

The effect of various parameters on the supercritical extraction of Moroccan oil shales: Application in the elaboration of carbon foams and graphitizable carbons

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Abstract. *This study evaluates the possibilities to produce new materials, starting from Moroccan oil shales, for different applications. More specifically, the authors aimed to demonstrate that the organic fraction of the oil shales could be used as a precursor of carbon foams and graphitizable carbons, after appropriate chemical treatments resulting in the “maturation” of this organic phase. First, the researchers studied the optimization of experimental conditions and the identification of various parameters influencing the yield and composition of oils obtained by the supercritical extraction of Moroccan oil shale. The effect of various experimental parameters, such as mineral matter, thermal treatment temperature (T), treatment duration (t) and solvent type, was studied. The experimental results obtained show clearly that the organic matter contained in the Moroccan Tarfaya oil shale (sub-layer R_2) can be recovered by phenol under the following optimal conditions: $T = 390$ °C, $t = 2.5$ hours using phenol as a solvent with an amount of 15 g for each 10 g of sub-layer R_3 carbonate-free oil shale (RH). The results reveal that the yield and composition of the oil obtained by extraction with phenol is markedly different from those obtained by extraction with toluene, quinoline or without*

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solvent. Furthermore, the phenol has a very significant role in increasing the recovery yield and the degree of maturation of the obtained oil. It was shown that phenol was a suitable extraction solvent to produce graphitizable carbon at a relatively low temperature, below 1800 °C.

Keywords: Moroccan oil shale, supercritical extraction, carbon foam, graphitizable carbon, phenol.

1. Introduction

Currently, natural gas and oil resources are extensively used, but these will not last indefinitely. So it is necessary to seek alternative energy resources. A lot of studies [1–4] have been carried out on shale oil whose world reserves are 500 times as high as those of oil [5]. However, the mineral matter contained in oil shale makes its use as a source of energy difficult. At the same time, the organic matter, which is present in oil shale and is rich in aromatic compounds, could find other applications [6, 7]. Hence, many studies have been performed on the methods of extraction of organic matter from oil shale [8–10]. Most of them concern the yield and quality of the extracted oil. The yield of organic matter is much higher by pyrolysis or supercritical extraction than by conventional extraction methods, just as is the quality of the recovered oil dependent on the operating conditions [11–14]. Some studies have shown that the addition of CO or H₂ upon extraction of shale and coal with water improves the efficiency and quality of the produced oil [15–17].

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 [18–24].

In this work, we explore the possibility of transforming oil shales to materials with high added value. More specifically, we have shown that the organic fraction of oil shales could be used as a precursor of low-cost carbon foams or graphitizable carbons, after appropriate chemical treatments resulting in the “maturation” of this organic phase.

Within this context, two principal objectives were fixed for the present research:

- a) to study the effect of several parameters (nature of solvent, mineral matter, temperature and duration of treatment) on the supercritical extraction of Moroccan oil shale in order to establish the optimal operating conditions allowing to have the best quality of oil with good recovery performance;
- b) to demonstrate that phenol was a suitable extraction solvent to produce graphitizable carbon at a relatively low temperature, below 1800 °C.

2. Experimental

2.1. Materials

The oil shale used in this work was from the Tarfaya deposit located in the south of Morocco (27.9375° N, 12.9263° W). This deposit consists of several layers that are in turn subdivided in sub-layers, each having a different amount of organic matter. The samples were obtained from the R₃ sub-layer, characterized by its high content of organic matter [25]. The chemical composition of this sub-layer is given in Table 1 [17].

The carbonate-free oil shale (RH) was obtained by dissolution of carbonates with HCl [26, 27]. The powdered R₃ shale (20 g, grain size 0.063–0.08 mm) and 80 mL of concentrated HCl (7 M) were introduced in an Erlenmeyer. The mixture was then magnetically stirred for 4 h. The formed CO₂ was trapped by bubbling through a barium hydroxide solution. After filtration, the solid residue (referred to as RH) was washed carefully with distilled water, dried at 100 °C and sealed in a plastic bag.

In order to eliminate silicates, RH was stirred with concentrated HF (4 ml g⁻¹ RH) for 4 hours. After filtration, the residue (K₃) obtained was first washed with dilute HCl solution and then with water, dried at 100 °C and sealed in a plastic bag.

