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Supercritical water extraction and characterization of Moroccan shale oil by different solvent

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Abstract

The aim of this work is study aimed to investigate the effect of the mineral matrix on supercritical water extraction of Moroccan oil shale (Timahdit area), to establish the best operating conditions likely to give a good yield of recovery (26.16%) with the best oil quality. The yield of the oil produced depends on the type of material used to extract the organic matter of oil shale: crude oil shale, oil shale decarbonized and the solvent (water, limewater, toluene and olive oil mill wastewater). Several results show that the mineral matrix and the olive oil mill wastewater has a significant effect on of the supercritical water extraction yield of shale oil, giving a better quality of the extracted oil. It is still another object to provide an efficient solvent extraction process for the recovery of oil shale wherein not toxic and law cost solvent can be employed and good percentages of oil shale can be recovered in a relatively inexpensive and easy. The FT-IR spectra show that, the extracted oil containing a substantial proportion of aromatic hydrocarbon compounds and fewer amounts of paraffins.

1. Introduction

Oil shale is the second largest solid fossil fuel deposit after coal in the world. Oil shale defined as a sedimentary rock containing solid, combustible organic matter in a mineral matrix, It contains organic matter in the form of kerogen. The other fraction called bitumen is soluble in organic solvent, but its total amount in the organic matter is small [1-3]. However, this organic matter rich in aromatic compounds could have other applications [4, 5]. Often shale oil contains significant amounts of olefins, aromatic compounds and heteroatoms, which make it compositionally different from conventional petroleum fuels [6]. It is a highly important unconventional petroleum product that has attracted increasing attention in the past several decades because of its massive geological reserves [7, 8]. Shale oil reserve in the world was up to 475 billion tons and 5.4 times equivalent to the natural oil, which would amount to a huge resource [9, 10]. It is important to note that the composition and properties of the shale oil can vary widely depending on the oil shale used and the retorting conditions [11, 12].

A lot of efforts and studies [13, 14] have been carried out to the direction of shale oil, whose world reserves are 500 times more important than those of oil [15], although the presence of mineral matter makes difficult its use as a source of energy. Also, oil shale have some potential for the production of several synthetic products such as cement, calcium, alumina, pitches, the carbon adsorbents, zeolites, carbon fibers and other chemicals. These various industrial applications of oil shale have generated in recent years many studies on methods for extracting these oils, such as soxhlet extraction, ultrasonic extraction, microwave irradiation, flotation technique, pyrolysis by conventional heating or under extraction with various solvents under sub and supercritical

