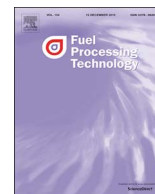




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# Fuel Processing Technology

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## Effect of microwave irradiation on the viscosity of crude oil: A view at the molecular level



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### ARTICLE INFO

#### Keywords:

Microwave irradiation  
Viscosity  
Composition  
Crude oil  
Heavy oil

### ABSTRACT

The increase in global energy demand and decrease in easily extractable light crude oil has generated a growing interest in heavy oil exploitation. However, the high viscosity of heavy oil leads to exploitation, transportation and refining challenges. In this context, microwave irradiation of crude oil samples from Sudan, China (Liaohe) and Venezuela were carried out to investigate the mechanisms of viscosity reduction. Saturate, aromatic, resin, and asphaltene (SARA) analysis of the crude oils was conducted according to the American Society Test and Materials standard, ASTM D4124-09. The SARA fractionation results demonstrated that microwave irradiation may affect the structure of resin/asphaltene micelles, thus leading to a change in the viscosity of the crude oil. The crude oils were further examined using the combined analytical techniques of electrospray ionization and Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS). The results from ESI FT-ICR MS analysis demonstrated that microwave irradiation of crude oil with a high proportion of O<sub>2</sub> compounds leads to polymerization, and ultimately an increase in the viscosity of the crude oil after microwave treatment. In other cases, cracking might occur due to the microwave heating.

### 1. Introduction

In recent years, factors such as increasing global energy demand, and rapid economic development of countries such as China and India, has led to the high consumption of petroleum products. To meet this demand, increased attention is focused on unconventional resources such as heavy oil and oil sands due to their enormous reserves. Heavy oil is defined as crude oil with a relative density higher than 0.92 or if the oil viscosity is higher than 100 mPa·s at the reservoir temperature. Heavy oil currently occupies at least half of the world's recoverable oil resources [1,2], and is mainly distributed in Venezuela, Canada, Russia, America and China [2,3]. However, drilling and transportation of heavy oils is a challenging task due to its high viscosity and high density, which can lead to flow and processing problems.

The main methods to reduce the viscosity of heavy oils include heating, dilution, emulsification, using chemical agents, catalytic reforming and microwave heating. Conventional heating is the predominant technique used for reducing viscosity due to crude oils high sensitivity to temperature. However, this is an energy intensive method, which necessitates the combustion of 1% of transported crude oil to meet the energy requirements. Moreover, heavy oil viscosity reduction

by the conventional heating method is a reversible process, thus, the viscosity level approaches the original value once the temperature decreases. Consequently, several heating equipment must be installed along the transport pipeline to maintain the viscosity at an acceptable level. As a result, the capital and operational costs of the conventional heating method is significantly high especially over long distances of pipelines [2].

Another widely used method for viscosity reduction is the dilution of heavy oil by mixing with lighter liquid hydrocarbons [1,4,5]. This is the simplest method, and it is more efficient for low wax content oil. For this method there must be a light oil resource and the crude oil needs to be dewatered before mixing. However, the physical properties of the crude oil will change if mixed with other oils. Another important drawback is that the transport capacity significantly increases. It is also important to highlight that the addition of light paraffin could lead to asphaltene precipitation, this may cause problems during the oil production [6,7]. Other viscosity reduction techniques, such as emulsification, chemical dosage, ultrasonic treatment and magnetic treatment, have been widely investigated but still have their limitations. There is currently no specific method to solve all the problems encountered in heavy oil transportation and exploitation.

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**Table 1**  
Key physical properties of the crude oil samples.

Item	Sudan	Liaohe	Venezuela
API°	22.3	15.2	16.1
Density (20 °C), kg·m <sup>-3</sup>	0.92	0.95	0.96
Oil classification	Middle-Naphthene based	Middle based	Naphthene based
Acid value, mg KOH·g <sup>-1</sup>	2.13	4.70	1.24
Viscosity (40 °C, cP)	202.1	1112.2	1546.4 (85 °C)
Carbon residue, %	7.53	9.00	11.13
Sulfur, %	0.75	0.34	2.49
Nitrogen, %	0.51	0.38	0.46
Nickel, µg·g <sup>-1</sup>	54	46.8	79
Vanadium, µg·g <sup>-1</sup>	0.9	1.54	396

Microwave heating effect arises from the interaction between the electric field and the charged particles in the material. If the charged particles are bound within regions of the material, i.e. in liquid or solid substances, the electric field will cause them to move until opposing forces balance the electric force. High frequency microwaves are responsible for collisions amongst the moving molecules due to the induced dipole moments produced by the applied electric fields. This in turn is responsible for heating [8]. In general, the higher the induced polarity, the greater the influence of microwaves. Therefore, microwave heating possesses the advantages of selective heating and volumetric heating.

