

## New Approach of Retorting of Huadian Oil Shale in Order to Reduce CO and CO<sub>2</sub> Emissions

Guy Roland Nguimbi<sup>1</sup>, Sun Youhong<sup>1</sup>, Phiri Cryton<sup>2</sup>

<sup>1</sup>Jilin University, No. 6 Ximinzhu Street, Changchun 130026, China

<sup>2</sup>College of Earth Science, Jilin University, Changchun 130061, China,

**Abstract:** - The combustion of oil shale can extract the kerogen and later transform the kerogen in to heavy oil .The only drawback of this technique is the decarbonation of mineral matter in shale by high temperatures. This process causes 60% to 70% of the CO<sub>2</sub> and CO emissions. The decarbonation of CaCO<sub>3</sub> and oxidation of fixed carbon causes the formation of CO<sub>2</sub> and CO .The aim of this study is to avoid the decarbonation by decreasing the temperature in the retort of combustion. During this experiment we tested the impact of two parameters: Firstly, decreasing the quantity of fixed carbon in the medium of combustion and secondly, increasing the amount of carbonates which acts as heat dissipater. It is demonstrated that increasing the amount of carbonates may only decrease the medium of combustion to temperatures not lower than 830°C which is still so high to avoid decarbonation. Moreover, the temperature can be decreased to avoid decarbonation by reducing the quantity of fixed carbon .When the medium reached the low temperatures, nearly all the fixed carbon is oxidized. In high temperatures decarbonation of the mineral matter present in oil shale produce huge emissions of CO<sub>2</sub>. We show, in this paper a new approach to controlling the temperature of the combustion to prevent this decarbonation .

**Keywords:** - decarbonation, Electrical combustion , Huadian , Oil shale

### I. INTRODUCTION

As the demand for energy is greatly increasing throughout the world, unconventional oil shale is regarded as a potential energy source to substitute oil and natural gas. And this has attracted researchers' attention for many years [1].The reserve for oil shale stands out as very important source of substitutes for petroleum. [2,3] Oil obtained from shale is similar products to those obtained from petroleum. [4] The thermal decomposition of oil shale, known as retorting or pyrolysis, converts the shale's solid organic material into liquid and gas. [5,6] This process on the other hand is a source of severe environmental pollutions.[7,8] During the recent past 10 years, one of the main problems of the oil shale industry has been to find an effective method of extracting Oil from oil shale with reduced emissions of large quantities of CO<sub>2</sub> from decarbonation. [9]

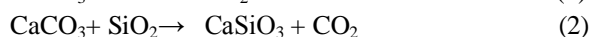
The major problem to oil shale industry is to find a process to recover oil from shale with less or without emission of CO<sub>2</sub>. Recently the retorting of oil shale has attracted the interest of many researchers [10,11,12], although most of research studies are concentrated on the method of retorting and the parameters of retorting oil shale. [12,13] However, our study focuses on the method to reduce the quantity of CO<sub>2</sub> and CO emission during retorting oil shale by controlling the temperature.

Huadian Oil shale composition has been studied by many researchers [10,14].Oil shale is a sedimentary rock consists of organic material (kerogen) [15], bitumen and inorganic matrix of quartz, Feldspars, clay and different types of carbonates (calcite, dolomite), pyrite and trace elements (Fe, V, Mo, Ni, Zn).

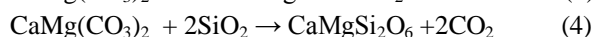
The decomposition of carbonate minerals such as calcite (CaCO<sub>3</sub>) and dolomite (MgCO<sub>3</sub>), during oil shale retorting are responsible for CO<sub>2</sub> emission. In this work, we refer these carbonate minerals as CaCO<sub>3</sub>.

The combustion of carbonates has been studied by Jeremy [9] and shown below:

**Calcite:**



**Dolomite:**



The above reactions occur when temperatures are up to 800°C.