conditions and combustion in fluidized bed reactors [16-21]. The organic matter of oil shale is accessible with much more significant yields by pyrolysis or supercritical extraction than by conventional extraction methods, just as the quality of the recovered oils depend on the operating conditions[21, 22] and the methods of extraction of organic matter from oil shale [23, 24]. Different organic solvents pure and combined were used for extraction [25, 26]. SCW has several potential applications, including extracting oil from oil shale lumps [27] and the cracking of heavy hydrocarbons into lighter fractions [28], thereby reducing the viscosity. Funazukuri et al. [29] studied supercritical fluid extraction of Chinese oil shale and found that polar components were more easily decomposed in SCW than in supercritical toluene (SCT). Yanik et al. [30] performed experiments to investigate the effect of pyrolysis, flash pyrolysis and SCW extraction on oil yield and the composition of the extract. The results showed that SCW extraction gave the highest oil yield, but this oil contained a high proportion of asphaltenes and polar compounds [22]. Olukcu et al. [31] reported that upgrading Beypazari oil shale in SCW gave a higher conversion but a lower oil yield than those in SCT. Oil obtained from SCT had more asphaltic and polar compounds than those from SCW. Wang et al. [32] studied the isothermal subcritical water extraction technique to extract organic matters from Huadian oil shale under different extraction conditions. The effects of particle size, extraction temperature, extraction time and water-oil shale mass ratio were investigated on the extracts yield. Similar results were obtained by Abu Al-Alla et al. [33] who also studied the effect of amount and type of solvent, time of extraction, and the temperature of retorting on the percentage yield of oil produced. They found that the percentage yield of oil increased as the volume of solvent increased the best result is obtained by using methanol as a solvent. The yield also increased by increasing time of extraction and stirring rate. El Harfi et al. [22], observed higher oil yields in SCW than in near pyrolysis conditions. Due to these interesting features and properties, supercritical fluid extraction (SFE) has received great efforts from many researchers [33-35].
Recently, Arrillaga et al. [36] use of water in hydrothermal and supercritical conditions as a medium to upgrade heavy oil fractions has shown promising results and presents an interesting alternative for heavy oil process. On the other hand, supercritical extraction of Jordanian oil shale was investigated experimentally using a batch autoclave device. Operating conditions such as solvent type, mixing time, temperature, pressure, and particle size effects on oil recovery from oil shale have been studied. The results indicated that oil yield increases with the increase of pressure and temperature. The maximum extract yields of 15 and 16 wt% were obtained at 42 bars and 318°C with toluene for El-Lajjun and Sultani oil shales, respectively. SFE has shown to be an efficient technique since the extracted yield was 55% more than the yield obtained using the classical Fischer Assay retorting process [37].
The aim objectives of present study were to investigate the effect of the mineral matrix and the type of solvent on the supercritical water extraction of Moroccan oil shale (Timahdit area) to establish the best operating conditions likely to give a good yield of recovery with the best oil quality.

2. Material and Methods

2.1. Precursor material

Oil shale deposits have been identified at ten localities in Morocco. The two deposits that have been explored most extensively are the Timahdit and the Tarfaya deposits; about 69000 analyses have been made of samples from 157 boreholes totalling 34632 m in length and from 800 m of mine workings.
The Timahdit deposit, located about 250 km southeast of Rabat, underlies an area about 70 km long and 4 to10 km wide within a north east-trending syncline (Figure 1). The moisture content ranges from 6 to 11 percent, and the sulphur content averages 2 percent. Total oil shale reserves are estimated at 18 billion tons within an area of 196 km^2, oil yields range from 20 to 100 L/t and average 70 L/t.

The oil shale specimen used in this investigation was obtained from the Timahdit (provide by the ONAREP: National Office of Petroleum Research and Exploitation) located in the mid-Atlas mountain at 35 km in the south of Azzrou. This deposit is a vein of oil shale 100–150 m in thickness and comprising several layers with variable contents of organic material [39]. The layer studied in this work is the Y layer whose mineralogical composition is illustrated in Table 1.

The raw rock (Y) were crushed, then ground in an electric grinder until we get a fine powder with a particle size <200 µm. At a mass of the powder (Y) was leached with concentrated hydrochloric acid (6N) [41, 42] and with stirring until no release of carbon dioxide [43]. Reactions that result from this process are:

$$CaCO_3 + 2HCl \longrightarrow CO_2 + CaCl_2 + H_2O \quad (1)$$

$$CaMg(CO_3)_2 + 4HCl \longrightarrow 2CO_2 + CaCl_2 + MgCl_2 + 2H_2O \quad (2)$$

