

Effects of Phenol Addition on Oil Extraction from Moroccan Oil Shale by Supercritical Toluene

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Abstract: In the present work, the effect of phenol on the supercritical extraction of the organic matter from Tarfaya's oil shale with toluene was evaluated. The experimental results showed clearly that phenol had a significant effect on the yield and the composition of the oils obtained. Moreover, it was shown that phenol was a very efficient modifier for oil shale, 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.

Keywords: Oil shale, Supercritical extraction, Toluene, Phenol, Pitch.

1. INTRODUCTION

Oil shale has been considered for a long time as 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 eventually demonstrated that more research is needed to make the oil produced cost effective and competitive against conventional petroleum.

Besides, oil shale has some potential for the manufacturing of synthetic products such as cement, calcium, alumina, pitches, carbon adsorbents, zeolites, carbon fibers and other chemicals [5-10]. As a result, in recent years many studies have been carried out on methods for oil extraction, 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]. Particularly, it has been demonstrated that the extraction yield and the quality of oils extracted depend on several parameters (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], and acetone [23] or hexane [24] to extract pesticide residues. Other authors have also used the reagents in order to degrade the solute molecules [25-27]. Lanças *et al.* [21] have studied the effect of certain solvents (acetone, hexane, methanol) on the extraction of the herbicide Diuron from sugar cane and orange samples with supercritical CO₂. They concluded that methanol enhanced significantly the extraction yield compared to other modifiers.

Meanwhile, Oliveira *et al.* [28] 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. Earlier studies had also shown that the addition of CO or H₂ when extracting oil from shale and coal with water improved the efficiency and quality of the oils produced [29, 30].

In this work, we chose phenol as modifier in oil extraction from Moroccan oil shale with supercritical toluene. This choice was dictated by the thermal stability of phenol, due to intermolecular hydrogen bonds. Besides, the highly reactive hydroxyl group could react with some organic functions present in the oil shale. The objective was to investigate the effect of phenol on the yield and the composition of the oil obtained by extraction with supercritical toluene.

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2. EXPERIMENTAL

2.1. Materials

The oil shale used in this work was from the Tarfaya deposit located in the South of Morocco. 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 R_3 sub-layer, which is characterized by its high content of organic matter [31]. The chemical composition of the R_3 sub-layer is given in reference [32].

The carbonate-free oil shale (**RH**) was obtained by dissolution of carbonates with HCl [33,34]. 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. The mixture was then subjected to magnetic stirring for 4 h. The CO_2 produced 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.

2.2. Methods

2.2.1. Preparation of the Pitches

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 and heating rate were controlled. The temperature of extraction was 390 °C with a heating rate of 16 °C min⁻¹ [35]. The maximum pressure reached during this treatment of 120 min was 8 MPa. After cooling 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 [36] 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.

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 [37]. After extrusion and mechanical stretching, the fiber was

thermoset by slow heating in dry air at atmospheric pressure to temperatures in the range of 60-280 °C. The oxidized fibers were pyrolyzed under nitrogen flow with the temperature being progressively raised up to 950 °C at a heating rate of 5 °C min⁻¹ [38].

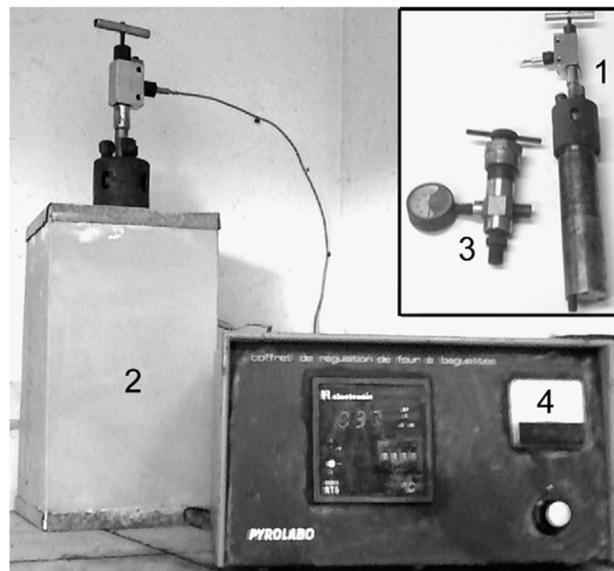


Figure 1: Schematic diagram of the apparatus used for supercritical extraction: (1) reactor; (2) furnace; (3) pressure gauge; (4) thermocouple; (5) regulator.

