AGEING OF KUKERSITE THERMOBITUMEN

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Ageing of the mix of thermobitumen and oil (TBO) formed at low-temperature pyrolysis of kukersite in autoclaves was studied, and the effect of pyrolysis conditions on the share of fractions soluble in hexane, benzene and tetrahydrofurane was described. The results reveal a decrease in the total weight of TBO and solid residue at storage. During a month of ageing in open air the additional weight loss of the initial organic matter reaches 10-15%. At that, the yield of TBO decreases and that of the solid residue increases. The fractions of TBO soluble in hexane (maltenes + oil) and in benzene (asphaltenes) decrease, and the fraction soluble in tetrahydrofurane (pre-asphaltenes) increases.

The initial yields of hexane and benzene solubles depend on the degree of TBO secondary cracking determined by the pyrolysis conditions. The share of the fraction soluble in hexane increases with pyrolysis temperature and duration and attains 40–50% from the initial organic matter on account of decomposition of asphaltenes concurred with decrease in the total yield of TBO to 60–70% because of gas and coke formation.

Introduction

The continually increasing demand for liquid fuels and steadily decreasing petroleum reserves have intrigued investigations aimed at more complete transformation of oil shale organic matter into liquid fuels.

The previous works have shown that the recovery of kukersite organic matter (OM) can be enhanced by its extraction with superheated solvents [1, 2] or by low-temperature pyrolysis of the shale at 340–380 °C [3–6] and subsequent dissolution of the high-molecular (650-1300 u) semi product, thermobitumen (TB), remained in the cubic residue in open retorts or of the mix of thermobitumen and oil (TBO) formed in autoclaves. Under the optimum conditions where the initial kerogen has decomposed almost entirely into TBO but its secondary cracking into coke has scarcely started,

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the high (up to 90%) extraction yield of TBO from the initial organic matter can be obtained in both devices.

A theoretical basis for the new technology describing the co-effects of pyrolysis duration, nominal temperature and non-linear heating rate on the kinetics of phase transformations in the both laboratory devices by a unified mathematical model was proposed [7–9]. The rate factors and apparent kinetic constants for the parallel decomposition patterns of kerogen into extract (TBO in an autoclave and TB in a retort) and volatiles (gas in autoclaves, and oil and gas in retorts), and for the secondary parallel decomposition of TBO in autoclaves or TB in retorts into gas and coke were estimated.

The next challenge would be the further upgrading of the TBO obtained into liquid fuels by hydrogenation. At that, the first problem revealed in the works mentioned above is instability of the extracts evident from formation of a solid phase in the solutions of TBO during storage.

Ageing of oil shale TBO has not been studied earlier. The structure of TBO that is far being fully understood is quite complex. At that, the free radicals evoking during thermal decomposition may take part in irreversible ageing reactions as polymerization, polycondensation and oxidation, and evaporation of lighter components.

The widely used analytical method chromatography, coupled with mass-spectrometry (GC-MS or LC-MS) is limited by volatility or solubility and cannot readily be adapted to examine high-molecular-mass materials. Currently, above the 450–500 u range, no single method is unambiguously capable of indicating molecular mass distribution or chemical structural features in complex fuel-derived mixtures, and advances in this field require a comparison of several independent analytical methods [10].

At the present time, 95% of the almost 100 Mt of natural and artificial bitumen obtained as the vacuum residue of petroleum distillation, are applied as asphalt mixes in the paving industry. Mainly rheological methods have been proposed to replicate the effect of ageing aimed to foresee bitumen behaviour during application and service life. In this field the first concern has been the effect of time on the viscosity at blending of hot mixes to be pumpable and to allow homogeneous coatings. Second, the coating has to become stiff enough to resist rutting at high pavement temperatures and, oppositely, soft enough to resist cracking at the lowest temperatures. Viscosity, penetration, softening point, and weight loss tests were applied to investigate the rheological properties of fresh and aged Arabian asphalts [11]. It has been shown [12, 13] that ageing produces fundamental modifications in the colloidal structure of both vacuum residues and their maltenes fractions shifting all the solubility classes (asphaltenes, resins and saturates plus aromatics) towards the preceding, adjacent less soluble class. However, in contrast to the previous findings, the macrostructure of asphaltenes both in solutions and in a vacuum residue was found not being representative of the age hardening process, in spite of the fact that the content of asphaltenes increased and the ratio of resins, aromatics and saturates against asphaltenes

decreased being strongly dependent on temperature ranges [14]. The chemical changes during ageing of several bitumens have been found to include the formation of carbonyl compounds and sulfoxides, and to increase in amount of large molecular associations and polydispersity [15].