Table 1. Chemical composition of sub-layer R₃ [17]

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

2.2. Apparatus

2.2.1. Preparation of asphaltenes

The supercritical extraction of the 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 [28]. 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 in order to precipitate the high-molecular fraction (asphaltenes) constituting the pitch [29]. After stirring for 12 h, the two fractions, soluble (maltenes) and insoluble (asphaltenes), were separated by filtration through Whatman Filter Paper,

and then dried for 12 h at 40 °C and 80 °C, respectively. The scheme of the autoclave is shown in Figure 1.

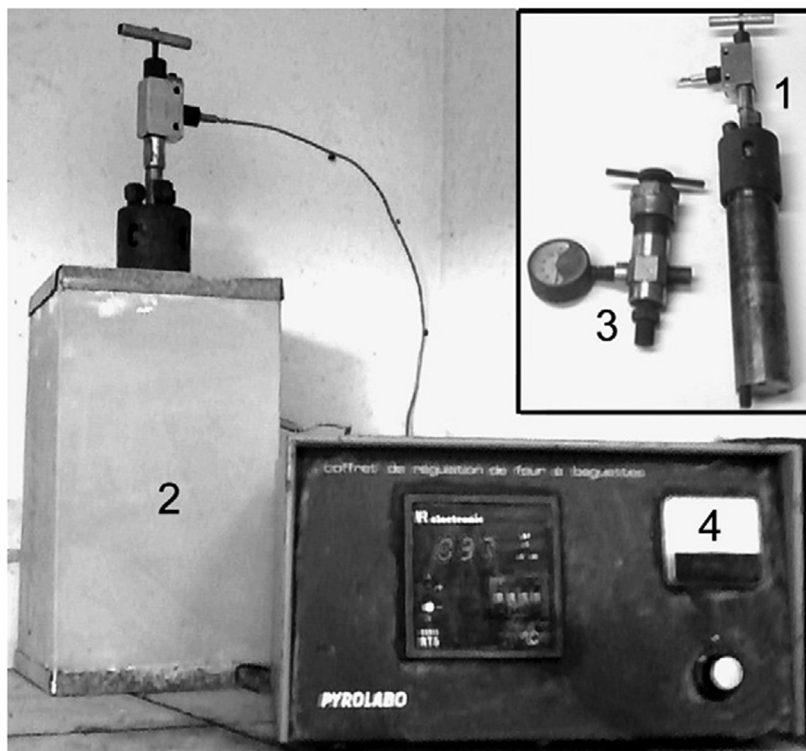


Fig. 1. Schematic diagram of the apparatus used for supercritical extraction: (1) reactor; (2) furnace; (3) pressure gauge; (4) regulator.

2.3. Analyses

Scanning electron microscopy (SEM) micrographs were taken with a Hitachi TM-1000 microscope. Fragments of about 0.5 cm² 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.

Raman spectra were obtained on a Labram 010 spectrometer (Dilor), using the 514.5 nm green line of an argon laser as excitation source. The samples were step-scanned in 1 cm⁻¹ 86 resolution between 500 and 2000 cm⁻¹.

Size exclusion chromatography (SEC) was carried out on a Waters analytical system (pump 510, refractometer 410 and UV/visible detector 486) with tetrahydrofuran (THF) as eluent at 1 mL min⁻¹ and using a TSK GMHXL column with a mixed porosity of 1500–10⁷ Å. Relative average molecular weights were calculated with a cubic, 12-point calibration curve obtained from monodisperse polystyrene standards.

3. Results and discussion

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

In order to study the effect of mineral matter on the recovery yield and composition of the extracted oils, we conducted extractions on three different samples according to the protocol described in the experimental part:

- Sample 1: sub-layer $R_3 \rightarrow R_3$;
- Sample 2: sub-layer R_3 without carbonates $\rightarrow RH$;
- Sample 3: sub-layer R_3 without carbonates and silicates $\rightarrow K_3$.

The results of study of the effect of mineral matter on the recovery yield and composition of the extracted oils have been published recently [30]. These results showed 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 gives evidence of 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.

According to the previous work by Abourriche et al. [30], the RH sample has several advantages, both in terms of preparation (less consumed products), and the results obtained (high recovery yield).

Moreover, the presence of fluorine in the organic matter resulting from sample K_3 complicates its use. These reasons made us use RH as the starting material to carry on the study.

3.2. Effect of temperature

To study the effect of temperature on the extraction yield, experiments were conducted at temperatures between 200 and 500 °C, while the other factors were maintained invariant (treatment time and amount of solvent).

