The experimental study of effect of microwave heating time on the heavy oil properties: Prospects for heavy oil upgrading

Jaber Taheri-Shakiba,b, Ali Shekarifardb,b,* Hassan Naderic

a School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran
b Institute of Petroleum Engineering, College of Engineering, University of Tehran, Tehran, Iran
c Research Institute of Petroleum Industry, Department of Research and Technology of the Rock and Fluid Reservoirs, Tehran, Iran

ARTICLE INFO

Keywords:
Heavy crude oil
Microwave
Sulfur
Asphaltene
Upgrading

ABSTRACT

A heavy crude oil sample from an oil field in southwest Iran was placed in a Fischer assay and heated by microwave for two-minute time steps until 14 min total heating time had elapsed. Unlike conventional heating technique (CHT), which caused light carbonic components to escape and raised C20+ components in oil samples, the value of light carbonic components increased under microwave heating technique (MHT) up to 6 min. These materials cannot escape the oil sample in MHT because the cracked components approach a superheated state, and in this study a large portion of them remained at 6 min. Moreover, in contrast to the CHT results, the C1-C20 components increased to 13.5 wt% in the analysis of cracked gases during MHT. In MHT, light components increased with heating time, and C7+ components fell. This is indicative of light components escaping after 6 min. Some components escaped as condensate. In CHT, the escape of only small amounts of condensates was observed at 12 and 14 min, while under MHT, this phenomenon started at 8 min and contained larger amounts. This phenomenon is due to secondary cracking in oil, which is created by an abrupt increase in the temperature of some components that have more capacity to absorb microwaves. The sulfur content of heavy oil in MHT tended to decrease over time, approaching 34 wt% at 14 min; in contrast, in CHT it remained constant. Sulfur was removed from the oil sample as H2S and SO2, predominantly in a gas state, but also as condensate, in increasing amounts over time. Sulfur removal from the heavy crude oil sample is highly important in the upgrading process because of its high coefficient of microwave absorption. H2S is produced from the start of MHT, but SO2 is observed only after 6 min, and then only in the produced gas. Saturation, Aromatic. Resin and Asphaltene (SARA) components analysis showed changes in the resin and asphaltene components. The amount of asphaltene components began to decline starting early in the heating process, and approached its lowest amount at 4 min (3.21 wt%). Reduction of resin components in MHT began at 8 min and reached 55% at 14 min. Asphaltenes have a high capability to absorb microwaves due to having SNO (Sulfur, Nitrogen and Oxygen) components that create hot zones in heavy oil; these hot zones enhance cracking and upgrading. Scanning electron microscopy images of asphaltene particles showed that microwaves caused some changes in the structure of these particles. Energy-dispersive spectroscopy analysis of these particles showed that SNO components under MHT declined over heating time. The results also suggest that after sulfur, nitrogen and oxygen have the highest potential to absorb microwaves.

1. Introduction

In recent years the development of heavy-oil upgrading has assumed great importance. Various techniques are used to produce high-quality oil from heavy and ultra-heavy oils; these techniques are being enhanced to recover more product with less cost. The objectives of these enhancements are to decrease time treatment, increase energy efficiency, better manage the fluid flow, reduce waste and waste materials, increase safety by using less equipment, and allow the use of equipment that is more easily controlled.

Microwaves can assist in the separation of oil and water in stable oil-water emulsions, and enhances the effect of demulsifiers [1]. Hasçakir et al. [2] showed that microwave raises production by heating specific components and reducing viscosity. Ranji [3] investigated the mechanism of MW effectiveness and stated that the existence of some heavy elements in oil with different absorption coefficients for MW creates hot zones. Jackson [4] incorporated some additives with a high capability to absorb microwaves into heavy oil, finding that this

http://dx.doi.org/10.1016/j.jaap.2017.10.012
Received 21 July 2017; Received in revised form 13 October 2017; Accepted 14 October 2017
Available online 18 October 2017
0165-2370/ © 2017 Elsevier B.V. All rights reserved.
improves the upgrading process. Hence, extensive research in the field of heavy-ultra-heavy oil using more efficient processes needs to be conducted.