Lamontagne [16] has shown, basing on the indexes of aromaticy ($A_{1600}/\Sigma A$), aliphatic [($A_{1460} + A_{1376}$) /ΣA], carbonyl ($A_{1700}/\Sigma A$) and sulphoxide ($A_{1030}/\Sigma A$) where $\Sigma A = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{2953,2923,2862)}$, that an hour of oxidation of road bitumens by the air inside a FTIR heated (163 °C) cell is equivalent to two years of ageing on site. This work demonstrated that during the first two years, an increase in aromatisation was observed.

Masmoudi [17] measured by FTIR a decrease in instauration index and an increase in carbonyl index during stability studies of cosmetic "oil in water" emulsions taking as instauration index $A_{3006}/(A_{3006} + A_{2921} + A_{2851})$ and as carbonyl index $A_{1746}/ \Sigma A$ (the sum of the area between 1800 and 650 cm^{-1}).

The over-year ageing of an hydrocracked extract of coal was examined using size exclusion chromatography assessed in terms of shorter elution times and parallel changes in UV-fluorescence spectra [18]. The extent of the changes in the first week of the study was significant. No further changes were detected after the first month. At that, the ageing phenomenon was more marked for the product kept at room temperature in the air than in a freezer in a non-oxidising atmosphere. It was supposed that the changes observed involve the formed less reactive free radicals that have not reacted during the hydrocracking reaction itself.

The most part of thermobitumen consists of difficult to process asphaltenes, the high-molecular very complex compounds insoluble in _n_-hexane (_n_-pentane) but soluble in benzene (toluene). Asphaltenes are made up from units of condensed aromatic nuclei carrying alkyl groups and hetero elements. The difference in the size of units and chemical structure of asphaltenes depend on their source. The tendency of asphaltenes to aggregate distinguishes them from other oil constituents. According to Evdo-kimov [19], asphaltenes form aggregate-free solutions only at concentrations below 1–5 mg/l, between 10–20 mg/l dimers become the predominant species, while at concentrations 90–100 mg/l quasispherical dimer pairs are formed, whereas Beer's law is fulfilled only at concentrations exceeding 700 mg/l. In more diluted solutions a non-monotonic multi-peak relationship exists in the plot of absorbencies versus concentrations at any wave-length. On the contrary, a linearity of that plot was demonstrated in the range 0–400 mg/l of asphaltenes at 532 nm in [20]. Later, kinetics of asphaltenes aggregation was studied by conifocal microscopy [21]. The authors con-cluded that the aggregation process depended on the nature of the crude oil studied, and it was affected by the asphaltenes concentration.

Thermo-optical studies of solutions of asphaltenes in toluene and tetra-hydrofurane [22] have shown that the solvent molecules can be trapped

during aggregation of asphaltenes resulting in minimum diffusivities (D) before 50 mg/l and an increase in D at higher concentrations until a constant value is reached near 2000 mg/l.

Basing on the Hansen solubility parameter for bitumen determing solubility data of bitumen in a set of 48 solvents with known solubility parameters, Masmoudi [23] found that the asphaltenes may be dissolved in the maltenes rather than dispersed, indicating that no asphaltene micelles can exist. It was shown that the small difference between solubility parameters of asphaltenes and maltenes of the paving asphalt contributes to its good aging resistance [24].

Ageing of bio-oils, in some ways, analogous to the behaviour of asphaltenes found in petroleum, was observed as a viscosity increase and some phase separations. This instability is believed to result from a breakdown in the stabilized micro emulsion and to chemical reactions, which continue to proceed in the oil [25].

The artificial maturation of asphaltenes has been studied by hydrous and confined pyrolysis. The results support the idea that a competition between water and hydro-aromatics as hydrogen sources exists in hydrogen transfer reactions [26]. It was suggested that hydrogen transfer reactions between water and the newly formed hydrocarbons are catalyzed by the asphaltenes.