Our objective is to reduce the temperature during retorting of Huadian oil shale, in order to avoid decarbonation of CaCO<sub>3</sub> which produce CO<sub>2</sub> and CO emissions. Controlling the temperature is necessary because during the heating process, the high temperature decarbonates the large quantities of mineral matter present in oil shale.

We demonstrated in this paper a new approach for controlling the temperature of the combustion to prevent this decarbonation. We have also attempted to show the influence of the proportions of calcium carbonate and the fixed carbon oxidization has on combustion.

We want especially to answer the following question: is it possible to extract oil in shale without decarbonating the calcium carbonate (CaCO<sub>3</sub>)? If yes, can we consider it as an alternative to the mixture of oil shale, calcium carbonate and sand to decrease the combustion temperature and prevent decarbonation and facilitate the Carbonation of CaO. This research concerns a process and an apparatus for extracting the kerogen from oil shale without negatively affecting the environment.

Martins [16,17] reported that the production of oil from oil shale by the pyrolysis process consists of many reactions including drying, devolatilization, FC oxidation and decarbonation of CaCO<sub>3</sub>. However, Fixed carbon (FC) oxidation and decarbonation of CaCO<sub>3</sub> are the most important reaction for the conversion of kerogen to bitumen and emission of CO<sub>2</sub> and CO during combustion of oil shale. Fixed Carbon Oxidation: this reaction has so many intermediate reactions which results in the production of CO<sub>2</sub> and CO. This reaction have been investigated by several researchers [18,9] it occur between 300°C and 550°C according to the simplified reactions below:



Under 500°C the combustion of oil shale generates: volatile matter, CaCO<sub>3</sub>, and inert matter and CO<sub>2</sub>. The CO<sub>2</sub> produced under this temperature represents 30% of the total CO<sub>2</sub> produced compared to the normal combustion. Less than 500°C the pyrolysis of oil shale is done without decarbonation.

Based on mass and flue-gas analysis it is possible to determine the the proportion of FC oxidized to CO, and the fraction of CaCO<sub>3</sub> that is decarbonated.

Decarbonation of CaCO<sub>3</sub> and carbonation of CaO; This reaction plays a major role during combustion of oil shale. Furthermore the decarbonation of CaO undergoes carbonation to CaCO<sub>3</sub>. The carbonation of CaO consumes CO<sub>2</sub>. [19]

In this work we demonstrate the decarbonation of CaCO<sub>3</sub> to produce CaO that in inturn undergoes carbonation to CaCO<sub>3</sub>. This theory is only proposed here for the interpretation of our experimental results. By reducing the temperature when the temperature is decreased we can totally avoid the decarbonation reaction and remain with the FC oxidation.

The decarbonation reaction of CaCO<sub>3</sub> is written as:



The carbonation reaction has been studied for a long time [20] according of the following reaction:



This reaction of decarbonation of CaCO<sub>3</sub> occur above 750°C [21].

