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# APPLIED PIROLYSIS

## Analysis of the asphaltene properties of heavy crude oil under ultrasonic and microwave irradiation



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#### ABSTRACT

Using new technologies are quite significant in the production and development of heavy oil reservoirs. In this study, the effects of microwave (MW) and ultrasonic (US) waves on the properties of Ellam heavy crude oil of the southwest oil reservoirs of Iran have been investigated. Experimental results show that different processes occur in samples under MW radiation for 5, 10, 15 and 20 min. Under MW for 5 and 10 min we have viscosity reductions from 15.836 mPa.s to 12.234 mPa.s and 11.122 mPa.s, respectively. This is due to volume expansion with decreasing viscosifying component and high absorption capacity of heavy molecules of oil toward MW that charges the cracking process. US waves increase the viscosity of oil for all time durations because the power from US waves causes the evaporation of light compounds. Next, the effect of MW and US radiation on the asphaltene clusters using microscopic images was investigated. Results of asphaltene particle size distribution show that increasing duration of wave radiation makes the particles smaller, and the size range of asphaltene particles in the samples under MW radiation is much smaller than for the samples under US wave radiation. Moreover, in samples under MW radiation, the large particles cannot be seen. Consequently, the average particle size of asphaltene is smaller in samples under US wave radiation. But the particle size range is high, and large-sized particles in different time intervals of US radiation are observed. The results of scanning electron microscopy show that microwaves make the asphaltene conglomerate forming particles smaller and more regular in shape than the primary state, whereas ultrasonic waves completely alter the structure of the asphaltene particles, creating asphaltene clusters with a different structure. Based on the Fourier transform infrared spectra, ultrasonic exposure increases the cracking rate of the weaker bands and the condensation of aliphatic bands more than does exposure to microwaves, due to an increase in the intensity of the spectra.

#### 1. Introduction

Asphaltene is one of the heavy components in crude oil. Any changes in the physical and chemical properties of asphaltene lead to precipitation that disturbs the suspension state of these particles, allowing them to form deposits on the surfaces of the reservoir rock as well as the pipeline and other processing equipment. Eventually, this causes expensive problems such as permeability reduction and considerable changes in wettability, in particularly heavy-oil fields. Finally, it affects oil production and the economic efficiency of the reservoir. To date, the oil industry has not yet found a comprehensive solution to the problem of asphaltene deposition. Existing solutions are only temporary, and the oil industry's need to extract oil from heavy-oil reservoirs makes the problems caused by asphaltene deposition incredibly important. Almost any change in the physical or chemical equilibrium of oil can cause asphaltene deposition. The most common changes are [1-4]:

- 1. Mixing fluids of different temperatures and composition.
- 2. Gas injection and changes in pH.
- 3. Effect of strong electrical charges and chemical material.
- 4. Drops in pressure and temperature.

Asphaltene particles are soluble in low-molecular-weight aromatics (such as benzene or toluene) and insoluble in low-molecular-weight alkanes (such as *n*-heptane or *n*-pentane); these alkanes stabilize emulsions to the greatest extent at or near the point of precipitation [5–7]. Numerous studies have been carried out that model the formation of asphaltene deposition and the kinetic solubility of these precipitants in different solvents [8–13]. For instance, Spiecker et al.

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studied the aggregation and solubility behavior of asphaltene and its subfractions [14]. Using chemical solvents to remove asphaltene depositions near wellbore is not economically efficient, as the process is inefficient, requiring large volumes of solvents. These solvents also cause formation damage near wellbore by changing the wettability of the rock [15]. Moreover, all chemical treatments pose many dangers to environmental and personal safety. Mechanical methods including pigging flow lines, wireline tubing and scrapers (containing a rod, wireline, flow line, and free-floating piston) are also used to manage asphaltene deposition, but they have a number of significant disadvantages [16–19]:

- 1. High operational cost.
- 2. Restrictions on the use of some equipment.
- 3. Long duration.
- 4. Danger of fishing of tools.
- 5. The possibility that perforations will become clogged.

