Effect of processing conditions on the improvement of properties and recovering yield of Moroccan oil shale

Abdelkrim Abourriche[(a)*], Mina Oumam[(b)], Said Mansouri[(b,c)], Mossaab Mouiya[(a,e)], Yassine Rakcho[(a)], Abdelaziz Benhammou[(a)], Younes Abouliatim[(a,d)], Jones Alami[(c)], Hassan Hannache[(b,c)]

[(a)] Laboratory Materials, Processes, Environment and Quality, National School of Applied Sciences, Safi, Morocco
[(b)] LIMAT-Thermostructural Materials and Polymers Team, Faculty of Science Ben M'sik, B.P. 7955 Casablanca, Morocco
[(c)] Department of Materials Science and Nanoengineering, University of Mohamed VI Polytechnic, Lot 660-Hay Moulay Rachid, 43150, Ben Guerir, Morocco
[(d)] Laboratory of Process and Environmental Engineering (L.P.E.E), Higher School of Technology of Casablanca, Hassan II University, Route del Jadida, km 7, BP 8012 Oasis Casablanca, Morocco

Abstract. *In the present work, Moroccon Tarfaya oil shale was treated by acids and different solvents under supercritical conditions, successively. Experimental results showed clearly that residual mineral matter had a significant effect on the yield and composition of the resulting organic fraction. Indeed, the oil yields obtained from some samples, 43% and 56%, respectively, were much higher than that from the sub-layer, 18%. In addition, the yield of recuperation and quality of extracted oils were largely dependent on the nature of solvents (toluene, water, shale oil). Thus, phenol was shown to be a very efficient modifier for the supercritical extraction of organic matter from Tarfaya oil shale with toluene, affording a good yield of recovery and a suitable maturation of organic matter. The pitches prepared by mixing phenol and toluene contained more aromatics and had a high char yield (46%) at 950 °C compared to those obtained by extraction with supercritical toluene alone.*

Keywords: *Tarfaya oil shale, mineral matter, supercritical extraction, water, toluene, phenol.*

* Corresponding author: e-mails *a.abourriche@uca.ma; krimabou@hotmail.com*

1. Introduction

Oil shale has been considered for a long time a great economic hope for those countries that possess large reserves. Thus, programs to operate oil shale as an energy source were launched by several countries such as Scotland, Australia, France and China [1–4]. These programs demonstrate that oil shale is far from substituting the products of oil, because of high costs and non-competitiveness against conventional petroleum.

Besides, oil shale has some potential for the production of synthetic products such as cement, calcium, alumina, pitches, carbon adsorbents, zeolites, carbon fibers and other chemicals [5–12]. Those applications have generated, in recent years, many studies on methods for extracting these oils, such as pyrolysis by conventional heating or under microwave irradiation, extraction with solvents under sub- and supercritical conditions or combustion in fluidized bed reactors [13–17].

Studies have demonstrated that the extraction yield and quality of oils extracted depend on several parameters like nature of solvent, modifier, temperature, pressure, duration of treatment, heating rate, grain size.

The effect of modifiers on the performance of supercritical extraction has been reviewed by several authors [18–20]. Solvents used were pentane for the extraction of food products [21], polycyclic aromatic hydrocarbons [22], acetone [23] and hexane [24] to extract pesticide residues. Other authors [25, 26] have also used reagents in order to degrade the solute molecules.

Lanças and Rissato [21] studied the effect of certain solvents (acetone, hexane, methanol) on the extraction of the herbicide Diuron in sugar cane and orange samples with supercritical CO_2. They concluded that the addition of methanol as a modifier enhanced significantly the extraction yield compared to other modifiers.

Dariva et al. [27] reported that the addition of organic solvents in the extraction of oil shale with supercritical water improved the yield and quality of the extracted oils.

Many researchers determined the thermal characteristics and kinetic parameters of oil shale samples by thermogravimetry (TG) and differential thermogravimetry (DTG) under non-isothermal heating conditions for both pyrolysis and combustion processes [28–32]. They also used differential scanning calorimetry (DSC) to determine the combustion kinetics of oil shale samples by an ASTM method. It was observed that higher heating rates resulted in higher reaction temperatures and higher heat of reactions.