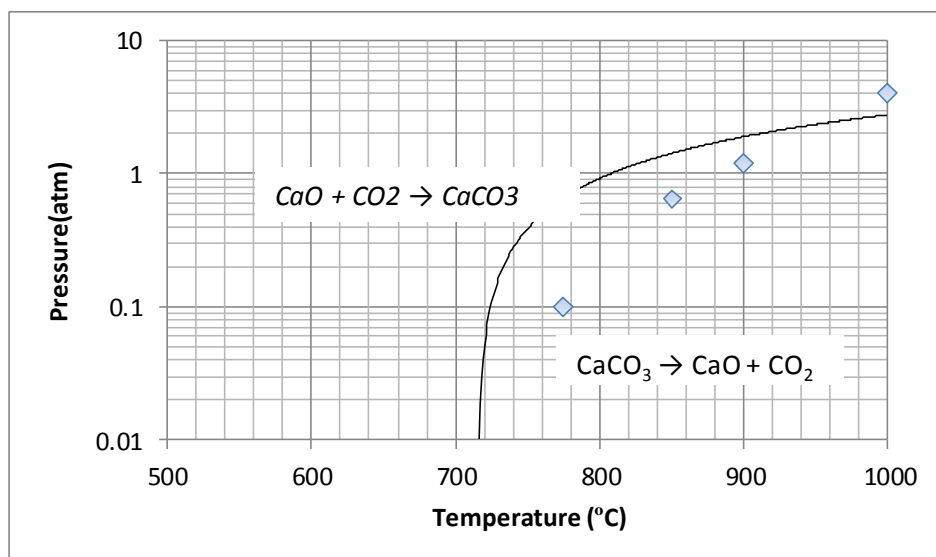


Figure 3. Equilibrium pressure in the temperature of CO<sub>2</sub> over CaCO<sub>3</sub>. Modified after [21]

This invention concerns a process and an apparatus for extracting the oil and gas from oil shale without negative environmental effects.

## II. EXPERIMENTAL

### 1. Materials

The investigated Oil shale samples were obtained from Huadian area located in Jilin province, northeast, China. Results of the proximate analysis and ultimate analysis of the sample are shown in table 1. The oil shale blocks pass through crushing and grinding operations to reduce the particle sizes. In the crushing stage the rocks are reduced to about 0.5-2 cm. After grinding, the particles are equal or inferior to 2 mm. The Fischer assay oil yield of Huadian oil shale is between 8 to 18 %. [22, 23, 14]

Table 1. Analysis result of Huadian oil shale by weight %

Proximate analysis				Ultimate analysis				
V <sub>ad</sub>	M <sub>ad</sub>	FC <sub>ad</sub>	A <sub>ad</sub>	C <sub>ad</sub>	H <sub>ad</sub>	O <sub>ad</sub>	N <sub>ad</sub>	S <sub>ad</sub>
31.75	12.62	4.86	50.79	64.57	8.33	14.74	1.49	1.84

Proximate analysis was carried out according to (GB/T 212-2008): the National Standard method of China for coal and analysis ultimate analysis was made by the element analyzer (CE440, EAI).

### 2. Experimental device

Figure 2. Is a schematic block diagram of the experimental apparatus. The experiments were conducted with a setup that consists of an iron-steel cylindrical body with an inner diameter of 25 cm and height of 35 cm that houses the samples. In the top of the cylindrical body, inserted one stem of heaters (1000 W), and this heater was connected to a temperature controller to increase the temperature of the system. The temperatures were controlled to obtain the desired retorting temperature and monitored by digital temperature controller. The two thermocouples are placed from the center of the tube heater T<sub>1</sub> and T<sub>2</sub> located at the top r=0 cm and r=12cm (Fig .2), making it possible to measure the temperature around the cell at different distance. This reveals whether the combustion front progresses or not as a vertical surface., and connected to the temperature controller to continuously record temperature values. Then, the sample holder was placed in another cylindrical cell, which has a 45 cm height and 35cm inner diameter. To minimize the heat losses, the space between two cylinders was filled by crushed perlite (low thermal conductivity). This installation is capable to control the temperature. The cylindrical body is pierced with one pipe on the underside that can recover the oil, water and gas by simple steam oil in graduated test tube. The products are cooled at the exit of the reactor with a direct water quench and flow to a container where the first gas-liquid separation takes place.

