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# Recovery of Turkish Oil Shales by Electromagnetic Heating and Determination of the Dielectric Properties of Oil Shales by an Analytical Method

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The effect of microwave irradiation on the recovery of three different oil shale samples was studied. To enhance the microwave efficiency, three different iron powders (Fe, $Fe_2O_3$, and $FeCl_3$) and their three different doses (0.1, 0.5, and 1% by weight, each) were added to the samples as microwave receptors. The doses of each receptor were optimized for each oil shale sample based on the highest oil or gas production value obtained experimentally. During the experimental studies, the temperature distribution and the emissions of CO, $H_2S$, $CH_4$, and $O_2$ gases were recorded. Temperature distributions obtained experimentally were modeled analytically to find the microwave power absorption coefficient of each oil shale sample. Experimental and analytical studies show that, oil recovery from oil shales is not only related to reaching the pyrolysis temperature, but also to the amount of time that temperature is maintained. Therefore, for the efficient recovery of oil shales, the best solution is found in a hybrid utilization of irradiation and conventional heat transfer: microwave heating for a rapid temperature rise and conventional heating for sustaining high temperatures effectively.

## Introduction

Energy development is getting more important each day, especially for developing countries like Turkey. In order to decrease the dependency on energy exporting countries, alternative fossil fuel resources of Turkey need to be further investigated. Oil shale resources are the second largest fossil fuel resources of Turkey and the proven reserve is around 2.22 billion tons with about 3 million tons of these reserves being mineable.[1,2]

The most effective way of processing oil shales is the retort technique which is converting kerogen into synthetic crude oil by pyrolysis, hydrogenation, or thermal dissolution.[3] The retort technique can be applied as surface or in situ retorting. For the mineable part of an oil shale resource, surface retorting is the most appropriate method. It is mostly a continuous process in which the raw oil shale undergoes pyrolysis under the effect of heat, yielding oil and waste products.[4] Since it is a continuous process, it demands applying heat for an extended time, requiring a significant amount of energy.[5]

To minimize the energy consumption in retort technique, electromagnetic heating can be employed as an alternative recovery method.[6,7] It is known that heating times using microwaves can often be reduced to less than 1% of those required using conventional heating methods.[8]

This difference in efficiency is due to how energy is transferred to the sample. Microwave energy generated by a magnetron is directly absorbed by the molecules of the material subjected to the microwave heating. This is in contrast to conventional heating, where heat is propagated into the material from a heating element. Because each wave has a positive and negative component, the molecules in the materials are jostled back and forth at twice the rate of the microwave frequency, so the microwave energy is converted to heat.[9] Dielectric properties of a material affect how the transmitted microwaves react with the material in the system.[10] The dielectric properties of the materials change with the frequency of the system, temperature, and the electrical properties of the materials. Different materials and even the different concentrations of a combination of materials can change these properties.[8,11]

Since crude oil has a low dielectric constant, it absorbs microwaves weakly.[11] This weak absorption poses a problem when standard microwave ovens are employed in the heating process. While different magnetron frequencies can be used by

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industrial microwave generators,[12] because of a constant magnetron frequency (2450 MHz), the steady-state temperature of a microwave oven cannot be changed. The only option for enhancing the microwave absorption in a material is then changing its dielectric properties. This can be accomplished by adding chemicals with high microwave absorption to the samples subjected to microwave irradiation. These materials are referred to as microwave receptors.[11−14] Of these materials, activated carbon, iron oxides, and methanol have been used to recover some heavy crude oil samples, while CuO and $V_2O_5$ have been used for the liquefaction of coal by electromagnetic heating.[11−15] Due to their very high microwave absorption coefficients, in some industries, microwave heating with SiC, $BaFe_2O_4$, and $TiO_2$ susceptors is also employed to increase the efficiency of the process and decrease its cost.[16,17]

In this research, the recovery of three different Turkish oil shales was investigated by using the electromagnetic heating method. To direct the microwave energy into the samples more effectively, several microwave receptors were used and their types and doses were optimized. Process performances were examined according to produced oil, emitted gases, and increasing temperature values.

Besides investigating a new technology for the recovery of oil shale, an analytical model was used to determine the dielectric properties of oil shales. Dielectric properties of materials vary in accordance to the molecular structure, atomic bond strength, and type. Research into dielectric properties is still lacking and corresponding relationships have failed to accurately predict the precise properties of material dielectric permittivity.[18] Therefore, in this study, an analytical model was used on the basis of experimental results to clarify the microwave absorption ability of the oil shales.

## Materials and Methods

**Sample Characterization.** The oil shale (OS) resources in Turkey are distributed mainly in middle and western Anatolia. Generally, marl, clay, and carbonates are the host rocks and organic matter is found in disseminated form.[19] Among the potential resources, OS1, OS2, and OS3 deposits are of the major importance in terms of quality, amount and exploitability. The characteristics of these three deposits are given in Table 1.[20,21]

Since these resources are the most important resources among the oil shale deposits in Turkey, recovery characteristics of these three oil shale samples were studied by using microwave heating.