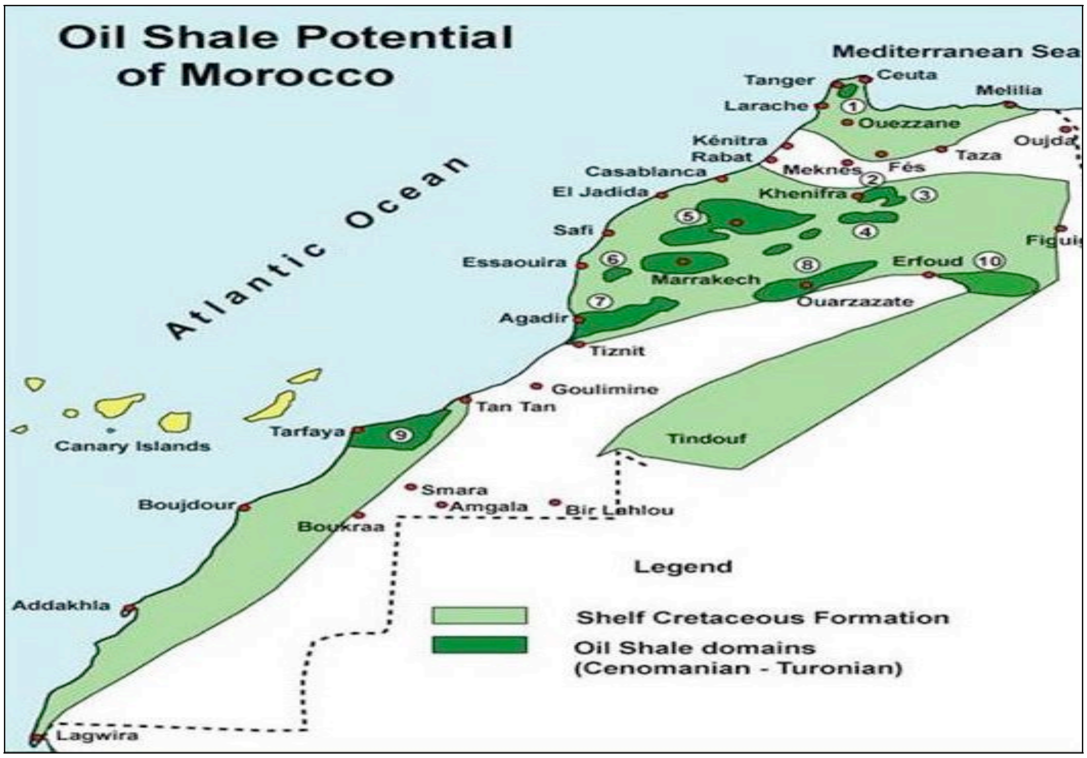

Figure 1: Oil shale deposits in Morocco [38].

Table 1: Mineralogical composition of Timahdit oil shale (Y layer) [40]

Compound	Calcite	Dolomite	Silica	Clay and other	Organic material
% by Weight	15.2	12.2	21.8	26.9	23.9

After filtration, the residue was washed by distilled water to eliminate excess acid. The product obtained, referred to as YH, then dried in oven at about 110 °C and stored for a possible future use (figure 2).

Figure 2: Fully-crushed oil shale.

2.2- Apparatus
An autoclave (high pressure reactor) manufactured by Amar equipment PVT. LTD. was used in this work. Figure 3 represent a photograph of the extraction unit. The autoclave consists of a stainless steel cylindrical vessel of 750 mL of capacity. The cylinder contains an agitator consisting of a Magnetic drive on a vertical shaft driven by an electric motor. An electric heating (furnace) is used for the heating process and a water cooling coil around the vessel is used for cooling. The temperature of the reactor was maintained at a desired temperature by using an on-off temperature controller (control panel).

2.3- Procedure
The oil shale (Y or YH) and solvent were placed in the vessel of the autoclave device. The autoclave's cover was placed over the vessel and closed tightly to ensure that no leakage takes place. After that, the unit was

heated to the desired temperature at a heating rate of 10 °C/min, and then kept at supercritical temperature of each solvent for the required period.