Due to the specific microwave heating mechanism, more and more applications have been employed to the oil industry, including petroleum exploration and transport. Research proves that microwave heating can irreversibly reduce the viscosity of heavy oils [9–11]. This technology is efficient, clean and generates no pollution. Microwave energy was first used in the 1950s for petroleum exploitation [12]. In 1977, Bosisi et al. [13] carried out the first experiment of microwave extraction of asphaltene from sand shale, they found that the average molecular weight of asphaltene after microwave heating is lower than that of conventional heating. Moreover, small amount of CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> gases were produced. Bosisi et al. [13] also found thermal cracking of asphaltene occurred under microwave irradiation, which could be attributed to the thermal effect of microwave.

Researchers have examined the technology of microwave assisted exploitation. Sresty et al. [14] found that 35% oil can be obtained from oil sand after microwave treatment. Pizarro et al. [15] conducted a low frequency electrical heating field trial in the RIO Panan oil field in Brazil, and showed that the output can be increased from 1.2 bbl/d to 10 bbl/d after 70 days at a heating power of 20 kW. Wall [16] proved by experiment that the exploitation of high pour point crude oil is more economical through microwave technology, the produced oil obtained lower water content relative to the oil generated from conventional heating.

Recent studies show that the combination of electromagnetic (EM) heating and gas injection can efficiently enhance the oil recovery, a recovery of 45% was achieved using the combination of electromagnetic heating and gas injection, however only 24% and 20% oil can be obtained by applying electromagnetic heating and gas injection respectively [17]. The electromagnetic heating reduces the viscosity of oil, whilst the injected gas sweeps the heated oil away towards the production well, thus providing improved recovery rates [17]. Combining solvent injection with EM heating has also proved to further reduce the energy intensity of the process [18,19]. The research of Hu et al. [18] shows that combined EM heating and solvent assisted gravity drainage could effectively enhance heavy oil recovery up to 83.59% by using alternate EM heating and n-octane injection. With EM heating alone, the recovery is only 12.37%.

There are two theories on the mechanism of microwave viscosity reduction of heavy oil: thermal effect and non-thermal effect [10,11,19–23]. For the thermal effect, microwave selective heating makes the temperature distribution within the treated material non-uniform, the temperature in the polar component (resin and asphaltene) area is much higher making these materials decompose into small molecule materials, thus reduced the viscosity [10,11,19,20,22]. The theory of non-thermal effect states that microwave heating could reduce the molecule's activation energy and then induce cracking at low temperatures [21–23].

Although many studies have shown that microwave radiation may reduce the viscosity of crude oil irreversibly, the principles are still unclear, and there is a lack of research at the molecular level to analyze the reduction mechanism. The aim of this work was to investigate the effect of microwave treatment on the viscosity, SARA content, and heteroatom compounds of crude oil samples from Sudan, Liaohe (China) and Venezuela. In order to examine the mechanism of viscosity reduction by microwave irradiation at a molecular level, SARA fractionation and ESI-FT ICR MS analysis were carried out.

## 2. Materials and methods

### 2.1. Materials

All solvents and reagents used in saturate, aromatic, resin and asphaltene (SARA) fractionation are of analytical grade without any further purification. The solvents used in ESI FT-ICR MS are of HPLC grade and used as received. The crude oil samples used in this study were obtained from Sudan, Venezuela and Liaohe (China). The characteristics of the crude oil samples are listed in Table 1.

### 2.2. Microwave-assisted viscosity reduction

Experiments were carried out using a 3 kW single mode microwave cavity system, operated at 2.45 GHz (Fig. 1). Fifty milliliters of crude oil

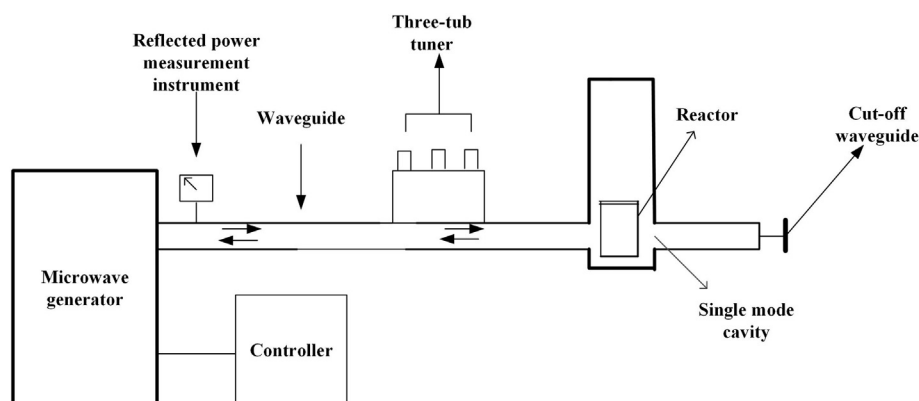


Fig. 1. Microwave treatment system.

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