Besides, alteration of the share of the maltenes and asphaltenes with pyrolysis conditions should affect the hydrogenation results. For example, the formation of two structurally different cokes during thermal hydro-cracking of Tabasco bitumen is attributed to differences in coking properties of the asphaltenes and the deasphalted heavy oils [27].

In this work, the ageing of TBO obtained at low-temperature pyrolysis of kukersite in autoclaves is studied for the first time, and the effect of pyrolysis conditions on the yield of hexane and benzene soluble fractions is described.

Experimental

In all the experiments 4.0 g of finely powdered (0.04-0.1 mm) kukersite, containing 0.9% moisture and 40.15% organic matter (OM) were poured into a glass tube with inner diameter 8 mm, weighed and put into a 20-cm^3 micro-autoclave. The autoclaves were placed in a muffle oven at room temperature. The desired nominal temperature (360–410 °C) was reached during 100 min. After two hours residence time the autoclaves were cooled to room temperature and opened. The mass of gas formed was determined by the weight loss after discharging. The solid residue was not removed from TBO to avoid any loss of the lighter fractions during evaporation of the organic solvents applied. So, it was possible to find out that the mass of the pyrolyzed products decreased with time. The samples were weight in open and closed tubes kept at room temperature and in a refrigerator during

3 months. After different durations of the storage, the solid pyrolyzed product was extracted exhaustively in Soxhlet extractor successively with hexane, benzene and tetrahydrofurane. The mass of the corresponding extracts – so-called maltenes, asphaltenes and pre-asphaltenes, was found from the decrease in the sample mass at the extraction after drying of the corresponding residue. The extracts obtained were dissolved in 100-ml measuring flasks. The absorbance of the solutions was recorded on the spectrophotometer SPECOL 10 at wave lengths 420–450 nm. At that, the too dark solutions of asphaltenes and pre-asphaltenes were diluted in the ratio 1:10 with tetrahydrofurane.

Iodine value for hexane and benzene extracts was determined according to ASTM D-1959.

Results and discussion

Ageing

Changes in the yield of the phases
Several series of pyrolysis experiments in the six on hand micro autoclaves were conducted in this study. The heating time (100 min.) up to the nominal temperature (380 °C) was chosen, like it was made in the major autoclaves (500 cm^3) used, and followed by two hours isothermal retention. Distribution of the pyrolysis products between the three phases: gas, hexane + benzene extract (TBO) and organic solid residue is depicted in Fig. 1.

One can see from Fig. 1 that the experimental results obtained in different series fluctuate. Nevertheless, a continuous increase in the yields of volatiles and solid residue on account of the target product, TBO, is evident at ageing.
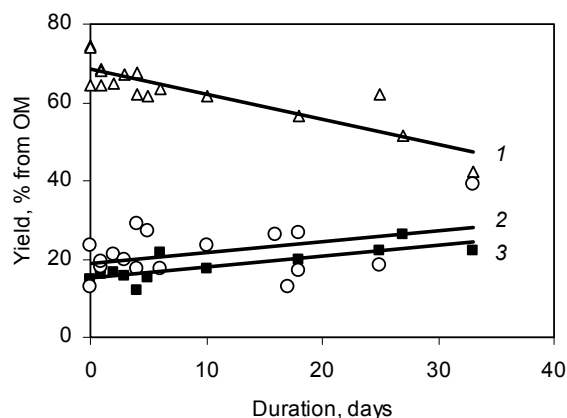

Fig. 1. Effect of ageing on the yield of different phases, % from initial OM: Total hexane and benzene extract, TBO (curve *1*), gas (curve *2*), and solid residue, coke and THF extract (curve *3*).

These changes in time (*t*) can be approximated to the following linear relationships:

$$Y(\text{Gas}) = 18.6(\pm1.6) + 0.39(\pm0.11)t \qquad (1)$$

$$Y(\text{Extract}) = 68.5(\pm1.4) - 0.58(\pm0.10)t \qquad (2)$$

$$Y(\text{Solid residue}) = 15.2(\pm1.0) + 0.222(\pm0.073)t \qquad (3)$$

The experiments above revealed an unexpected result – the mass of pyrolysates consisting of TBO and solid residue decreased at ageing. This phenomenon was studied in more details monitoring in time the weight of the glass tubes containing pyrolysates obtained at different nominal tempera-tures in several parallel experiments from different series. The results pre-sented in Fig. 2 prove that, independently of the initial gas yield depending on the pyrolysis conditions, a sharp increase in the yield of volatiles occurs during the first week of ageing followed by a trivial monotonous increase even after three month.

