°C and pyrolysis at 480-600°C in the presence of water vapour.

3.2.1. Step-wise oxidation with potassium permanganate at ambient temperature.

The thirteen-step alkaline permanganate degradation of oil shale kerogen concentrate at ambient temperature is carried out. The amount of KMnO_4 is determined from previous investigations [Angelova et al., 1982]. The oxidized products are separated according to scheme, presented in Figure 3. A high total yield of oxidation products (90.1%) and minimum yield of gaseous products (2.79%) are obtained.

The ether eluates (II, III and V) and the extract(I) (acids, extracted with water vapour) contain low molecular products. The acetone eluates contain the polyfunctional acids (PFA). The total amount of the both fractions polyfunctional acids (acetic extracts IV and VI) is approximately constant for all steps of oxidation. The distribution between them only differs with the progress of the oxidation. The amount of the soluble polyfunctional acids (acetic extract IV) decreases in comparison with insoluble polyfunctional acids (VI). This change in the proportion of the both polyfunctional acids is probably due to the different positions in the structures of the macromolecule of kerogen from which they are obtained. Also, the differences in bonding affects this difference. The molecular mass of the acid

solution insolubles PFA (1670) is much bigger than that of the solubles (450). NMR spectra show mainly a content of hydrogen in phenolic groups and methyl and methenyl groups, connected with aromatic rings for soluble, and a high content of aliphatic protons for insoluble acids. The results from IR spectra confirm the presence of aromatic structures in soluble PFA and more expressed aliphatic structures for insoluble PFA.

The basic parts of the ether extracts are acids: n-monocarboxylic (MKA), n-dicarboxylic acids (DKA) and benzenecarboxylic acids (BKA). Having in mind that the conditions of the oxidation are mild, we may assume that the composition of aliphatic carboxylic acids brings undoubtedly structural information. On the basis of the quantity and the content of DKA one can say that about 20% of the organic matter of the kerogen is contained in carbon chains with length of the right chain about 25 C atoms. These chains can play a connecting and netting function. The content of oxalic and malonate acids decreases with extensive oxidation, the distribution of the rest of the acids are similar in all three stages. The whole quantity of MKA is only 1%, which shows the low contents of embranchments in the kerogen macromolecule. Their length changes from 9 to 24 atoms. The aliphatic monocarboxylic acids with length of chain up to C₁₀ are determined in the extract I (extracted with water vapor) and higher homologues in the etheric extracts II, III and V respectively. The content of benzenecarboxylic acids (BKA) is 3.14 %. All members of the homologous number are identified. The content of phthalic acids is the highest. BKA as the primary products of oxidation are representative of aromatic fragments, which are connected with unstable bonds. The schematic picture of the destruction of the kerogen to PFA, DKA, MKA and BKA is presented on Figure 4.