Özgür et al. [33] studied the effect of co-firing of biomass fuels with oil shale on combustion, using a thermogravimetric analysis (TGA) and DSC. They observed that the biomass (10% and 20% by weight) blended with oil shale was a good option for co-firing owing to the formation of a sufficient amount of volatile matter to maintain stability in ignition and combustion.

Other studies [34–36] have also shown that the addition of CO or H_2 when

extracting shale and coal with water improves the efficiency and quality of the oils produced.

In this work, we chose phenol as a modifier in the extraction of oil shale with supercritical toluene. This choice was dictated by the compound's thermal stability because phenols are associated by intermolecular hydrogen-type bonds. In addition, the highly reactive hydroxyl group could react with some organic functions present in oil shale. Therefore, two principal objectives were fixed for the present research:

(a) to study the effect of three factors (mineral matter, solvent and phenol as modifier) on the supercritical extraction of Moroccan oil shale to establish the optimal operating conditions likely to give a good yield of recovery with the best oil quality;

(b) to demonstrate that phenol was a very efficient modifier for oil shale, giving a good yield of recovery and a suitable maturation of organic matter.

2. Experimental

2.1. Materials

The oil shale used in this work was from Tarfaya deposit located in South Morocco. This deposit consists of several layers that are in turn subdivided into sub-layers, each comprising a different amount of organic matter. The samples were obtained from sub-layer R_3, which is characterized by a high content of organic matter [37]. The chemical composition of R_3 is given in Table 1 [38].

Table 1. Chemical composition of sub-layer R_3

Composition	Mass%
Carbonates	70.0
Kerogen	20.0
Silicates	7.1
Pyrite	1.0
Bitumen	0.9

The carbonate-free oil shale (RH) was obtained by dissolution of carbonates with HCl [39, 40]. The powdered R_3 shale (20 g, grain size 0.063–0.08 mm) and 80 mL of concentrated HCl (7 M) were introduced in an Erlenmeyer flask. The mixture was then subjected to magnetic stirring for 4 h. The formed CO_2 was trapped by bubbling in a solution of barium hydroxide. After filtration,

the solid residue (referred to as RH) was washed carefully with distilled water, dried at 100 °C and stocked in a sealed plastic bag.

The carbonate-free shale was stirred with concentrated hydrogen fluoride (4 ml g^{-1} RH) for 4 h. After filtration, the residue (K$_3$) obtained was first washed with dilute HCl solution and then with water and dried at 100 °C and stocked in a closed plastic sachet.

2.2. Apparatus

2.2.1. Preparation of the pitches

The supercritical extraction of sample RH (10 g) with toluene as solvent was conducted in a 120 mL stainless steel autoclave equipped with a stirrer and heated in a tubular furnace whose temperature, as well as heating rate, were controlled. The temperature of extraction was 390 °C with a heating rate of 16 °C min^{-1} [41]. The maximum pressure reached during this treatment of 120 min was 8 MPa. After being cooled to room temperature, the mixture was extracted in a Soxhlet apparatus with chloroform for 12 h. After removing the solvent under reduced pressure, the organic material was dried for 12 h at 40 °C and weighed. The recovered oil was treated with *n*-hexane in a 1/10 oil to solvent mass ratio [42] in order to precipitate the high-molecular fraction (asphaltenes) that constitutes the pitch. After stirring for 12 h, the two fractions, soluble (maltenes) and insoluble (asphaltenes), were separated by filtration through Whatman paper, and then dried for 12 h at 40 °C and 80 °C, respectively. The scheme of the autoclave is shown in Figure 1.
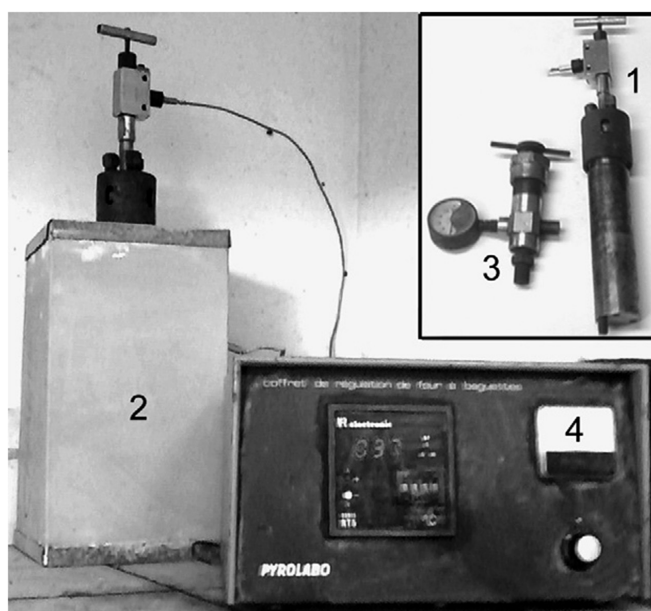