Noteworthy is that when the initial gas yield is subtracted from the current yield (curve 4), the loss of volatiles stored under the same conditions practically coincides independently from the pyrolysis temperature. It suggests that evolution of the light components dissolved and saturating TBO can take place. The opinion is supported by the fact that storage of the glass tubes with pyrolysate under different conditions (Fig. 3) affects the weight loss.

So, the rate of weight loss at room temperature (curve *1*) overcomes that in the refrigerator (curve *2*), both approaching the same constant value. Probably, in open air the content of volatiles at equilibrium conditions between TBO and gas phase approaches the total exhaustion of the light
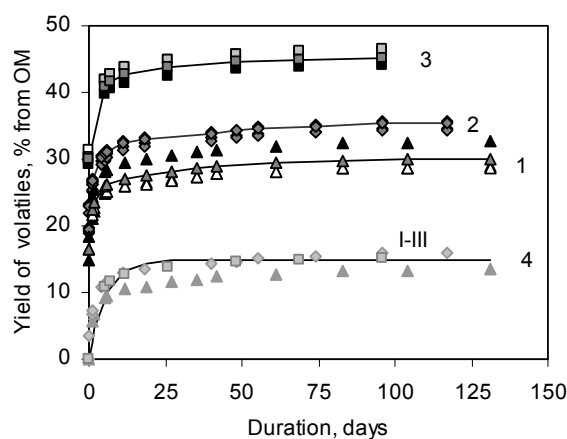

Fig. 2. Effect of ageing on the total yield of volatiles from the pyrolysate obtained at nominal temperatures, °C: 360 (curve *1*), 380 (curve *2*), 410 (curve *3*), and on the corresponding weight losses at room temperature storage (points *I-III*, curve *4*). Points experimental, curves calculated means.
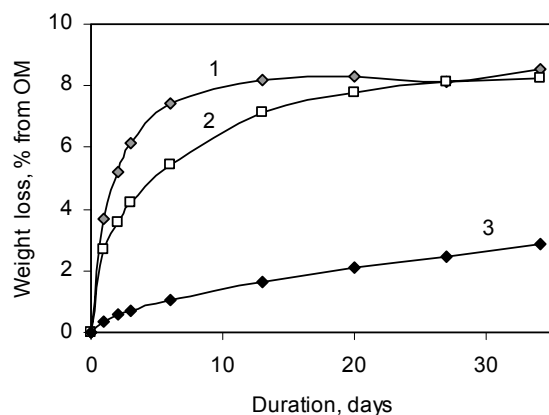
Fig. 3. Effect of ageing conditions on the weight loss of pyrolysate at storage in open tubes at room temperature (curve *1*), in open tubes in a refrigerator (curve *2*) and in closed tubes at room temperature (curve *3*).

fractions in TBO. Somewhat surprising weight loss of the closed tube (curve 3) can be explained by the volatiles leaving through the cork under the gas pressure increasing with time.

Extracts
The results obtained extracting the pyrolysates after different storage duration in Soxhlet apparatus subsequently with hexane (here and after maltenes), benzene (asphaltenes) and tetrahydrofurane (pre-asphaltenes) are presented in Fig. 4.

The experimental points in the figure show again pretty diffusive clouds of the extract yields, probably because the pyrolysates from different series
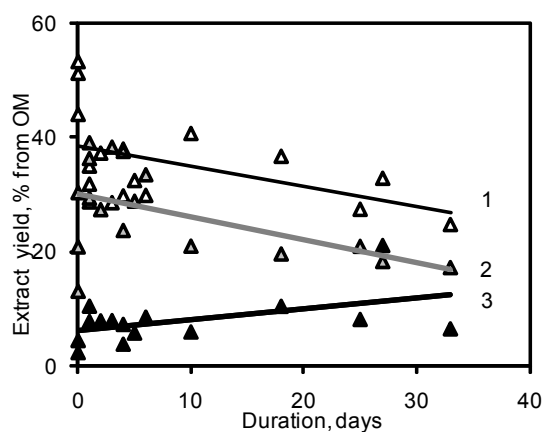