Oil shale is a complex mixture of kerogen and a wide range of minerals. Therefore, the thermal degradation of oil shale is too complex to be described by an individual chemical reaction.[1] In the initial stages of pyrolysis, distillation of low molecular mass species occurs. However, as the temperature is raised, in addition to the increased rate of volatilization due to the progressive evaporation of larger molecules, cracking of the compounds may also occur to produce volatile fragments. For OS1, OS2, and OS3, distillation takes place up to ∼230 °C and visbreaking and cracking occur in between 270 and 525 °C, and pyrolysis of oil shales generally starts in between 450 and 550 °C.[1,22] Moreover, the inorganic constituents of each oil shale sample and the behavior of each constituent may play an important role during the pyrolysis of oil shales.

For OS1, the major inorganic constituents, in the organic rich zones are calcite, dolomite, silica, and considerable amounts of pyrite, for OS2, calcite, dolomite, quartz, and smectite, and for OS3, quartz, dolomite, calcite, and clay minerals such as muscovite, Illite, and smectite.[19,21−25]

Calcite decomposes to CaO and $CO_2$ after reaching 825 °C.[26] Decarbonation of dolomite begins at 777.7 °C.[27] Silica decomposition in an inert atmosphere starts at 2800 °C and carbothermic reduction of silica starts around 1530 °C.[28]

Presence of clays and fine sands in the matrix favor increased rates of fuel formation. Rock minerals such as pyrite, calcite, and smectite also favor fuel-forming reactions.[29]

Therefore, during the pyrolysis of oil shales, not only the distillation, visbreaking, and cracking reactions associated with the decomposition of kerogen occur, but also decomposition of rock can take place after reaching necessary temperatures.

## Experimental Section

Experimental studies were conducted with the setup shown in Figure 1. This experimental setup consists of a conventional microwave oven, a temperature controller, a gas analyzer, and a computer. The microwave oven has a 1400 W input power, a 900 W output power, and a 2450 MHz frequency (BOSCH HMT 72G420). The temperature controller was used to measure the temperature of the samples during the experiments. The gas analyzer was used to measure the emitted gases in terms of

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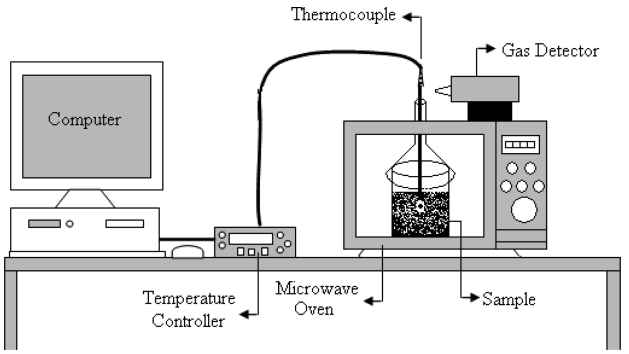


**Figure 1.** Experimental setup.

$H_2S$, CO, $CH_4$, and $O_2$. Both the gas analyzer and the temperature controller were connected to the computer. With the help of two different software, each measured value was recorded continuously. Oil shale samples subjected to the microwave heating were placed in a 500 mL glass beaker. To measure the temperature and emitted gases continuously a hole was drilled at the top center of the microwave oven. A glass funnel was placed at the top of the beaker and the tip of funnel was placed through the drilled hole. This was done in order to direct the emitted gases to the inlet of the gas analyzer, and to prevent the dispersion of emitted gases inside the microwave oven for protecting the magnetron. The gas detector was placed at the tip of the glass funnel, outside the microwave oven. A special thermocouple which is capable of measuring high temperatures (≈1500 °C) was placed at the center of the samples through the glass funnel (Figure 1). All of the experiments were conducted under ambient air atmosphere.

To enhance the microwave energy application, three different microwave receptors were used.[11] These receptors were Fe, $Fe_2O_3$, and $FeCl_3$, and were added to the samples in a powdered form. Three different doses by weight (0.1, 0.5, and 1%) were used to determine the optimum doses of receptors. Optimization of iron-powder type and doses for each sample was accomplished by considering the maximum oil or gas production. All recoveries were determined in a weight basis.