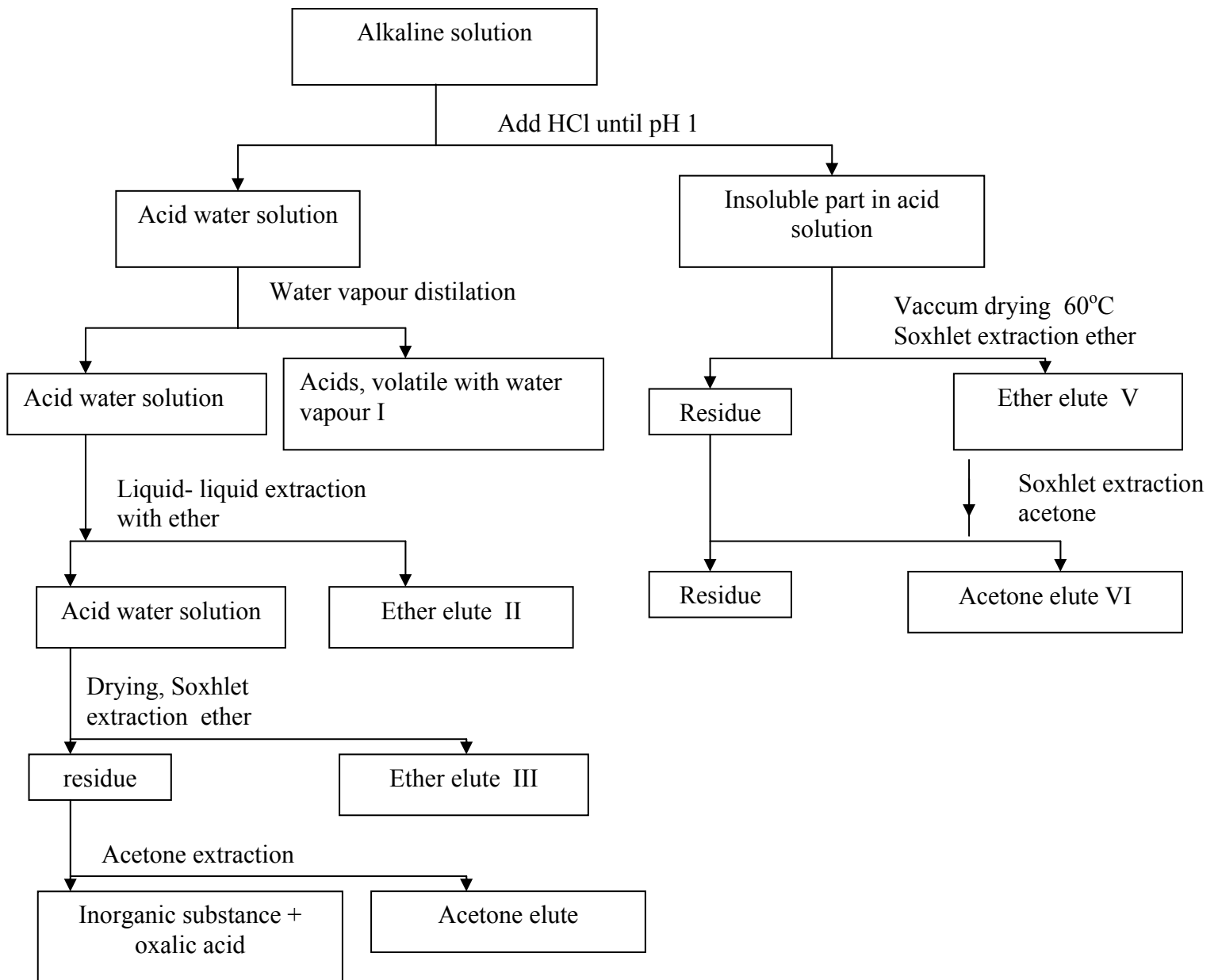


Figure 3. Scheme of the separation of the oxidized products.

3.2.2. Step-wise oxidation of the kerogen with potassium permanganate at 90°C.

The oxidation at higher temperature gives information about the content of stable aromatic structures. That is why the oxidation was carried out at 90 °C to achieve complete destruction of kerogen at the five steps. The products are examined according to scheme, presented in Figure 3.

The distribution of the carbon in the products of oxidation shows a large loss of carbon as CO₂ – 36.4%, while this value is only 2.7% for oxidation at ambient temperature.

The content of carbon in PFA insoluble and soluble in acidic solution is different too. The total amount of PFA sharply decreases with increase in the oxidation temperature.

The low molecular weight products are the main part of the whole oxidized products (86.3%). The dominant part of the fractions are acids. The presence of benzene and naphthalene carboxylic acids has been established. The bigger part of acids, which are formed by oxidation are probably received as a result of secondary processes. The composition of acids (higher content carboxylic groups in ortho-position and polysubstituted acids) does not exclude participation of aromatic rings in polycyclic structures.