Figure 2 shows that the mass loss of the RH product is low up to 300–350 °C, then increases sharply in the temperature range of 350–400 °C. This is in agreement with the results of earlier works [31, 32]. The oil yield obtained has been shown by several authors to increase with temperature rising from 380 to 420 °C. In the current study, the oil yield was determined at the following temperatures: 380, 390, 400, 410 and 420 °C. It turned out that the oil yield was higher at $T = 390$ °C (4.5 g of organic matter recovered, which corresponds to the yield of 201.7% compared to the Fisher test). Therefore, the temperature was set at this value to optimize the other factors. The drop in oil yield at temperatures above 390 °C can be explained by the thermal cracking of the aliphatic substituents, which generate a strong gas evolution at the expense of the oils.

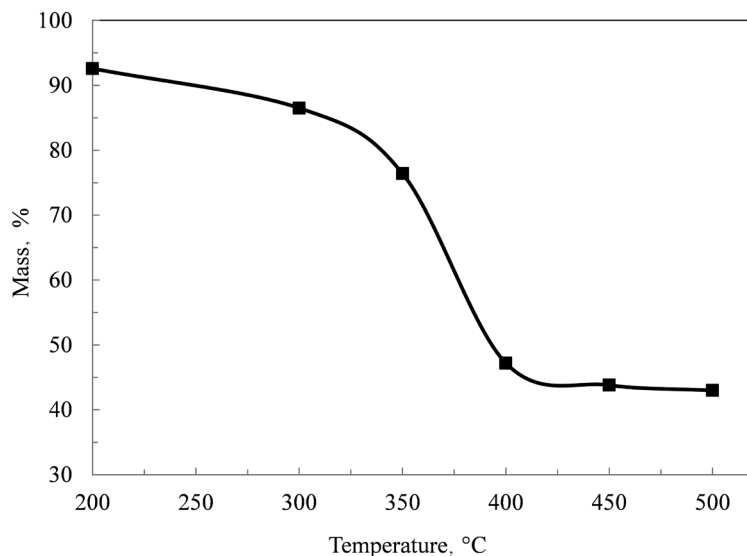


Fig. 2. Variation of the insoluble material in CHCl_3 as a function of temperature.

3.3. Effect of treatment duration

The results of study of the effect of treatment duration are shown in Figure 3. The mass insoluble in chloroform varies considerably as a function of treatment duration. This mass decreases and reaches minimum within 2.5 h, then increases for a longer time. This increase can be explained by the condensation reactions which cause the formation of coke.

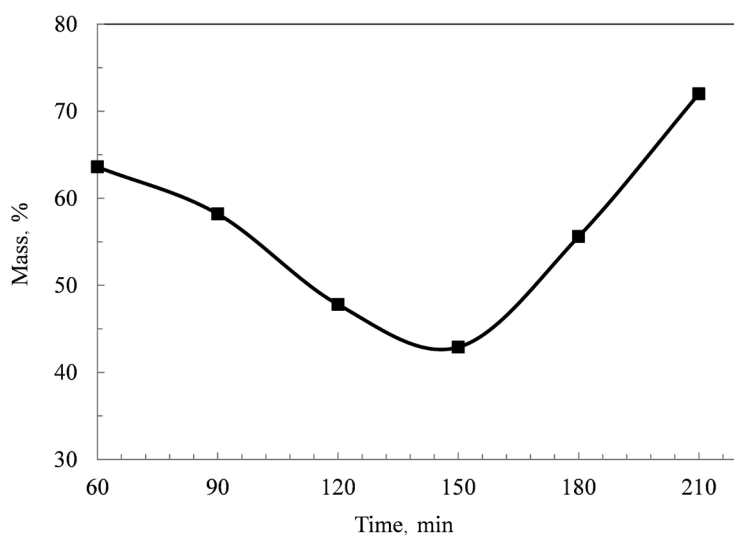


Fig. 3. Variation of the insoluble material in CHCl_3 as a function of treatment duration.

3.4. Effect of the nature of solvent

In order to study the effect of solvent on the yield of recuperation and composition of oil, an extraction was carried out with 10 g of sample RH without and with different solvents (toluene, quinoline, phenol) under the conditions described above. The yields and composition of the oil obtained under different conditions are presented in Table 2.