**Analytical Modeling Theory.** The temperature-distribution equation derived by Abernethy in 1976 was used in the analytical modeling study.[30] The net heat input rate into the cylindrical element was derived in this paper as

$$\left(\frac{dQ}{dt}\right)_{net} = \left\{ \underbrace{\frac{\alpha P(r)}{4.18}}_{\text{radiation term}} + \underbrace{\rho_o q_o S_o \left(\frac{\partial T}{\partial r}\right)}_{\text{convection term}} + \underbrace{2\pi h K \frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)}_{\text{conduction term}} \right\} dr = 2\pi r h \rho_t S_t \left(\frac{\partial T}{\partial t}\right) dr \quad (1)$$

where α is the power absorption coefficient ($cm^{-1}$), $P(r)$ is the total power radiated cross the radius $r$ (watts), $\rho$ is the density ($gm/cm^3$), $q_o$ is the flow rate ($cm^3$/sec), $S$ is the specific heat (cal/g°C), h is the height of the cylinder (cm), $K$ is the total heat conductivity (cal/sec/°C/cm), $T$ is the temperature (°C), $r$ is the radius (cm), and the indices o and t denote oil and total, respectively.

$P(r)$ and $\rho_t S_t$ are defined by the following formulas:[30]

$$P(r) = 2\pi h \Phi(r) = P_o e^{-\alpha(r-r_o)} \Rightarrow P_o = P(r_o) \quad (2)$$

$$S_t \rho_t = \rho_r S_r (1-\phi) + \rho_o S_o \phi (1-\sigma_w) + \rho_w S_w \phi \sigma_w \quad (3)$$

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**Table 1. Characteristics of the Major Oil Shale Deposits in Turkey**[1]

| | deposit | | |
|---|---|---|---|
| parameter | OS1 | OS2 | OS3 |
| proven reserve ($\times 10^6$ tons) | 66 | 78 | 83 |
| total reserve ($\times 10^6$ tons) | 66 | 360 | 122 |
| total organic carbon (wt%, average) | 3.2 | 5.6 | 6.9 |
| oil content (wt%, average) | 4.6 | 5.3 | 5 |
| total sulfur (wt%, average) | 0.9 | 1.3 | 0.9 |
| calorific value (j/g) | 4540 | 3235 | 4205 |
| water (%) | 12.9 | 1.6 | 2.8 |
| ash (%) | 60.5 | 66.2 | 70.9 |
| C (%) | 13.6 | 5.63 | 8.58 |
| H (%) | 1.5 | 1.3 | 1.4 |
| O, N (%) | 10.48 | 3.89 | 4.39 |
| S (%) | 0.99 | 1.25 | 0.19 |

where Φ(r) is the power density (watts/$cm^3$), $r_o$ is the well bore radius (cm), $\phi$ is the rock porosity (fraction), $\sigma_w$ is the connate water saturation, (fraction), and the indices r and w denote rock and water, respectively.

By substituting eq 2 and 3 into eq 1, the following derivation is obtained:[30]

$$\frac{\partial T}{\partial t} = \frac{1}{2\pi r h \rho_t S_t}\left\{\frac{\alpha P_o e^{-\alpha(r-r_o)}(r)}{4.18} + \rho_o q_o S_o \left(\frac{\partial T}{\partial r}\right)\right\} \quad (4)$$

Equation 4 is solved to obtain the temperature distribution. The setup dimensions shown in Figure 1 are not big enough to produce a large amount of shale oil. Therefore, to calculate the power absorption coefficient, eq 4 is solved for unsteady-state no-flow conditions. The following temperature distribution was obtained for this case:[30]

$$T(r,t) = T_o \frac{\alpha P_o e^{-\alpha(r-r_o)} t}{4.18 \times (2\pi h \rho_t S_t) r}, q = 0 \quad (5)$$

The most important parameter to determine the effectiveness of microwave heating is the power absorption coefficient of the medium. However, the power absorption coefficient does not exist for oil shales in literature. Therefore, in this study, experimental results are used to find the power absorption coefficients of each oil shale samples by using the aforementioned equations above.

To fully exploit the advantages provided by microwave heating over conventional heating such as heating times and energy consumption, materials with high power-absorption coefficients need to be employed. Therefore, to increase the power-absorption coefficient of oil shale samples, three different microwave receptors were added in powdered form to the oil shale samples. Furthermore, optimization of these microwave receptors was achieved by using three different doses of each receptor. Thus, the change of power-absorption coefficient after the addition of iron powders was also examined.

## Results and Discussion

**Experimental Results.** First, three minutes was used as the heating period in all the experiments. Each sample was selected to have a weight of 100 g, so that according to the oil content values given in Table 1, OS1, OS2, and OS3 samples contain approximately 4.6, 5.3, and 5 g oil, respectively.[1] Recoveries were calculated by dividing the produced oil weight by these oil content values for each shale sample.