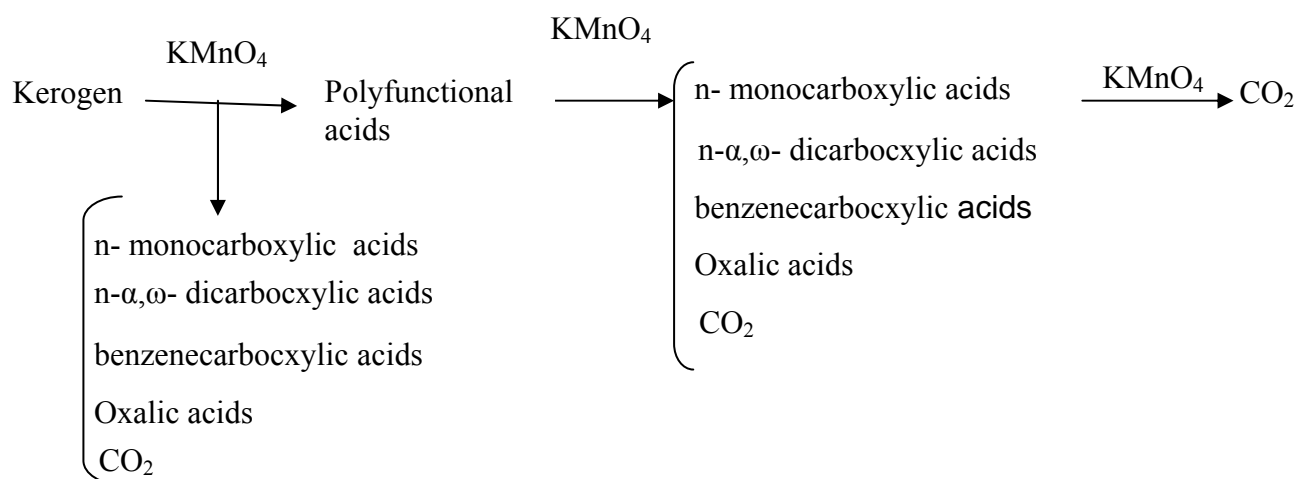


Figure 4. Sheme of the oxidation of the kerogen

3.3. Pyrolysis of the kerogen in the presence of water vapor.

The high yield of the volatile products ($V_{daf} = 80.56\%$) shows that organic substances of oil shales undergoes deep changes during the thermal destruction, but application of thermal steam destruction at mild conditions may give valuable information about the primary products obtained from decomposition of the macromolecule of the kerogen.

As a result of thermal steam destruction 50% of the volatile products from the kerogen are evaporated (30% swelling oil). The group chemical analysis shows that the basic part (78.4%) from swelling oil represents neutral. This oil is separated to six fractions by application of column chromatography and they are investigated by GC and GC-MS (Figure 5).

The first and second fractions contain alkanes, alkenes and cyclohexanes (Table 5 and Table 6). The content of cyclohexanes represents only 1.85% from neutral oil. The content of alkanes and alkenes is dominant (33% from neutral oil). The third and fourth fractions contain aromatic hydrocarbons. The content of benzene hydrocarbons is the highest – 56% from the identified compounds. The number of carbon atoms in alkyl substitutes reaches 20 in which the substituted benzenes are highest (1.9% from the swelling oil – Table 7). The number of carbon atoms in the alkyl substitutes reaches up to 20. The

amount of naphthalenehydrocarbons is low (0.45 % from swelling oil) and the substitutes are with shorter chains. In this way the presence of aromatic structures in the structure of the kerogen is confirmed. The number of aromatic cycles of the compounds obtained at the pyrolysis like oxidation at 90°C does not exceeds two cycles, as the presence of the monocycles is dominant between them. In contrast to oxidation, the pyrolysis of kerogen gives an information about the kind of the substitutes in the kerogen structure.

Fractions V and VI contain tar components. These compounds probably represent the fragments of the structure of kerogen, which at the mild oxidized destruction formed polyfunctional acids.

