

STEAM PYROLYSIS OF BULGARIAN OIL SHALE KEROGEN

M. RAZVIGOROVA^(a), T. BUDINOVA^{*(a)}, B. PETROVA^(a),
B. TSYNTSARSKI^(a), E. EKINCI^(b), M. F. FERHAT^(b)

^(a) Bulgarian Academy of Sciences, Institute of Organic Chemistry,
Sofia 1113, Acad. Bonchev Str. bl. 9, Bulgaria

^(b) Istanbul Technical University, Department of Chemical Engineering,
Maslak, Istanbul 34469, Turkey

The effect of water vapor on the yield and composition of products formed at thermal treatment of Bulgarian oil shale kerogen at atmospheric pressure has been studied. It was found that water steam reacts with oil shale organic matter significantly affecting the yield and composition of liquid and gaseous products. As for the yield of liquid products, it is about 20% higher than the yield obtained at Fischer Assay. The yield of semicoke is about 10% less. Liquid products formed in the presence of water vapor are richer in aromatic and aliphatic hydrocarbons among which long-chain paraffins with up to 33 carbon atoms predominate.

Introduction

Oil shales occur all over the world and their deposits are large. For many countries oil shale represents a valuable potential source of liquid hydrocarbons and energy. The role of oil shale in energy production has not yet been estimated well enough because its contribution to today's world energy budget is minimal compared to common energy sources such as petroleum and coal. However, with the development of global economy accompanied by increasing costs of petroleum and coal, the utilization of oil shale will become more important [1, 2].

Pyrolysis is the principal method used to convert oil shale to liquid fuels. Since organic matter of oil shale contains much hydrogen (7–12%), its majority (75–85%) is converted to volatile products at low-temperature pyrolysis [3–5].

During the process of heating of solid fuels up to the temperature of their thermal destruction, organic matter undergoes degradation, associated with

* Corresponding author: e-mail goriva@orgchm.bas.bg

breaking of chemical bonds and formation of reactive products, most probably free radicals, which, according to their stability, could become coupled to each other forming more complex molecules. In the absence of hydrogen (semi-coking and coking), the process is shifted towards the formation of products of condensation, i.e. semi-coke and coke. In the presence of mobile hydrogen, free bonds formed after destruction of the molecules are stabilized at the expense of intramolecular redistribution of hydrogen or due to additional hydrogen inserted, and as a result the yield of the ultimate products of destruction is altered and the yield of the liquid products increased. In the case of steam pyrolysis water acts as a physical factor influencing heat transfer and favouring fast desorption of low-molecular products from the solid-phase surface, whereby their subsequent cracking is avoided. This helps to increase the yield of liquid products, and as a result the evaporated volatile products will reserve specific features of the kerogen structure, which allows to use thermochemical destruction as an analytical method for investigation of oil shale composition [6–8].

The aim of this work was to study thermal treatment of one sample of oil shale from the Krasava deposit, which is the most prospective deposit of mixed humin-sapropelic origin in Bulgaria. The influence of water vapour on the yield and composition of destruction products at atmospheric pressure was studied.

Experimental

Sample

Oil shale sample was obtained from the Krasava deposit located near the town Radomir in the west of Bulgaria (60 km from the capital Sofia) [9]. For pyrolysis experiments, the sample was crushed and thereafter ground in a jaw mill until the desired particle size was obtained. The sample was sieved to obtain the size fraction < 0.2 mm and subjected to a successive demineralization process. The results of elemental analysis of raw and demineralized oil shale sample are given in Table 1.