Before and after each experiment, all of the equipments were weighed using a very sensitive balance with a 0.1 mg readability. The differences between these two measurements give the gas production in weight basis. A glass filter was placed at the bottom of the beaker and the produced oil was collected underneath this filter. By measuring the weight

**Table 2. Microwave Experiment Summary for OS1**

| | | total gas emission (ppm) | | production (g) | | |
|---|---|---|---|---|---|---|
| receptor name | addition (%) | CO | $H_2S$ | gas | oil | spent shale |
| Raw | | 106.1 | 2.6 | 1.61 | 0.04 | 98.35 |
| | 0.1 | 1383.7 | 67.3 | 11.34 | 0.24 | 88.42 |
| Fe | 0.5 | 28.9 | 0.0 | 1.61 | 0.02 | 98.37 |
| | 1 | 8.0 | 0.1 | 1.47 | 0.01 | 98.52 |
| | 0.1 | 6.1 | 0.0 | 1.45 | 0 | 98.55 |
| $Fe_2O_3$ | 0.5 | 365.4 | 16.2 | 5.26 | 0.13 | 94.61 |
| | 1 | 15.4 | 0.2 | 3 | 0.05 | 96.95 |
| | 0.1 | 25.3 | 0.1 | 2.65 | 0.01 | 97.34 |
| $FeCl_3$ | 0.5 | 27.9 | 0.6 | 2.29 | 0 | 97.71 |
| | 1 | 0.0 | 0.0 | 1.66 | 0.04 | 98.3 |

**Table 3. Microwave Experiment Summary for OS2**

| | | total gas emissions (ppm) | | production (g) | | |
|---|---|---|---|---|---|---|
| receptor name | addition (%) | CO | $H_2S$ | Gas | Oil | Spent Shale |
| Raw | | 12.5 | 0.1 | 0.81 | 0 | 99.19 |
| | 0.1 | 38 | 0.2 | 0.55 | 0 | 99.45 |
| Fe | 0.5 | 1.3 | 0 | 0.24 | 0 | 99.76 |
| | 1 | 3.9 | 0 | 0.2 | 0 | 99.8 |
| | 0.1 | 49.7 | 0.3 | 0.41 | 0.05 | 99.59 |
| $Fe_2O_3$ | 0.5 | 3.6 | 0 | 0.24 | 0 | 99.76 |
| | 1 | 2.5 | 0 | 0.03 | 0 | 99.97 |
| | 0.1 | 68.7 | 0.8 | 0.67 | 0.005 | 99.33 |
| $FeCl_3$ | 0.5 | 0 | 0 | 0.46 | 0.01 | 99.54 |
| | 1 | 100.9 | 0 | 1.27 | 0 | 98.73 |

of this filter before and after each experiment, the produced oil amount was determined.

To enhance the microwave efficiency, hence the oil recovery, three different microwave receptors (Fe, $Fe_2O_3$, and $FeCl_3$) and their three different doses (0.1, 0.5, and 1%, by weight) were added to each oil shale sample. The type and dose of the microwave receptors was optimized according to oil or gas production. For the determination of recovery characteristics of each oil shale samples by electromagnetic heating, 10 experiments for each sample were conducted.

The experimental results are summarized in Tables 2−4 . The temperature distributions for each experiment are shown in Figures 2−4.

The general trend of these figures is very similar to what is available in literature showing temperature variations in pyrolysis reactions.[14,15] Hence, we can safely assume that pyrolysis dominates the reactions, and the small amount of combustion occurring at the surface of the samples has a negligible effect, and therefore can be ignored.

Because the highest oil production was obtained after the addition of 0.1% Fe, it was selected as the optimum type and dose of iron powders for OS1 (Table 2). Also, the greatest temperature value is observed for this dose of iron.

The highest CO and $H_2S$ emissions and gas production were observed after the addition of 0.1% Fe (Table 2). So, the produced gases mostly consist of CO and $H_2S$ after the addition of 0.1% Fe.

The presence of hydrogen sulfide is an evidence of the occurrence of hydrodesulphurization. Microwave pyrolysis

**Table 4. Microwave Experiment Summary for OS3**

| | | total gas emissions (ppm) | | production (g) | |
|---|---|---|---|---|---|
| receptor name | addition (%) | CO | $H_2S$ | Gas | Spent Shale |
| Raw | | 2.4 | 0.1 | 3.48 | 96.52 |
| | 0.1 | 0 | 0 | 2.29 | 97.71 |
| Fe | 0.5 | 0 | 0 | 7.27 | 92.73 |
| | 1 | 298 | 1.4 | 2.41 | 97.59 |
| | 0.1 | 0 | 0 | 2.36 | 97.64 |
| $Fe_2O_3$ | 0.5 | 0 | 0 | 2.23 | 97.77 |
| | 1 | 0.2 | 0 | 2.36 | 97.64 |
| | 0.1 | 48.3 | 0.4 | 2.06 | 97.94 |
| $FeCl_3$ | 0.5 | 2.9 | 0.1 | 2.30 | 97.70 |
| | 1 | 26.7 | 0.6 | 2.86 | 97.14 |

