The Effect of microwave frequency on dielectric properties and Pyrolysis of oil shales

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ABSTRACT

In the present work, the effect of in situ electromagnetic retorting technologies on the oil shales was reviewed. In this literature review on oil shales dielectric properties, we found that the relative dielectric constant (ε') and imaginary permittivity (ε'') decrease with increased frequency and remain constant at higher frequencies. Formation fluids and mineral-bound water also affect measured dielectric properties. This review presents and synthesizes prior work on the influence of applied frequency on the dielectric properties of oil shales that can aid in the future development of frequency specific in situ retorting technologies and oil shale grade assay tools. The results obtained revealed that this process can be efficiently used for the purpose. The oil shale seems related to the retorting of the shale and the products of the degradation of the kerogen. In addition, the obtained oil has interesting characteristics. It is more maltenic, less polar than the oils obtained by conventional pyrolysis.

Key words: Oil Shales; Microwave; Pyrolysis; Frequency; Dielectric Properties.

INTRODUCTION

Oil shale, one of unconventional oil sources, is a fine-grained sedimentary rock containing kerogen, a mixture of organic chemical compounds with huge molecular weight. Also, oil shale have some potential for the production of several synthetic products such as cement, calcium, alumina, pitches, the carbon adsorbs, zeolites, carbon fibres and other chemicals (Miao et al., 2011). These various industrial applications of oil shale have generated in recent years many studies on methods for extracting these oils, such as pyrolysis by conventional heating or under microwave irradiation. Microwaves heating is one of the best known and the most widely used methods of heating. But there are many advantages and disadvantages of this method. Microwave heating makes use of different wavelengths of electromagnetic waves from the surface of objects to translate into heat for heating the objects from inside to outside. In recent years, there are many foreign reports about the thing of microwave heating bituminous coal and lignite, compared to the conventional heating, microwave heating techniques were to be faster 1 to 2 orders of magnitude (Zhao et al., 1993). Because conventional pyrolysis would be a time-consuming process, microwave heating might serve as an alternative method for drying, pyrolyzing and gasifying these materials in one single step. A clear advantage of microwave systems is the short heating time needed to achieve in minutes what might otherwise take hours with conventional heating methods (Mujundar 1995). In recent years, the use of microwave heating has been employed not only in analytical and environmental chemistry (Zlotorzynski 1995) but also in the pyrolysis of materials such as biomass (Kriegerbrocket 1994), coal (Monsef-Mirzai et al., 1995), oil shales (harfii et al., 1999; Chanaa et al., 1994) and various organic material (Kenneth 1995).

This review addresses the literature related to the dielectric properties and electromagnetic heating of oil shales (average 10 types of oil shales formation) and specific parameters that affect our ability to use electromagnetic energy to produce shale oil. The primary objectives for this review are: to identify the influence of minerals and water on the ability for oil shale to absorb electromagnetic energy; to determine the influence of applied frequency on oil shale dielectric properties and to enhance the oil yield and the oil quality.

ELECTROMAGNETIC HEATING CONCEPTS

A number of investigators studied the dielectric permittivity of oil shales in order to develop electromagnetic probes for kerogen layer identification, and to investigate the potential for in situ oil shale retorting using electromagnetic energy in a volumetric heating process (Judzis 1978; Scales et al., 2006; Bridges et al., 1982). In all of these studies, investigators used oil shale dielectric properties as indicators of oil shale electromagnetic energy absorption. The complex relative permittivity is used as an indicator of the amount of electromagnetic energy that can be stored by a material (Judzis et al., 1980):

\[ \varepsilon_r = \frac{\varepsilon^*}{\varepsilon_0} = \varepsilon' - j\varepsilon'' \]  

Where \( \varepsilon_r \) is the complex relative permittivity, \( \varepsilon^* \) is the complex permittivity, \( \varepsilon_0 \) is the permittivity of free space (8.8542×10−12 F/m), \( \varepsilon' \) (the real part of the complex relative permittivity) is the relative portion of the dielectric constant, and \( \varepsilon'' \) (the imaginary portion of the complex permittivity) is the dielectric loss. The loss tangent, tan\( \delta \) (where tan\( \delta = \varepsilon''/\varepsilon' \)), is a measure of a material’s tendency to heat during exposure to electromagnetic energy. Generally, \( \varepsilon' \) is an indicator of the energy that passes through a material, so...
that a high value indicates that the material is transparent to electromagnetic energy. On the other hand, \( \varepsilon'' \) and \( \tan\delta \) are indicators of energy absorbed by a material, so that a high value indicates that the material absorbs (is not transparent) to electromagnetic energy and therefore likely heats. It is important when considering information on dielectric properties that the definition of these parameters is well-established. For the purposes of this review article, we will adhere to the conventions as defined previously.