Table 1. Characteristics and elemental composition of oil shale and its kerogen, %

Sample	W	A ^{mf}	OM	CO ₂	S _{pyr}	S _{tot}	C ^{maf}	H ^{maf}	N ^{maf}	H/C
Oil shale	0.41	59.00	24.62	16.38	1.20	1.20	75.80	8.70	1.20	1.37
Kerogen	0.20	8.10	91.90	–	3.14	7.67	70.89	7.40	1.30	1.26

maf – moisture and ash-free material

mf – moisture-free material

OM – organic matter

CO₂ – amount of carbon dioxide

Demineralization

Oil shale sample was demineralized with 10% HCl and HF using a standard method [10]. 100 ml of 10% HCl was added to 10 g sample of oil shale. The resulting slurry was stirred for 8 hours, thereafter filtered, and 200 ml of 10% HCl was added again to the residue. The solid residue stayed for 10 hours at room temperature, thereafter it was filtered and washed with distilled water till the disappearance of Cl^- ions. The sample was dried at 50 °C under vacuum for 24 hours.

Nearly 30 g of the sample was demineralized with 10% HCl and thereafter treated with 100 ml conc HF for 1 h at room temperature. After removal of the acid, the sample was treated with 50 ml conc HCl for 30 minutes. The treatment was repeated, and the sample was filtered and washed with distilled water till the disappearance of Cl^- ions, and finally dried under vacuum at 50 °C for 24 hours.

Pyrolysis of the kerogen in the presence of water vapour

A sample of kerogen (25 g) was subjected to pyrolysis in a stream of water vapour under atmospheric pressure at the heating rate of 30 °C/min to the final pyrolysis temperature of 400 °C. The duration of pyrolysis at this temperature was 25–30 min. Volatiles formed were collected in a vessel in order to condense. Liquid products were separated from the condensed water vapor and thereafter separated to organic bases, carboxylic acids, phenols and neutral shale oil according to the scheme presented in Fig. 1.

Separation of the neutral part of the shale oil was performed according to the procedure of Sawatski [11], but at atmospheric pressure and in a glass column. The neutral oil was separated in a column filled with Al_2O_3 and silica gel. The scheme of the separation of the neutral shale oil is presented in Fig. 2.

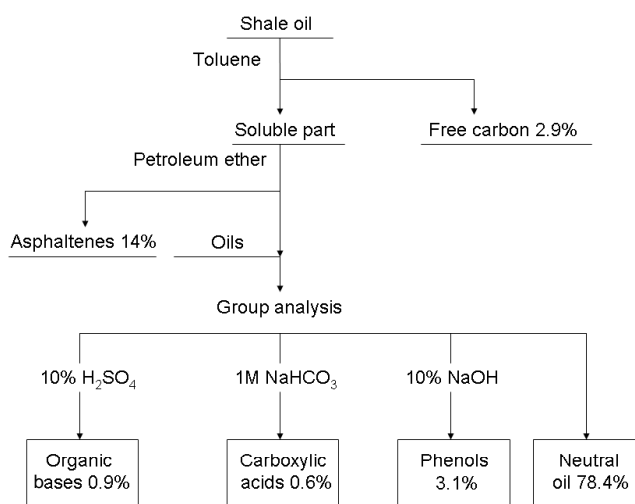


Fig. 1. Scheme of chemical group analysis of shale oil.

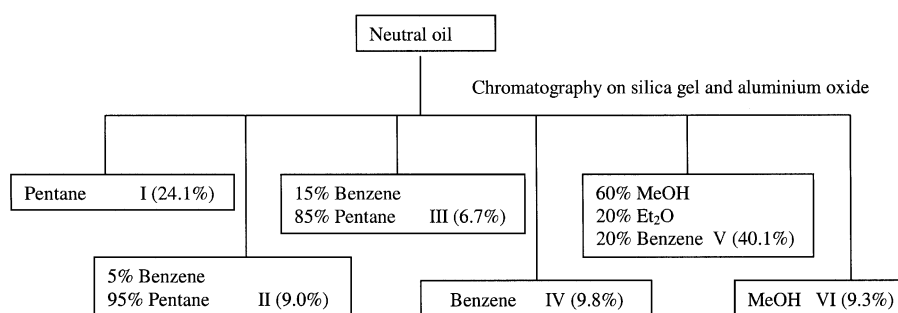


Fig. 2. Scheme for separation of neutral oil.