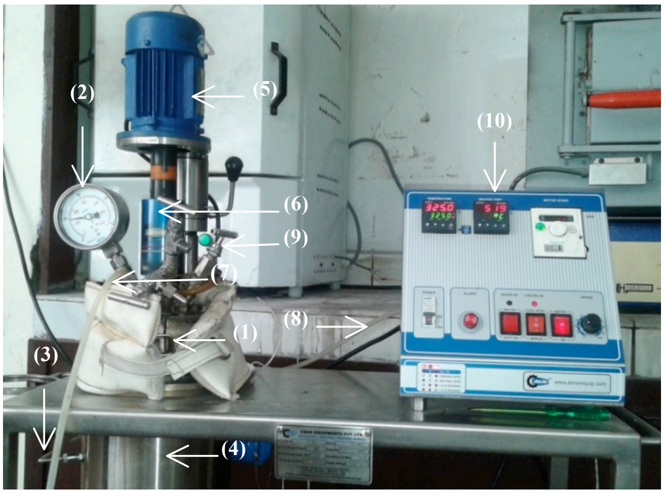

Figure 3: Photograph of the apparatus used for sub-critical water extraction
1. Autoclave stand; 2. Manometer; 3. Thermocouple; 4. Furnace; 5. Electric stirrer motor; 6. Magnetic drive; 7. Inlet cooling water; 8. Outlet cooling water; 9. Gas outlet valve; 10. Control panel (Temperature, Motor speed,…).

The heating rate of the device was measured experimentally and by plotting the reactor temperature versus time. At the end of each experiment, the extractor vessel was cooled down to a temperature less than the boiling point of the solvent using circulating tap water through the cooling coil of the autoclave device. Then, the extractor was depressurized and the contents were removed, filtered, and washed with water. After being cooled to room temperature, the mixture was extracted by soxhlet apparatus with 200 mL of chloroform which was heated at 40°C for 12h [4]. The shale oil was recovered by removed the solvent under reduced pressure using rotary evaporator, and was dried at 40°C for 12h [4] and weighed. The shale oil yield was determined by the following relationship.

$$\text{Oil (\%)} = \frac{m_E}{m_0} \text{x}100 \qquad (3)$$

Where m_0(g) and m_E(g) are the mass of the organic material contained in the raw oil shale (Y) and oil shale decarbonized (YH) the mass of the extract, respectively.

2.4- Analyses
Infrared (IR) spectra were recorded between 400 and 4000 cm^{-1} with a BURKER TENSOR 27 FT-IR spectrometer by summing 32 scans at 2 cm^{-1} resolution. Pellets were prepared by dispersing 2 mg of raw oil shale (or oil shale decarbonized) into 198 mg of potassium bromide (KBr). IR Spectra were obtained with a resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Characterization of Precursor material
An infrared analysis was performed on raw oil shale (Y) and the oil shale decarbonized (YH). IR spectrum shown in Figure 4 and all the band assignments are listed in Table 2. IR spectrum showed signification change in position of peaks. After decarbonization process, we note the disappearance of the bands located at 1426 cm^{-1}, 878 cm^{-1} and 707 cm^{-1} is the characteristic of carbonate ($CaCO_3$) and the bands corresponds of organic material (OM) of oil shale remains unchanged.

3.2. Mineral matrix and solvent effect on extraction yield of shale oil
To study the influence of mineral matrix and the type of solvent on the extraction yield of shale oil, a various experiments was performed to different solvents (water, limewater, OMW and toluene), the amount of solvent, time of contact and the supercritical temperature of each solvent [4] remaining constant. The results of this various experiments are given in Table 3 and Table 4 in Figure 5.