Table 2 reveals that the maturation treatment in the presence of chemical agents allowed the degradation of organic matter. The yields of oil obtained are relatively high and give evidence of significant amounts of asphaltenes. Under these experimental conditions, toluene can be seen in its supercritical state, (the critical point of the liquid corresponds to $T_c = 320\text{ }^\circ\text{C}$ and $P_c = 4.16\text{ MP}$). Its thermodynamic properties are then altered, resulting in very significant physical phenomena. On the one hand, the low viscosity promotes the transfer of material and on the other hand, the impregnation and solubilization of the products are more thorough; therefore, the extraction yields are higher than under normal conditions. It is also observed that the yield of oil obtained by quinoline and phenol is significantly higher than that of oils extracted with toluene or without solvent.

Table 2. Yields and composition of oils extracted from RH by different solvents

Extracts	Ex(0)	Ex(T)	Ex(Ph)	Ex(Q)
Solvents	Without solvent	Toluene	Phenol	Quinoline
Mass of sample, g	10	10	10	10
Amount of solvent	–	60 ml	15 g	60 ml
Heating rate, $^\circ\text{C}, \text{min}^{-1}$	16	16	16	16
Temperature, $^\circ\text{C}$	390	390	390	390
Time, min	150	150	150	150
Pressure, MPa	0.3	4.5	1.2	1.3
Recovered oil, g	4.21	3.2	5.71	7.1
Maltenes, wt%	59	47	62	65
Asphaltenes, wt%	41	53	38	35
Softening temperature of asphaltenes, $^\circ\text{C}$	116	84	88	93

3.5. Analysis of organic extracts obtained by different solvents

3.5.1. Analysis of organic extracts by SEC

Knowledge of average molecular weights has come into common use in the specification of macromolecules whose molecular distribution directly influences the kinetics of polymerization. Steric exclusion chromatography (SEC) makes it possible to predict the physical behavior of different extracts; it is widely used to determine the molecular distribution and characteristics of pitches. The respective study may involve comparison of the profile of the molecular distribution of an extract with that of a reference material, or identify parameters whose determination CES allows: molecular weight (M_w), number average molecular weight (M_n) and polymolecularity index (I_p).

M_w is the molecular weight of a fictitious homogeneous polymer which would have the same properties as the mixture studied, M_n is the number average molecular weight, M_w is the molecular weight of the peak. I_p is the polymolecularity index, it is the quotient M_w/M_n , which represents the heterogeneity of the mixture. It is equal to 1 only when dealing with a homogeneous polymeric substance, while for industrial polymers it can reach or even exceed 10.

Oil shale extracts obtained by different solvents were analyzed by SEC; the chromatograms obtained are shown in Figure 4 and the corresponding characteristics are grouped in Table 3.

The analysis of these characteristics displays that quinoline promotes the degradation of kerogen, resulting in a low average molecular weight. The molecular distribution of the extract is relatively dispersed, but remains less pronounced than that of extracts obtained by maturation in the presence of toluene (in supercritical conditions) or without a modifying agent. In the presence of phenol, the extract obtained has different characteristics. Its average molecular weight is relatively high, but the dispersion of the mixture is very low. Its properties seem more attractive than those of the extract obtained in the presence of quinoline (very low average molecular weight) and are responsible for the isotropic character of the carbon fibers formed [33].

Table 3. Analysis of extracts by SEC

Solvent	\bar{M}_w^a	\bar{M}_n^b	I_p
Without solvent	2804	494	5.68
Toluene	2916	570	5.12
Phenol	2313	1353	1.71
Quinoline	466	135	3.45

^a Weight average molecular weight; ^b number average molecular weight;

I_p – polydispersity index = \bar{M}_w / \bar{M}_n .