GC-MS analyses of eluates from silica gel and Al_2O_3 column were performed on a gas chromatograph directly coupled to the Jeol-D 300 mass spectrometer. Capillary columns with OV-17 and OV-101 stationary phases were used.

Results and discussion

Characteristics of oil shale and kerogen samples

For many years petroleum geochemists have been interested in obtaining mineral-free and chemically unaltered concentrated materials of natural origin. The convenient hydrochloric/hydrofluoric acid treatment is effective in removing carbonate, oxide and monosulfide minerals from sedimentary rocks, and during this treatment kerogen and pyrite remain almost fully unaffected [12, 13].

Tha data in Table 1 show that the sample of Krasava oil shale contains relatively much carbon dioxide and pyritic sulphur. The content of organic matter is 24.62%. The consecutive demineralization of the oil shale sample decreases the mineral content from 59 to 8.10%. The content of pyritic sulphur (S_{pyr}) in kerogen is relatively high – 3.14%. Most likely, due to high dispersion of organic matter and high content of pyrites, it is difficult to decrease the content of mineral components below 8%. Effective removal of pyrite is usually the main problem. The magnitude of the change in organic matter depends on the chemical nature of kerogen as well as on the reaction conditions. Quantitative removal of pyrite is not possible without alteration of the composition of organic matter [14]. For that reason we did not use HNO_3 to decrease the content of pyritic sulphur. According to the Van Krevelen diagram (plot of atomic H/C vs. O/C ratios) the kerogen is classified as type II [14]. Type II kerogen originates from deposits with autochthonous organic matter formed from phytoplankton, zooplankton and microorganisms (bacteria), accumulated in a reductive environment. Kerogen (type II) of oil-producing rocks and shales is usually formed in this way.

Characteristics of the shale oil obtained by pyrolysis of kerogen in a stream of water vapour

Table 2 presents the results of oil shale pyrolysis both in the presence of water vapour and in Fischer retort [3, 5]. The yields of liquid product, with respect to the organic substance content, are 74% (pyrolysis with water vapour) and 50% (Fischer method), respectively, at hydrothermal treatment, while the yield of semicoke is lower (17 and 29%, respectively). The elemental composition of the shale oil is: C – 82.3% and H – 8.26%.

The high yield of volatile products shows that the dominant part of oil shale organic matter is converted to oil during the process of pyrolysis with water vapour in mild conditions, which allows to investigate the primary products formed after decomposition of kerogen.

IR spectra of the shale oil obtained by both pyrolysis with water vapour and Fischer method are presented in Fig. 3. The juxtaposition of both spectra shows that the IR spectrum for shale oil obtained by pyrolysis with water vapour clearly shows dominant presence of long aliphatic chains (a band at 720 cm^{-1}), relatively high concentration of $-\text{CH}_3$ aliphatic groups (bands at 1380 and 2860 cm^{-1}), methylene $-\text{CH}_2-$ and alicyclic groups at 1465 and 2940 cm^{-1} , in comparison with the shale oil, obtained in Fischer retort.

Table 2. Yield of the products obtained from kerogen at pyrolysis in the presence of water vapour and in Fischer retort

Products	Yield, wt. %	
	Pyrolysis with water vapour	Fischer retort
Semicoke	17.0	29.0
Shale oil	74.0	50.0
Gas + pyrolytic water + losses	9.0	21.0