Fig. 1. Photograph of the apparatus used for supercritical extraction: (1) reactor; (2) furnace; (3) pressure gauge; (4) regulator.

2.2.2. Preparation of carbon fibers

The pitch was melted at 180 °C, in a laboratory-made spinning device equipped with a single spinneret and a filter to remove solid particles from the melt [43]. After extrusion and mechanical stretching, the fiber was thermoset by being slowly heated in dry air at atmospheric pressure to temperatures in the range of 60–280 °C. The oxidized fibers were pyrolyzed under nitrogen flow, the temperature was progressively raised up to 950 °C at a heating rate of 5 °C min^{-1} [44].

2.3. Analyses

Elemental analysis was performed at the Service Central d'Analyse du CNRS, France.

The analyses by X-ray photoelectron spectroscopy (ESCA-XPS) were carried out in an Escalab VG220i-XL apparatus.

Infrared (IR) spectra were recorded between 400 and 4000 cm^{-1} with a Nicolet 205 FT-IR spectrometer by summing 32 scans at 2 cm^{-1} resolution. Pellets were prepared by dispersing 2 mg of sample into 198 mg of KBr.

Thermogravimetric analyses were performed with a TGS-2 Perkin–Elmer analyzer under high purity argon flow (40 mL min^{-1}). Samples of about 12 mg were heated from 50 to 950 °C at a heating rate of 5 °C min^{-1}.

The surface areas of the fiber were measured by nitrogen adsorption at 77 K with a Micromeritics Flowsorb II 2300 instrument using the Brunauer–Emmet–Teller (BET) method. Before adsorption measurements the samples were outgassed at 160 °C for 24 h.

Scanning electron microscopy (SEM) micrographs were taken with a Hitachi TM-1000 microscope. Fragments of about 0.5 cm^2 cut from the corresponding samples were mounted on a carbon tab, which ensured a good conductivity. A thin layer of gold-palladium was sputtered prior to analysis.

Size exclusion chromatography (SEC) was carried out on a Waters analytical system (pump 510, refractometer 410 and UV/visible detector 486) with teterahydrofuran (THF) as eluent at 1 mL min^{-1} and using a TSK GMHXL column with a mixed porosity of 1500–10^7 Å. Relative average molecular weights were calculated with a cubic, 12-point calibration curve obtained from monodisperse polystyrene standards.

[1]Hydrogen nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AC 250 spectrometer (250 MHz). The samples were placed in 5 mm-ID tubes with CDCl$_3$ as solvent. The chemical shifts are given in ppm relative to TMS δ = 0 ppm.

3. Results and discussion

3.1. Effect of mineral matter on the yield of recuperation of the obtained oil

In order to show the effect of mineral matter on the yield of recuperation and composition of the extracted oils, we conducted extractions of three different samples according to the protocol described in the experimental part: sample 1, sub-layer R_3; sample 2, sub-layer R_3 freed of carbonates RH; sample 3, sub-layer R_3 freed of carbonates and silicates K_3.

Before carrying out the supercritical extraction of the samples, X-ray Photoelectron Spectroscopy (XPS) analyses were performed to identify the composition of the starting materials and to follow the evolution of this composition throughout the demineralisation process. By comparing the results given in Table 2, it can be noted that sample RH is characterized by the absence of Ca and Mg, which confirms the fact that the treatment of the rock by HCl dissolved completely the carbonates. We also noticed that HF dissolved silicates and clays (sample K_3).

