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# New Integral Processes Enrichment of Moroccan Oil Shale using Mineral and Hydrometallurgical Methods

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## ABSTRACT

*In this work, we increase the calorific value of Moroccan oil shale, which is the main element in the combustion of fossil fuels. In particular, we consider the shale of Timahdit, enriching it by hydrometallurgical and mineral processing methods in order to use it to generate thermal and electrical energy. Although different studies have been conducted for the development of Moroccan oil shale, but they have not dealt with the axis as we have. Direct combustion of raw shale is difficult due to the presence of high carbonate content with 23.2% in the Timahdit oil shale and 40.2% in Tarfaya, and a total content of organic matter, respectively 17.7 and 16.25% [Bekri O. Possibilities for oil shale Development in Morocco. CAER-University of Kentucky, Center for Applied Energy Research 1992. 3(5) ]. During pyrolysis of raw shale, organic waste (residual carbon) obtained for both shales depends on the rate of heating (5 to $40°Cmin^{-1}$) [Barkia H., Belkir L. and Jayaweera S. A. A. Journal of Thermal Analysis and Calorimetry 2003. 71. 97p]. It turns out that there are three phases in the whole process: first, the concentration of carbon residue decreases with increasing heating rate. It stabilizes around $12°Cmin^{-1}$, then it continues to decrease at higher heating rates. The activation energies are determined using the Coats-Redfern. Our results in this paper show a change in the reaction mechanism at around 350°C. Below this temperature, the activation energy is $41.3 kJmol^{-1}$ for the decomposition of Timahtid oil shale, and $40.5 kJmol^{-1}$ for Tarfaya oil shale. Otherwise, the respective values are 64.3 and $61.3 kJmol^{-1}$. Using Timahdit oil shale of initial kerogen content of 17.7%, calorific value 1436 kcal/kg, and by performing a physicochemical treatment, we augment the organic matter to 60%. We get a calorific value $\geq 4500$ kcal/kg and remnant products (sous-products), which depend on the nature of the used acid.*

***Keywords***: *Leaching, combustion, carbon, kinetics, oil shale, thermogravimetry, enrichment, calorific value, by-products: $CaCl_2$, $CaSO_4$, $Ca_3 (PO_4)_2$, and ash*

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## INTRODUCTION

Currently, the global dependence on energy is affixed. The raw materials required for energy production, which is the nerve center of a growing global economy, have fueled a tremendous competition not only among developed countries but also the countries in development to gain a monopoly. So, after conventional resources such as oil, gas, and coal there are those so-called unconventional resources such as oil, gas extracted from oil shale for its direct use in energy production. Morocco holds a large reserve of one of these indigenous energy sources including 15% of global oil shale, and given that Morocco imports more than 90% of its energy, the exploitation of this resource allows Morocco not only to produce shale oil and gas by pyrolysis, but also electricity by direct combustion [1]. The resulting ash is a potential material for cement and the road construction

industries. Attention has been focused on the most important Moroccan deposits of Timahdit and Tarfaya oil shale [2–4]. There is an important difference between oil shale, coal, and tar in their mineral content, as oil shale has a mineral content of 33% or higher, much higher than that of coal and tar [2]. Extensive studies have been conducted on the physical and chemical properties of Timahdit and Tarfaya oil shale to commercially exploit these deposits [5, 6]. Oil shales are very heterogeneous in their chemical composition and physical property. Thus, during their thermal decomposition, a complex set of sequential and parallel reactions occur, for example, changes in water vapor, the conversion of kerogen to bitumen, their dissociation into hydrocarbons of low volatility and high volatility (gas and oil), oxidation of residual carbon, etc. In the treatment of oil shale, combustion results in fully oxidized products, while pyrolysis leads to condensable products and a solid residue; Crawford et al. have discussed the enthalpies of combustion for samples of raw and spent oil shale [7]. Docker showed that shale having an oil content of more than 83 $dm^3 ton^{-1}$ produce sufficient coke, complete combustion of which can produce sufficient energy for retorting the oil shale [8]. In this work, we developed new methods to increase the calorific value of Moroccan oil shale, which is poor in kerogen but rich in carbonates and clays, which are characterized by intimate physicochemical liaison between the organic matter (kerogen)