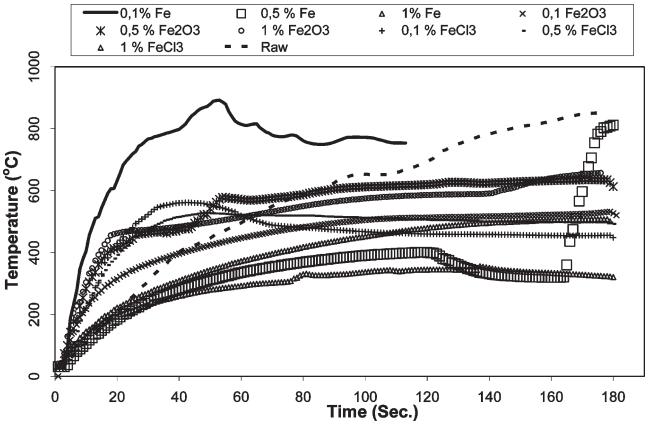


**Figure 2.** Temperature distributions of experimental results for OS1.

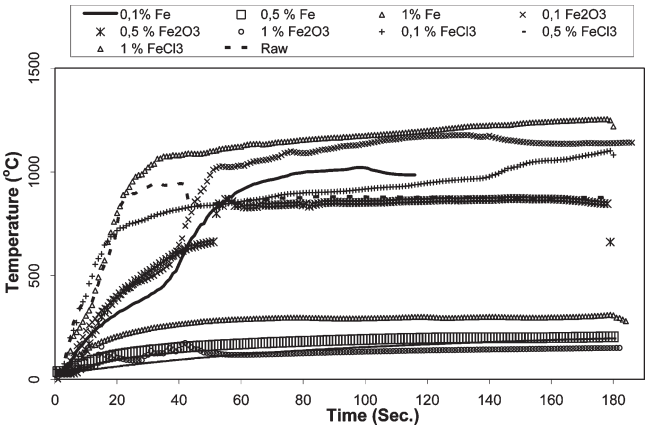


**Figure 3.** Temperature distributions of experimental results for OS2.

of OS1 after the addition of 0.1% Fe caused an increase in pyrolysis reactions and hydrodesulphurization reactions. Hydrodesulphurization (HDS) is a catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petroleum, jet fuel, kerosene, diesel fuel, and fuel oils.[31,32] Since oil

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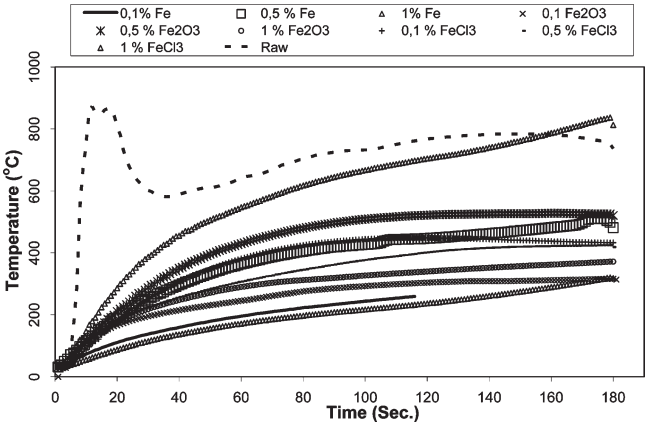


**Figure 4.** Temperature distributions of experimental results for OS3.

shales contain numerous complex compounds which contain sulfur, it is obvious that microwave heating helps to remove this impurity from these resources by hydrodesulphurization. The hydrodesulphurization process also helps to decrease the oil viscosity by increasing the temperature.

The oil content of OS1 is assumed as 4.6 g for 100 g oil shale sample.[1] The total production of gas and oil is, however, higher than 4.6 g for 0.1% Fe, and 0.5% $Fe_2O_3$. This is evidence that rock decompositions occur during the pyrolysis of OS1. Thus, it can be said that over 635 °C, rock decomposition of OS1 occurs at atmospheric condition. Experimental results in Table 2 are not sufficient to determine when the rock decomposition starts for OS1. Furthermore, it is not evident which minerals decompose.

The temperature distribution results for the experiments conducted with OS1 are summarized in Figure 2. For OS1, temperature distributions generally have two different regions. At the beginning of the experiments, the temperatures increase very fast, and then stabilize.

The highest temperature is observed after the addition of 0.1% Fe (Figure 2). Thus, it can be said that, 0.1% Fe is a good microwave receptor for the recovery of OS1.

In order to understand the mechanisms of microwave heating of oil shales better, gas emission, oil production, and gas production results should be considered together. Results obtained for OS2 were summarized in Table 3 and temperature distributions are given in Figure 3. For OS2, since the highest oil production was obtained after the addition of 0.1% $Fe_2O_3$, this was determined as the optimum dose for the recovery of OS2.