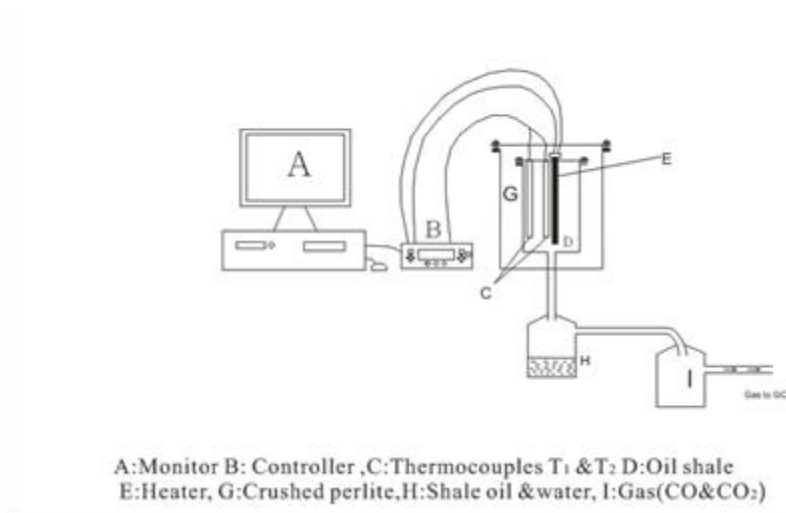


Figure 2. Schematic diagram of the fixed bed reactor

### III. PROCEDURE

We used the electrical heating to heat oil shale during whole experiment. . The heating rate and final temperature were controlled. During our experiments the gas was collected using gas bags during pyrolysis time .The pyrolysis gas composition was analyzed. Oil shale sample was placed in four drawers.

Both the gas analyzer and the temperature controller were connected to the computer. Two experiments in the same conditions were carried out all the time .the experimental work follows the detail below. All detail about composition of mixture is in (Fig.3) and the experimental results are in (Table 2).

We used reference experiment in (Fig 3) to make Thermogravimetric Analysis (TGA).

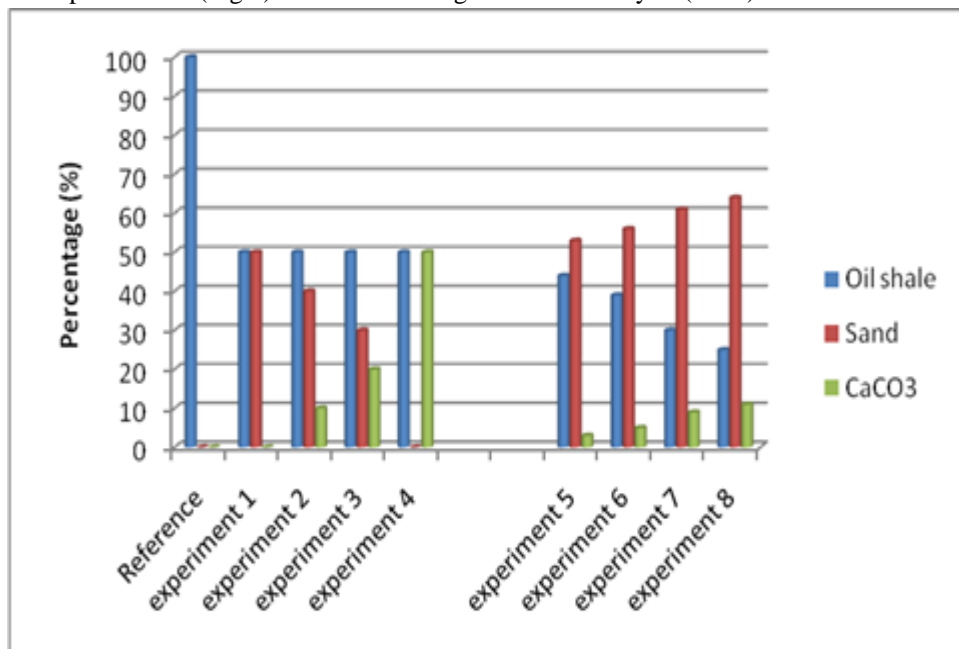


Figure 3. The composition of the mix in different experiment

Table 2. Experimental conditions and results for all experiments

No.	Experimental conditions			Results				
	Oil Shale %	Sand %	Added CaCO <sub>3</sub> %	T/°C	FC Oxidation %	CaCO <sub>3</sub> decarbonation %	CO %	CO <sub>2</sub> %
reference	100	0	0	1100	98.6.	98.2	6.25	18.4
1	50	50	0	1017	97.8	93	6	18
2	50	40	10	1037	97.0	95.0	7.94	18.6
3	50	25	25	900	96.4	69.0	6.20	22.0
4	50	00	50	820	96.6	61.4	5.97	25.2
5	44	53	03	750	96.4	58.1	4.01	15.6
6	39	56	05	720	95.9	21.4	3.7	12.4
7	30	61	09	640	95.6	8.20	3.6	7.8
8	25	64	11	590	95.2	7.6	3.2	6.2

