EXTRACTION OF OIL FROM JORDANIAN ATTARAT OIL SHALE

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Abstract. *A short overview of the previous works concerning oil extraction from Jordanian oil shale is presented. The results of the systematic experimental study obtained in this work on the effects of temperature (320–420 °C) and exposure time (0–10 h) at nominal temperature on the yield of pyrolysis products from Attarat oil shale generated in autoclaves without any solvent and in the presence of benzene, water and tetralin are described. The yields of solid residue, gas, pyrolytic water and subsequent extracts with benzene (thermobitumen and oil (TBO) including asphaltenes and hexane solubles) and tetrahydrofurane (asphaltols) were estimated. The compound groups of TBO were assessed. The highest yield of TBO, 59.4% of organic matter (OM), was obtained at a temperature of 420 °C and duration 0.25 h. The 20% lower yield of TBO from Jordanian oil shale OM in comparison with that from Estonian Kukersite OM is explained by close values of the apparent kinetic constants estimated for the overall decomposition of the Attarat oil shale OM, and for the secondary decomposition of TBO.*

Keywords: *Jordanian Attarat oil shale, pyrolysis, autoclaves, kinetics.*

1. Introduction

The proven amount of Jordanian oil shales is about 5×10^{10} tons [1]. So, there is interest in attaining a maximum utilization potential of the local energy source reducing Jordan's dependence on imported oil. The eight most important deposits – Juref ed Darawish, Sultani, Wadi Maghar, El-Lajjun, Attarat Um Ghudran, Khan ez Zabib, Sigawa and Wadi Thamad, are located in west-central Jordan. Recovery of liquid fuels from the shales of different deposits amounts to 8–12%. The best-explored deposits are El-Lajjun, Sultani, Juref ed Darawish and to some extent Attarat Um Ghudran [2, 3].

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The oil shales have shown unexpected structural and reactivity differences despite they were deposited at roughly the same time in the same region [4].

Oil shale organic matter (OM) consists of organic solvents soluble bitumen and insoluble kerogen. A special feature of Jordanian oil shale is that there are quite a lot of foraminifera shells (diameter < 20 μm) filled with bitumen or kerogen instead of the usual calcite [1]. Beneficiation of the oil shale by froth flotation has shown a poor recovery of oil-rich components (maximum 3%) just due to the fact that during crushing and milling kerogen and bitumen wet most of the oil shale particles, making it difficult to adjust surface properties [5].

Kerogen can be extracted from the oil shales only after its thermal or chemical decomposition.

1.1. Extraction of bitumen

In Jordanian oil shale the share of OM soluble in organic solvents without thermal decomposition (bitumen) is quite high. Al-Harasheh [6] and Shawaqfeh and Al-Harasheh [7] have studied the extraction of bitumen from El-Lajjun and Sultani oil shales using different types of solvents by continuous contact mixing. The oil yield obtained in the Fischer Assay of the samples was respectively 9.38 and 12.45%. The weight loss of the samples in the extraction without thermal decomposition increased from 2 to 6% in the row of the solvents: diesel, butanol, kerosene, propanol, ethanol, benzene, methanol, ethyl acetate, cyclohexane, solvent mixture (toluene, methanol, and chloroform), toluene, xylene and carbon disulfide, and was 9.5% with high polarity dimethyl sulfoxide. It can be supposed that the weight loss exceeding the oil yield in the Fischer Assay could partly be the result of dissolution of the mineral part of the shale in the polar solvents. The solubility in cyclohexane was found to increase with an increase in mixing time (1–6 h), temperature (25–50 °C) and solvent/shale ratio (2/1, 3/1, 5/1 g/g), and to decrease with an increase in grain size (100–1600 μm). The yield of bitumen depended on the solvent type and deposit and decreased from 3 to 0.5% in the row: chloroform, toluene, hexane and ethanol for the Sultani deposit whereas for the El-Lajjun deposit hexane was the weakest solvent. It was proved in [6] that distribution of aliphatic and aromatic hydrocarbons, hetero-compounds and asphaltenes was affected by polarity of solvents. Guo [8] explained that the solubility in different solvents depended upon their ability to disrupt the non-covalent bond interactions between bitumen and kerogen. The oil yield obtained by continuous mixing at 50 °C was 0.3–1.2% lower than that obtained using a Soxhlet apparatus at a boiling temperature of solvents.

Matouq et al. [9] and Matouq and Alayed [10] reported that the efficiency of various solvents can be substantially increased assisted by low frequency ultrasound or gamma-ray radiation. It was shown that the fraction extracted from El-Lajjun oil shale was 90% of the total extract obtained already after 10 minutes of sonication. Using tetrahydrofurane (THF) as the solvent, the

extraction time was decreased four-fold while the fraction extracted was increased thrice at room temperature by using ultrasounds under 20 kHz frequency. After gamma radiation exposure for 72 h at room temperature without any mixing source, the yield of the extract from the Fischer Assay increased from 13 to 71% in the row: water, benzene, acetone, acetone + water and acetone + benzene [10].

1.2. Retorting

Usually solid fuels are liquefied by semicoking in the course of which the thermal decomposition of OM under inert atmosphere in an open retort by heating up the sample to a nominal temperature (450–500 °C), keeping the temperature during a prescribed period, and separation of the liquids (oil and water) and non-condensable gaseous products are conducted. The effect of OM content on the oil yield of Jordanian oil shale from the main five deposits described in [11] is depicted in Figure 1.

The linearity of the dotted trendline *A* with a slope of 0.377(±0.013) reveals that the oil yield in the Fischer Assay increases nearly proportionally (correlation coefficient R^2 = 0.88) with increasing OM content. Actually, the curve *B* depicting the oil yield on the basis of OM shows a practically constant value, 37.9(±0.5)%, being close to the slope of *A,* when OM content is 25% or higher only, and decreases for poorer samples with decreasing OM content like for any other oil shale [12]. The decrease can be explained by increasing surface of the mineral matter adsorbing the oil formed and accelerating catalytically the secondary decomposition of the adsorbed oil layer into coke and gas.

Jaber et al. [13] showed, using a fixed bed reactor at a nominal temperature of 500 °C, that the oil yield from El-Lajjun and Sultani oil shales increased from 10 to 15% with an increase in particle size from 0.85
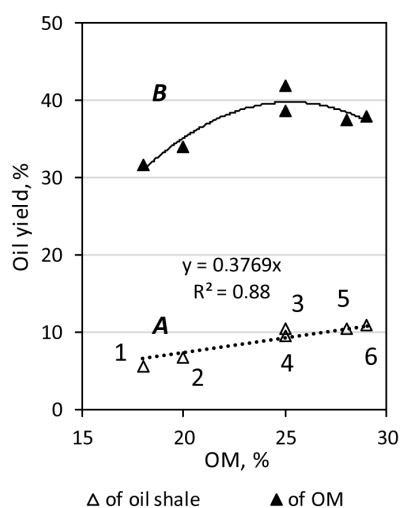

Fig. 1. Effect of organic matter (OM) content on the oil yield on the basis of oil shales (*A*) [11] and of their OM (*B*) in the Fischer Assay from the deposits: 1 – Jure Ed-Darawish, 2 – Wadi Maghar, 3 – El-Thamad, 4 – Sultani, 5 – El-Lajjun, 6 – Attarat Um Ghudran.

up to 5.6 mm whereas the gas yield of the samples decreased respectively from 6.1 to 5.6% and from 5.6 to 5.0%. The phenomenon was explained by the fact that the small particles had a greater surface area per mass unit, favoring the adsorption of oil and its secondary cracking. The yield of water (hygroscopic and pyrogenetic) was invariably about 10%.