Fig. *4.* Effect of ageing on the yield of the fractions soluble in hexane (curve *1*), benzene (curve *2*) and tetrahydrofurane (curve *3*).

were applied for extraction. Yet, the results prove that the decrease in TBO yield described above by curve 1 in Fig. 1 is compiled from decreases in the yield of both maltenes and asphaltenes, and the yield of solid residue increases due to the increase in the yield of preasphaltenes. The changes can be approximated to linear relationships as follows:

$$Y(\text{Maltenes}) = 38.4(\pm 2.3) - 0.31(\pm 0.17)t \qquad (4)$$

$$Y(\text{Asphaltenes}) = 29.8(\pm 2.2) - 0.42(\pm 0.16)t \qquad (5)$$

$$Y(\text{Pre-asphaltenes}) = 5.8(\pm 1.4) + 0.14(\pm 0.10)t \qquad (6)$$

It can be concluded that a condensation of the both TBO fragments takes place at ageing. The noteworthy changes in the group composition of the extracts are evident in the results of thin layer chromatography presented in Fig. 5.

A decrease in the share of aliphatic compounds in the hexane fraction could be explained by their volatilization from the pyrolysate. Appearance of Nhet, PCHC and MCHC in benzene fraction, and the decrease in the share of HPhet compounds in benzene and tetrahydrofurane can be explained by their aggregation. As far the yields of the extracts are different, it is more informative to compare the changes of the compounds by yields of the chemical groups from the initial kerogen (Table 1). The results in Table 1 explain that depicted in Fig. 1 decrease in the total yield of the extract at ageing takes place mainly in the fraction of hexane soluble, especially aliphatic hydrocarbons, and in the fraction of high-polar heterocompounds precipitating due to stabilization of the unsaturated intermediate products by aggregation.
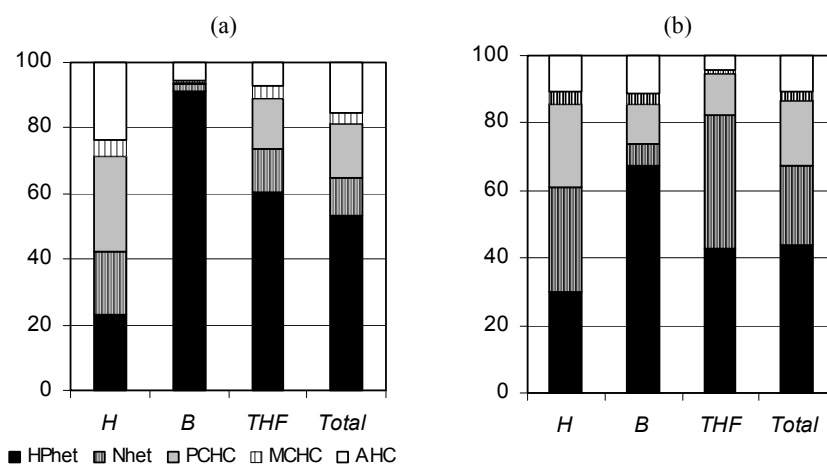

Fig. 5. Chemical group composition of the fractions soluble in hexane (column *H*), benzene (column *B*), tetrahydrofurane (column *THF*) and total extract (*Total*) separated from the fresh pyrolysate (*a*) and after its 34 days ageing (*b*).