Table 2. XPS analysis of the starting materials, atomic %

Element	R_3	RH	K_3
Fe (2p3)	0.2	0.1	0.1
O (1s)	36.5	26.9	19.3
N (1s)	0.4	1.3	1.0
C (1s)	43.4	56.0	73.3
Cl (2p)	2.5	0.4	–
S (2p)	0.8	2.1	2.8
Al (2s)	2.4	3.7	2.8
Si (2p)	3.2	8.2	–
Ca (2p)	9.3	–	–
Mg	0.1	–	–
Na	0.2	–	–

"–" not determined

Extraction yields obtained for samples R_3, RH and K_3 are given in Table 3. The yields of recuperation were calculated from the total amount of organic matter contained in each sample.

Table 3. Extraction of the treated shale by toluene

Sample	R_3	RH	K_3
Mass of sample, g	10	10	10
Solvent, mL	60	60	60
Heating rate, °C min^{-1}	16	16	16
Temperature, °C	390	390	390
Time, min	150	150	150
Pressure, MPa	4.5	4.5	4.5
Recovered oil, g	0.5	3.0	4.3
Yield of recuperation, %	18	43	56

Results in Table 3 show that the yield of recuperation varies considerably among the different samples. Indeed, the yields obtained for samples RH and K_3 are more significant than for sample R_3, which shows the effect of mineral matter. The poor yield obtained for sample R_3 can be explained by the high porosity of carbonates, which allows organic matter to be retained in the mineral matrix and consequently delays its extraction. To study the effect of mineral matter on the composition of the oils, elemental analyses of the oils obtained from samples R_3, RH and K_3 were conducted. The results are presented in Table 4.

Table 4. Elemental analyses of the oils, atomic %

Oil	C	H	N	S	O*	H/C	O/C
Oil R_3	41.34	55.11	0.55	0.73	2.26	1.33	0.055
Oil RH	40.81	53.33	0.55	1.04	4.04	1.31	0.099
Oil K_3	42.25	54.10	0.72	1.06	1.87	1.28	0.044

* O is determined by difference

Atomic ratios H/C and O/C of the three oils are shown in the Van Krevelen diagram (Fig. 2) demonstrating the effect of mineral matter on the degree of maturation of the obtained oils. From this diagram it can be noticed that the maturation degree of the oil shale's organic matter varies considerably with the samples used in supercritical fluid extraction. Indeed, the oil K_3 exhibits a considerably higher maturation degree, compared to oils R_3 and RH. The oils obtained range from an immature organic matter of I-a type (oil R_3) to
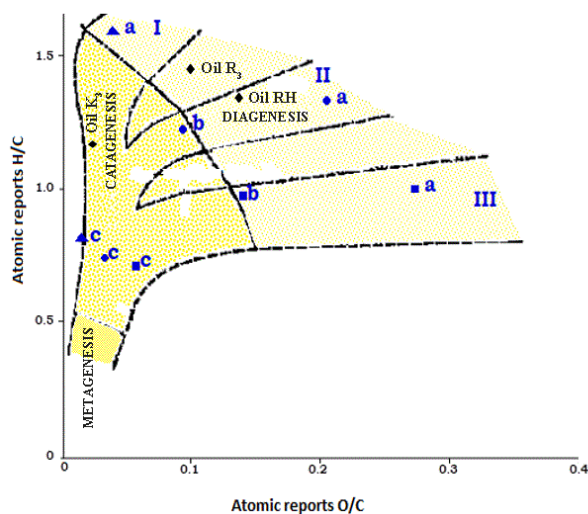
Fig. 2. Classification of the oils extracted from the shale materials by the Van Krevelen diagram.

an immature organic matter of II-a type (oil RH), or a more mature organic matter, rich in carbon and which is related to standard catagenesis II-b (oil K_3). Those results were confirmed by SEC analyses (Table 5).

The comparison of those values shows that the oil obtained with sample K_3 has the highest value of the average molecular weight ($\bar{M}_w$), compared to oils R_3 and RH. This suggests that, under these conditions, toluene is able to extract large molecules from kerogen.