and mineral gangue. The objectives of these wet processes, in particular, were to liberate the kerogen and separate it from the mineral phase by leaching dilute acid followed by a flotation, depending on the chemical reagents used (hydrochloric acid, sulfuric acid, or phosphoric acid). In this paper, we achieved rich shales with an organic matter content greater than or equal to 60% depending on the nature of the acid used, which can be used directly as fuel to generate thermal and electricity energy because of its calorific value, or they may undergo pyrolysis to prepare oil shales. Thus, from the Timahdit oil shale with a grading of 17.7 and 23.2% kerogen carbonates, 45% quartz, pyrite, clays, and other minerals, we obtained oil shale containing 60% enriched kerogen, 0% carbonates, and remnants were clays and quartz that remained bound to the kerogen structure. The remnant products of these processes are $CaCl_2$, $CaSO_4$, $Ca_3 (PO_4)_2$, and ash extracted from the combustion of oil shale enriched. This work is part of a larger program to study the combustion and thermal analysis of Moroccan oil shale.

## EXPERIMENT

### Apparatus

In this section, we explain our experimental work, in particular, the samples on which we worked, the separation process, the calorific value, as well as the devices that have been used. For the separation, we used the flotation

method and acid attacks with a stirring reactor. The calorific value has been determined by using an adiabatic calorimeter with a pressure of 30 bar in a calorimetric bomb, using a sample of 0.5 g.

**Samples**

The oil shale samples used in this work have been obtained from Timahdit and Tarfaya deposit (Morocco). Table I shows the general characteristics of the two slates

**Table I** The General Characteristics of the Two Slates.

| Characteristics | Timahdit | Tarfaya |
|:---:|:---:|:---:|
| Humidity (%wt) | 7.0 | 17.5 |
| Density (g/cm³) | 2.423 | 2.276 |
| PCS (Kcal/kg) | 1436 | 1100 |
| Oil (1/t) | 85 | 74 |
| $CO_3$ (%wt) | 23.2 | 40.2 |
| Kerogen (%wt) | 17.7 | 16.26 |
| Ash (%wt) | 65.3 | 54.9 |
| Carb. org (%wt) | 12.9 | 11.3 |
| Carb. min. (%wt) | 4.6 | 8.0 |
| Carb. tot. (%wt) | 17.5 | 19.3 |
| Soufre. org. (%wt) | 1.6 | 1.7 |
| Soufre. min. (%wt) | 0.7 | 0.3 |
| Soufre. tot. (%wt) | 2.3 | 2.0 |

For each heating in the oil shale, the rate was determined after heating all the samples in flowing nitrogen atmosphere (35 cm³min⁻¹) at 500°C and holding for 1 h at this temperature. Air was then introduced to obtain the amount of organic carbon remaining in the shale [9]. Figure 1 shows the extent of reaction where $\alpha$ is a function of temperature for Timahdit and