Nazzal [14] pyrolized El-Lajjun oil shale in a fixed bed reactor at heating rates of 2–30 °C/min under the atmosphere of N_2 and the mixture of N_2/water steam as sweeping gases. The maximum yields of different products were observed at different flow rates. So, the maximum yield of oil was 8.9% under N_2 and 10.3% under N_2/water steam at the heating rate of 10 °C/min. The corresponding gas yield was 9.64 and 9.9% at 30 °C/min, and of water, 5.7 and 6.6% at 15 °C/min. Thereby, it was not explained how the yield of water was found in the presence of N_2/water steam.

Tucker et al. [15] compared the retorting and supercritical extraction of El-Lajjun oil shale. Retorting in the Fischer Assay (heating rate 10 °C/min, residence time 50 min at a nominal temperature of 500 °C) gave the oil yield of 11.7 L/kg under N_2 and 12.0 L/kg under CO_2. Extraction of the shale in supercritical CO_2 and water gave respectively 8.8 and 17.7 L/kg of oil. A bit more mid-distillate and narrower molecular weight compounds were found using CO_2. The most promising conditions resulting in 61% of oil from OM obtained using supercritical water will be described below in Part 1.4 concerning solvent extraction.

1.3. TGA

The thermogravimetric analysis (TGA) represents an alternative to the retorting process in an open device. In this procedure some milligrams of a sample are decomposed under an inert atmosphere monitoring changes in temperature and weight loss with time. So, the rate of changes in the transformation degree of oil shale expressing evolution of total volatiles (including oil, water and gas) can be tracked, and the corresponding apparent kinetic constants can be estimated.

The total weight loss of El-Lajjun and Sultani oil shales in TGA within the temperature range of 300–500 °C has been 22 and 18%, respectively [13].

Al-Harahsheh et al. [16] reported that the total weight loss of El-Lajjun oil shale between 200 and 550 °C was about 20%, and about 70% of its OM isolated by sequential HCl and HCl/HF digestions. It was concluded that the mineral matter enhanced the catalytic cracking of the oil shale.

TGA in the temperature range of 120–550 °C of Jordanian oil shale from five deposits gave the weight loss as follows, %: Sultani 23.14, El-Lajjun 19.05, Ma'an 17.72, Yarmouk 16.54, and Attarat 13.57 [4, 17]. Subtraction from the total volatiles of gas yields being between 5 and 8% in the Fischer retort would give the oil yields close to the values obtained in the Fischer Assay discussed in Part 1.2.

Increase in the heating rate from 3 to 40 °C/min increased the weight loss in TGA of two another oil shale samples from the Attarat deposit from 23.1 to 24.93% and from 20.61 to 21.11% [18]. So, the pyrolysis behavior of Attarat shale was analogous to that of the more surveyed El-Lajjun and Sultani oil shales described above.

The possibility for an exact monitoring of the transformation rate and temperature in TGA has given a favorable technique to investigate effects of various parameters on the pyrolysis kinetics. The isothermal and non-iso-thermal integral and differential methods have been developed, approximating the complicated thermal decomposition mostly to a single, but also to parallel or consecutive apparent reactions. Mainly, the simple first order kinetic reactions have been assumed. The values of the apparent activation energy have varied between 7 and 112 kJ/mol [13–19], depending on the degree of transformation, temperature interval, heating rate, particle size and OM content.

1.4. Solvent extraction under sub- and supercritical conditions

As described above, the yield of oil obtained from Jordanian oil shale in laboratory conventional open retorts is below 40–50% of OM, being 10–25 % lower than the corresponding value of Estonian Kukersite OM, 60–66%. So, modification of the thermal liquefaction process has been of interest for a more complete utilization of Jordanian oil shale OM. With the aim to increase the oil yield, liquefaction of Jordanian oil shale has been investigated in the presence of several solvents under sub- and supercritical conditions.

Tucker et al. [15] conducted a 2-hour supercritical (SC) extraction of a 20 g El-Lajjun oil shale sample at 375 °C and 14.3 MPa in SC-CO_2 and at 439 °C and 24.9 MPa in SC-H_2O, giving in both the experiments the same solvent density, 0.119 g/cm^3. It is noteworthy that the reaction temperature in the SC solvents applied was significantly lower than in the Fischer Assay (500 °C). The oil yield obtained in SC-H_2O was higher than that obtained in N_2 retorting and amounted to 177 cm^3/kg of the shale or 61% of OM. In SC-CO_2 the oil yield was only 88 cm^3/kg or 30% of OM. It can be supposed that the 2-hour duration used was insufficient for the thermal decomposition at 375 °C. Unfortunately, the scheme and solvents applied for oil separation from the solid residue and water were not described. So, we cannot be sure that part of water remained in the liquid product in the experiments with SC-H_2O.

Fei et al. [20] treated El-Lajjun oil shale (24.2% OM) in 27 ml autoclaves for 1 and 5 hours at temperatures of 300, 355 and 425 °C without water, and in the medium of water to oil shale ratios of 1:1 and 1:3 in the presence of N_2, CO and H_2 by adding various catalysts. The conversion degree of OM into hydrocarbon gas and products soluble in THF (oil + water + asphaltenes + asphaltol) was 86% at 355 °C (5 h), and close to 100% at 425 °C (1 h). The summary yield of oil and water was respectively 9–12 and 17–18% on

the basis of oil shale, corresponding to 37–50 and 70–74% of OM. Thereby it is possible that the sum of oil plus water of OM is overestimated because part of pyrogenetic water could be originated from the crystal water of minerals. The presence of N_2, CO and even H_2 (3 MPa, at room temperature) gave similar conversions of the shale at the same temperature and duration. The yields without water and in the presence of 1 g/g water were close. Increasing the water to oil shale ratio to 3 g/g generally decreased the oil yield and increased the yields of gaseous hydrocarbons and CO_2. Addition of $NaAlO_2$, $Cu(OAc)_2$, $Fe(OAc)_2$, SnO_2 and $Ni(OAc)$ having proved themselves as catalysts in coal conversion gave no significant increase in the yields of useful products from Jordanian oil shale.

Allawzi et al. [21] found that a relatively high oil yield can be obtained in a fixed bed autoclave using CO_2 (12.5 ml/min) supercritical extraction with co-solvents like acetone or hexane. The highest oil yield, 10% of El-Lajjun oil shale, actually not surpassing that in retorting (Fig. 1), was obtained at 450 °C and 22.5 MPa with hexane as a co-solvent.