These results show that the macromolecule of the kerogen does not contain polycyclic aromatic compounds (more 2-3 cycles). The identified alkanes, alkenes and substituted cyclohexanes show considerable parts of saturated structures. They are probably precursors for obtaining the aliphatic monocarboxylic and di-carboxylic acids.

Table 5. Identified compounds in fraction I

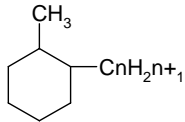
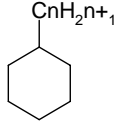
Compounds	Amount, %	Compounds	Amount, %
1. Alkanes /C ₁₃ - C ₂₆ / C _n H _{2n+2}	47.99	1 Alkenes /C ₁₃ - C ₂₆ / C _n H _{2n}	33.19
2. Isoalkanes /3- methylheptadecane, 2- methyl-octadecane/	0.39	2  /Number of C _{alk.} = 11- 16/	1.87
3. Isoprenoides /2,6,10- trimethylpentadecane, 2,6,10,14- tetramethylpentadecane/	2.99	3  /Number of C _{alk.} =14, 17, 20/	1.12

Table 6. Identified compounds in fraction II.

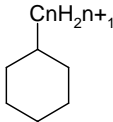
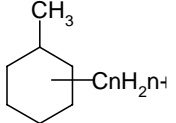
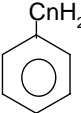
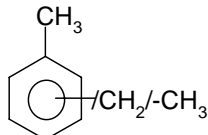
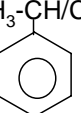
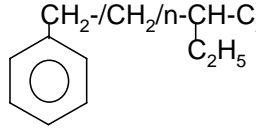
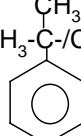
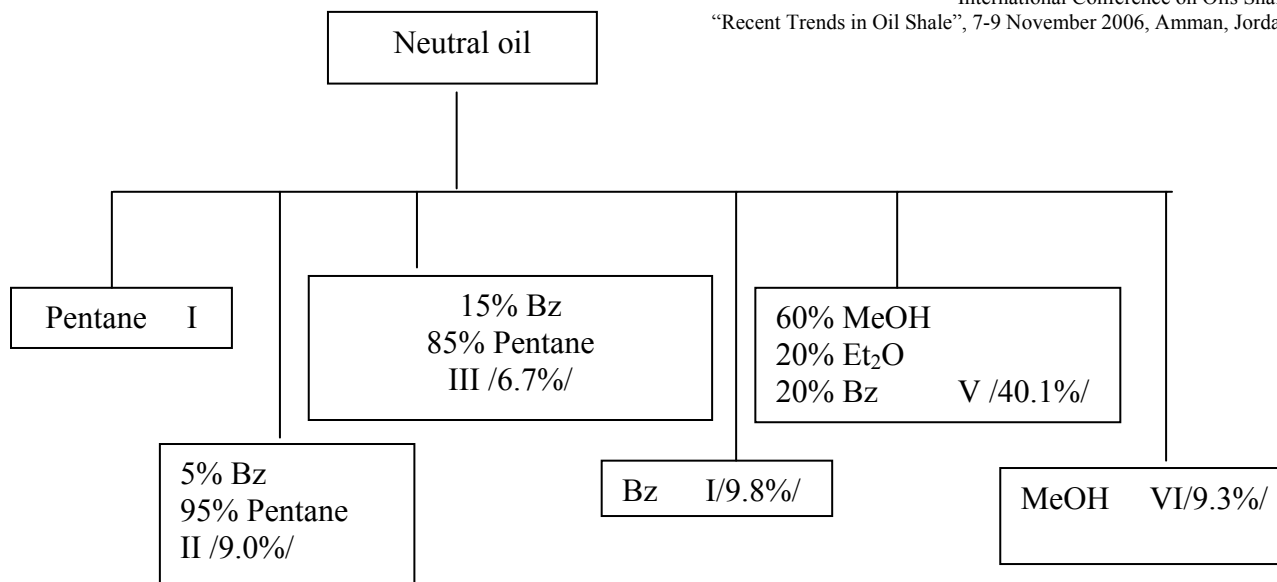
Compounds	Amount, %	Compounds	Amount, %
1 Alkanes /C ₁₄ - C ₃₃ / C _n H _{2n+2}	45.65	1. Alkenes /C ₁₄ - C ₁₈ / C _n H _{2n}	0.51
		2  /Number of C _{alk.} = 11- 17/	9.20
		3  /Number of C _{alk.} =13- 15/	3.81