Tarfaya oil shale crude to four heating rates ranging from 5 to 40°Cmin⁻¹. For both shale, thermal decomposition began at 200°C and reached a maximum rate around 420°C for the lowest heating rate and moved to higher temperatures with increasing heating rate.
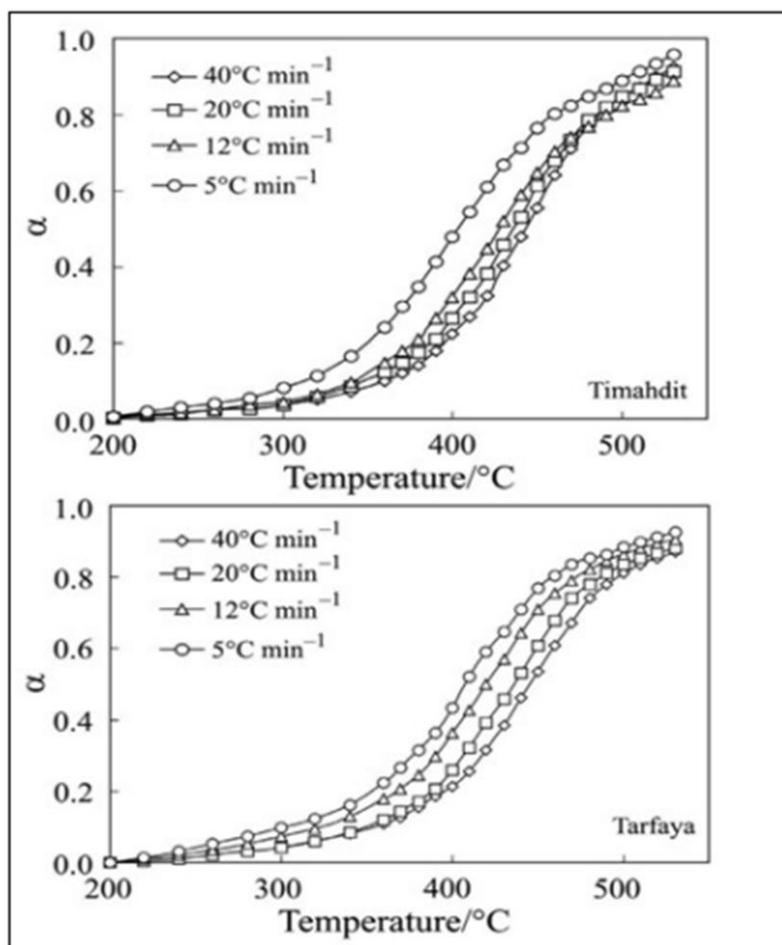
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**Fig. 1** The extent of reaction where α is a function of temperature.

## RESULTS AND DISCUSSION

### Preparation and Combustion of Kerogen from Timahdit Oil Shale

To have a reference sample of isolated kerogen (standard), we processed a single batch of Timahdit oil shale (crushed to a particle size less than 2 mm) by HCl/HF to isolate almost all of kerogen with 96% organic matter content. The objective of the leaching is to destroy existing liaison between carbonates, kerogen, and clays without affecting the organic matter. Thus, the role of HCl is to dissolve the carbonates, while HF can destroy the clay to liberate the kerogen. This method of isolation of kerogen is very expensive; it is only of analytical interest.

### Methods of Attacks by SBB Acids

After grinding SBB (raw oil shale) to a particle size of about 2 mm, the product is placed in a flotation reactor. Liquid phase is separated slowly to avoid foaming and oxidation and diluted thrice with hydrochloric acid, sulfuric

acid, or phosphoric acid with a mechanical stirring until the total release of carbon dioxide. This selective leaching process lasts 2 h. After the carbonate attack, the pH of the reaction mixture should be 1.5 to 2. Then, the separation procedure of solid phase depends on the acid used: in case sulfuric acid is used and a frother such as methyl iso-butyl ketone (MIBC) is added, we get schisto-gypsum ($CaSO_4$) and a part of clay. The non-float is composed mainly of shale-enriched SBES. In case of the use of phosphoric acid, we add the reagent in excess to prevent the formation of solid $Ca_3(PO_4)_2$, which complicates the operation of phase separation in the flotation cell containing a mixture of oil shale enriched (SBEP) mixed with clays, silica, and $Ca^{++}+H_2PO_4^-$ to a pH below 2. The procedure of separation from the aqueous phase to solid phases is by filtration, and then the separation of clay and silica is done by reverse flotation. Thus, the resultant non-float is composed mainly of oil shale enriched (SBEP) to 60%. In the case of using hydrochloric acid, there is one single solid phase, consisting of just filteration and washing to isolate enriched oil shale (SBECl). These methods have been submitted to the national patent office in the Moroccan Industrial and Commercial Protection (OMPIC) filed on 08/09/2009, application number 32207. Depending of the acid used, we obtained either liquid discharge due to the reactions of bases $Ca^{++}+2Cl^-$ with hydrochloric acid:

$$CaCO_3+2HCl \rightarrow Ca^{++}+2Cl^-+CO_2 \qquad (1)$$
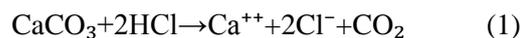
or a strong rejection ($CaSO_4$) in the case of sulfuric acid:

$$CaCO_3+H_2SO_4 \rightarrow CaSO_4+H_2O+CO_2 \qquad (2)$$

or $Ca_3(PO_4)_2$ solid after neutralization with slaked lime:

$$Ca^{++},2H_2PO_4^-+2OH^- \rightarrow Ca_3\,(PO_4)_{2solid}+2H_2O \qquad (3)$$
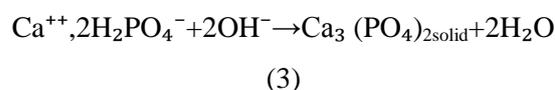
These results led us to propose three processes that we have given according to Figure 2. The photos 1, 2, 3, 5, 6, 7, 8, and 9 in Figure 3 show successively isolated samples of:

(i). Crude oil shale (SB) Timahdit crushed to 2 mm
(ii). SB Timahdit kerogen isolated for use as a standard to 96% organic matter
(iii). Shale enriched by attack with HCl (SBECl)
(iv). Shale enriched by attack with $HSO_4$ (SBES)
(v). Shale enriched by attack with $H_3PO_4$ (SBEP)
(vi). $CaCl_2$ residue obtained after evaporation of water
(vii). $CaSO_4$ from the $H_2SO_4$ attack
(viii). $Ca_3\,(PO_4)_2$ obtained by $H_3PO_4$ attack
(ix). The ashes from the complete combustion of shale enriched

Photos 10 and 11 show the flotation cell used for the separation phase and direct test of combustion of oil shale obtained. The secondary products obtained from three lanes $CaCl_2$, $CaSO_4$, and $Ca_3(PO_4)_2$ and ash from the combustion of SBE have a chemical value. The advantages of using sulfuric acid or phosphoric acid instead of hydrochloric acid are multiple:

- Sulphuric acid is cheaper than hydrochloric acid.
- The attack by hydrochloric acid (HCl) releases more toxic gas that is harmful to the environment.

- Sulfuric acid and phosphoric acid are less corrosive than hydrochloric acid.
- Attacks by sulfuric acid or phosphoric acid lead to the production of solid waste such as calcium sulfate ($CaSO_4$) and calcium phosphate ($Ca_3(PO_4)_2$) that can be readily isolated. But attack by hydrochloric acid lead to ($Ca^{++}+2Cl^-$) solutions that are difficult to evaporate and isolation of solid $CaCl_2$ is very hygroscopic.
- Phosphoric acid is a national product of value for treating rich oil shale because we can regain the phosphate $Ca_3(PO_4)_2$ after neutralization with caustic soda.