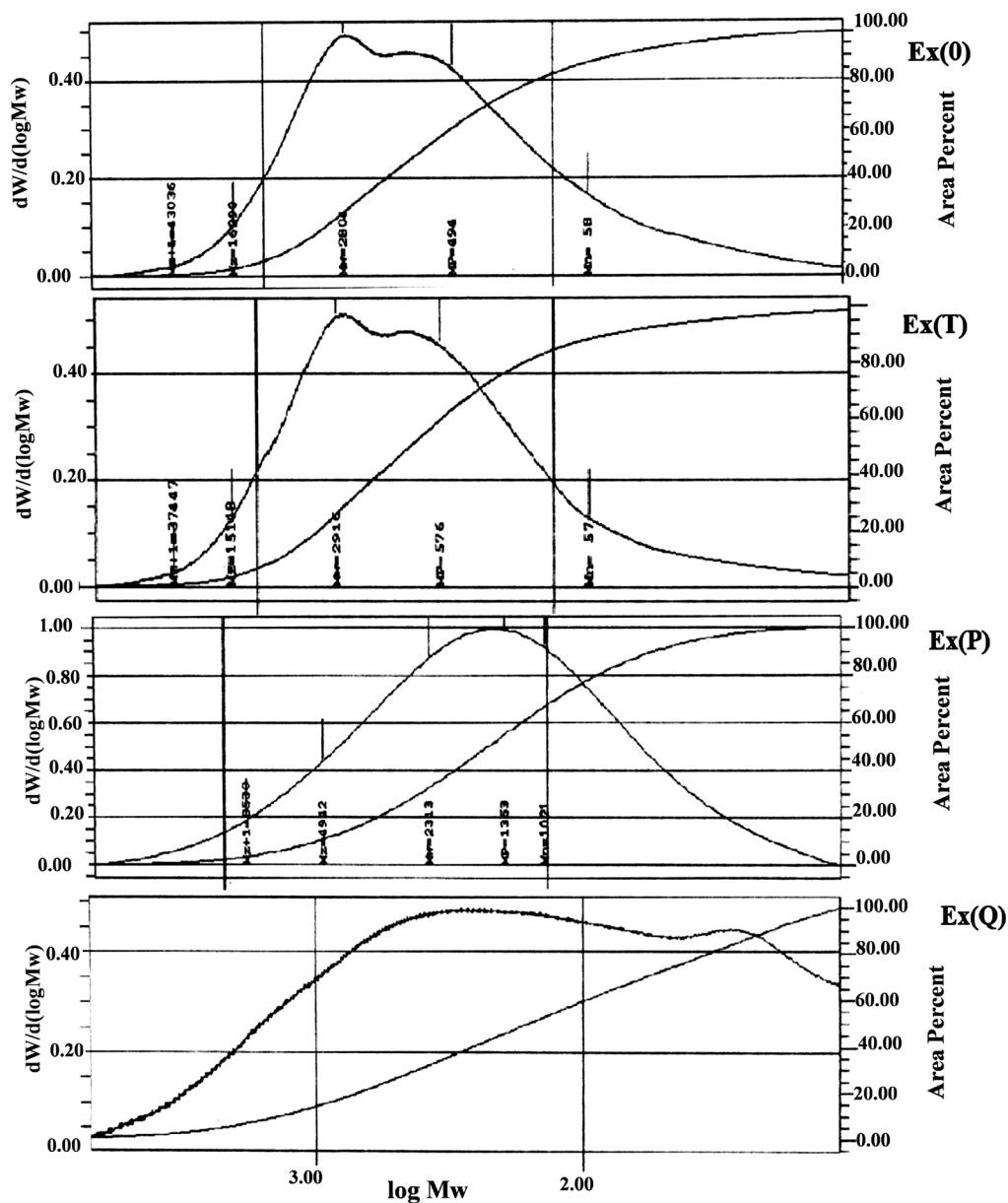


Fig. 4. Chromatograms of extracts obtained by different solvents.

3.5.2. Raman spectroscopy

The spectrum of monocrystalline graphite has been studied earlier in several studies [34–36]. Two active vibration modes are observed in Raman scattering E_{2g}^1 at 42 cm^{-1} and E_{2g}^2 at 1582 cm^{-1} (G band). These two bands correspond to vibrations of sp^2 -type C-C bonds in the graphene planes. E_{2g}^1 is difficult to observe and E_{2g}^2 is in practice the only one of these two lines which can be used to characterize carbonaceous materials.