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.

The electron probe X-ray microanalysis (EPMA) was carried out in a Cameca SX 100 apparatus.

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.

Thermogravimetry (TG) was 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 fibers were measured by nitrogen adsorption at 77 K with a Micromeritics Flowsorb II 2300 instrument using the 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 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.

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

¹H NMR spectra were recorded on a Bruker AC 250 (250 MHz) spectrometer. The samples were placed in 5 mm-ID tubes with deuterated chloroform (CDCl₃) as solvent. The chemical shifts are given in ppm relative to TMS ($\delta = 0$ ppm).

3. RESULTS AND DISCUSSION

3.1. Effect of Phenol on Yield of and Composition of Obtained Oil

In order to study the effect of phenol on the yield and the composition of the oil obtained by supercritical extraction with toluene, two series of experiments were carried out under the conditions described in the experimental part (section 2.2.1), with increasing volumes of toluene. The results obtained are given in Figure 2.

The shape of the two plots is the same, the mass of insoluble being lower in the case of the mixture (toluene + phenol) than for toluene alone. This shows that the addition of phenol increased the extraction yield without modifying the conditions of extraction by toluene, especially pressure. Figure 2 displays two zones of extraction, in the first one, the yield of recovery decreases with the increasing volume of toluene. A similar result was reported by Zhuang and Thies [39] during the supercritical extraction of petroleum pitch by toluene. They observed that the output of extraction was high for a solvent to pitch ratio equal to 2 and low for a ratio of 3. This can be explained by repulsion forces between oil molecules in solution. In the second zone, the output of extraction increases as the volume of toluene grows.

At 390 °C, the pressure in the autoclave reached 5.3 MPa and 7.5 MPa for a volume of 50 mL and 70

mL, respectively. In these conditions, toluene exceeds its critical point (320 °C, 4.2 MPa), which confers it a good solvent capacity and consequently led to an increase in the output of extraction. Comparable results were obtained by Canel and Missal [40] on the extraction of oil shale of Gôynük (North-Western Turkey) by supercritical water. They concluded that the output of extraction increased as the pressure was increased.

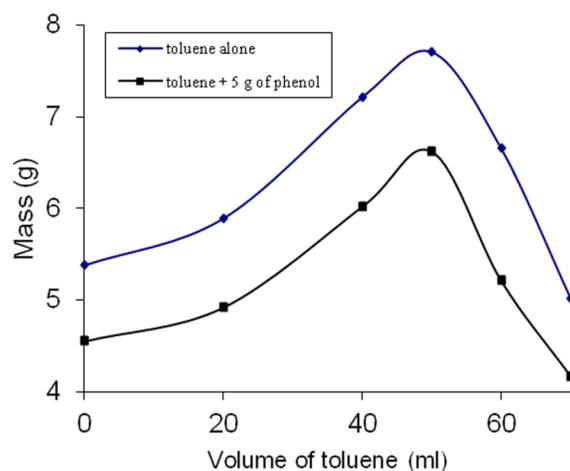


Figure 2: Variation of the insoluble material in CHCl₃ as a function of the toluene volume.

As two extraction zones were identified above, two volumes of toluene were selected to study the effect of phenol on the extraction yield: $V_1 = 40$ mL of toluene (zone 1) and $V_2 = 60$ mL of toluene (zone 2).

The analysis of the results obtained (Figure 3) shows that the plots obtained in both cases have a similar shape and the weight of the insoluble material in chloroform decreases as the amount of phenol increases. It reaches its minimum for a mass of phenol

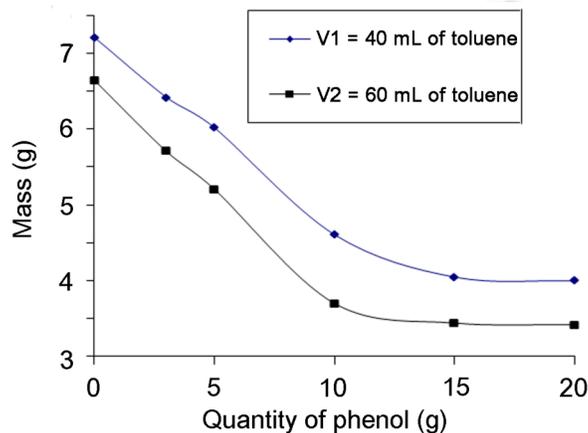


Figure 3: Variation of the insoluble material in CHCl₃ as a function of the phenol mass.