Measurements before start out: Mass of the medium .Measures after the experiment: Final mass of the medium, color of the bed and quantities of oil recovered and gas (CO<sub>2</sub> and CO).The gases collected from micro-sampling device were analyzed using a Peak Performer 1 FID [24] .Two species were chosen to be separated: CO, which represents one gas formed only by oil shale devolatilization and oxidation of Fixed Carbon .CO<sub>2</sub> that is formed during oil shale devolatilization, by decarbonation of CaCO<sub>3</sub>.

#### IV. EXPERIMENTAL RESULTS AND DISCUSSION

##### 1. TGA Analysis

Thermogravimetric Analysis (TGA) (Fig 4).is used as reference to monitor the weight of oil shale sample when exposed to an increase in temperature. By exploiting the results we can characterize the kinetics of chemical reactions of materials. TGA experiments were carried out with a heating ramp of 5°C /min up to 1100°C. The several steps of decomposition of the shale sample are shown in (Fig. 4).

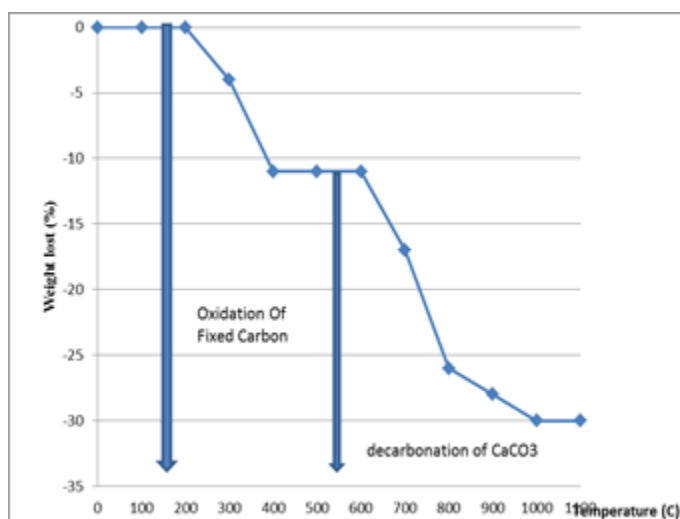


Figure 4. Thermogravimetric Analysis (TGA).

Subsequently both decarbonization and FC oxidation zone were estimated according to the transition period and the speed of layer considered, as determined before (Fig 4.) Particular attention is paid to the fraction of CaCO<sub>3</sub> that is decarbonated at the front passage and the fraction of carbon that is oxidized to CO and not CO<sub>2</sub>.

Two parameters influence the temperature during Huadian oil shale combustion namely: the fraction of fixed carbon oxidized to CO and CO<sub>2</sub> and the fraction of CaCO<sub>3</sub> carbonate to CO<sub>2</sub>. Thermocouple T<sub>1</sub>, a peak close to 1050°C. all the experimental result is reported in Table 2.

## 2. Influence of the fraction of calcium carbonate on the temperature

On the experiment 1,2,3 and 4 we study the influence of the fraction of calcium carbonate on the temperature. And the (Fig 5) show the evolution of temperature during combustion as a function of the total mass of CaCO<sub>3</sub>. By keeping the amount of FC to 4.86% we vary the amount of CaCO<sub>3</sub> by adding CaCO<sub>3</sub> from 12.62% to 63%.