Microwaves are electromagnetic waves with a frequency range of 300 MHz to 300 GHz, corresponding to wavelengths of 1 mm to 1 m. Current estimates indicate that microwave technology in various industries can result in considerable savings in energy consumption and processing time. Moreover, microwaves create a uniform and homogeneous heating in substances. Microwaves affect some materials profoundly and others weakly [5]. Energy absorption varies depending on microwave frequency and power, sample composition and dielectric properties, and temperature. The dielectric properties of a substance and the result of applying electromagnetic waves on that substance can be studied. To optimize electromagnetic heating, these properties should be examined, as they have different values at different frequencies of electromagnetic waves. This interaction can be used to selectively heat specific sites in a sample [6,7]. In selective heating, only a selected volume of the target material is exposed to microwave radiation.

The most difficult obstacle to increasing the efficiency of production from heavy-oil reservoirs is that a large amount of energy is required in the process of heat injection. The usual method of transferring energy from the source to the sample takes advantage of the benefits of electromagnetic radiation over conventional thermal processing. MHT delivers energy directly, and offers a long thermal gradient, high penetrating capacity, and volumetric heating [8]. The chemical reactions that occur when microwaves are used to heat the oil are still largely unknown [9]. Much attention is focused on the microwave enhancement of changes and cracking of oil components because microwave irradiation has been shown to accelerate these processes. The effect of factors such as temperature, heating rate, and type of heating must be investigated. Moreover, understanding the kinetics of oil is also significant. Changes in the properties of heavy oil under various heating conditions have not been extensively studied. Because the quality of oil recovered from a heating process (conventional or microwave) is a light crude oil, additional upgrading processes are required [10]. The results reported in this paper can somewhat reduce the ambiguities in the use of microwave technology in the oil industry, particularly with respect to enhancing production from heavy- and ultra-heavy-oil reservoirs, and can suggest additional ways to apply microwaves in oil reservoirs in the future.

2. Materials and Methods

A 150 ml sample of Sarvak oil (Viscosity: 943.66, API: 15) from an oil field in the southwest of Iran was subjected to MHT in a Fischer assay apparatus (Fig. 1). MHT was performed at a frequency of 2450 MHz and a power of 400 W and 900 W. All parts of the device were first filled with helium so that heating could take place without the presence of oxygen and other reactive gases; this was because the volume and components of outlet gas would be measured when heating the oil sample. The sample was subjected to heating in the Fischer assay at time intervals of 2, 4, 6, 8, 10, 12, and 14 min. The gas extracted by heating the oil sample was stored in a gas meter (VINCI-Numero serie N*200). Gas composition was determined using gas chromatography (GC). The outlet condensate from the crude sample was gathered in a receiving flask using a condenser. The condensate components were determined by GC (ASTM D6729), and its sulfur content was also measured using a Vario Max-CHNS elementar (Carbon, Hydrogen, Nitrogen and Sulfur) (ASTM D4294). The heated crude sample was stabilized in a cold environment for one day. Carbon and CHNS components were measured using gas chromatographic simulated distillation (GC-Sim Dis) and the Vario Max-Chns elementar, respectively (ASTM D5291, ASTM D4294). Saturations, aromatics, resins (ASTM D-4124), and asphaltenes (IP-143) were determined using SARA analysis. Scanning electron microscopy (SEM) images of asphaltene particles under MHT were taken to observe changes in their structure. The asphaltene particles under MHT were examined using electron-dispersive spectroscopy (EDS) to determine amounts of CSNO (Carbon, Sulfur, Nitrogen and Oxygen), V (Vanadium), and Ni (Nickel) components. All tests were also conducted using CHT for comparison. After each heating period, we immediately measured the temperature with a thermometer. Because the thermometer had a metal wire, we could not put it inside the microwave. Therefore, after the heating time was completed, we immediately measured the temperature. In CHT, we adjusted the oven based on the heating time. For example, if the temperature in the microwave oven reaches 44 °C at 4 min, the typical oven temperature is set to 44 °C at 4 min. In some cases, it was not possible to reach expected temperature at a given time interval. In these circumstances, we changed the temperature rate of the oven to reach the desired temperature. The temperature of the crude oil sample at different time durations is displayed in Fig. 2 (2450 MHz and 400 W). The reason for choosing time intervals of 2 minutes is that we did not observe a significant change between different steps at intervals of 1 minute. A total heating time of 14 minutes was selected because after 10 minutes the rate of the changes had nearly approached zero. Microwave irradiation imparts energy directly to the oil sample by the interaction between an electric field and the electric charges of molecules, or molecular interaction within the generated electromagnetic field [11]. Therefore, the components of the material can be heated individually and instantaneously by applying energy as high-frequency electromagnetic waves, overcoming limits imposed by the material’s heat-transfer characteristics. MHT to 10 minutes considerably increased the samples’ temperature (84 °C), after which their capacity to absorb microwaves decreased.