equal to 15 g in the first series of experiments (40 mL of toluene) and 10 g for the second series of experiments (60 mL of toluene). Moreover, the mass of the insoluble material in chloroform is lower in the case of the second series of experiments.

In summary, the addition of phenol on oil extraction from Moroccan oil shale with supercritical toluene increases the extraction efficiency.

In view of SEC analysis results (Table 1), it appears that the value of the weight average molecular weight, \bar{M}_w , for the oil recovered by mixing toluene and phenol is, as expected, lower than that for the oil (HT70) obtained using toluene only.

Elemental analysis of the obtained oils (Table 2) showed that the oil HT70PH5 possesses a very low sulfur content and a higher aromaticity factor (low H/C) compared to HT70 oil. These results confirm the role of phenol as modifier of extraction with supercritical toluene in reducing the level of sulfur in oils extracted.

3.2. Analyses of the Pitches

3.2.1. Analysis of the Pitches by SEC

The results of the SEC analyses of the pitches are shown in Table 3. 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.

3.2.2. TG/DTA

The results of thermal analysis (TG/DTA) of the pitches (Figure 4) show that the pitch PHT70 is characterized by a mass loss that starts around 100 °C and ends at 550 °C, with a peak around 420 °C. The residue yield at 950 °C is about 32%. Secondly, the thermogram of the pitch PHT70PH5 is completely different from the former. It exhibits a mass loss that spreads over the same temperature range as pitch PHT70, but with the appearance of a complex phenomenon consisting of 3 successive mass losses at 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. This could be explained by the fact that the pitch PHT70PH5 consists of lighter molecules but quite thermally stable compared to the pitch PHT70.

Table 1: Analysis of the Oils by SEC

Oil	\bar{M}_w^a	\bar{M}_n^b	I_p^c
HT70	1650	200	8.2
HT70PH5	1190	410	2.9

^aWeight average molecular weight; ^bNumber average molecular weight. ^c I_p : polydispersity index = \bar{M}_w / \bar{M}_n . HT70: oil extracted using 70 mL of toluene. HT70PH5: oil extracted using 70 mL of toluene + 5 g of phenol.

Table 2: Elemental Analysis of the Obtained Oils (wt%)

Fraction	C	H	N	S	O
HT70	41.09	53.7	0.056	1.2	4.06
HT70PH5	45.80	51.2	0.038	2.2	0.05

(O was determined by difference). HT70: oil extracted using 70 mL of toluene. HT70PH5: oil extracted using 70 mL of toluene + 5 g of phenol.

Table 3: 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

^aWeight average molecular weight; ^bNumber average molecular weight. ^c I_p : polydispersity index = \bar{M}_w / \bar{M}_n . PHT70: pitch obtained from oil HT70. PHT70PH5: pitch obtained from oil HT70PH5.

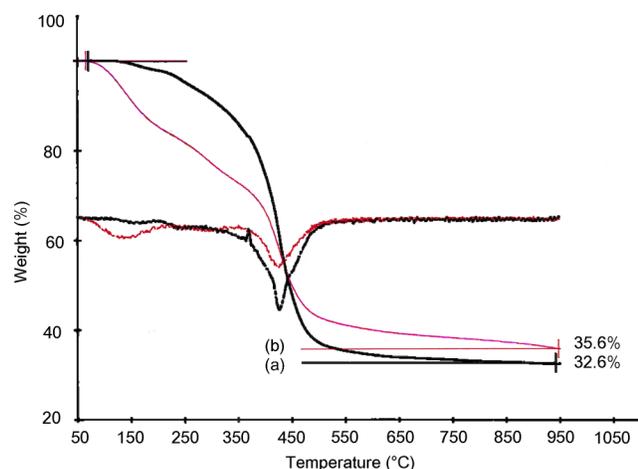


Figure 4: Thermograms of the pitches: (a) PHT70, (b) PHT70PH5.