**DIELECTRIC PROPERTIES OF OIL SHALES**

Typical minerals present in oil shales include quartz, feldspars, clays (illite and chlorite), carbonates (calcite and dolomite), pyrite, and other minor minerals. Kerogen, the organic material in oil shales, is the target of unconventional fuels production. Elemental composition estimates for all kerogen include, as weight percent of the organic matter: C (80-82%); H (10-11%); N (2-3.5%); S (1-2%); and O (5-6.5%) (Baughman 1978; Smith 1961). Although more oil shales are a targeted layer for oil shale unconventional fuel processing due to its high kerogen content, oil shale mineral composition and kerogen elemental composition in other organic-rich layers can differ with depth and geographic location (Robinson 1976). Most organic matter in chemically-extracted oil shale samples is associated with the carbonate mineral matrix as opposed to the silicate mineral fraction (Jeong et al., 1983). An understanding of the dielectric properties of individual components of oil shales, such as the dielectric response of the minerals and water present in the marlstone, can aid in interpreting and predicting the overall dielectric properties of oil shales. For a typical oil shale mineral matrix consisting of dolomite (32-34%), calcite (16-17%), silica (15-18%), clays (35-35.5%) and a combination of naticolite, dawsonite, siderite, pyrite, ferroan and other minerals (2-5%) the marl matrix \( \varepsilon' = 5.324 \) and \( \varepsilon'' = 0.029 \) at 500 MHz (Judzis 1980). Although individual minerals that comprise the inorganic marl matrix have dielectric properties that remain generally constant across a wide range of frequencies, the relative proportions of these minerals differ both geographically and with depth. Due to this variability, some investigators recommend against the use of \( \varepsilon' \) as an indicator of oil shale grade, or as a parameter that indicates absorption of energy by kerogen, and instead suggest the use of \( \varepsilon'' \) and \( \tan\delta \) as parameters (Judzis 1970). Tisot (1969) reported that surface area estimates for oil shales suggest that only a small amount of the organic matter present is bonded physically or chemically to minerals. Absorption of electromagnetic energy by kerogen therefore may occur independently of energy absorption by the mineral matrix. In using electromagnetic energy to identify and pyrolyze kerogen in oil shales, applying energy at different frequencies other than those preferentially absorbed by water and high permittivity minerals may specifically target and increase the efficiency of electromagnetic energy absorption by kerogen. Some investigators hypothesized that certain physicochemical effects and the presence of formation water affect observed trends in oil shale dielectric properties. Nottenburg et al. (1979) measured the dielectric properties of 10 types of oil shales across the frequency range of 50 Hz to 1 MHz at room temperature. They observed a decrease in the \( \varepsilon' \) magnitude with increased numbers of drying cycles (for each cycle: pre-heat to 110 °C for 24 h, then cool to room temperature for measurement) for oil shale samples cored perpendicularly to the bedding plane, and similar results were observed for samples cored parallel to the bedding plane. Scatter in \( \varepsilon' \) and \( \varepsilon'' \) versus oil shale grade was reduced with increased numbers of drying cycles (at 1 MHz applied frequency) [Figure 1]. Reduction in the magnitude of \( \varepsilon' \) and the decrease in scattering effects from interfacial polarization may be explained by the removal of pore water (e.g., non-mineral-bound) from the oil shale matrix with each drying cycle. However, it appears that not all of the pore water was removed due to continued changes in the measured dielectric properties with increased numbers of drying cycles. Nottenburg et al. (1979) noted that interfacial polarization effects on dielectric measurements in wet samples at frequencies <100 kHz were not as prominent in wet samples measured at frequencies >100 kHz. Therefore, they suggested that dielectric heating methods should be employed at the higher end of the frequency spectrum in order to avoid interfacial polarization effects, although potentially long pre-heating times may be necessary in order to remove water from tight oil shale pore space. Although interfacial polarization can be a frequency-specific phenomenon, and in dried samples may reflect irreducible water trapped within the marl matrix, the lack of a relationship observed between \( \varepsilon' \) and oil shale grade also has been explained by others as an effect of varied inorganic mineral distribution within the oil shale matrix.