Table 5. Analysis of the oils by SEC

Oil	$\bar{M}_w{}^a$	$\bar{M}_n{}^b$	Ip
Oil R_3	1170	160	7.3
Oil RH	1340	200	6.8
Oil K_3	1650	200	8.2

^{a} – weight average molecular weight; ^{b} – number average molecular weight;
Ip – polydispersity index = $\bar{M}_w / \bar{M}_n$

According to the results above sample RH presents several advantages, not so much on the level of preparation (less consumed products), but on the level of the results obtained (high yield of recuperation). Moreover, the presence of fluorine in the organic matter resulting from sample K_3 makes its use difficult. Oumam [44] has previously reported that during the carbonization of the

organic matter resulting from K_3, the walls of the silica tube were gradually attacked by carbonization gases rich in fluorine. These reasons led us to use RH as the starting material to carry on our study.

3.2. Effect of the solvent

In order to study the effect of solvent on the yield of recuperation and composition of the oil, the extraction was carried out with 10 g of sample RH by using 60 mL of different solvents (toluene, water, shale oil) under the conditions described above. The yields and compositions of the oils obtained under different conditions are given in Table 6.

Table 6. Yields and composition of the oils extracted from RH by different solvents

Solvent	Toluene	Water	Shale oil
Mass of sample, g	10	10	10
Volume of solvent, mL	60	60	60
Heating rate, °C min^{-1}	16	16	16
Temperature, °C	390	390	390
Time, min	150	150	150
Pressure, MPa	4.5	28.5	20
Recovered oil, g	3	4.8	3.7
Yield of recuperation, %	43	68.6	55.7
Maltenes, g	1.1	1.6	1.2
Maltenes, w%	36.7	33.3	32.4
Asphaltenes, g	1.6	3.0	2.1
Asphaltenes, w%	53.3	62.5	56.7

The results demonstrate that the yield and composition of the oil obtained by extraction with water are obviously different from those of the oil obtained by extraction with toluene or shale oil. The oil's higher yield and maltene content indicate that water not only acts as an extraction solvent, but also reacts with the molecules of kerogen. It also reacts with the double and triple bonds of the decomposition products, resulting in alcohols and aldehydes [45, 46]. The results of elemental analysis of the obtained oils are presented in Table 7. Those results show clearly that water is an optimal solvent, offering the highest maturation of the organic matter of oil shale. This reinforces a hypothesis that, under these conditions, water is able to degrade large molecules contained in kerogen.

Table 7. Elemental analyses of the oils obtained from RH, atomic %

Oil	C	H	N	S	O*	H/C	O/C
Oil (water)	45.41	49.00	1.52	1.28	2.54	1.02	0.050
Oil (toluene)	40.81	53.33	0.55	1.04	4.04	1.31	0.099
Oil (shale oil)	40.40	50.85	1.00	1.36	5.2	1.26	0.13

* O is determined by difference

The disadvantage of using water is the high pressure generated during the supercritical extraction of oil shale with water (Table 6). To overcome this problem, we proceeded to the extraction of oil shale with toluene by adding phenol as a modifier.

In order to study the effect of phenol on the yield of recuperation and composition of the obtained oil, the extraction was carried out with 10 g of sample RH by using different volumes of toluene and 5 g of phenol according to the same conditions as described previously. The results obtained are shown in Figure 3.

By comparing the two curves (Fig. 3) it can be seen that their appearance is the same, but the mass of the insoluble material is lower in the case of a mixture (toluene + phenol). The decrease in the mass of the chloroform-insoluble material with the addition of phenol can be explained by the fact that phenol can react with the molecules of kerogen which causes the decomposition of large molecules and therefore leads to molecules of smaller sizes [47]. It may be noted, for example, that the transalkylation reactions were observed by Leach [47] to take place between 350–550 °C. Moreover, the transformation of phenol to phenolate, in the
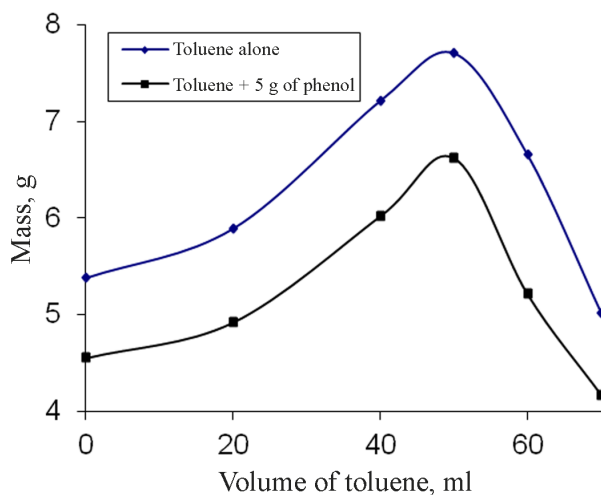

Fig. 3. Variation of the insoluble material in $CHCl_3$ as a function of toluene volume.

presence of traces of water or bases in the medium gives it a character of good nucleophile which can attack different carbonyl groups. A previous work by Koel et al. [48] on using neoteric solvents in oil shale studies shows that solvents attack kerogen and its chemical modification or degradation occurs.