The effect of temperature between 355 and 425 °C on the pyrolysis during 1 h of Jordanian oil shale from five deposits in autoclaves without solvents under N_2 and H_2 gas (3 MPa at room temperature) was reported in the paper of Amer et al. [4]. The yields of extraction fractions estimated on the basis of OM varied in wide ranges depending on the conditions and decreasing in the row as follows: CH_2Cl_2-solubles + H_2O + gas (39.8–93.6%) including oil + H_2O (31.6–89.7%) and insoluble in hexane asphaltenes (1.7–29.9%), and soluble in THF asphaltols (0.6–5.7%), gaseous hydrocarbons + H_2S (0.0–9.1%), and CO_2 (0.0–3.5%). As an example, the effect of temperature on the yield of CH_2Cl_2 soluble oil + H_2O is depicted in Figure 2 using the data published in Table 4 in [4].
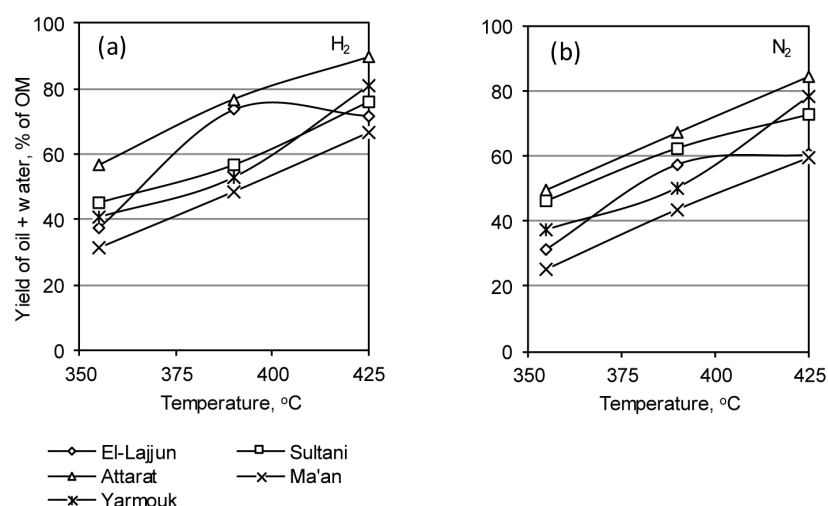

Fig. 2. Effect of temperature on the yield of oil + water in the 1-h pyrolysis in autoclaves in the presence of hydrogen (a) and nitrogen (b). The data are taken from [4].

Figure 2 shows that the yield of oil and water fraction extracted after the 1-h pyrolysis increases proportionally with increasing temperature. Apparently, this effect is amplified with the insufficient reaction time applied. The most reactive is Attarat and the least reactive Ma'an oil shale OM. As an exception, the oil shale from the El-Lajjun deposit attains a steady state already at 390 °C. It can be supposed that the secondary cracking characteristic of the oil formed particularly from El-Lajjun oil shale prevents further increase in oil yield. The atmosphere of H_2 increases the yield of oil + water by 2–16%, in comparison with N_2, however, the curves depicting pyrolysis are similar under both the gases. The yields of oil + water obtained in the work [4] extracting the pyrolysates produced in autoclaves without solvents are close to the oil yields obtained in water medium and without water published earlier [20]. Noteworthy is that the data depicted in Figure 2 are about twice higher than the oil yields presented in Figure 1 where the yield of water was not included.

According to Haddadin [22], the samples of El-Lajjun oil shale undergo softening and molecular rearrangement up to 330 °C. Thereafter, heating up to 500 °C results in evolution of oil and gas corresponding to the weight loss by 23% in the untreated shale and by 42% in the decarbonated shale. It was reported that up to 90% of OM was transformed into decomposition products by dissolution conversion when 2 g/g of tetralin was added as a hydrogen donor solvent at a temperature of 315°C.

1. 5. Flash pyrolysis and pyrolysis in a solid heat carrier unit

Fluidized bed pyrolysis appears to be a promising procedure since a rapid evolution of volatiles due to a fast heating rate can avoid the secondary cracking of the valuable oil formed. Nazzal and William [23] treated the oil shale samples from the Sultani deposit in a semi-continuous fluidized bed reactor under N_2 and N_2/water steam atmosphere in the temperature range of 400–540 °C. The fluidized medium was quartz sand. The residence time of the vapor phase was 30 s and of the shale 45 min. The maximum oil yield obtained at 540 $^{\circ}$C was 8.7% of the initial shale under nitrogen, and 9.8% under nitrogen/steam atmosphere. The results are close to the oil yield from the shale under standard conditions in the Fischer Assay, 9.2% (Fig. 1).

Yorudas and Gavrilov [24] processed 15 kg/h of oil shale from the El-Lajjun deposit, containing 21.26% of conditional OM $[100 - A^d - (CO_2)_{mineral}{}^d]$, in a solid heat carrier unit using the Galoter method. The oil yield from the sample was 10.7% (50% of OM), being 81% of the oil yield found in the Fischer Assay.

1.6. Comparison of the thermal liquefaction of Jordanian and Estonian Kukersite oil shales

The yield of pyrolytic oil from an oil shale depends on its OM content and composition of both the organic and mineral parts [12].

The investigations described above have revealed that independently of the liquefaction procedure applied, typically, about 10–13% of oil can be extracted from the initial Jordanian oil shale, corresponding to 40–60% on the basis of OM. Whenever higher yields were reported, like in TGA and solvent extraction, water and/or gases were included.

It was shown in our previous works [12, 25] that the oil yield at a low-temperature pyrolysis of Estonian Kukersite using open retorts at 350–370 °C was also up to 40% of OM. But when the high-molecular thermo-bitumen (TB) was extracted from the cubic residue after retorting or from the total pyrolysate obtained in autoclaves, the total yield of the liquid product, stating the sum of thermobitumen and oil (TBO), exceeded 80% of OM.

Formation of the thermobitumen intermediate is a common feature in the thermal decomposition of highly aliphatic organic matter of Baltic, Colorado, Green River and Australian oil shales whereas more aromatic oil shales such as Turkish, Kentucky New Albany, and Mississippi are prone to quick condensation of the aromatic rings and formation of insoluble in benzene coke [3]. According to Fei et al. [20], a solid state ^{13}C NMR spectrum of the acid-washed shale showed the atomic ratio of C_{ar} to C_{aliph} of 0.21:0.79, indicating a high aliphatic content with an H/C atomic ratio of 1.44 for the total organic material. So, the formation of TB may be characteristic of Jordanian oil shales.

The goal of this study was to elucidate conditions for obtaining a maximum yield of liquid product, TBO, from Jordanian Attarat oil shale. For this purpose, a systematic experimental study of the effects of temperature and time on the yield of pyrolysis products from Jordanian oil shale in autoclaves without any solvent and in the presence of benzene, water and tetralin was conducted.

2. Experimental

2.1. Characterization of the initial sample

The oil shale sample studied was taken from Jordanian Attarat deposit and delivered by Indrek Aarna, Head of R&D Department, Eesti Energia AS.

The conditional OM (weight loss in incineration at 550 °C) of the sample was 21.44%, ash content (weight loss in incineration at 825 °C) 61.9%, carbon dioxide 20.4% and moisture 0.68%.