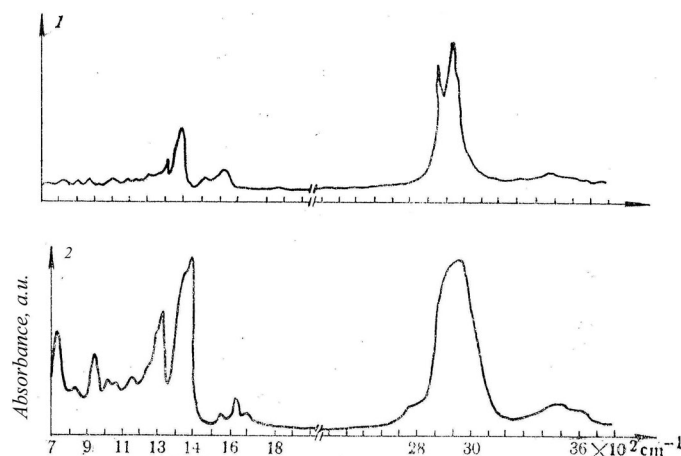


Fig. 3. IR spectra of shale oil: 1 – shale oil obtained in Fischer retort, 2 – shale oil obtained by pyrolysis in the presence of water vapour.

NMR ^1H spectrum of shale oil shows that the dominant amount of hydrogen is in aliphatic groups not connected with aromatic ring. Phenolic aromatic protons and protons of alkyl chains connected with aromatic rings have been established, too (Table 3).

Chemical group analysis (Fig. 1) shows that the main part of shale oil is represented by neutral oil (78.4%) and heteroatomic compounds, mainly phenols (3.1%).

Table 3. Distribution of hydrogen

Major assignments	H shift range (ppm)	%
$\text{H}_{\text{al}}(\text{CH}_3)$	0.5–1.1	19.4
H_{al} and $\text{H}_{\text{alicycl}}(=\text{CH}_2, =\text{CH}-)$	1.1–1.9	47.1
$\text{H}_{\text{al}}(\text{CH}_3, =\text{CH}_2, =\text{CH}-)$, bonded to Ar. structures	1.9–3.5	21.3
$\text{H}_{\text{al}}(=\text{CH}_2, =\text{CH}-)$, bonded to oxygen	3.5–6.5	2.6
$\text{H}_{\text{Ar}}(=\text{CH}-)$ and H_{phen}	6.5–9.0	9.6

H_{al} – aliphatic hydrogen

$\text{H}_{\text{alicycl}}$ – alicyclic hydrogen

H_{phen} – hydrogen in phenolic groups

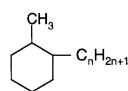

H_{Ar} – hydrogen in aromatic structures

Investigation of neutral shale oil

Neutral shale oil was separated out into six fractions by application of column chromatography, and the fractions were investigated by GC and GC-MS (Fig. 2).

The first fraction was eluted with pentane. Alkanes and alkenes dominate in the first fraction (81% of the mixture). Cyclic and branched structures amounts to 19% (Table 4). The presence of unsaturated structures is generally accepted to be an indicator of the development of cracking processes. Quantitative distribution of the paraffinic and olefinic hydrocarbons is similar. The dominance of long-chain hydrocarbons evidences for marginal development of cracking processes.

Table 4. Compounds identified in fraction I

Compounds	Amount, %	Compounds	Amount, %
1. Alkanes $\text{C}_n\text{H}_{2n+2}$ (C_{13} - C_{26})	47.99	1. Alkenes C_nH_{2n} (C_{13} - C_{26})	33.19
2. Isoalkanes (3- methylxptadecane, 2-methyl-octadecane)	0.39	 (Number of $\text{C}_{\text{alk}} = 11-16$)	1.87
3. Isoprenoids (2,6,10- trimethylpentadecane, 2,6,10,14- tetramethylpentadecane)	2.99		
		 (Number of $\text{C}_{\text{alk}} = 14,17,20$)	1.12

The second fraction (Table 5) contains paraffinic, olefinic and naphthenic hydrocarbons uneluated with pentan. Naphthenic hydrocarbons are represented by monocyclic compounds with different substitutes. The maximum number of carbon atoms in the substitutes is 17.