**Enrichment diagram**
**For a ton of raw oil shale crushed to 2mm**
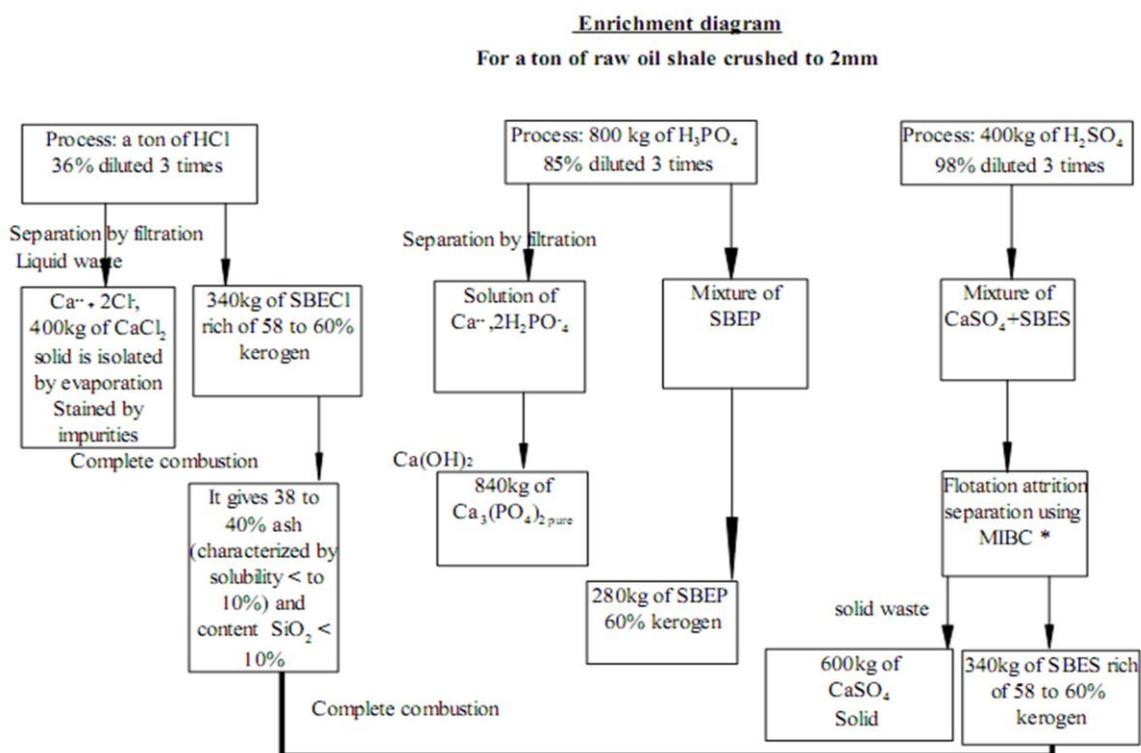
**Fig. 2** Enrichment diagram.
MIBC (Methyl Isobutyl Ketone)
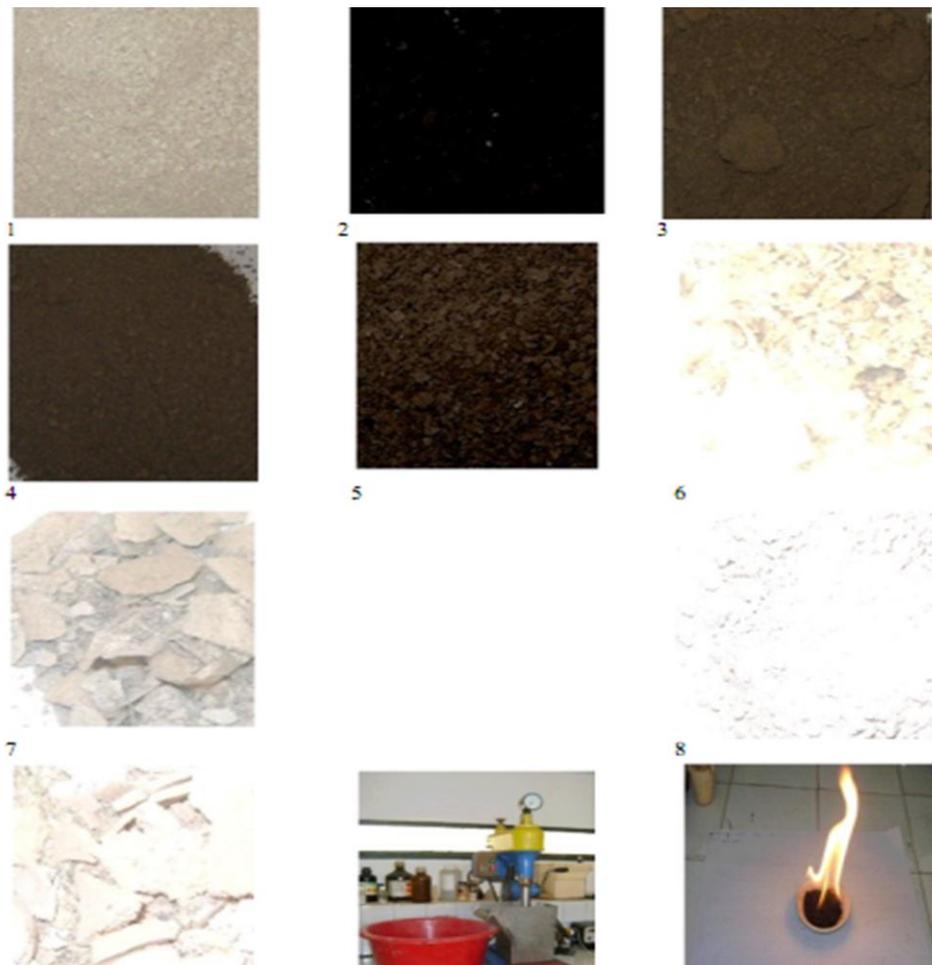
**Fig. 3** Photos 1, 2, 3, 5, 6, 7, 8, and 9 are successively isolated samples.