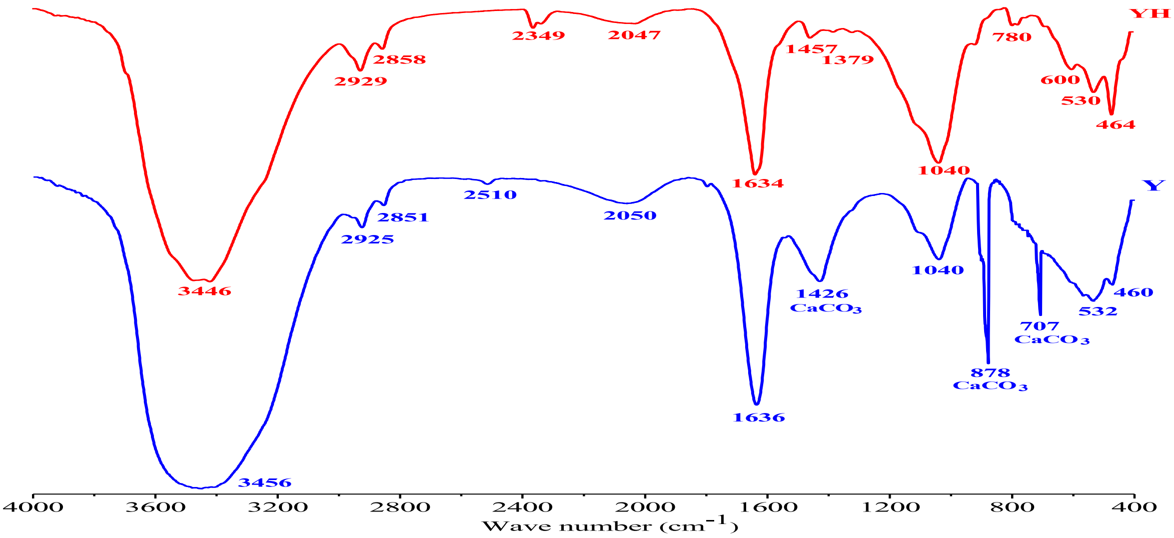

Figure 4: FT-IR spectrum of raw oil shale (Y) and the oil shale decarbonized (YH).

Table 2: Major bands in the infrared spectra of raw oil shale (Y)

bands (cm^{-1})	Assignments	References
3456	O–H stretching vibrations (alcoholic, phenolic, carboxylic)	[44]
2925	C–H stretching (CH_2 et CH_3, asym)	[44]
2851	C–H stretching (CH_2, asym)	[44]
2510	S–H bending	[45]
2050	C≡C bending	[46]
1636	C=O stretching (carbonyls et carboxyls)	[45, 46]
1426	$CaCO_3$ bending (calcium carbonate)	[47]
1040	C–C bending (aliphatic and aromatic alkane)	[48]
707, 878	$CaCO_3$ stretching (calcium carbonate)	[47]
530, 460	C-H bending (aliphatic alkane)	[48]

Table 3: Solvent effect on supercritical water extraction process of raw oil shale (**Y**)

Solvent	Amount of solvent (g)	Temperature (°C)	Pressure (bar)	[a]Oil yield (%)
Water	50	374	212	10.38
Limewater	50	374	194	14.78
OMW	50	374	136	**18.56**
Toluene	50	320	48	12.26

[a]Calculated from the amount of OM contained in Y: 25 g of Y contains 5.98 g of OM.

Table 4: Solvent effect on supercritical water extraction process of oil shale decarbonized (**YH**)

Solvent	Amount of solvent (g)	Temperature (°C)	Pressure (bar)	[b]Oil yield (%)
Water	50	374[c]	208	14.85
Limewater	50	374[c]	190	21.26
OMW	50	374[c]	132	**26.16**
Toluene	50	320[c]	45	17.74

[b]Calculated from the amount of OM contained in YH: 25 g of YH contains 9.25 g of OM.
[c]supercritical temperature of solvent.