3.3. Analyses of the pitches

3.3.1. Analysis of the pitches by SEC

The results of the SEC analysis of the pitches are presented in Table 8. The pitch obtained using 70 mL of toluene (PHT70) has a high value of $\bar{M}_n$, i.e. toluene is able to recover large molecules without degradation of kerogen. In contrast, in the case of extraction by mixing toluene and phenol, the $\bar{M}_w$ value obtained for the PHT70PH5 pitch is very low. This suggests that phenol has a degrading action, thus providing a pitch formed of low molecular weight molecules.

Table 8. Analysis of the pitches by SEC

Oil	$\bar{M}_w{}^a$	$\bar{M}_n{}^b$	$I_p{}^c$
PHT70	2670	230	11.6
PHT70PH5	1270	217	5.8

[a] – weight average molecular weight; [b] – number average molecular weight;
Ip – polydispersity index = $\bar{M}_w/\bar{M}_n$
PHT70 – pitch obtained from oil HT70

PHT70PH5 – pitch obtained from oil HT70PH5

3.3.2. TGA/DTA

The results of thermal analysis (TGA/DTA) of the pitches (Fig. 4) show that pitch PHT70 is characterized by a mass loss that starts around 100 °C, with a peak around 420 °C, and ends at 550 °C. The residue yield at 950 °C is about 32%. It is also noted that the thermogram of pitch PHT70PH5 is completely different from that of the former. It exhibits a mass loss that spreads over the same temperature range as that of pitch PHT70, but with the appearance of a complex phenomenon consisting of 3 successive mass losses at temperatures of 150 °C, 300 °C and 450 °C. Furthermore, we note that the residue yield at 950 °C for this pitch (36%) is somewhat higher than that of PHT70. A possible explanation for the agreement with the measurements by SEC could be that pitch PHT70PH5 consists of light, but thermally quite stable molecules compared to pitch PHT70. These results are in good agreement with SEC measurements.
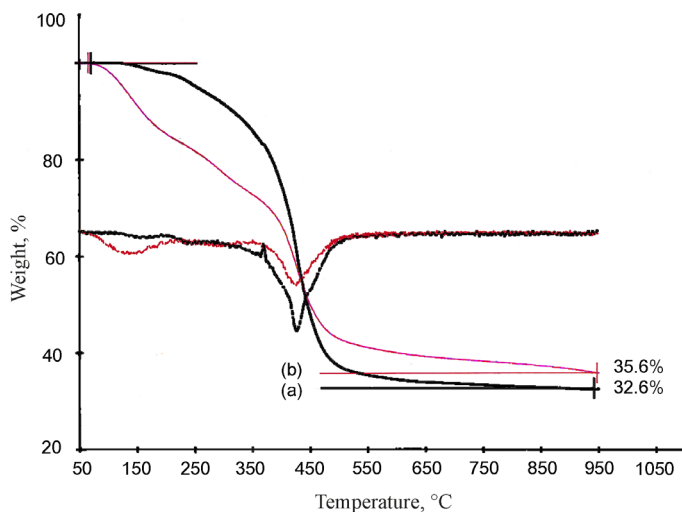
Fig. 4. Thermograms of the pitches: (a) PHT70, (b) PHT70PH5.

3.3.3. Elemental analysis

The elemental analysis of the obtained pitches (Table 9) showed that pitch PHT70PH5 possessed a very low sulfur content and a higher aromaticity factor (low H/C) compared to pitch PHT70.