1. SB Timahdit 2. Kerogen SB Timahdit standard 3. SBECl 4. SBES 5. SBEP 6. Residual $CaCl_2$ obtained after evaporation of water 7. $CaSO_4$ from the $H_2SO_4$ attack 8. $Ca_3(PO_4)_2$ obtained by means of $H_3PO_4$ attack 9. The ashes from the complete combustion of shale enriched 10. The flotation cell used for phase separation 11. The test of direct combustion of oil shale obtained.

**Calorific Power**

Use of oil shale of higher calorific value improves the technical efficiency of the equipment used [10]. Transportation expenditures are reduced. Also, use of oil shale of higher heat value results in reduced amounts of ash. The useful component of oil shale is kerogen (organic matter). The main quality indicators are calorific value (Q) and oil yield (T). Calorific value and oil yield of oil shale are proportional to kerogen content. If kerogen's calorific value is $\xi \pm \varepsilon MJ/kg$, the formula of oil shale calorific value is:

$$Q = \xi K, \text{ MJ/kg} \quad (4)$$

Where K is the share of kerogen (100% = 1), and oil yield is:

$$T = \Gamma K = (\Gamma/\xi) Q\% \qquad (5)$$

Where $\Gamma$ is the coefficient of proportionality between T and K.

There are two sources of $CO_2$ from oil shale combustion: decay of carbonate minerals and combustion of kerogen. Higher heat value of oil shale indicates lower share of carbonate minerals and this can be improved by using different treating techniques in mines. The $CO_2$ from combustion of kerogen will be introduced as carbonous $CO_2$ but decreasing it is not possible by mining. The amount of $CO_2$ formed by full decay of carbonate minerals of oil shale also depends on the content of organic matter in fuel. Ash content also depends on the quality of oil shale. Our enrichment methods of Moroccans oil shale, in particular that of Timahdit, allowed us to not only to increase the quantity of organic matter, but also to triple their heat in passing from 1436 kcal/kj to 4500 kcal/kj and more depending on the nature of the acid used. (Table II).

**Table II** Calorific Value by Different Reagents.

| Acids | HCl/HF | HCl | $H_2SO_4$ | $H_3PO_4$ |
|---|---|---|---|---|
| PCS (kcal/kg) | 4705 | 4700 | 4600 | 4500 |

**CONCLUSIONS**

In this paper, we have developed new methods to increase the value of Moroccan oil shale. In particular, we have dealt with Timahdit shale, which have been enriched by using hydrometallurgical and mineral processing methods. Among other results, we have shown that the calorific value, being the main element in the combustion of fossil fuels, gets increased. This result displays an interesting medium in the direct combustion of oil shale. It also influences positively in the pyrolysis process for extracting oil shale. Enrichment through hydrometallurgical processes has allowed us to increase the content of Timahdit oil shale kerogen from 17.7 to 60%, the calorific value from 1436 to more than 4500 kcal/kg, and generate by-products of great value that opens new ways to develop research into industrial applications, including preparation for the manufacture of pure phosphates.

**ABBREVIATIONS**

SB: oil shale
SBE: shale enriched
SBECl: shale enriched by HCl
SBES: shale enriched by $H_2SO_4$
SBEP: shale enriched with $H_3PO_4$

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