3.2.3. Elemental Analysis

Elemental analysis of the obtained pitches (Table 4) showed that the pitch PHT70PH5 possessed a very low sulfur content and a higher aromaticity factor (low H/C ratio) compared to pitch PHT70.

Table 4: Elemental Analysis of the Pitches

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

^aO is determined by difference. PHT70: pitch obtained from oil HT70. PHT70PH5: pitch obtained from oil HT70PH5.

3.2.4. ¹H NMR

The pitches were also characterized by ¹H NMR spectroscopy (Figure 5). The spectrum of pitch PHT70 presents predominantly signals corresponding to aliphatic protons located between 0.5 and 3 ppm, while 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 the elemental analysis carried out on this pitch. This confirms that phenol was an efficient modifier likely to give a good yield of recovery and a better quality of oil.

3.3. Characterization of the Filaments

The carbonization yield at 950 °C was of about 49%. Elemental analysis of the pyrolyzed filaments (C: 98.83; S: 1.08; Fe: 0.03 and Si: 0.06 in at.%) showed that the organic matter extracted contained a minimum of metal impurities.

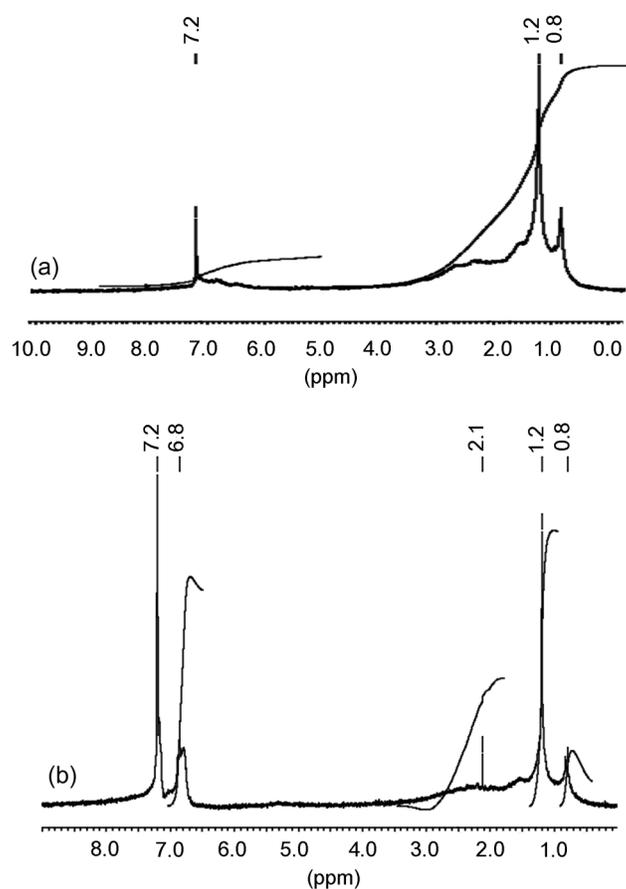


Figure 5: ¹H NMR spectra of the pitches: (a) PHT70, (b) PHT70PH5.

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

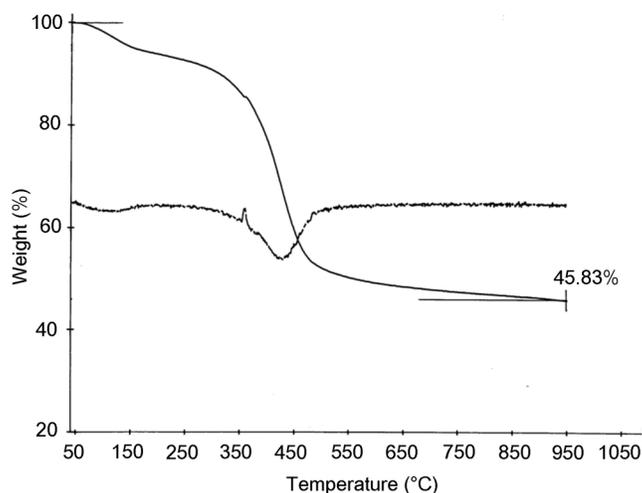


Figure 6: Thermal curve of the pitch PHT70PH5M.