The third fraction contains aromatic hydrocarbons (Table 6). The content of substituted aromatic hydrocarbons and structures is high (55.6% of the

Table 5. Compounds identified in fraction II







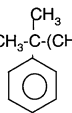
Compounds	Amount, %	Compounds	Amount, %
1. Alkanes C_nH_{2n+2} (C ₁₄ - C ₃₃)	45.65	1. Alkenes C_nH_{2n} (C ₁₄ - C ₁₈)	0.51
		2.  C_nH_{2n+1} (Number of C _{alk} = 11-17)	9.20
		3.  C_nH_{2n+1} (Number of C _{alk} = 13-15)	3.81

Table 6. Compounds identified in fraction III

Compounds	Amount, %	Compounds	Amount, %
1.  C_nH_{2n+1} C_nH_{2n-6} (Number of C _{alk} = 8, 10, 17)	2.93	4.  $(CH_2)_n-CH_3$ (Number of C _{alk} = 10-13, 15, 16, 20)	14.71
2.  $CH_3-CH(CH_2)_n-CH_3$ (Number of C _{alk} = 9, 11-16)	9.67	5.  $CH_2-(CH_2)_n-CH-C_2H_5$ (Number of C _{alk} = 9)	0.31
3.  $CH_3-C-(CH_2)_n-CH_3$ (Number of C _{alk} = 18)	0.80		
Compounds		Amount, %	
C_nH_{2n-12} (Naphthalene derivates)			
1. Number of C _{alk} = 2		0.40	
2. Number of C _{alk} = 3		2.77	
3. Number of C _{alk} = 4		2.12	
4. Number of C _{alk} = 5		0.52	
5. Number of C _{alk} = 10		0.60	
C_nH_{2n-18}	phenantrene/anthracene	2.40	
C_nH_{2n-16}	2,3-dimethylfluorene	2.50	
C_nH_{2n-8}	alkyltetrahydronaphthalene	11.99	

identified compounds). The number of carbon atoms in the substitutes reaches 20. The content of naphthenic hydrocarbons is less (12.7%) and chains of their substitutes are shorter (up to 8 carbon atoms). Substituted polycyclic aromatic hydrocarbons have not been identified. In addition, phenanthrene (or anthracene) is present. There is no reason to consider it a product formed by destruction. Phenanthrene probably originates from kerogen matrix being released after destruction of kerogen macromolecule. Taking into consideration that the investigated products are obtained as the result of thermal destruction, which creates conditions for additional aromatization, we can assert that kerogen macromolecule does not contain highly condensed aromatic structures. Substituted tetralin structures detected evidence of the presence of hydroaromatic cycles.

The fraction IV contains no new classes of compounds. This fraction contains alkylsubstituted benzenes.

The fractions V and VI eluted with strong polaric solvents probably contain tar components. Using another method for separation we established pentacyclic triterpenes in the fraction eluted with dichlorethylene. Some of them have hopane structure ($C_{30}H_{50}$ and $C_{30}H_{52}$) and others – perihydropycen structure ($C_{29}H_{50}$, $C_{30}H_{50}$, $C_{30}H_{52}$). The established component composition of the investigated fractions evidence that kerogen macromolecule does not contain polycyclic aromatic compounds (compounds with more than 2–3 rings). The content of naphthalene structures in the neutral part of the shale oil is low – 0.45%. Saturated hydrocarbons (acyclic and cyclic ones) represent the main part of the identified compounds (fractions I and II). Cyclic saturated hydrocarbons are represented by cyclohexanes (1.85% of the neutral oil). A considerable amount of paraffinic and olefinic hydrocarbons as well as long alkyl substitutes of cyclohexane and aromatic rings form a large part of kerogen macromolecule, which consists of unbranched chains. Tertiary and quaternary carbon atoms or cycles (cycloalkanes, benzene, naphthalene), can probably become centers of netting as places for breaking of such chains.

The presence of pentacyclic triterpenes is considered an evidence for the progress of widely running microbial processes.