Table 7. Identified compounds in fraction III

Compounds	Amount, %	Compounds	Amount, %
1	C_nH_{2n+1}  C_nH_{2n-6} /Amount of $C_{alk.} =$ 8, 10, 17/ 2.93	4	 /Number of $C_{alk.} =$ 10- 13, 15, 16, 20/ 14.71
2	$CH_3-CH/CH_2/n-CH_3$  /Amount of $C_{alk.} =$ 9, 11- 16/ 9.67	5	 /Number of $C_{alk.} = 9/$ 0.31
3	 $CH_3-C-CH_2/n-CH_3$ /Amount of $C_{alk.} =$ 18/ 0.80		
Compounds		Amount, %	
C_nH_{2n-12} /Naphtalene derivates/			
1. Amount of $C_{alk.} = 2$		0.40	
2. Amount of $C_{alk.} = 3$		2.77	
3. Amount of $C_{alk.} = 4$		2.12	
4. Amount of $C_{alk.} = 5$		0.52	
5. Amount of $C_{alk.} = 10$		0.60	
C_nH_{2n-18}	phenantrene/antracene	2.40	
C_nH_{2n-16}	2,3- dimethylfluoren	2.50	
C_nH_{2n-10}	alkyltetrahydronaphtalene	11.99	



Bz-benzene; MeOH-methanol; Et₂O-ethanol

Figure 5. Sheme of separation of the neutral oil.

4. Some trends of the studies of the oil shale utilization.

4.1. Oxidation with nitric acid.

The oxidation of oil shales with nitric acid is carried out to obtain the polyfunctional acids with the high amount of nitrogen (to 5-6 %) for the purpose of obtaining nitrogen containing groups, including nitrogen oxide. Polyfunctional acids from nitric acid oxidation (acetone extracts) were used as active substance (as water soluble potassium salts) as stimulators for the some plants. The stimulators are obtained by the oxidation with 57 % HNO₃. They are investigated as stimulators for rice and cucumbers plants. The highest effect is achieved with 40 mg/dm³ concentration of the activated substance.

4.2. Thermal treatment at 480-550°C.

Pyrolysis of oil shale in the range of 480-560 °C was carried out at 2 kg/h capacity. The maximum yield of swelling oil (70-72 %) is received at 500 °C. The gaseous products contain 20-30% H₂ and around 10-20% CH₄. The liquid products contain a low sulphur content(0.45 %).

CONCLUSIONS

The differentiated method is used to decompose the organic oil shales substance of the under different conditions gave a possibility to elucidate the characteristic of peculiarities of the structure of the oil shale macromolecules.

It is established by selective extraction and hydrolysis of the organic substance that the acids and acidic oxygen groups have important role in the bonding between kerogen, bitumen and mineral components. A big part of the kerogen macromolecule (40 %) is built from higher molecular fragments, which contain two types structures. One of them has aromatic character and take place mainly in the periphery of the macromolecule. The other type is higher molecular weight and are built mostly of aliphatic structures.

About 20% of the organic substance of the kerogen is contained in hydrocarbon chains with length of the straight sections up to 33 carbon atoms. These chains have connecting and netting role. The content of the embranchments in the kerogen macromolecule is low (~1% from the organic matrix). Their length ranges from 9 to 24 carbon atoms.

The characteristic of the organic matrix of oil shale show the possibility of its application for obtaining of high qualitative liquid and gaseous fuels, raw material sources for chemical industries and as a fertilizer for the agricultural utilization.

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