Table 1. **Effect of ageing on the yield of chemical groups at subsequent extraction of the pyrolysate into hexane (H), benzene (B) and tetrahydrofurane (THF), % from OM**

Compound	After 0 day				After 34 days			
	H	*B*	*THF*	*Total*	*H*	*B*	*THF*	*Total*
Hydrocarbons:								
aliphatic (AHC)	9.02	1.70	0.17	10.89	3.15	2.01	0.22	5.38
aromatics:								
monocyclic (MCHC)	1.96	0.06	0.08	2.10	1.01	0.53	0.05	1.59
polycyclic (PCHC)	11.17	0.24	0.35	11.76	7.10	2.05	0.60	9.75
Neutral hetero compounds (Nhet)	7.30	0.57	0.30	8.17	9.04	1.21	1.97	12.22
High polar hetero-compounds (HPhet)	8.95	27.24	1.37	37.56	8.57	11.86	2.11	22.54
Total yield of the extract	38.40	29.81	2.27	70.48	28.87	17.66	4.95	51.48

Iodine value

Estimation of an unsaturation characteristic, iodine value, depicted in Fig. 6, reveals that there is no practical change in the iodine values of remaining soluble malthenes and asphaltenes (clouds of experimental points *1* and *2*) at ageing.

The mean iodine value for maltenes is 15.6 g/100 g and for asphaltenes 26 g/100 g. But iodine value of the total pyrolysate including solid residue (experimental points *3*) shows a tendency to decrease a little according to the trendline

$$Y \text{ (Iodine value of total pyrolysate)} = 39.1 - 0.42t \qquad (7)$$

According to Fig. 1 the yield of solid residue increases with time. Obviously, such a precipitation of maltenes and asphaltenes by condensation
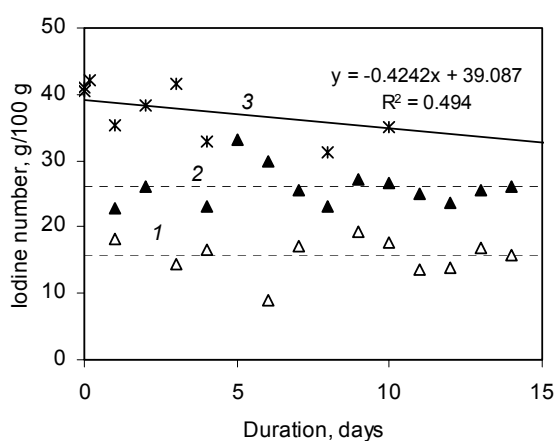

Fig. 6. Effect of ageing on the iodine number of the fractions soluble in hexane (curve *1*), benzene (curve *2*) and total OM in the pyrolysate (curve *3*).

on account of their double bonds and unsaturated radicals decreases the total iodine value of the pyrolysate. The remaining dissoluted maltenes and asphaltenes do not change their unsaturation degree per mass unit.

Discussion

Independently on the mine and content of mineral matter, the kerogen of kukersite is unique in composition, and products of its thermal decomposition contain large quantities of acid and neutral oxygen compounds as well as unsaturated, saturated, and aromatic hydrocarbons. According to Lille [28] the macromolecules of kerogen are highly aliphatic, with the ratio of aliphatic to aromatic carbons *ca* 4–5. The model of the kerogen empirical formula is $C_{421}H_{638}O_{44}S_4NCl$ which corresponds to the elemental composition, %: C – 76.9; H – 9.7; O – 10.7; S – 1.9; N – 0.2; Cl – 0.5, and the atomic ratio of H/C 1.515. The composition and physical characteristics of polycomponental TB reflect the structural groups of kerogen and depend on pyrolysis conditions. There were found various polycyclic compounds of different molecular masses in the composition of TB. For example after pyrolysis of the kerogen concentrate during 132 hours at 330 °C and 4 hours at 360 °C, Kask [29] estimated the elemental composition of thermobitumen as follows, %: C – 86.9 and 83.6; H – 8.43 and 9.56; O+N – 4.4 and 6.3; S – 0.40 and 0.50, and the corresponding atomic ratio of H/C 1.16 and 1.37. The decrease in the H/C ratio in TB and the high content of oxygen can be the main causes of TB ageing.

The experimental results above have revealed that at ageing of the pyrolysate obtained at low-temperature pyrolysis of kukersite in an autoclave an aggregation of the compounds takes place that shifts maltenes and asphaltenes to the preceding adjacent class – pre-asphaltenes and solid residue, and the content of aliphatic, monocyclic and polycyclic hydrocarbons soluble in hexane decreases and those soluble in benzene increases. The aggregation might be resulted by chemical condensation reactions between phenolic and neutral oxygen groups or by formation of hydrogen bonded complexes between oxygen-containing molecules. At the same time an opposite process takes place – the yield of the volatile phase increases. It might be supposed that the weight decrease would be brought about volatile side-products of condensation or just by evolution of trapped in TBO light fractions. A decrease in the yield of aliphatic hydrocarbons supports rather the latter idea. The chemical changes in the products will be a challenge of the future works.