After microwave heating of raw OS2, 0.81 g gas was produced. 0.81 g gas covers the 12.5 ppm CO and 0.1 ppm $H_2S$ and the other gases exerted during the process which cannot be detected by the gas analyzer. After the addition of 0.1% Fe, while the CO and $H_2S$ emissions are increased in volume basis, gas production in weight basis decreased. Since CO and $H_2S$ are the byproducts of the pyrolysis process, the results indicate that 0.1% Fe addition accelerates pyrolysis reactions. Iron also accelerates hydrodesulphurization reaction by forming $H_2S$.[33] In other words, these reactions help to remove the impurities (O and S) from the oil shale, by forming CO and $H_2S$.[34] For the other doses of Fe, $H_2S$ emission was not observed, so the optimum dose of Fe for OS2 can be determined as 0.1%.

After the addition of $Fe_2O_3$, high CO emissions were observed, but the gas production is still less than the gas production of the raw sample by weight. The same line of thought can be applied for all of the doses of $Fe_2O_3$.

The greatest temperature value was observed around 1300 °C after the addition of 1% $FeCl_3$. Since at this temperature all of the light and moderate fractions and even the heaviest part of the oil are evaporated, no oil production and the greatest CO production were observed.[35]

For OS2, as for OS1, temperature distributions generally have two different regions. At the beginning of the experiments, temperature increases very fast and stabilizes at an approximately constant value (Figure 3).

At the beginning of the experiment, 1% $FeCl_3$ yielded the greatest temperature value, but resulted in no oil production. At the end of the experiments, not only 1% $FeCl_3$ but also samples with 0.1% $Fe_2O_3$ and 0.1% Fe additions reached higher temperatures than raw oil shale reached. The greatest oil recovery was obtained for 0.1% $Fe_2O_3$. Therefore, 0.1% $Fe_2O_3$ is selected as the optimum type and dose for the recovery of OS2.

Because no oil production was observed for OS3, the optimum type and dose of the microwave receptors were determined on the basis of the greatest gas production. Thus, the optimum type and dose is selected as 0.5% Fe (Table 4).

The highest gas production was observed after the addition of 0.5% Fe. However, CO and $H_2S$ emissions were not detected for this dose of Fe, which means that the produced gases were different than CO and $H_2S$. The highest doses of Fe and all doses of $FeCl_3$ help to remove impurities in the form of CO and $H_2S$.

Besides the fact that no oil was produced from OS3, the addition of microwave receptors also reduced the temperature values compared to raw oil shale temperature values (Figure 4). Therefore, none of the receptors provide any benefit for the recovery of OS3 by electromagnetic heating.

Since rock decomposition is an endothermic process, it causes the temperature to decrease. This decrease is obvious in Figure 4 for raw OS3. Thus, at atmospheric conditions, it can be said that rock decomposition starts at around 873 °C for OS3 and decomposition could be in the form of carbonate.

Because OS1 is known as high grade shale in literature, recovery of this oil shale is generally greater when compare to OS2 and OS3.[1]

**Analytical Modeling Results.** Experimentally obtained temperature distribution data were used to solve eq 5 to find microwave power absorption coefficients of each oil shale sample.

Figure 5 represents the analytical modeling results for raw oil shales, and oil shales containing the optimum type and dose of microwave receptors.

In Figure 5, circles represent the temperature distribution results of experiments conducted with each raw oil shale sample, dashes correspond to the temperature distribution results of experiments conducted with each oil shale sample after the addition of optimum type and dose of microwave receptors, and straight lines show the analytical modeling results for both cases.

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**Table 5. Calculated Power Absorption Coefficient Values for All Experiments**

| | | OS1 | | | | | OS2 | | | | | OS3 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| receptor name | addition (%) | $\alpha^a$ | $T^a$ | $t^a$ | oil$^a$ | gas$^a$ | $\alpha^a$ | $T^a$ | $t^a$ | oil$^a$ | gas$^a$ | $\alpha^a$ | $T^a$ | $t^a$ | gas$^a$ |
| | raw | 4 | 411.5 | 42 | 0.86 | 4.04 | 30 | 913.6 | 25 | 0.0 | 5.9 | 37 | 861 | 11 | 19.9 |
| | 0.1 | 13 | 683.1 | 22 | 5.21 | 28.70 | 10 | 933.7 | 63 | 0.0 | 4.0 | 2 | 1445 | 33 | 13.1 |
| Fe | 0.5 | 2.7 | 241.6 | 30 | 0.43 | 4.07 | 2.7 | 125.5 | 23 | 0.0 | 1.8 | 3 | 256.2 | 31 | 41.6 |
| | 1 | 4 | 236.1 | 23 | 0.22 | 3.70 | 7 | 197.6 | 18 | 0.0 | 1.5 | 4 | 417.9 | 34 | 13.8 |
| | 0.1 | 8.5 | 295.4 | 16 | 0.00 | 3.66 | 15 | 1018 | 51 | 0.9 | 3.0 | 5 | 150.5 | 15 | 13.5 |
| $Fe_2O_3$ | 0.5 | 1 | 398.8 | 17 | 2.81 | 13.24 | 2 | 395.2 | 15 | 0.0 | 1.7 | 1 | 198.5 | 19 | 12.7 |
| | 1 | 10 | 459.4 | 19 | 1.08 | 7.57 | 2 | 144 | 45 | 0.0 | 0.2 | 3 | 186.5 | 22 | 13.5 |
| | 0.1 | 7 | 465.9 | 23 | 0.22 | 6.67 | 25 | 740 | 23 | 0.1 | 4.9 | 4 | 287.2 | 36 | 11.8 |
| $FeCl_3$ | 0.5 | 6 | 439.6 | 25 | 0.00 | 5.76 | 1.2 | 110.4 | 52 | 0.2 | 3.3 | 3 | 213.3 | 27 | 13.2 |
| | 1 | 3.3 | 192.7 | 20 | 0.87 | 4.19 | 25 | 1063 | 33 | 0.0 | 9.3 | 1 | 182 | 67 | 16.4 |