Conclusions

Pyrolysis of Bulgarian oil shale sample in the presence of water vapour has been carried out. The amount of the liquid product resulting from this hydrothermal treatment is 24% higher than that obtained by Fischer method. Pyrolysis in water vapour is suggested to be an appropriate procedure for structural studies of organic matter of oil shale, since a large quantity of informative products is obtained. The data obtained indicate that the macromolecule of kerogen is built of two types of structures. The first one is of more expressed aromatic character occupying the peripheral parts of the

macromolecule. Structures of the second type are mostly of aliphatic nature. Organic matter of kerogen contains straight hydrocarbon chains with the length of up to 33 carbon atoms. These chains can play connecting and netting role. Benzene and naphthalene are dominating aromatic structures in kerogen. The composition of the products shows that diagenesis of oil shale has been soft owing to what oil shale cannot bear high temperatures and pressures.

REFERENCES

1. *Raukas, A.* Oil shale industry and sustainability – governance through dialogue // *Oil Shale*. 2005. Vol. 22, No. 1. P. 3–4.
2. *Oja, V.* A brief overview of motor fuels from shale oil of kukersite // *Oil Shale*. 2006. Vol. 23, No. 2. P. 160–163.
3. *Gubergrits, M. J.* Thermal Processing of Oil Shale Kukersite. – Tallinn: Valgus, 1966. 356 p. [in Russian].
4. *Lazarov, I., Dimitrova, Tz., Georgiev, N., Vilkov, V., Shipkov, P.* Thermal treatment of oil shale // *Bulgarian Oil Shales*. Bulgarian Academy of Sciences, 1983. P. 127–131.
5. *Razvigorova, M., Angelova, G.* Comparative characteristics of neutral oils of low-temperature carbonization of some Bulgarian oil shale deposits // *Petrol. Coal Geol.* 1979. Vol. 10. P. 25–31.
6. *Minkova, V., Razvigorova, M., Goranova, M., Ljutzkanov, L., Angelova, G.* Effect of water vapour during the pyrolysis of solid fuels on the yield and composition of the liquid products // *Fuel*. 1991. Vol. 70, No. 6. P. 713–719.
7. *Minkova, V., Razvigorova, M., Gergova, K., Goranova, M., Ljutzkanov, L., Angelova, G.* Effect of water vapour on the pyrolysis of solid fuels. II. Effect of water vapour during the pyrolysis of solid fuels on the formation of the porous structure of semicoke // *Fuel*. 1992. Vol. 71, No. 3. P. 263–265.
8. *Razvigorova, M., Minkova, V., Goranova, M.* Effect of water vapour on the low molecular part of the organic matter during mild pyrolysis of bituminous coal // *Comptes Rendus del l'Académie Bulgare des Sciences*. 1994. Vol. 47, No. 2. P. 49–52.
9. *Panov, G.* Review of the deposits of oil shale Bulgaria // *Bulgarian Oil Shales*. 1983, Bulgarian Academy of Sciences, 1983. P. 7–21 [in Russian].
10. *Radmacher, W., Mohrhauer, P.* Entmineralisierung der Steinkohlen für analytische Ziele // *Brennstoffchemie*. 1956. Vol. 37. P. 353–358.
11. *Sawatsky, H., George, A. E., Smiley, G. T., Montgomery, D. S.* Hydrocarbon-type separation of heavy petroleum fractions // *Fuel*. 1976. Vol. 55, No. 1. P. 16–20.
12. *Acholla, F. V., Orr, W. L.* Pyrite removal from kerogen without altering organic matter: chromous chloride method // *Energy&Fuels*. 1993. Vol. 7, No. 3. P. 406–410.
13. *Larsen, J. W., Pan, C. S., Shawver, S.* Effect of demineralization on the macromolecular structure of coal // *Energy&Fuels*. 1989. Vol. 3, No. 5. P. 557–561.

14. *Saxby, J. D.* Isolation of kerogen in sediments by chemical methods // *Chem. Geol.* 1970. Vol. 6. P. 173–184.
15. *Tissot, B. P., Welte, D. H.* *Petroleum Formation and Occurrence.* – Berlin: Springer-Verlag, 1984.

Presented by J. Soone

Received August 6, 2007