Effect of pyrolysis conditions on the share of maltenes and asphaltenes in TBO

The experimental results above have revealed that asphaltenes overcome malthenes in their ageing rate and iodine number. Besides, production of liquid fuels by hydrogenation from asphaltenes is more complicated than from maltenes. So, conditions where maltenes prevail would be of interest. It

is known that the share of maltenes and asphaltenes in TBO depends on the pyrolysis conditions [4], but the effect is not quantitatively clear.

In this part of work, the effects of pyrolysis temperature and duration on the yield of maltenes and asphaltenes from oil shale were elaborated.

Basing on the photometric measurements described in [19–21] an attempt was done to evaluate the effect of main factors of the low-temperature pyrolysis on changes in the optical densities (E) of the solutions (Fig. 7).
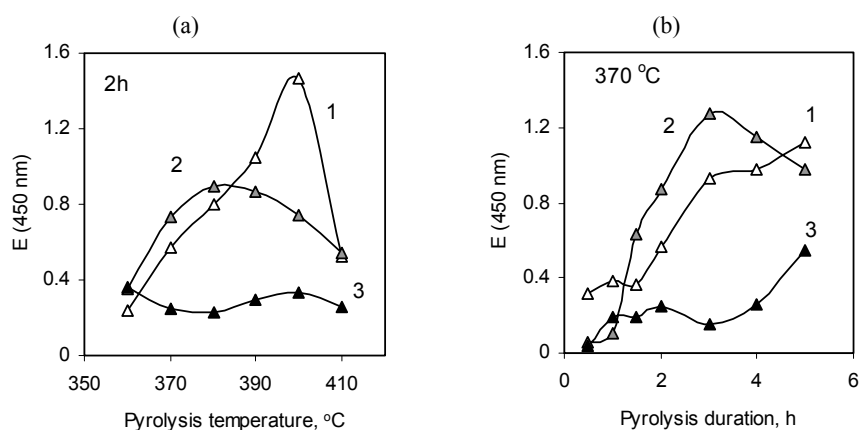

Fig. 7. Effect of pyrolysis nominal temperature (*a*) and pyrolysis duration (*b*) on the optical density of the solutions of the fractions soluble in hexane (curve *1*), benzene (curve *2*) and tetrahydrofurane (curve *3*).

The results obtained prove that at 2-h duration the maximum in optical density of the hexane solutions occurs at 400 °C, and of the benzene solutions at 380 °C, whereas the temperature effect is insignificant for the tetrahydrofurane solutions. The increasing duration increases optical density of the hexane and tetrahydrofurane solutions on account of the benzene solution at 370 °C.

Building of calibration curves evidences that the special absorbance per gram of the extracts having pale yellow to dark brown colour increased in the row: maltenes<asphaltenes<<pre-asphaltenes. The graphs obtained by dilution of any definite sample followed good linearity. But the graphs built using diluted extracts from different pyrolysis series resulted in a cloud of discursive experimental points with quite unsatisfactory linear regression. Besides, the solutions became darker and turbid in time. Therefore, the optical density measurements were excluded in the further study.

The analogous but much more informative and authentic is depiction of the effect of pyrolysis conditions on the yield of the main products. The effect of pyrolysis nominal temperature on the yield of products extracted on the next day after 2-h pyrolysis duration is given in Fig. 8a. One can see that an increase in the temperature increases the yield of gas, and decreases the