![Schematic of microwave Fischer oven.](image-url)
3. Results and Discussion

3.1. Carbon components

The GC-Sim Dis results in Fig. 3 shows the distribution of different types of hydrocarbons in the samples affected by the heating processes (2450 MHz and 900 W). Experimental results show that MHT yielded lighter components than CHT at the same temperature. Three different scenarios of interaction between the microwave energy and the crude-oil components occurred, which led to the vibration and rotation of the material’s molecules: absorption, conduction, and reflection. The absorption of electromagnetic waves causes in-situ movement of crude oil molecules, which contributes to the generation of heat caused by friction [12]. Based on the experimental results, there was a significant difference in final components obtained using MHT as compared to CHT.

At the time interval of 2 min, CHT decreased C1–C10 from 1.7 wt% to 1.56 wt%, C11–C19 from 13.35 wt% to 13.43 wt%, and C20+ components of crude oil from 84.97 wt% to 85.09 wt%. In MHT these values were 6.4 wt%, 17.32 wt%, and 76.66 wt%, respectively. At 2 min heating, no significant change occurred in the carbon components of the CHT sample, while under MHT the C1–C10 and C11–C19 components increased to 4.34% and 3.97%, respectively, while C20+ components declined to 8.31%. The largest increase under MHT was observed in the C6–C10 components (3.55 wt%), and the greatest reduction was associated with the C26–C40 components (6.21 wt%).

At 4 min, under CHT the C1–C10 and C11–C19 components declined by 0.57 wt% and 1.2 wt%, respectively, and the C20+ components increased by 1.77 wt%. However, under MHT, the C1–C10 and C11–C19 components increased by 6.35 wt% and 10.32 wt%, respectively, while C20+ components declined by 16.52 wt%. The largest increase under MHT was observed in the C10–C19 components (5.57 wt%), and the greatest reduction was observed in the C26–C40 components (10.36 wt%).

At 6 min, under CHT, the C1–C10 and C11–C19 components declined by 0.82 wt% and 3.13 wt%, respectively, and the C20+ components increased by 3.95 wt%. However, under MHT, the C1–C10 and C11–C19 components increased 13.5 wt% and 17.62 wt%, respectively, and the C20+ components declined by 31.11 wt%. The largest increase under MHT was observed in the C11–C13 components (14.16 wt%), and the greatest reduction was observed in the C26–C40 components (17.29 wt%).

At 8 min, under CHT, the C1–C10 and C11–C19 components declined by 1.19 wt% and 4.45 wt%, respectively, and the C20+ components increased by 5.66 wt%. However, under MHT, the C1–C10 and C11–C19 components increased by 12.75 wt% and 16 wt%, respectively, and the C20+ components declined by 28.74 wt%. The largest increase under MHT was observed in the C11–C13 components (13.87 wt%), and the greatest reduction was observed in the C26–C40 components (16.42 wt%).

At 10 min, under CHT, the C1–C10 and C11–C19 components declined by 1.56 wt% and 7.44 wt%, respectively, and the C20+ components increased by 9.06 wt%. However, under MHT, the C1–C10 and C11–C19 components increased by 9.25 wt% and 15.17 wt%, respectively, and the C20+ components declined by 24.35 wt%. The largest increase under MHT was observed in the C11–C13 components (12 wt%), and the greatest reduction was observed in the C26–C40 components (14.12 wt%).

At 12 min, under CHT, the C1–C10 and C11–C19 components declined by 1.54 wt% and 8.85 wt%, respectively, and the C20+ components increased by 10.1 wt%. However, under MHT, the C1–C10 and C11–C19 components increased by 0.66 wt% and 3.91 wt%, respectively, and the C20+ components declined by 4.55 wt%. The largest increase under MHT was observed in the C11–C13 components (3.27 wt%), and the greatest reduction was observed in the C40+ components (4 wt%).