In the case of poorly organized carbons, the Raman spectra show, in addition to the G band around 1600 cm^{-1} , a D band around 1350 cm^{-1} and, possibly, a shoulder D' of the G band. These bands represent a characteristic structural disorder. Thus, for a disordered carbon, the intensity of the D band at 1350 cm^{-1} increases with disorder [37]. Studies carried out on heat-treated coke have revealed that the degree of graphitization of the carbonaceous material increases with treatment temperature. This results in the reduction in the width at mid-height of the band D, located around 1350 cm^{-1} . A decrease in the width of the G band is also observed when the degree of graphitization of the carbonaceous material increases [38]. A study by Johnson et al. [39] has highlighted the appearance of a new band around 1620 cm^{-1} , it was observed in carbonaceous materials with a low degree of graphitization. This band combines with the E_{2g}^2 G band to give a massif centered around 1600 cm^{-1} . The main elements that the Raman spectrum can compare for a carbonaceous material are:

- The D band which appears between 1300 and 1400 cm^{-1} corresponds to the deformation vibrations of poorly organized monocrystalline structures. This is the so-called forbidden band in the case of graphite.
- The G band which appears between 1500 and 1700 cm^{-1} reflects the existence of graphitic planes.
- The 2D band which reflects the structural disorders appears between 2500 and 2700 cm^{-1} .
- The D + G band which appears between 2800 and 3000 cm^{-1} is the combination of the D peak relating to the disorder and the G peak of the graphite.

The analysis of the Raman spectra of the samples used in this work (Fig. 5) shows that the asphaltenes APh obtained from the phenolic extract have interesting characteristics. Indeed, the Raman spectrum presents a G band around 1580 cm^{-1} which testifies to the structural organization for this sample and a massif around 3000 cm^{-1} (D + G band); the D band relating to the disorder is weaker compared to the other samples, in particular the AT sample obtained in the case of toluene, whose D and D + G bands are more marked and more intense compared to the asphaltenes AQ obtained using quinoline and A0 obtained without a solvent.

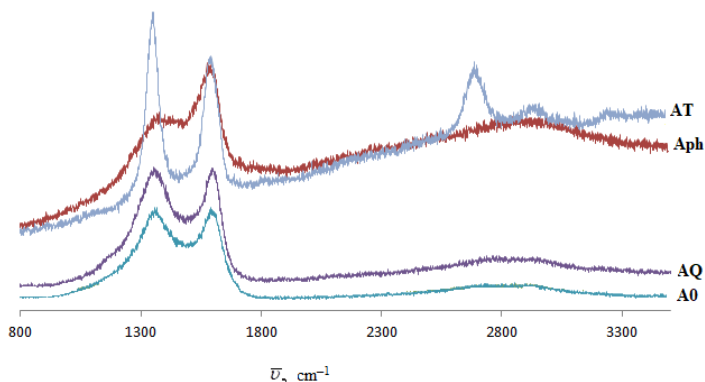


Fig. 5. Raman spectra of different samples: A0 – asphaltenes obtained without solvent; AT – asphaltenes obtained by toluene; AQ – asphaltenes obtained by quinoline; APh – asphaltenes obtained by phenol.

3.6. Transformation of asphaltenes into carbon foams

The Raman spectra of different samples (Fig. 5) reveal that the asphaltenes APh obtained from the phenolic extract have interesting characteristics. Indeed, the Raman spectra present a G band around 1580 cm^{-1} , which testifies to the structural organization of this sample and a massif around 3000 cm^{-1} (R + G band); the D band relating to the disorder is weaker compared to the other samples, in particular the AT sample obtained by toluene whose D and D + G bands are more marked and more intense compared to the AQ and A0 samples [37, 38]. This induced us to conduct the study with three samples (A0, AT and APh), which we had transformed into carbon foams. The operation consisted in introducing the pitch into a mold and then treating it at $550\text{ }^{\circ}\text{C}$. The low molecular weight elements were transformed into gases and their release promoted the creation of pores within the material giving rise to the form of desired foams. Optical microscopy photos of the elaborate carbon foams are presented in Figure 6. As can be seen from the figure, the nature of the solvent used has an impact on the foam structure. The carbon foam obtained by phenol has a homogeneous porous structure compared to other samples.

3.7. Carbonization and graphitization of elaborated carbon foams

The M0, MT and MPh carbon foams, produced from asphaltenes A0, AT and APh, underwent heat treatment under an inert atmosphere for one hour and at temperatures between 1100 and $2800\text{ }^{\circ}\text{C}$. Figures 7, 8 and 9 present the Raman spectra of the materials obtained.