The elemental analysis gave: C 20.6%, $C_{organic}$ 15.0%, H 2.1%, N 0.3%, S_{total} 3.11%, $S_{organic}$ 2.67%, and $S_{pyritic}$ 0.28% of the dry shale.

The yields of the pyrolysis products in the Fischer Assay on dry shale were as follows: oil 10.4%, semicoke 84.6%, pyrogenetic water 0.8% and gas + losses 4.2% of the dry shale.

2.2. Liquefaction procedure

Pyrolysis of the oil shale was carried out in glass test tubes placed in 58 cm^3 autoclaves. The tubes facilitating to wash out the pyrolysis products were omitted only in the test series with water medium corroding glass at the temperatures applied.

In each experiment 10 g of the air dried shale powdered to 0.04–0.1 cm or 8, 6 or 5 grams of the shale and 8, 12 or 15 grams of the solvent (to achieve a ratio of the solvents to shale of 1, 2 and 3 g/g) were used. The samples were placed into a cold muffle oven. The constant nominal temperature varying from 320 to 420 °C was attained for the period of 60 minutes. The pyrolysis duration was measured from the time when the muffle oven reached the nominal temperature prescribed.

Efficiency of the liquefaction process was evaluated by the yield of pyrolysis products: gas, subsequent extracts with benzene (TBO) and THF (asphaltols), and solid residue. TBO, representing the total benzene solubles (bitumen, thermobitumen and oil), was divided into hexane soluble maltenes and hexane insoluble asphaltenes. The asphaltols were less soluble and higher molecular hetero-compounds than TB.

2.3. Analysis

The mass of gas formed was determined by the weight loss after discharging the volatiles from the open autoclave at room temperature. The pyrolysis liquid products consisting of TBO and asphaltol were extracted exhaustively with boiling benzene, and subsequently with THF in a Soxhlet extractor. The mass of the solvents insoluble solid residue (SR) was weighted after drying at 105–110 °C during 1–2 h. The solvents applied were removed from the TBO and asphaltol solutions in a vacuum rotation evaporator at 60–70 °C. The distillation residues of the benzene and THF extracts obtained in the rotation evaporator were left in the open flask and weighted after 24 h for evolution of the solvent traces remained. Like in the authors' earlier works, removing traces of benzene from TBO has been a problematic procedure. The quantity of TBO can be underestimated due to evaporation of low-boiling destruction products or overestimated when part of the solvent, having a higher boiling temperature than the lighter fractions or being incorporated into destruction products, is not removed. So, the mass of TBO was preferred to determine by subtracting the mass of gas, water, THF extract and solid residue from the initial mass of the shale.

TBO was divided into two fractions: soluble in hexane maltenes (oil) and insoluble in hexane asphaltenes, the latter being undesirable as a fraction more prone to coke formation. For this purpose, 10 g/g of hexane was added to an aliquot of the incompletely dried benzene extract. After 24 h the precipitate of asphaltenes was filtrated, dried and weighted.

The compound groups of TBO were estimated by preparative thin-layer chromatography separating 500 mg samples on 24 × 24 cm plates coated

with a 2 mm silica gel layer (60 mm, Fluka), and using *n*-hexane as the eluent. Five groups of compounds were separated and extracted from silica gel with ethyl ether: aliphatic hydrocarbons (AlHC), monocyclic hydrocarbons (MCHC), polycyclic hydrocarbons and some sulfur compounds (PCHC), neutral hetero-atomic (Nhet) and polar hetero-atomic (Phet) compounds.

3. Experimental results and discussion

3.1. Pyrolysis without solvents in autoclaves

Soxhlet extraction of bitumen from the initial sample without thermal decomposition yielded, % of the dry shale (% of OM): benzene extract 1.09 (5.14), THF extract 0.53 (2.49), and solid residue 98.38 (92.37).

Yields of the pyrolysis products from the dry oil shale obtained in the test series conducted at various temperatures and isothermal durations are presented in Table 1.

The results in Table 1 show that at any temperature series the gas yield increases with time whereas the yield of TBO has a maximum and that of SR a minimum shifting with increasing temperature to shorter durations. The maximum yield of TBO achieved is only 12%, and the maximum transformation degree of the oil shale is 17–18% of the dry shale. The yields are close to those obtained at semicoking of Jordanian oil shales in the Fischer Assay [6, 7, 11, 13, 14] and depicted in Figure 1.

As the products given in Table 1 are generated in the thermal decomposition of OM, the better characterization of the process can be obtained when the yields are depicted on the basis of OM. Effect of pyrolysis duration at various nominal temperatures on the yields of the main decomposition products – gas, TBO, asphaltols, and solid residue of OM, are presented in Figure 3.

The data in Figure 3 prove that increasing the temperature and duration results in a steady increase in gas yield. The yield of TBO has a maximum amounting 55–60% of OM at nominal temperatures of 320, 360, 380, 400 and 420 °C respectively after 10, 1.5, 1.0, 0.75 and 0.25 h. The maximum yield of TBO surpasses the oil yield of Attarat oil shale estimated in the Fischer Assay (Fig. 1) by 17–22% of OM. The optimum duration for obtaining a minimum yield of SR, about 20%, agrees with the duration for attaining a maximum TBO yield. It has been firstly revealed that the time dependence of the yield of asphaltols, the most condensed extract defined as the product being insoluble in benzene but soluble in THF, is complicated and has two maximums. It can be supposed that during the first maximum the kerogen molecules decompose into intermediate products being precursors of TBO, and the second maximum reflects the secondary condensation of TBO into precursors of coke.

Table 1. Effect of nominal temperature and isothermal duration on the yield of pyrolysis products from Attarat oil shale in autoclaves, % of oil shale