Table 9. Elemental analysis of the pitches

Pitch	C	H	N	S	O*
PHT70	42.3	52.6	1.09	1.7	2.26
PHT70PH5	45.17	48.6	0.88	1.34	3.99

* O is determined by difference
PHT70 – pitch obtained from oil HT70
PHT70PH5 – pitch obtained from oil HT70PH5

3.3.4. ^{1}H NMR

The preceding pitches were also characterized by ^{1}H NMR spectroscopy (Fig. 5). In the spectrum of pitch PHT70, signals corresponding to aliphatic protons located between 0.5 and 3 ppm are prevalent. On the contrary, aromatic protons are very marginal. On the other hand, the spectrum of pitch PHT70PH5 reveals the presence of aliphatic and aromatic protons. Presumably, aromatic-rich compounds were extracted from heavy molecules in that case, which corroborates the results of elemental analysis of this pitch. This confirms that phenol was an efficient modifier likely to give a good yield of recovery and a better quality of oil.
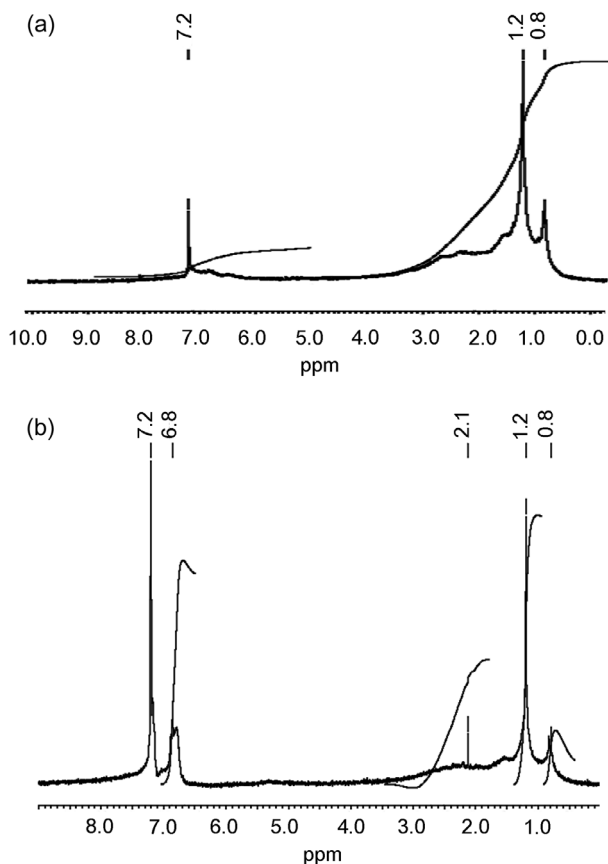
Fig. 5. ^{1}H NMR spectra of the pitches: (a) PHT70, (b) PHT70PH5.

3.4. Characterization of the filaments

At 950 °C the carbonization yield was about 49%. The elemental analysis of the pyrolyzed filaments (C 98.83, S 1.08, Fe 0.03, Si 0.06%) showed the extracted organic matter to contain a minimum of metal impurities.

Mechanical tensile tests performed on monofilaments of about 20 μm in diameter revealed a tensile strength of 320 MPa and a Young's modulus of 30 GPa. These values are modest when compared to those found for fibers elaborated from precursors with oriented textures. They are however comparable to those of fibers obtained from coal tar or petroleum isotropic pitches [49–51].

In order to improve the mechanical properties of the fibers, we tried to increase the pitches softening temperature by adding a supplement step in their preparation. This step consisted firstly in precipitation of oils with ethanol followed by washing with hexane. This was intended for elimination of the majority of light ends and, of the polar functional groups since the presence of
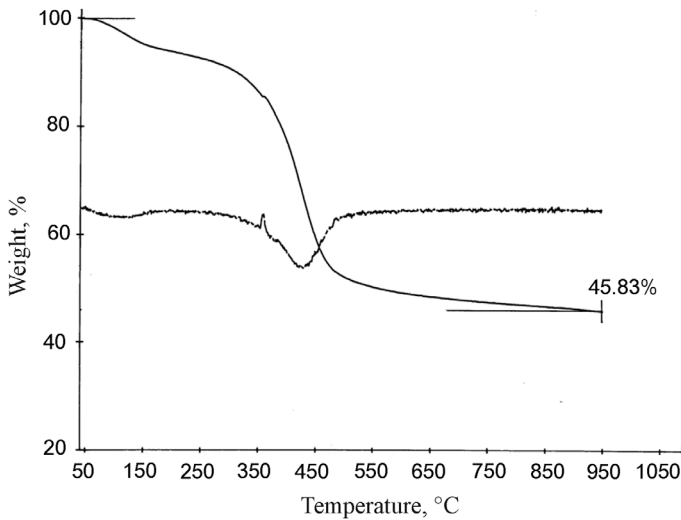
Fig. 6. Thermal curve of pitch PHT70PH5M.