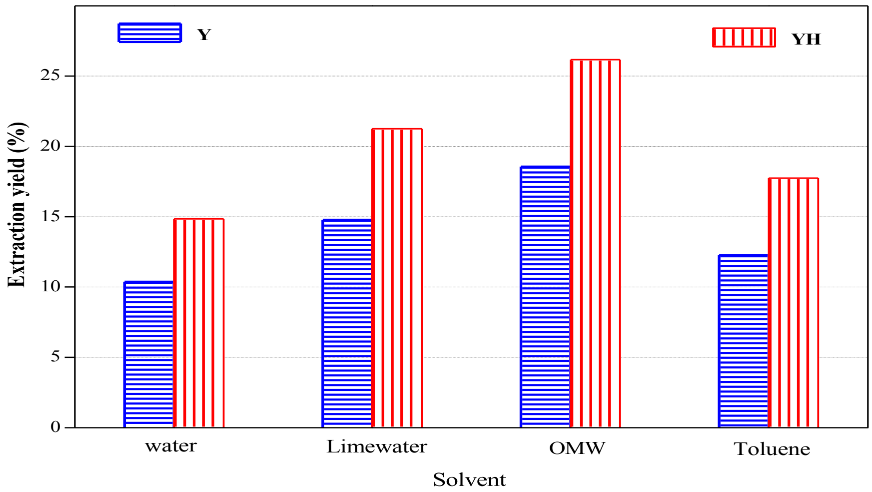

Figure 5: Effect of mineral matrix and solvent on extraction yield

The effect of solvents on extraction yields was studied by a few experiments as shown in Figure 5. For comparison, it can be seen that OMW is the strongest solvating power than the other solvents, it have given the lowest oil than the other solvents. On the other part, that the amount of organic material recovered from YH is more important than that recovered from the raw rock Y at supercritical temperature of each solvent [4], which shows the influence of the mineral matrix on extraction. This result can be explained by the fact that crude oil shale contains carbonates that have a high porosity [24] which results in a retention of organic matter through the pores of the mineral. If the force of attraction between the bitumen and the solvent is greater than that between the solvent molecules or of the dissolution of the bitumen, then the bitumen can be easily extracted [49]. Different organic solvents pure and combined were used for extraction [50, 51].

3.3. Effect of the polyphenols of OMW on the extraction yield of organic materials

To study the effect of polyphenols of OMW on the extraction yield, three experiments was performed to different solvent, the other parameters remaining constant. The results of extraction solid-liquid of experiments are given in Table 5.

Table 5: Effect of polyphenols of OMW on supercritical water extraction process of oil yield

Solvent	Quantity of OMW (g)	Temperature (°C)	^{b}Oil yield (%)
Raw OMW (without treatment)	50	374	**26.16**
Delipidated OMW	50	374	18.26
Dephenolated OMW	50	374	10.26

^{b} Calculated from the amount of OM contained in the YH: 25 g of YH contains 9.25 g of OM.

The results of Table 4 show that raw OMW had a significant effect on the amount of OM extracted, On the other hand, the dephenolization of the OMW reduces the extraction yield, it shows that the polyphenols of the OMW have a great degrading power of the organic material. This result has been observed by several works [24, 45, 52] in the extraction of the Tarfaya oil shale by different solvents, they have found that phenol is the power extraction solvent. And this trend may be due to that the rate of extraction of bitumen depends on the type of organic solvent used so if the force of attraction between bitumen and solvent is greater than that between the solvent molecules of the dissolution of bitumen, then bitumen can be easily extracted.

3.4. Analysis of shale oil extract by OMW

The FT-IR spectrum of the shale oil extract referred HYHW (figure 6), shows that the sample is rich in carbon and oxygen. The relatively high intensity of the broad OH band is found at 3460 cm^{-1}. The sharp bands at 2960 cm^{-1}, 2925 cm^{-1} and 2851 cm^{-1} are due to aliphatic C-H stretching of CH_3 and CH_2 and deformation vibrations [45]. It was also observed that the peaks at 2368 cm^{-1} and 2336 cm^{-1} represent (C ≡ C) bonds [46]. The band at 1706 cm^{-1} belongs to the C=O stretching vibration of carboxyl and carbonyl groups [52, 47]. The strong band at

1626 cm^{-1} is due to aromatic C=C stretching, and bands located at 1055 cm^{-1} and 1216 cm^{-1} region are assigned to C-O vibrations of various functions (esters, alcohols,…) [53]. The peak at 1455 cm^{-1} is due to the C-H bending of CH_3 [53]. The IR spectra show an intense aromatic matrix in the oil shale and successive aromatic band of C-H and C-C (885 and 610 cm^{-1}) are due to high organic matter content of the sample [54, 55].We also note the disappearance of the bands located at 530 cm^{-1} and 464 cm^{-1} is the characteristic of alkane.