| Temperature, °C	Time, min	Gas	Benzene extract (TBO)		THF extract (asphaltols)	Pyrogenetic water	Solid residue (SR)
			total	including asphaltenes			
320	0	0.00	0.55	0.28	0.77	0.19	98.49
	60	0.95	6.07	3.50	0.42	0.54	92.03
	90	1.25	7.20	3.81	1.32	0.57	89.66
	120	1.63	8.67	3.91	1.87	0.30	87.53
	150	1.81	9.04	3.98	2.58	0.08	86.48
	240	2.06	10.21	4.69	1.85	0.21	85.67
	300	2.32	11.26	5.35	1.69	0.30	84.44
	360	2.34	11.73	5.72	1.61	0.38	83.95
	420	2.47	11.70	5.87	1.70	0.38	83.75
	480	2.50	11.62	4.21	1.89	0.36	83.64
	600	2.52	12.33	5.40	1.96	0.35	82.85
360	0	0.00	0.80	0.40	0.73	0.22	98.25
	30	1.50	7.69	4.02	2.65	0.35	87.82
	45	1.96	10.17	4.40	2.50	0.46	84.91
	60	2.27	12.53	5.75	0.90	0.62	83.69
	90	2.69	12.1818	5.58	0.77	0.43	83.93
	120	2.86	11.54	3.66	1.81	0.16	83.63
	150	3.05	10.71	3.52	2.49	0.22	83.53
	180	3.78	10.35	3.14	2.14	0.30	83.89
	240	3.55	10.00	2.82	1.75	0.52	84.18
	300	3.82	9.73	2.31	1.14	0.60	84.71
	360	3.92	8.75	1.78	1.29	0.63	85.42
380	0	0.03	1.03	0.68	1.02	0.20	97.72
	15	0.95	6.06	2.71	2.18	0.28	90.54
	30	1.56	11.20	4.60	2.86	0.42	83.97
	45	1.87	12.47	4.49	1.84	0.64	83.18
	60	2.65	12.35	5.79	1.51	0.63	82.86
	90	3.33	10.20	2.48	1.39	0.32	84.77
	120	3.63	10.29	1.87	1.28	0.27	84.54
	240	4.60	8.49	1.10	1.19	0.37	85.35
400	0	0.00	1.67	0.94	0.50	0.32	97.51
	15	1.74	8.39	4.60	1.65	0.42	87.80
	20	1.96	7.15	2.90	2.80	0.55	87.53
	30	2.52	10.44	5.47	2.86	0.81	83.36
	45	3.12	11.52	3.80	0.89	0.59	83.88
	60	3.81	10.40	2.17	0.62	0.43	84.75
	90	4.39	9.13	1.04	0.64	0.27	85.58
	120	4.78	8.75	0.83	0.53	0.19	85.75
	180	5.49	7.87	0.60	0.29	0.15	86.20
	240	5.65	6.98	0.44	0.62	0.22	86.52
420	0	0.00	2.14	1.06	0.59	0.44	96.83
	5	0.59	1.45	0.99	1.58	0.51	95.87
	15	2.18	12.61	6.29	2.10	0.96	82.14
	20	2.46	10.85	3.32	1.57	0.73	84.39
	30	3.35	10.48	2.05	0.99	0.30	84.88
	60	4.72	8.46	0.70	0.09	0.15	86.58
	120	6.33	6.30	0.35	0.37	0.21	86.78
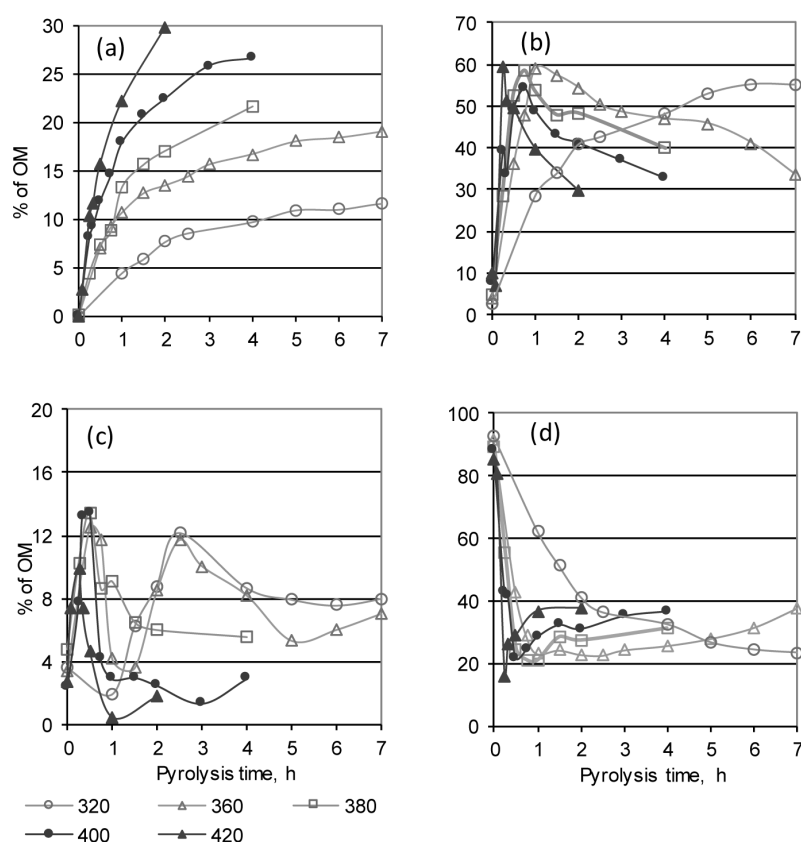
Fig. 3. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of gas (a), TBO (b), asphaltols (c) and solid residue (d).

The maximum total yield of benzene and THF extracts (the sum of TBO and asphaltol) reaches about 65% of OM (Figs. 3 and 4). Nevertheless, the yield of liquid products is 15–20% lower than that obtained from Estonian Kukersite [25].

The effect of pyrolysis duration and temperature on the formation of pyrolytic water has been studied for the first time. The experimental results depicted in Figure 4a evidence that in autoclaves the yield of pyrolytic water passes two maximums like that of asphaltols (Fig. 3c). The first maximum appears at the duration corresponding to the exhaustion of the initial kerogen and attains 2–4.5% of OM. Thereafter, the yield of pyrogenetic water decreases to a minimum, 0.5–1.5% of OM, in the stage of condensation of TBO into asphaltols. After that, a second increase in the yield of water could be explained by the subsequent coke formation from the intermediate product, asphaltol.
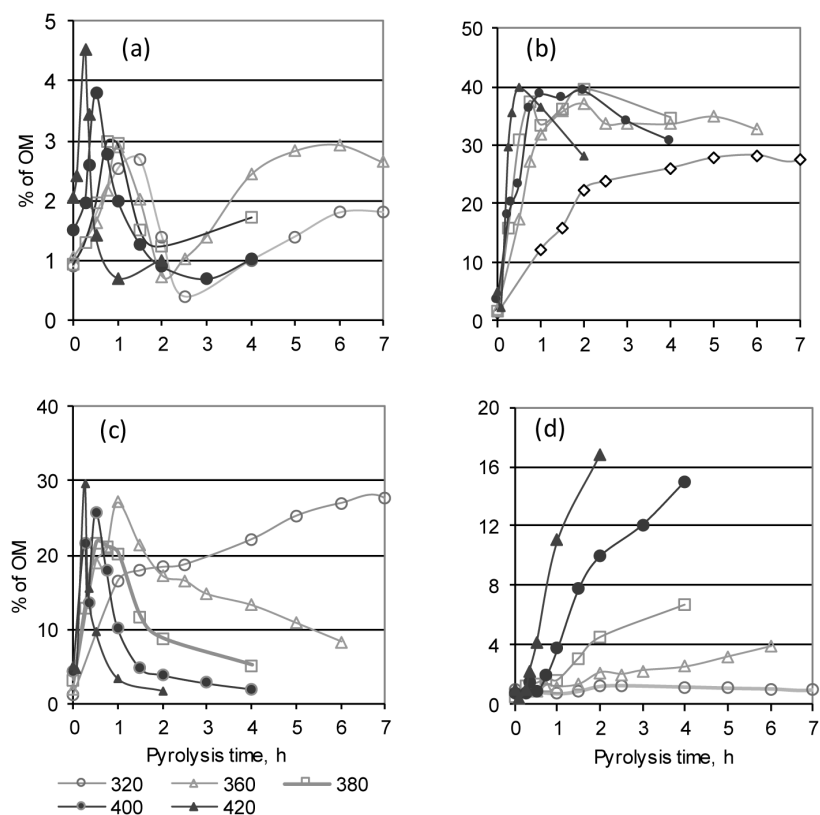
Fig. 4. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of pyrolytic water (a), asphaltenes (b) and maltenes (c), and on the ratio of maltenes/asphaltenes (d).