At 14 min, under CHT, the C1–C10 and C11–C19 components declined by 1.59 wt% and 8.7 wt%, respectively, and the C20+ components increased by 10.3 wt%. However, under MHT, the C1–C10 and C11–C19 components increased by 0.62 wt% and 2.41 wt%, respectively, and the C20+ components declined by 3 wt%. The largest increase under MHT was observed in the C11–C13 components (3.07 wt%), and the greatest reduction was observed in the C26–C40 components (3.75 wt%).

Overall, the 6 min time duration showed the greatest changes, with the largest increase observed in the C1–C10 and C11–C19 components, and the largest reduction in the C26–C40 components. In fact, at 2, 4, and 6 min, the C1–C10 and C11–C19 components showed a rising trend and the C20+ components a dropping trend, while at 8, 10, 12, and 14 min these trends were reversed. Under CHT, all samples showed a decline in C1–C10 and C11–C19 components and an increase in C20+ components.

Under MHT, due to the high amounts of energy received, the temperature increases quickly; this rapid increase does not allow the components and bonds to be separated and reach vapor phase even at the normal evaporation (condensation) point. Therefore, light hydrocarbon components do not have enough time to escape the crude oil. This phenomenon causes the MHT 2, 4, 6 min samples to show a high concentration of C1–C10 components, especially at 6 min. Under MHT, the materials pass the normal evaporation (condensation) temperature but fail to reach to the vapor phase, becoming superheated. The cracking process needs high temperatures, and thus this superheated state would eventually increase the intensity of cracking. The approach
to the vapor phase is an endothermic process. Thus, the sample needs to absorb thermal energy from the ambient environment to reach vapor phase. This absorption leads to a decrease in energy decrease and either stability or a decrease in the temperature of the environment. The materials need to acquire latent heat for condensation to reach the steam phase a normal evaporation temperature. Under the exothermic process of MHT, materials receive latent heat energy, unlike CHT; this increases the temperature of the bonds and prevents energy loss to achieve their separation. Consequently, this reduction in energy loss as the bond temperature increases leads to an increase in the temperature of the material to a higher-than-normal evaporation (condensation) point \([13,14]\). This superheating process also helps to increase the temperature in these zones, and eventually results in the cracking of those components of the material that have not previously reached the cracking point. At time durations more than 6 min, under MHT, there is enough time for existing C_1–C_{10} components to escape due to the increased temperature; thus these components begin to escape from the crude oil. This issue can be observed in outlet gases and produced condensate due to MHT cracking, which will be discussed below.

### 3.2. Sulfur content

Fig. 4 shows the sulfur content of crude oil heated using MHT at different time intervals. At all durations, the sulfur content of the sample had an almost constant value. Similarly, heating with CHT showed no change in sulfur content over time due to the evaporation of other components. Under MHT, between 4 min and 10 min, we observed a linear reduction in sulfur content, after which we observed a steep reduction followed by a gradual decrease in sulfur content. In 10 min, as shown in Fig. 2, a dramatic rise in temperature occurred that

---

**Fig. 3.** Histogram of hydrocarbons composition of the MHT and CHT samples.
Generally, the oils with higher concentrations of sulfur components as well as heavy molecules (i.e. asphaltenes) had high absorption coefficients, which caused rapid increases in temperature [15]. Heavy-molecule components containing sulfur, such as asphaltenes, play a key role in carrying charges in heavy crude oil and have higher dielectric properties. These properties, along with high amounts of these components in the heavy oils, lead to increases in temperature under MHT. The concentration of these heavy components, which are good microwave receptors, create local regions that absorb comparatively more energy, creating micro-zones of higher temperature [16,17]. These micro-zones, also called “hot zones”, contribute more to upgrading at an earlier time. The difference between heat distribution for MHT and CHT caused a higher yield range of condensable product during microwaving (Fig. 5). In MHT, the measured bulk temperature was lower than the local temperature adjacent to the hot zones. This caused the heavier carbon chains to reach their cracking threshold, increasing the lighter component fractions. The C1–C10 and C11–C19 components increased under MHT, which can also be due to such zones resulting from cracking of heavier components. These zones have more capability to absorb microwaves and their temperature can rise rapidly, which can cause secondary cracking in heavy components. Secondary cracking occurs adjacent to the hot zones under MHT. In hot zones, the concentration of sulfur is higher than in other parts of the crude oil, and
thus, the possibility of heavier components cracking in these regions is higher than usual [16,17].