heteroatoms makes the materials obtained either crosslinkable or graphitizable [52]. So we used this method to prepare a new pitch from HT70PH5 oil. The softening temperature rose to 260 °C.

We analyzed this new pitch, PHT70PH5M, by TGA/DTA (Fig. 6) in order to compare the results to those obtained for pitch PHT70PH5. The mass loss corresponding to molecules of low mass observed in Figure 4b between 180 and 300 °C for pitch PHT70PH5 has completely disappeared. We also noted an increase in the residual rate from 36% for pitch PHT70PH5 to 46% for the new pitch PHT70PH5M. This result confirms that the new method of preparation of pitches leads to materials containing heavier molecules.

We tried to spin the new pitch on the same principle of the spinning described above. The fibers obtained in this case are very thick, $d = 850$ mm, and they have the shape of rods. This can be explained by the fact that the spinning temperature is the decomposition temperature of the pitches. Furthermore, we noticed that those rods had a very clear porous structure. Therefore, analyses by SEM were performed on the rods (Fig. 7). The SEM pictures show highly
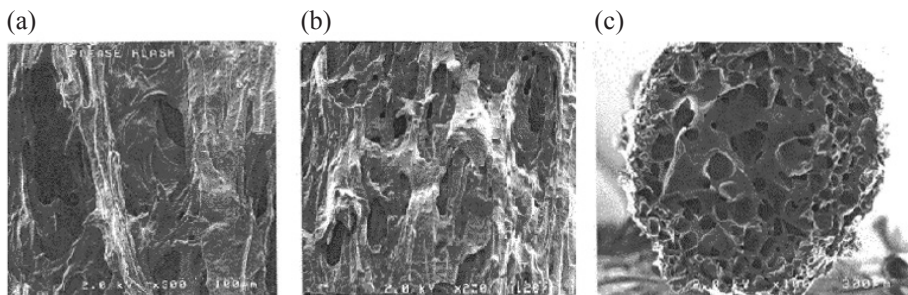
(a)   (b)   (c)

Fig. 7. SEM micrographs of the stick.

porous structures. The micrographs (Fig. 7a, 7b) demonstrate the distribution of pores throughout the wand and Figure 7c indicates the presence of pores in the heart of the stick. The SEM analysis displays a higher homogeneity of the pores within our sticks. It therefore seemed to us very interesting to determine the specific surface of these rods. To this end, we determined the surface area of rods by using nitrogen sorption measurements. The resulting value S_{BET} is of the order of 300 m^2 g^{-1}, which suggests that activation of these fibers can result in activated carbon of good quality that could be used as adsorbent or filter in environmental applications.

4. Conclusions

In conclusion, we can remark that the yield and composition of the obtained oils depend on the solvents and the nature of material used to extract the organic matter from oil shale. In addition, the yield and composition of the oil obtained by extraction with water are markedly different from those of the oil obtained by extraction with toluene or shale oil. The oil's higher yield and maltene content indicate that water is an optimal solvent, offering the highest maturation of the organic matter of oil shale.

The disadvantage of using water is the high pressure generated during the supercritical extraction of oil shale with water. To overcome this problem, we proceeded to the extraction of oil shale with toluene by adding phenol as a modifier. The current study showed that phenol was a very efficient modifier for the supercritical extraction of the organic matter from Tarfaya oil shale with toluene, giving a good yield of recovery and a suitable maturation of the organic matter. The pitches prepared by mixing phenol and toluene contain more aromatics and have a high char yield at 950 °C compared to those obtained by extraction with supercritical toluene alone. We also noticed that the chemical modification of the pitches afforded very thick fibers with a highly porous surface, which suggests that activation of these fibers can result in activated carbon of good quality that could be used as adsorbent or filter in environmental applications.

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