3.2. Pyrolysis in solvent medium

With the aim to increase the yield of liquid products and reduce the coke formation, the liquefaction was tested in the medium of 1–3 g/g of benzene, water or tetralin. The procedure was conducted during 1 h, being the optimal duration at a temperature of 380 °C. The yields of pyrolysis products on the basis of the initial shale are presented in Table 2. The yields of the most characteristic products, TBO and SR, on OM basis, are depicted in Figure 5. It was impossible to estimate directly the yields of gas and pyrogenetic water dissolved partly in the solvents. So, the data were taken from the corresponding results of experiments conducted without any solvent and presented in Table 1.

The data in Table 2 evidence that the addition of solvents increases the yield of TBO of the shale by 1–3% only. The influence of the benzene medium is the smallest. Tetralin, being supposed to act as a potential hydrogen donor, is not much more efficient at 380 °C tested. In this work, the summary yield of liquid products (TBO, asphaltols and water) in tetralin

Table 2. Effect of solvent/shale ratio on the yield of pyrolysis products at various temperatures and durations, % of oil shale

T, °C	Time, min	Solvent/OS, g/g	Gas[1]	Benzene extract (TBO)		THF extract (asphaltols)	Pyrogenetic water[1]	SR
				total	including asphaltenes			
In benzene								
360	180	0	3.32	10.35	3.78	2.14	0.30	83.88
		1	3.32	11.61	3.61	0.51	0.30	84.26
		2	3.32	12.03	5.11	0.55	0.30	83.79
		3	3.32	12.28	3.27	0.62	0.30	83.48
380	60	0	2.65	12.35	5.79	1.51	0.63	82.86
		1	2.65	12.92	2.73	0.35	0.63	83.51
		2	2.65	12.91	3.05	0.28	0.63	83.58
		3	2.65	12.61	3.70	0.94	0.63	83.22
	120	0	3.63	10.29	1.87	1.28	0.27	84.53
		2	3.63	11.73	1.27	0.75	0.27	83.62
In water								
	60	0	2.65	12.35	5.79	1.51	0.63	82.86
		1	2.65	12.50	n. d.	0.46	0.63	83.77
		2	2.65	11.97	n. d.	0.08	0.63	84.68
		3	2.65	13.94	5.28	0.49	0.63	82.30
	120	0	3.63	10.29	1.87	1.83	0.27	82.95
		2	3.63	10.91	2.75	0.94	0.27	84.47
In tetralin								
	60	0	2.65	12.35	5.79	1.51	0.63	82.86
		1	2.65	13.57	n. d.	1.49	0.63	81.67
		2	2.65	14.21	n. d.	0.92	0.63	81.59
		3	2.65	11.57	n. d.	2.91	0.63	82.24

[1]Taken from Table 1; n. d. – not determined.

is 74% of Attarat oil shale OM like in the work of Fei et al. [20] on EL-Lajjun oil shale OM. The yield of TBO remains roughly 60% of OM in various solvents, being characteristic of the maximum yield attained in autoclaves at various nominal temperatures without any solvent (Fig. 3).

The group compositions of TBO extracted from the pyrolysates produced in an optimum combination of temperature and duration, 380 °C and 1 h, without any solvent, and in benzene and water are presented in Table 3, and on the basis of total OM in Figure 6. The analogous data in tetralin are absent because it was impossible to separate the solvent (b. p. 208 °C) from the pyrolysis oil without losses of the lighter fractions. For comparison, the yields of compound groups of Estonian Kukersite oil shale under the same conditions taken from [26] are depicted in the same figure.
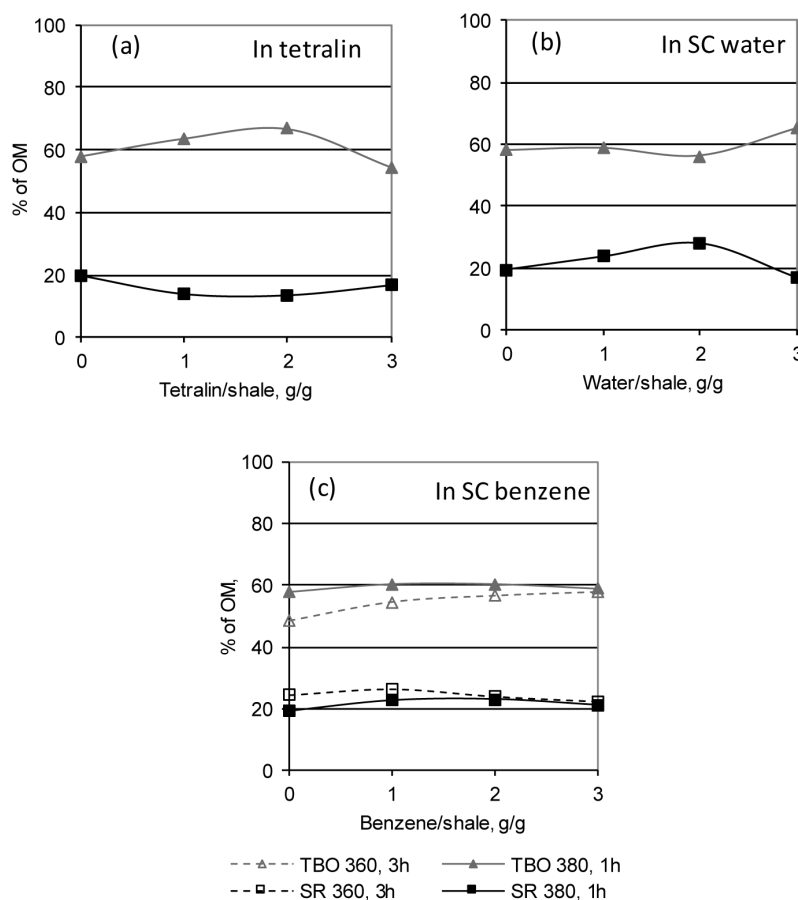
Fig. 5. Effect of solvent/shale ratio on the yield of TBO and solid residue in tetralin (a), SC water (b) and SC benzene (c) on OM basis (SC – supercritical).