$^a$ $\alpha$ power absorption coefficient [$(\times 10^{-6})$ cm$^{-1}$]; $T$, the first peak temperature (°C); $t$, time necessary to reach the first peak temperature (sec); oil (%), oil recovery in percentage; gas (%), gas recovery in percentage.

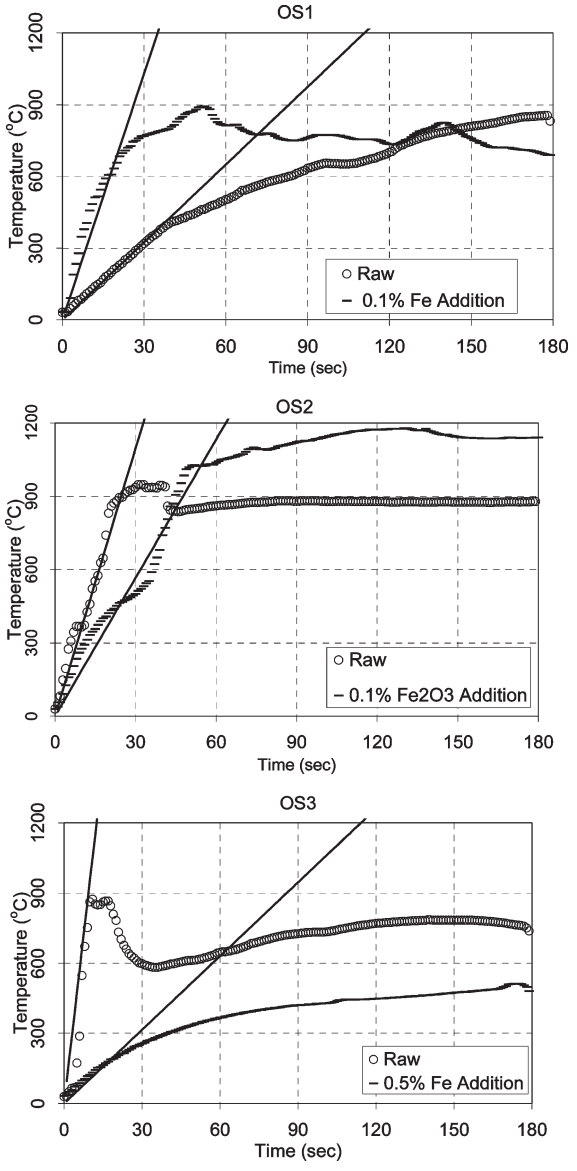


**Figure 5.** Experimental and analytical modeling results for raw oil shale and oil shales with optimum type and dose of microwave receptors.

Dielectric properties of materials vary in accordance to the molecular structure, atomic bond strength, and type.[18] The

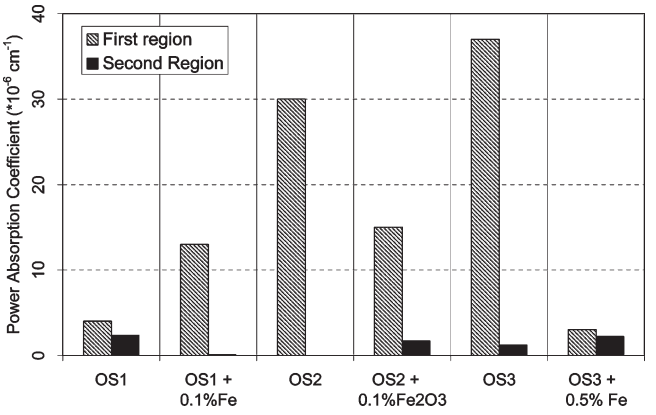


**Figure 6.** Power absorption coefficient variations with temperature.

oil shale compositions are changing during the electromagnetic heating due to the pyrolysis of oil shale and/or decomposition of the rock, hence the dielectric properties of the mediums are also expected to change. This is evident in the experimentally obtained temperature distribution graphs which can be represented by approximately two different regions (rapidly increasing temperature that varies slowly afterward). Therefore, the power absorption coefficients need to be defined at least for these two regions for each experiment. The changes in the power absorption coefficients for these regions are summarized in Figure 6. Figure 6 shows that the power absorption coefficients in the second region are not as high as in the first region.