The Raman spectra of MT materials treated between 1100 and $2800\text{ }^{\circ}\text{C}$ (Fig. 8) indicate that the intensity of the D band located around 1380 cm^{-1}

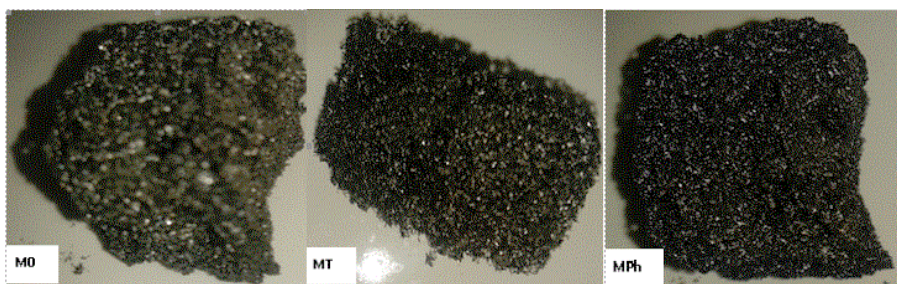


Fig. 6. Optical microscopy photos of the elaborate carbon foams: M0 – carbon foams obtained without solvent; MT – carbon foams obtained by toluene; MPh – carbon foams obtained by phenol.

increases as the treatment temperature increases. These spectra are comparable to that of non-graphitizable carbon treated at high temperatures [40]. The decrease in the degree of graphitization of MT with the increase in temperature can be explained by the presence of a higher level of oxygen in the pitch, which delays its graphitization. The MPh and M0 materials demonstrate that the higher the treatment temperature, the more the intensity of the G band, characteristic of graphite planes, increases and that of the D band, which corresponds to disorder, decreases. The MPh material spectrum (Fig. 9) treated at 2800 °C exhibits a higher intensity of the line located at 1590 cm^{-1} . This displays that its degree of graphitization is very high. The analysis of these spectra also reveals that the graphitization of these materials occurs below 1800 °C. The structural evolution of the material appears around 1400 °C, but the degree of graphitization of the material depends significantly on the material preparation method.

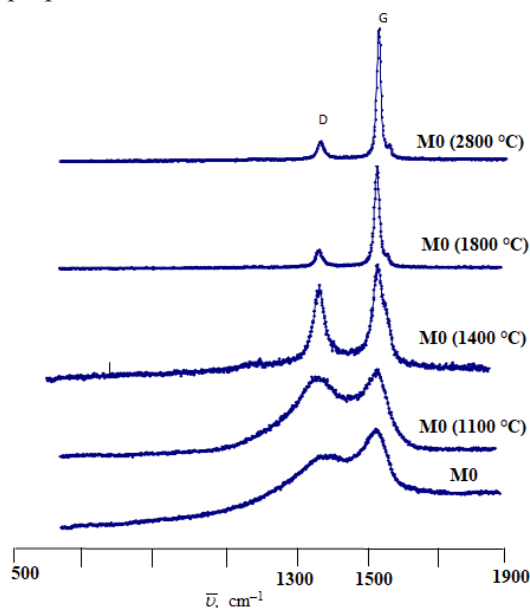


Fig. 7. Raman spectra of carbon foams M0 treated at different temperatures.

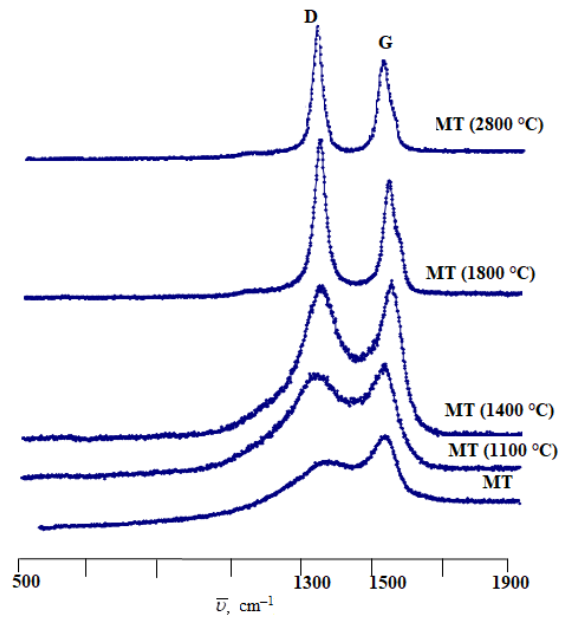


Fig. 8. Raman spectra of carbon foams MT treated at different temperatures.