Table 3. Group composition of TBO (1 h, 380 °C), %

Compound group	Symbol	Solvent			
		–	Benzene	Water	Tetralin
Aliphatic hydrocarbons	AlHC	8.2	7.5	6.2	8.2
Monocyclic hydrocarbons	MCHC	8.4	5.4	3.4	8.4
Polycyclic hydrocarbons	PCHC	32.9	39	32.8	32.9
Neutral hetero-atomic compounds	Nhet	13.2	10.8	12.1	13.2
Polar hetero-atomic compounds	Phet	37.3	37.3	45.5	37.3

According to Table 3 and Figure 6, the main compound groups in the benzene extract obtained in the pyrolysis of Jordanian oil shale in benzene, water or without any solvent at 380 °C are polycyclic hetero-atomic compounds and polycyclic hydrocarbons surpassing totally 40–50% of OM. The yields of desired aliphatic and monocyclic hydrocarbons are below 5%. The
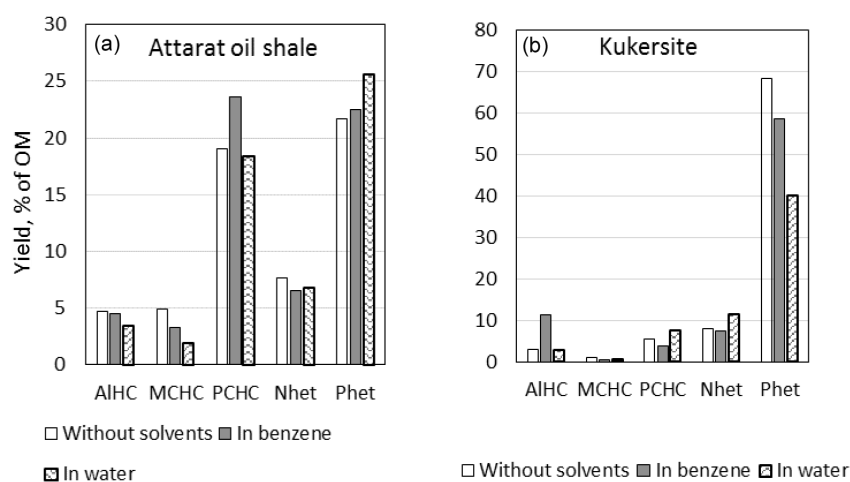
Fig. 6. Yield of compound groups of TBO from pyrolysis of Attarat oil shale (a) and Estonian Kukersite (b).

highest yield of polar hetero-atomic compounds in the water medium suggests that the yield of TBO could be increased due to the incorporation of some water molecules into the liquid product. Differently, in the Kukersite origin benzene extract polar hetero-atomic compounds (mainly oxygen compounds) prevail whereas the yields of the other groups are lower than those from the pyrolysis of Jordanian oil shale.

3.3. Kinetics of OM decomposition

The results of this work agree with published ones establishing that the yields of liquid products on the basis of Attarat oil shale OM in open retorts, in autoclaves without solvents, and in the medium of various solvents are 15–20% lower than those of Estonian Kukersite oil shale under the same conditions.

The time-dependence of the yields depicted in Figure 3 shows that the exhaustion of the initial OM of Jordanian oil shale takes place approximately twice faster than that of Estonian oil shale [25].

In this work, for approximate characterization and comparison purposes, the kinetics of the complicated pyrolysis process consisting of several parallel and consecutive reactions, the time-dependence of changes in the yield of solid residue (Fig. 3d) reflecting the total conversion of kerogen into gas, TBO, asphaltols, pyrolytic water and coke, and the total subsequent decomposition of TBO (Fig. 3b) into gas and coke were discussed only.

The rate factors for the isothermal decomposition of kerogen (k_1) and TBO (k_2) at any nominal temperature tested were estimated presuming a simple first order reaction as follows:

$$\ln(C_0/C) = -k_i(t - t_0), \tag{1}$$

where C_0 is the maximum yield of SR or TBO, t_0 is the corresponding duration, and C is the yield after duration t. The values of k_1 were calculated using only the linear part of the function described by Equation (1) where the coke formation was insignificant and SR represented unreacted kerogen only.

The apparent kinetic constants, frequency factor A and activation energy E, were found from the slope (b) and reciprocal (a) of the linear trendlines of the logarithmic form of the Arrhenius relationship:

$$\ln k = \ln A - E/(RT). \tag{2}$$

The trendlines obtained introducing into Equation 2 the values of k estimated at various nominal temperatures using experimental data found for the overall decomposition of Attarat oil shale (Fig. 3d) and for the intermediate product TBO (Fig. 3b), and the corresponding total factors deduced from the rate factors of Estonian Kukersite published in [25] are depicted in Figure 7.

The regression coefficients, a and b, of the linear trendlines in Figure 7, and the corresponding apparent kinetic constants ($A = \exp(a)$, $E = -bR$, $R = 0.008314$ kJ/mol K) are given in Table 4.
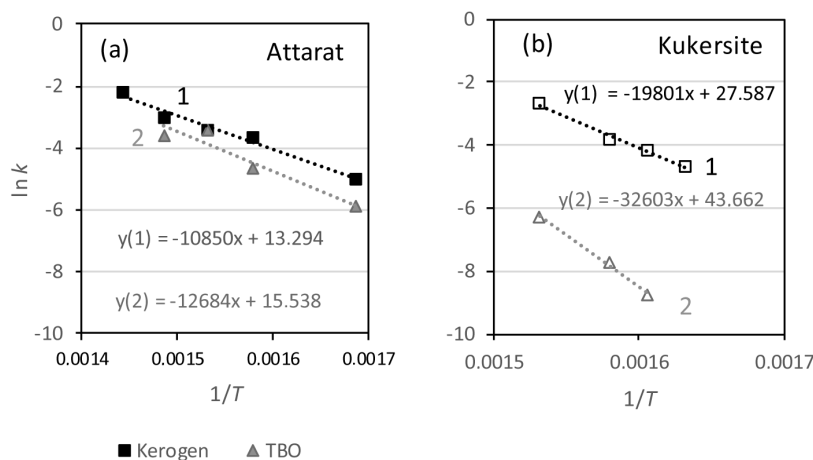

Fig. 7. Arrhenius plot of rate factors for the overall decomposition of initial kerogen and TBO of Attarat oil shale (a) and Estonian Kukersite (b).

Table 4. Apparent kinetic constants for decomposition of kerogen and TBO in autoclaves

Oil shale	Initial object	a	$-b$	A, 1/min	E, kJ/mol
Attarat	Kerogen	13.3	10850	5.91×10^5	90.2
Attarat	TBO	15.6	12684	5.61×10^6	106
Kukersite [25]	Kerogen	27.6	19801	9.69×10^{11}	165
Kukersite [25]	TBO	43.7	32603	9.15×10^{18}	271

The kinetic constants (E_1 and A_1) estimated for decomposition of Attarat oil shale kerogen in this work are comparable with those for decomposition of El-Lajjun oil shale found by Al-Ayed et al. [27], 98–120 kJ/mol and $(5.7–7.0) \times 10^7$ 1/min, under non-isothermal conditions (350–550 °C), and with the activation energy, 99.6 kJ/mol, found by Khraisha [28] under isothermal conditions. The kinetic constants E_2 and A_2 for the secondary decomposition of the intermediate product, TBO of Attarat oil shale, have been estimated in this work for the first time.

Noteworthy is that the analogous apparent activation energies, E_1 and E_2 for Estonian Kukersite kerogen and TBO, are respectively 1.8 and 2.6 times higher, and the logarithms of the frequency factors 2.1 and 2.8 times higher than those of Jordanian oil shale.

As a rule, an increase in E occurring with an increase in A follows a linear relationship called the compensation effect. The plot of kinetic constants in Table 4 depicted in Figure 8 indicate that the linear regression

$$\ln A = 0.169(\pm 0.008)E - 1.73(\pm 1.39) \tag{3}$$

is kept ($R^2 = 0.9955$) between the apparent kinetic constants of Attarat oil shale and Estonian Kukersite.