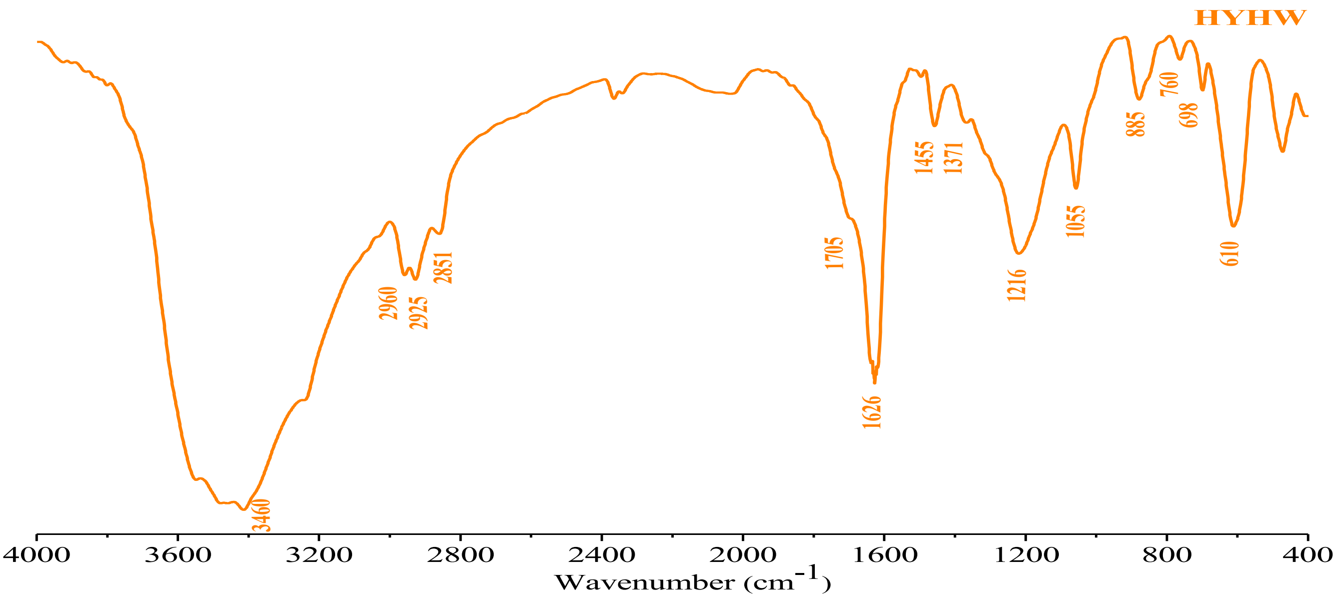

Figure 6: FT-IR spectrum of oil shale extract.

Conclusion

In this work, the supercritical water extraction technique has been investigated using Moroccan oil shale deposits such as Timahdit area. The important parameters that may affect the mechanism of oil production such mineral matrix and type of solvent will be examined. The result show that the yield of the oil produced depends on the solvent and the type of material used to extract the organic material of oil shale: raw oil shale, oil shale decarbonized. The oil yield obtained by olive oil mill wastewater extraction is significantly higher than those obtained by other solvents. The FT-IR spectra show that, the extracted oil containing a substantial proportion of aromatic hydrocarbon compounds and fewer amounts of paraffins. However for a sustainable environment and to try to address environmental issues, we could develop these effluents (liquid wastes) as a natural solvent of extraction of Moroccan oil shale.

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