**ANALYSIS OF 10 SAMPLES OF OIL SHALES UNDER MICROWAVE**

In the case of conventional pyrolysis, oil shale particles (20 g, 1–1.25 mm) were heated to 550°C at a heating rate of 10°C min⁻¹ in a stream of nitrogen gas with a flow rate of 0.151 min⁻¹. In the case of pyrolysis by microwave irradiation, a shale sample of 20 g, mixed with a small percentage (approximately 0.5 wt.%) of carbon grains to allow uniform heating, is placed in the sample holder. A constant flow of carrier gas (nitrogen) with a flow rate of 0.151 min⁻¹ is supplied immediately after the microwave field is applied.
The yields and the composition of the oil recovered from the oil shale after microwave pyrolysis and conventional heating are given in Table 1. The yields obtained for $\pi_i = 300$ W and 450 W are almost similar to those of the conventional pyrolysis. However, the yield decreases for $\pi_i = 600$ W. This result can be explained by the fact that during pyrolysis, the temperature increases rapidly and reaches high values which favors the reactions of gasification and cracking of the oil. In addition, solvent fractionation of the oils (Table 1) shows that oils resulting from microwave pyrolysis are less asphaltinic and polar than those produced by conventional heating. The percentage of maltenes, aromatics and polars increases when the incident power is increased. This is due to the degradation of the large molecules of kerogen and asphaltenes leading to small molecules of aromatics and polars that are soluble in alkanes. Similar results were observed for pyrolysis by conventional heating (Noble RD et al., 1980, 1981; Wang et al., 1983; Nguyen 1990).

**Table 1.** Yields and composition of shale oils obtained by microwave pyrolysis and conventional heating

<table>
<thead>
<tr>
<th>Products</th>
<th>Conventional pyrolysis</th>
<th>Microwave pyrolysis</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\pi_i = 300$ W</td>
<td>$\pi_i = 450$ W</td>
</tr>
<tr>
<td>Oil (wt.%)$^a$</td>
<td>6.6 ± 0.1</td>
<td>6.1 ± 0.2</td>
</tr>
<tr>
<td>Spent shale (wt.%)$^a$</td>
<td>86.8 ± 0.1</td>
<td>67.8 ± 0.4</td>
</tr>
<tr>
<td>Water (wt.%)$^a$</td>
<td>2.6 ± 0.1$^b$</td>
<td>16.8 ± 0.2</td>
</tr>
<tr>
<td>Gas + Losses (wt.%)$^a$</td>
<td>4 ± 0.1</td>
<td>9.3 ± 0.2</td>
</tr>
<tr>
<td>Asphaltenes (wt.%)$^a$</td>
<td>10.9 ± 0.1</td>
<td>7.2 ± 0.1</td>
</tr>
<tr>
<td>Maltenes (wt.%)$^a$</td>
<td>88.7 ± 0.2</td>
<td>91.7 ± 0.3</td>
</tr>
<tr>
<td>Paraffins (wt.%)$^a$</td>
<td>18.6 ± 0.5</td>
<td>16.1 ± 0.4</td>
</tr>
<tr>
<td>Aromatics (wt.%)$^a$</td>
<td>58 ± 0.7</td>
<td>64.3 ± 0.6</td>
</tr>
<tr>
<td>Polars (wt.%)$^a$</td>
<td>11.9 ± 0.4</td>
<td>5.8 ± 0.3</td>
</tr>
<tr>
<td>Time (min.) required to obtain the maximum quantity of oil</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

$^a$ Based on oil shale.
$^b$ After previous drying at 100°C.
$^c$ Based on oil.
CONCLUSION
Use of techniques employing electromagnetic energy to assess oil shale formation potential and to retort oil shales appears technically feasible, however, the geologic and processing parameters affecting energy absorption by oil shales need to be considered when designing a large-scale project. The current literature shows that both pore water saturation and mineral-bound water, in addition to mineral content, can affect the measured dielectric properties of oil shales. Dielectric properties remain constant at higher frequencies, although the amount of energy absorbed by oil shales is related to organic content. The geometry of organics and inorganics within the oil shale also can affect dielectric heating techniques. Dielectric properties differ in heated and retorted samples, as shown by temperature dependent effects on measured dielectric properties.

The oil shales seems to be related to the retorting of shales and the degradation products of the kerogen. These results have to be confirmed by measuring the dielectric and magnetic properties of the material as a function of time and temperature. During pyrolysis under microwave irradiation, the temperature increases rapidly and reaches higher values, thus favoring the cracking reaction of oil shale. This is in agreement with the observed lower percentage of paraffins in the oils of microwave pyrolysis (Table 1, \( \pi = 450 \) W). The obtained oil has interesting characteristics. It is more maltenic, less polar than the oils obtained by conventional pyrolysis. In addition, a fast pyrolysis 40 min (\( \pi = 300 \) W), 25 min (\( \pi = 450 \) W) 8 min (\( \pi = 600 \) W) instead of 60 min in the case of conventional pyrolysis.

REFERENCE