yield of asphaltenes and pre-asphaltenes, whereas the yield of maltenes has its maximum at 400 and the yield of solid residue its minimum at 370 °C. The effect of pyrolysis duration on the yield of products at the temperature found as the maximum for separation of OM from mineral matter, 370 °C, is presented in Fig. 8b. The results show that the changes in the yields with increase in duration are analogous to the increase in temperature – the decomposition degree of the products increases, whereas preasphaltenes and organic solid residue have a minimum before the secondary cracking of asphaltenes starts. At 410 °C and after two hours also decomposition of the benzene solubles starts. The behaviour of the curves explains that the secondary cracking of asphaltenes increases mainly the yield of benzene solubles but unwontedly also the coke and gas yields.
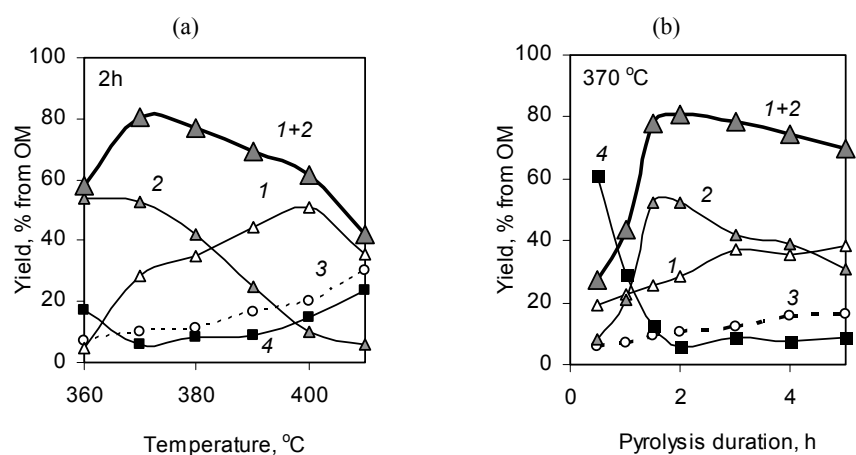

Fig. 8. Effect of pyrolysis nominal temperature (*a*) and duration (*b*) on the yield of the fractions soluble in hexane (curve *1*), benzene (curve *2*), and of the total TBO (curve *1+2*), gas (curve *3*) and solid organic residue (curve *4*). Heating-up time 100 min.

In all the experiments above the heating-up time was 100 minutes. The data in Table 2 explain that when the heating-up time is shorter the yields of gas, TBO and pre-asphaltenes decrease, the yield of solid residue increases, whereas the yield of asphaltenes has a maximum and that of maltenes a minimum. The results prove that under the pyrolysis duration 2 hours and nominal temperature 370 °C formation of TBO and its secondary cracking start before the nominal temperature is attained.

The experimental results in Figures 8*a* and 8*b* and Table 2 agree with the maximum in the yield of total TBO and minimum of the organic solid residue under an appropriate combination of pyrolysis temperature and duration described earlier mathematically in [7, 8].

Table 2. **Effect of heating up time to 370 °C on the yield of kerogen decomposition products, % from OM**

Product	Heating-up time, min, and (rate, °/min)		
	6 (58)	60 (5.8)	100 (3.5)
Gas	8.38	9.73	10.18
Maltenes + oil	12.3	10.45	28.24
Asphaltenes	65.67	69.66	52.43
TBO	77.97	80.11	80.67
Pre-asphaltenes	1.15	4.15	4.8
Organic solid residue	14.73	7.26	5.7

Conclusions

The target product, a mix of thermobitumen and oil (TBO), forming at low-temperature (360-410 °C) pyrolysis of oil shale in autoclaves, is not stable. The following phenomena have been revealed at storage of the product:

- An additional volatilization of the light fractions captured in the sticky TBO leads to the continuous decrease in the weight of the total product. Independently of the pyrolysis temperature, the weight loss reaches in open air 10–15% from the initial organic matter during a month of ageing.
- The yield of extractable with organic solvents products decreases on account of the increasing yields of solid residue and gas.
- The yields of hexane solubles (maltenes + oil) and benzene solubles (asphaltenes) decrease and of tetrahydrofurane solubles (pre-asphaltenes) increases.
- The main decrease in the hexane solubles takes place in the most preferable fraction – aliphatic hydrocarbons – and also in the fraction of aggregating high polar heterocompounds.
- The initial yield of maltenes and asphaltenes at pyrolysis depends on the degree of secondary cracking of TBO. The share of the hexane-soluble fraction increases with pyrolysis temperature and duration and attains 40-50% from the initial organic matter on account of the decrease in the total yield of TBO to 60-70%.
- The process of upgrading of TBO to liquid fuels by hydrogenation should follow the pyrolysis process as soon as possible to avoid any loss at ageing.

Acknowledgements

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