Therefore, there is a need for technologies that can effectively remove asphaltene depositions in heavy-oil reservoirs. A combination of two (or more) of the methods described above (for example, mechanical and chemical) can be combined to form an effective solution. MW treatments have been proposed as a superior means of reducing viscosity and thermal-cracking and upgrading of heavy oil processes [20,21]. US treatment can be a continuous phase to provide adhesive and ductile properties to dispersed asphaltenes [22]. US radiation decreases the size of asphaltene clusters, thus increasing the suspension of asphaltene in crude oil and reducing or preventing its tendency to precipitate [23]. Other studies compared the efficiency of US waves in inhibiting asphaltene flocculation in crude oils with different gravities (API) [24]. US irradiation has been shown to change the rheology of asphaltenic crude oils, which may be due to changes in the crude oil's chemical and physical properties induced by sonication [25]. Yudong et al. (2013) found that US treatment can change the average structure of the residue, and changes in the content and structure of asphaltenes are the main causes leading to changes in the oil's properties [26]. US radiation has negative impacts on the distribution of the asphaltene particles' diameters, kinetic growth rates and oil viscosity [27] and removing the inorganic scale in porous media [28-30]. The mechanism by which MW heating induces chemical reactions is still unknown [31]. Much attention has been focused on the MW enhancement of changes and cracking of oil components because MW irradiation has demonstrated the ability to accelerate these processes; however, to date no report has been published that examines the effect of MW on asphaltene particles. Therefore, evaluation of the impact of MW on oil components is essential. The investigations and results of this paper can somewhat decrease the ambiguities in how MW technology can be applied in the oil industry, both on a wider scale and specifically in heavy/ultra-heavy oil reservoirs. In this study, the effect of ultrasonic (US) and microwave (MW) for different lengths of time on the components and viscosity of heavy crude oil from one of the southwest reservoirs of Iran has been studied. Effect of these waves on asphaltene particle size and the structure of asphaltene clusters using microscopic images analysis, as well as by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectra. From the results of this study, we can show how to use new technologies, by applying MW and US, for the improvement of heavy crude oil reservoir production by decreasing the viscosity and removing asphaltene precipitation.

#### 2. Experimental procedure

The heavy oil used in this study were obtained from the Ellam reservoir in southwest Iran. Saturations, aromatics, resins (ASTM D-4124) and asphaltenes (IP-143) in the heavy oils were determined using SARA experiments. The characteristics of the heavy oil are shown in Table 1. The onset of asphaltene precipitation in crude oil was measured using a

Table 1
Heavy oil composition.

Heavy oil properties	
Saturates (wt.%)	11.15
Aromatics (wt.%)	49.65
Resin (wt.%)	27.86
Asphaltene (wt.%)	11.34
Viscosity (mPa.S) @ 22 °C	796.28
°API	17

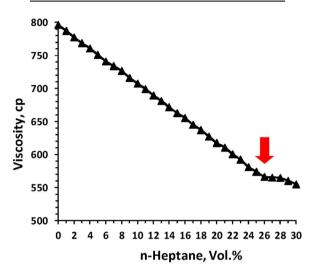
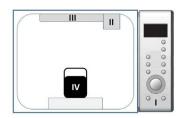


Fig. 1. Onset of asphaltene aggregation.

Controller II. Magnetron III. Waveguide IV. Oil sample

viscometer with different n-heptane percentages [32]. The measured onset occurred with a mixture of crude oil and *n*-heptane measured by a viscometer in 26 vol% of *n*-heptane and 79 vol% of crude oil (Fig. 1). A 150 ml crude oil and sample of 26 vol% of *n*-heptane and 79 vol% of crude oil was subjected to MW and US waves for 5, 10, 15 and 20 min. The reason for stopping after 20 min is that after this period the values for the measured components remained almost constant. A schematic of the MW apparatus used in this study is shown in Fig. 2. Samples were exposed to MW at various time durations at a 2450 MHz frequency and 400 W power. A schematic of the US wave apparatus used in this study is shown in Fig. 3. The sample was subjected to US radiation at 20 KHz frequency and 400 W power at different time ranges. The irradiated oil was cooled for one day at ambient temperature to allow it to stabilize. After the MW and US radiations were completed for the specified time interval, they cooled and the viscosity at standard temperature (25 °C) measured. After mixing the solution, sometime is required that the flocculation to be formed. Four drops of samples are observed using magnification times microscope. The optical polarizing microscope consists of a high-resolution video camera, a PC, a high-resolution image monitor and images were stored in high pixels. Solutions radiated with MW and US radiations for different time intervals.



I. Controller II. Magnetron III. Waveguide IV. Oil sample

Fig. 2. Schematic of microwave oven.

Controller II. Ultrasonic radiation generator III. Horn IV. Oil sample

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