Pyrolysis reactions start at around 450 °C.[22] In the experiments, this temperature is reached within less than one minute. We define this rapid rise in the temperature distribution graphs as the first region. In the second region, after reaching the pyrolysis temperature, oil shales lose their absorptive properties very fast. Therefore, the power absorption coefficients are only examined for the first region of all the experiments, as summarized in Table 5. In this table, temperature values represent the greatest temperatures to calculate the represented power absorption coefficients and time values represent the required process time to reach these temperature values in the first region.

Different microwave receptor additions show different results. When processing of each oil shale is considered individually and reorganized for increasing temperature, the following results are obtained: for OS1 raw oil shale,

and 0.5% $FeCl_3$, 1%$Fe_2O_3$, 0.1% $FeCl_3$, and 0.1% Fe addition cases can reach the pyrolysis temperature. The greatest oil production was obtained after the addition of 0.1% Fe. For OS2, 0.1% $FeCl_3$, raw oil shale, 0.1% Fe, 0.1% $Fe_2O_3$, and 1% $FeCl_3$ maintain higher temperatures than the temperature necessary to start pyrolysis reactions. The greatest oil production is observed at 1018 °C and 51 s is enough to reach that temperature after the addition of 0.1% $Fe_2O_3$. For OS3, just for raw oil shale and 0.1% Fe addition case the temperature rises over the pyrolysis temperature. No oil production is observed. It is obvious from these results, that microwave receptors favor the pyrolysis of the oil shales.

During the pyrolysis of oil shales by conventional heating, it is expected to observe shale oil production after reaching pyrolysis temperature. Since microwave irradiation is a substantially faster process than conventional pyrolysis, oil production or greater gas production is observed when temperature values are higher than the pyrolysis temperature.[14] This means that not only reaching the pyrolysis temperature, but also staying at that temperature for a certain amount of time is important for the pyrolysis and/or the catalytic cracking of oil shales.[22,36]

Viscosity reduction for the shale oil samples is due to the increasing temperature, referred to as thermal cracking. A common observation on reaction rates is that the higher the temperature, the faster a given chemical reaction will proceed. The basic reason for this is that at higher temperatures, the probability that two molecules will collide is higher.[37] Besides increasing the temperature, a catalyst can also be utilized to increase the rate of the reactions. Using a catalyst helps molecules achieve the correct geometry by providing a more efficient way to react. Catalysts increase the reaction speeds by decreasing the activation energy of the reaction.[38] At higher temperatures, catalysts work even better.[39]

Since molecular collisions are increasing with increasing temperature, the power absorption coefficients shown in Table 5 yield the greatest values for the temperatures higher than the temperature to initiate pyrolysis reactions. For all of the experiments the greatest power absorption coefficients were obtained for the lowest processing time when the medium still contains the materials that have high absorptive characteristics.

## Conclusions

Microwave heating was used for the pyrolysis of three different oil shale samples. Different microwave receptors were employed to enhance the microwave absorption characteristics of the oil shales and their doses were optimized.

Due to the compositional difference of the oil shales (Table 1) and different types and doses of iron powders employed, the dielectric properties for each sample are different. These differences result in significant differences in the oil and gas production for each oil shale sample. Since OS1 has a higher oxygen and hydrogen concentration than OS2 and OS3 and known as a high grade shale in the literature, oil recovery with electromagnetic heating generated the best results for OS1 (Table 1).[1,13] The results show that the oil shale recovery depends on both the oil shale characteristics and the microwave receptor types and doses. Therefore, it is important to find the dielectric properties of the material, for a better understanding of the effectiveness of a potential field application of microwave heating. For this purpose, an analytical model was used to find power absorption coefficient of the oil shales.

Thermal degradation of oil shales starts when the activation energy barrier is exceeded by reaching the pyrolysis temperature. More time is needed using conventional heating to reach this temperature compared to microwave heating.[36] It is possible to reach the pyrolysis temperature within one minute or less by employing microwave heating.

While the greatest oil production is obtained after reaching the pyrolysis temperature for conventional heating, for microwave heating this is observed after reaching temperatures much higher than the pyrolysis temperature. Although the highest recovery was obtained as 80% for the retorting of OS1,[36] it was obtained as 5.3% for the electromagnetic heating of OS1. Thus, not only reaching pyrolysis temperature but also maintaining that temperature for an extended time is important for the recovery of oil shales.

Our conclusion in view of these results is that for the efficient recovery of oil shales, a hybrid heating method can be employed. The substantially higher heating rate of microwave irradiation should be exploited to rapidly reach the pyrolysis temperature. Afterward, the heating method can be switched to conventional heating so that the temperature is sustained more effectively.

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