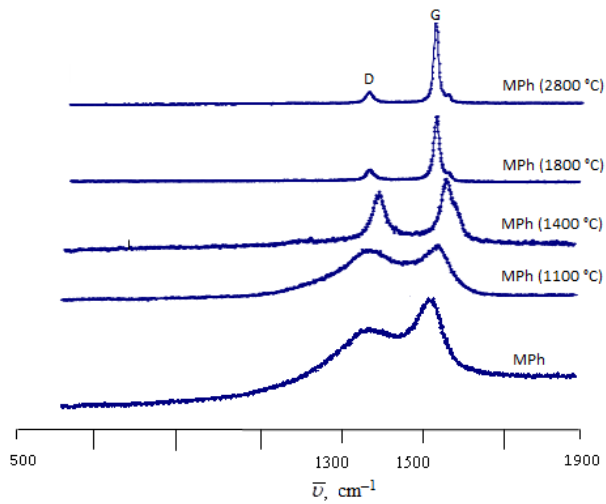


Fig. 9. Raman spectra of carbon foams MPh treated at different temperatures.

The elaborate carbon foams, treated at 2800 °C, were observed under a scanning electron microscope (Fig. 10). The SEM micrographs confirm the results obtained by Raman spectroscopy. The three materials differ in several aspects: MT has a poorly organized texture with many defects, M0 has a moderately organized texture, with some structural defects, while MPh foam has a laminated structure, characteristic of well-organized carbon.

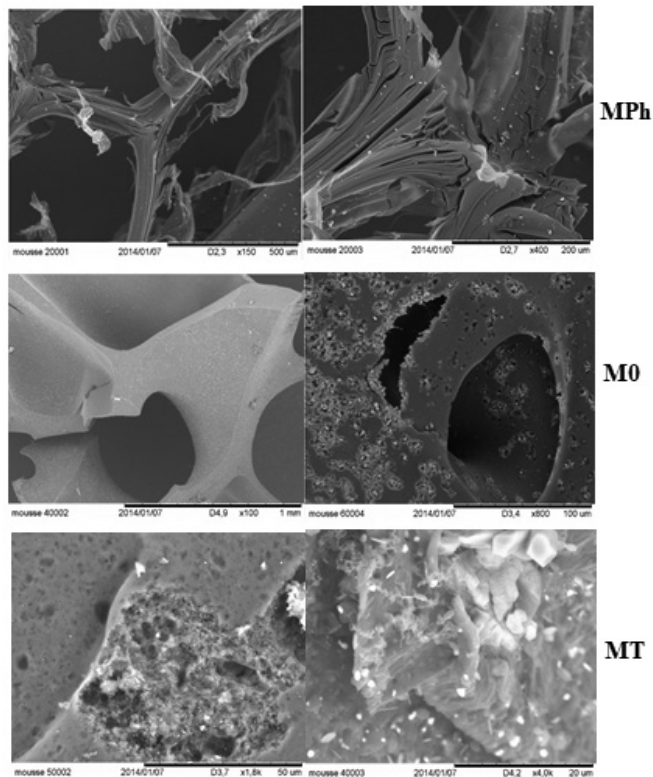


Fig. 10. SEM micrographs of the carbon foams treated at 2800 °C.

4. Conclusions

In this work, the authors have demonstrated the following:

- 1) The yield and composition of the oil produced depend on the nature of material used to extract organic matter from oil shales of sub-layer R_3 , free carbonates sub-layer (RH) or free carbonates and silicates sub-layer (K_3).
- 2) Processing temperature and duration of treatment have a significant effect on the recovery efficiency of organic matter from oil shale. Indeed, the yield increases with the increase in temperature and duration of the treatment, but exceeding a certain limit ($T = 390$ °C and $t = 2.5$ hours) it decreases.

3) It is possible to transform the heavy fraction of shale oils (asphaltenes) into foam carbon and graphitizable carbon. The asphaltenes obtained from the organic matter extracted from oil shale after maturation have an appearance similar to that of Ashland 240 petroleum pitch. The quantities as well as quality of the materials extracted depend significantly on the operating conditions and the solvent used. The use of phenol as a modifier during the maturation treatment of organic matter allows the formation of graphitizable carbons.

The materials obtained, using toluene as a solvent, exhibit a disordered structure. This may be due to the high dispersion of the molecular weight and also to the presence of heteroatoms, more particularly of oxygen which causes cross-linking and blocks the process of graphitization. The Raman spectrometry analysis clearly indicates that phenol is a good degradation agent, which makes it possible to obtain a well-organized carbonaceous material. These results were confirmed by scanning electron microscope observations.

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