The result for Table 3 showed that increasing the fraction of CaCO<sub>3</sub> from 12.62% to 63% decreases the temperature inside from 1100°C to 820°C. The temperature remained stable at 800°C even with the increase in the quantity of CaCO<sub>3</sub>. At this temperature, only 29% of initially present carbonates are decarbonated. Indeed when the temperature is above 800°C, the CaCO<sub>3</sub> is decarbonated rapidly, whereas when the temperature is less than or equal to 820°C it decarbonated slowly and behaves like an inert medium. At the temperature of 820°C or lower, the decarbonation of CaCO<sub>3</sub> is not significant and the CaCO<sub>3</sub> no longer acts as a heat sink but instead, acts as an inert medium.

For these experiments, it is interesting to calculate the absolute quantity of CaCO<sub>3</sub> that is decarbonated. The values obtained for the whole experiment vary between 22 and 60% initial CaCO<sub>3</sub> were nearly the same. It can be concluded that the temperature can decarbonate up to 28% CaCO<sub>3</sub>. In the reference case, only 22% was present, all of it was decarbonated, while in the other cases where CaCO<sub>3</sub> was present in quantities larger than 28% mass, only this later quantity was converted. The remaining carbonates behaved as inert materials.

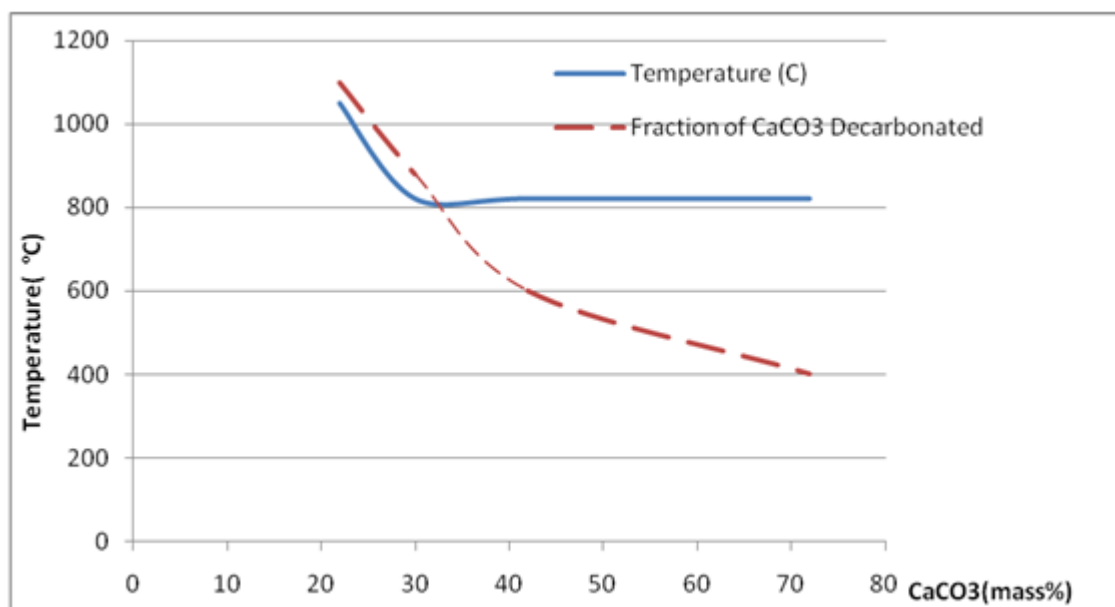


Figure 5. Variation of CaCO<sub>3</sub> in different temperatures.

## 3. Influence of the temperature on decarbonation of carbonate

Fig.5 gives the effect of the temperature on the on decarbonation of CaCO<sub>3</sub> as a function of the total mass of CaCO<sub>3</sub>. During experimental 1, 2,3 and 4 we vary the amount of CaCO<sub>3</sub> from 22% to 66% by added CaCO<sub>3</sub>. The result for (Table 2). showed that increasing the fraction of CaCO<sub>3</sub> from 22% to 66% while the amount of FC remains at 4.86%. decreases the temperature inside from 1100°C to 975°C. The temperature

remained stable at 900°C even with the increase in the quantity of CaCO<sub>3</sub>. This temperature is not low to avoid the decarbonation. Indeed, when the temperature of the mixture is above 800 ° C, the CaCO<sub>3</sub> decarbonates to CO<sub>2</sub> and fixed carbon oxidized to CO and CO<sub>2</sub>.