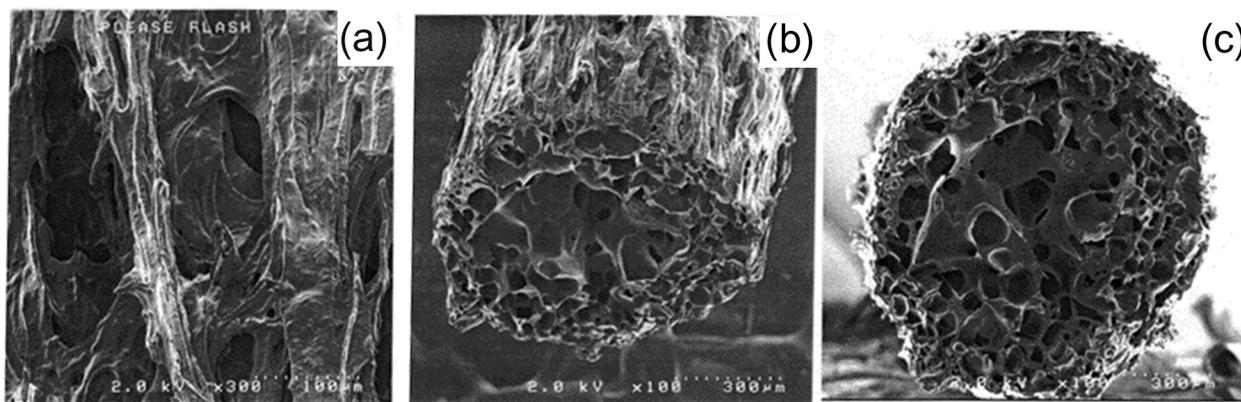


Figure 7: SEM micrographs of the stick.

those of fibers obtained from coal tar or petroleum isotropic pitches [41, 42].

In order to improve the mechanical properties of the fibers, we tried to increase the pitches softening temperature by adding a stage 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 both light ends and polar functional groups since the presence or not of heteroatoms makes the materials obtained either crosslinkable or graphitizable [43]. Therefore, we used this method to prepare a new pitch from HT70PH5 oil. The softening temperature rose to 260 °C.

This new pitch (PHT70PH5M) was analyzed by TG/DTA (Figure 6) in order to compare the result with that of pitch PHT70PH5. The mass loss observed in Figure 4b between 180 and 300 °C for pitch PHT70PH5 (corresponding to molecules of low mass) has completely disappeared. We also noted an increase in the residual rate from 36% for PHT70PH5 pitch 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 as described in Section 2.2.2. The fibers obtained in this case were very thick, $d = 850 \mu\text{m}$, with a rod-like shape, probably because the spinning temperature is the decomposition temperature of the pitch. Furthermore, we noticed that these rods had a very important porous structure, thus analyses by SEM were performed (Figure 7). The SEM micrographs show highly porous structures. Figures 7a and 7b show pores throughout the outer surface and Figure 7c shows the presence of pores in the heart of the stick. It therefore seemed to us very interesting to determine the specific surface area of these rods. To this end, nitrogen sorption measurements were

conducted and values of the order of $300 \text{ m}^2 \text{ g}^{-1}$ were found.

4. CONCLUSIONS

Within the framework of the development of Moroccan natural resources, we have carried out a study on Moroccan oil shale in order to prepare new pitches. The following conclusions can be drawn from the present investigation on the effects of phenol addition on oil extraction from Moroccan oil shale by supercritical toluene:

- The oil yield obtained by toluene/phenol mixtures is significantly higher than that of oil extracted by toluene only.
- The study of the influence of phenol on the extraction of organic matter from oil shale with toluene indicates that phenol plays a very important role in increasing the extraction efficiency of organic matter and a small change in mass of phenol results in a net increase in efficiency.
- The pitch prepared by mixing phenol and toluene contains more aromatics and a high residue rate at 950 °C compared to that obtained by extraction with supercritical toluene only.
- Chemical modification of the pitches afforded very thick fibers with important porous surfaces, which suggest that their activation may result in activated carbon of good quality that might be used as adsorbent or filter in environmental applications.

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