The co-effect of the kinetic constants having an opposite influence on rate factor is explained by the Arrhenius exponential equation:

$$k = A\exp(-E/RT). \tag{4}$$

The values of k at various temperatures calculated introducing the kinetic constants from Table 4 into Equation (4) are depicted in Figure 9.
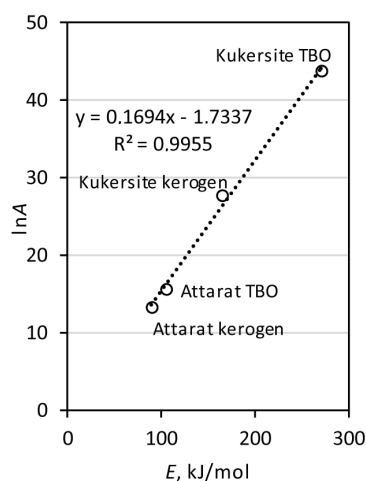

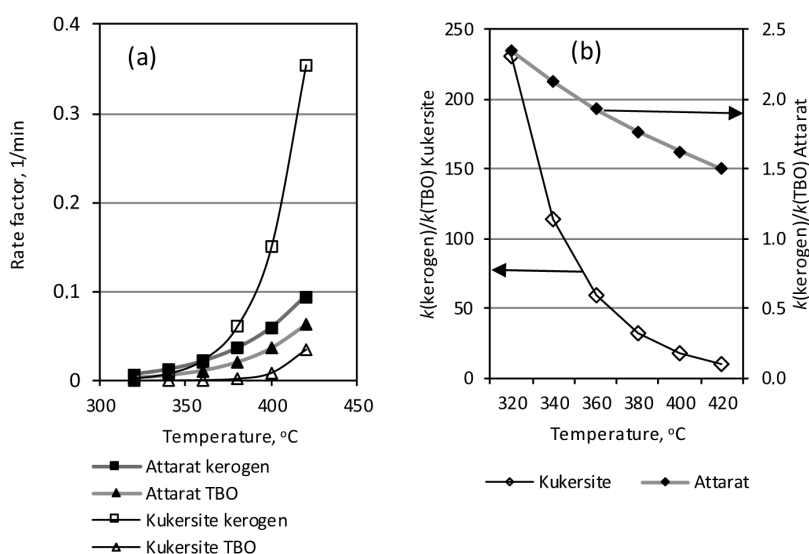Fig. 8. Kinetic compensation effect (A, 1/min).

Fig. 9. Effect of temperature on the rate factors for the overall decomposition of Attarat and Estonian Kukersite oil shale kerogen and TBO (a) and on the ratio of the factors (b).

The curves in Figure 9a show that the effect of temperature on the rate factors is vital above 360 °C having a really great influence on the rate of Kukersite decomposition, being a controlling stage before the maximum yield of TBO has been attained. When the temperature increases from 320 to 425 °C, the ratio of the factors (Fig. 9b) of Estonian Kukersite decreases from 230 to 10, while that of Attarat oil shale from 2.4 to 1.5 only. So, the decomposition rate of TBO of Attarat oil shale is comparable with its formation rate from the initial kerogen at any temperature tested. As a result, the maximum yield of liquid products from Attarat oil shale remains essentially lower than that from Estonian Kukersite. The addition of any solvent tested or variation in pyrolysis conditions could not suppress the secondary decomposition of TBO in autoclaves.

Both the oil shales are highly aliphatic: $C_{ar}/(C_{al} + C_{ar})$ of Attarat oil shale is 0.21 [3], and the corresponding ratio of the peak areas in the ^{13}C MAS NMR spectrum of Estonian Kukersite 0.217 [29]. The H/C atomic ratio of Attarat oil shale is 1.69 and of Kukersite 1.50. So, the obviously quicker coke formation from Attarat oil shale than from Estonian Kukersite is surprising and the reasons need further investigation.

4. Conclusions

In the low-temperature (320–420 °C) pyrolysis of Jordanian Attarat oil shale in autoclaves during the exposure time of 0–10 h at nominal temperature, the

gas yield and the ratio of maltenes to asphaltenes increase with time and temperature. In the optimum combination of temperature and duration the yield of benzene extract, consisting of bitumen, an intermediate product thermobitumen and oil (TBO), and its components, asphaltenes and maltenes, pass a maximum, and the yield of solid residue a minimum. The yields of pyrogenetic water and THF extract (asphaltols) have two maximums, the first one at the optimum duration of the TBO formation, and the other one in the stage of the secondary decomposition of TBO.

Increase in the nominal temperature from 320 to 420 °C decreases the optimum duration from 10 to 0.25 h.

The maximum yield of TBO extracted under optimum conditions amounts to 55–60% of organic matter (OM) and that of asphaltol to 10–12%. The maximum total yield of the liquid products extracted (TBO + asphaltols) is 65–70% of OM, being 20% lower than that from Estonian Kukersite oil shale, and exceeds the yield of oil from Attarat oil shale OM by 25–30% as estimated in the Fischer Assay.

The addition to Attarat oil shale of 1, 2 and 3 g/g of supercritical benzene or water, or tetralin, known as a hydrogen donor, has an unimportant effect on the yield of the pyrolysis products.

The main compound groups in TBO obtained from Attarat oil shale in pyrolysis without any solvent and in benzene or water are polycyclic hydrocarbons and polar hetero-atomic compounds, making both 30–45% of TBO. Differently, in TBO from Estonian Kukersite where the single polar hetero-atomic compound group prevails attaining 64–80% of TBO, the share of polycyclic hydrocarbons is in the range of 5–12% of TBO only.

The lower yield of TBO from Attarat oil shale than from Estonian Kukersite is explained by their decomposition kinetics. The apparent kinetic constants estimated in this work for the consequent decomposition of Attarat oil shale kerogen and the intermediate TBO in autoclaves are quite close. The activation energy for the overall primary decomposition of kerogen into gas, TBO, asphaltols and coke, E_1, is 90.2($\pm$9.9) kJ/mol, and for the overall secondary transformation of TBO into gas, asphaltols and coke, E_2, 106($\pm$25) kJ/mol. The corresponding frequency factors (A_1 and A_2) are 5.91×10^5 and 5.61×10^6 1/min. So, the yield of liquid products from Attarat oil shale is suppressed due to the intensive transformation of TBO into gas, asphaltols and coke.

The values of E_1 and E_2, and A_1 and A_2 for the decomposition of Estonian Kukersite kerogen and TBO are much higher, essentially differing from each other: 165 and 271 kJ/mol, and 9.69×10^{11} and 9.15×10^{18} 1/min, respectively. The co-effect of the values of E and A on the rate factors results from that the primary reaction of Kukersite kerogen decomposition prevails over the much slower secondary transformation of TBO.

The next challenges to solve would be characterization of the unstable and complicated TBO and asphaltols, and upgrading of the polycyclic and polar hetero-compounds into market-value liquid fuels.

Acknowledgements

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