If we describe the fraction of the decarbonation according to the temperature, as shown in Figure 3, it can be observed that it gradually increases with temperature. At about 590 ° C, only 8% CaCO<sub>3</sub> are decarbonated. Table 3 shows the main result of this work. It is therefore possible to avoid CaCO<sub>3</sub> decarbonation by keeping the temperature lower to 590°C (Table 2).

#### **4. Influence of the fixed carbon (FC) on the temperature.**

Based on the experimental results 5,6,7 and 8 as reported in (Table 2, Fig 6) we study the influence of the FC on the temperature by changing the quantity and composition of the fixed carbon in mixture while the amount of CaCO<sub>3</sub> remains at 12.62%.

By decreasing fixed carbon from 4.86 to 1.86 % ,the temperature of the combustion was decreased from 820°C to 562 °C .As the temperature decreased, the FC oxidation kinetics slowed down and at 562°C only 12% of the carbonates are decarbonated when almost all FC is oxidized., The temperature falls to 562°C , and only 12 % of the CaCO<sub>3</sub> is decarbonated so It is therefore possible to avoid the decarbonation

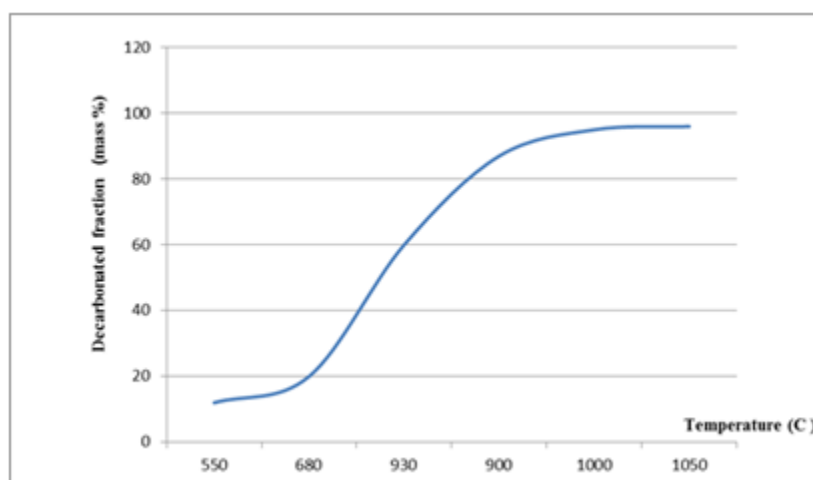


Figure 6. Decarbonated fraction at different temperatures

Whatever the experimental conditions, even at the lower temperatures, no fixed Carbon left in the mixture after combustion. It was found that 19% to 35% of fixed carbon was oxidized into CO and in CO<sub>2</sub> .

#### **V. CONCLUSION**

These results provide the approach of pyrolysis oil shale without the decarbonate mineral and less CO<sub>2</sub> emission. It has been clearly found that the composition (oil shale, sand and Carbonates) of the mixture influenced the temperature during combustion of oil shale. Increasing the fraction of CaCO<sub>3</sub> allow to reduce the temperature of 1100°C to 820°C but not low . The temperature is been decreased from 900°C to 562°C by reducing the fraction of Fixed Carbon at 4.86% to 1.8%. At 590°C , the temperature combustion decarbonate only 12% carbonate initially present and Fixed Carbon is oxidized .The percentage of Fixed Carbon oxidized increased with temperature .During this work we show how to avoid CO<sub>2</sub> by limiting the decarbonation of CaCO<sub>3</sub>.

This work presents a promising method to extracting oil contained in oil shale without decarbonation of minerals. These results provide one of the approaches to control a combustion temperature in the case of oil shale.

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