To investigate how the reduced sulfur contents left the crude oil sample under MHT, a process of produced gas and condensate was required. The volume of produced gas at various time ranges is shown in Fig. 6. The gases were placed inside a gas meter at 12.58 psi pressure and 70 °F temperature during the heating process. As the figure shows, the cracked volume of gas under MHT was much greater than under CHT – as much as four times greater at 14 min. One of the most important factors in the heating profile of oil is the heating mechanism. If the heating mechanism is such that the temperature rises in the middle of the sample, it will have the best heating profile and the best yield according to reaction processes, as long as the temperature is kept high. In contrast to CHT, MHT increases the temperature in the whole sample simultaneously without intervention by the vessel wall. This means that the heating proceeds uniformly throughout the vessel, reaching completion simultaneously. This effect also influences the general scalability of reactions and cracking, as an identical heating profile can be achieved regardless of the volume of the vessel. MHT is assisted synthesis, in that the ability to raise the temperature of a reaction well above the boiling point of the oil increases the speed of reactions by a factor of 10–1000 [18]. Unlike CHT, reactions in MHT are thus completed in minutes or even seconds. Heating time is very short, and thus cracking and reaction procedure can be fully optimized in a short time. Due to this reason, MHT yields a greater volume of cracked gas than CHT. Cracked-gas components at different time intervals are displayed in Table 1. After placing the cracked gas in the gas meter during CHT and MHT heating, gas chromatography was used to determine the gas composition. In cases where not enough gas was obtained, helium was added to make up the minimum volume needed to determine the sample’s composition using gas chromatography.
3.3. Cracked gas

As shown in Table 1, MHT yielded lower amounts of C1–C6 components of cracked gas than CHT; in CHT most light components left the sample in the form of gas. C6 components were measured in greater amounts than C1–C5 components under MHT in the initial heating time, although they declined as heating time increased. C7+ components, like C6, tended to decrease over heating time, and their content varied from 38.202 mol% to 9.634 mol% at 14 min. C6 and C7+ components showed irregular changes, and had lower values at the initial time compared with MHT. Released nitrogen under MHT is always more than under CHT; however, at the initial time interval it had a low value, then rose from 0.223 mol% to 22.94 mol% at 14 min. CO2 under MHT process showed an increasing trend, reaching 2.345 mol% at 8 min, and a dropping trend thereafter. In contrast, CO2 under CHT showed irregular changes. Under MHT, sulfur within the crude oil heated rapidly, activating the liberation of H2S and SO2. However, under CHT, the temperature was not sufficient to cause this reaction[19]. Sulfur exists at the center of heating zones under MHT; the heat in these zones causes sulfur-bearing components to crack and produce H2S and SO2. Another possible reason for the lower sulfur content in the heavy crude oil under MHT is related to bonding activation[20,21]. It is accepted that microwaves particularly affect the sulfur bonds in polar or hydrocarbon components, resulting in the breakage of current bonds and the production of activated sulfur. The activated sulfur can react with the hydrogen present in the crude oil to create hydrogen sulfide. Hydrogen bonds between sulfur and carbon are the smallest and weakest of the hydrocarbon bonds. Thus, the decrease in sulfur content during the cracking phase under MHT most probably is the result of the bonds’ energy. Production of hydrogen sulfide from these reactions resulted in decreased hydrogen and sulfur content and increased carbon content in the MHT sample. However, because of the low sulfur content and intermediate rate of this reaction, the hydrogen fraction was not lowered significantly.

Existing oxygen in heavy components such as asphaltene (which have a high capacity to absorb microwaves) can be separated from the asphaltene under MHT, forming SO2 with the released sulfur. Oxygen, nitrogen, and sulfur are polar components of asphaltene that have high potential to absorb microwaves. As shown in Table 1, the amount of SO2 value in the CHT samples was zero, and the H2S value was nearly zero except in at 6 and 12 min, when minimal amounts were measured. The sulfur content of crude oil is affected by microwaves under MHT because it is a polar component of the oil, and therefore, selective heating occurs. In the current study, under MHT, the H2S value increased with heating time, and at 10 min approached its maximum (9.643 mol%); after that, its value stayed nearly constant (decrease 0.13 mol%).

Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>MHT</th>
<th>CHT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol%</td>
<td>mol%</td>
</tr>
<tr>
<td>C1</td>
<td>0.064, 0.076, 0.113, 0.148, 0.164, 0.234, 0.487</td>
<td>Trace, 33.292, 21.573, 1.039, 0.069, 0.038, 0.838</td>
</tr>
<tr>
<td>C2</td>
<td>0.124, 0.188, 0.175, 0.194, 0.267, 0.547, 0.774</td>
<td>Trace, 23.401, 16.137, 11.117, 7.165, 9.159, 17.193</td>
</tr>
<tr>
<td>C3</td>
<td>1.267, 4.364, 9.54, 4.57, 5.29, 6.37, 6.25</td>
<td>Trace, 18.356, 15.284, 13.486, 22.387, 19.218, 15.103</td>
</tr>
<tr>
<td>C4</td>
<td>0.918, 1.921, 4.26, 3.94, 4.84, 3.26, 5.24</td>
<td>Trace, 1.521, 2.172, 5.334, 5.963, 12.155, 12.922</td>
</tr>
<tr>
<td>n-C5</td>
<td>16.197, 15.616, 11.457, 13.286, 12.044, 11.498, 7.216</td>
<td>Trace, 2.733, 4.73, 12.385, 8.351, 15.247, 7.616</td>
</tr>
<tr>
<td>N2</td>
<td>0.223, 1.354, 3.63, 8.612, 11.256, 16.25, 22.94</td>
<td>Trace, 0.063, 0.097, 0.124, 0.081, 0.113, 0.052</td>
</tr>
<tr>
<td>CO2</td>
<td>0.269, 0.922, 1.642, 2.345, 2.123, 1.651, 1.223</td>
<td>Trace, 0.114, 0.222, 0.324, 0.162, 0.215, 0.167</td>
</tr>
<tr>
<td>H2S</td>
<td>0.141, 1.933, 3.616, 6.785, 9.643, 9.511, 9.601</td>
<td>Trace, Trace, Trace, Trace, Trace, 0.051, Trace</td>
</tr>
<tr>
<td>SO2</td>
<td>Trace, Trace, 0.081, 0.227, 0.364, 0.552, 1.164</td>
<td>Trace, Trace, Trace, Trace, Trace, Trace, Trace</td>
</tr>
</tbody>
</table>

Fig. 6. Gas volume cracked from crude oil during CHT and MHT processes.
mol% and 0.042 mol% at 12 and 14 min, respectively). The SO2 value under MHT at 2 and 4 min was zero, but SO2 began to form at 6 min and continued to increase over time.

According to Table 2 the condensate produced under both CHT and MHT did not take place at the initial times. Under MHT condensation began at 8 min and continued through to 14 min. Under CHT condensation occurred only at 12 and 14 min. In cases where sample amounts were small, we repeated the experiment many times to determine the components. MHT produced more condensate than CHT, which is associated with the type of cracking mechanism. The difference between the bulk temperature of the sample and the local temperature at hot zones was due to the linear form of liquid molecules, which need higher equilibrium time for movement of convective flow from the hot zones to the further viscose layers. Also, under MHT, the measured temperature is the average temperature, which is reported due to the difference in the liquid layers’ temperature. Temperature increases in MHT are quite abrupt and cause overheating at hot zones, impeding volatilization at the early stage [22]. Volatilization is an endothermic process which is accompanied by the absorption of energy from the surrounding hot zones. Temperature increases at the early phase of microwave absorption depend on the total energy generation.

The volatilization process consumes much energy to reach the vaporizing stage, which causes decreases in the surrounding temperature. Surprisingly, MHT at the early stage acts against the volatilization process at hot zone because of its significant heating rate with respect to the time; this leads to superheating and prevents boiling at the components’ normal boiling point [23]. Preventing the volatilization of heavy components keeps the surrounding temperature constant and prevents them from consuming energy to change phase at the early stage. In contrast, CHT has a slow rate of heating, which gives the molecule bonds time to detach and change their phase.

The aromatic components (C6–C12) under MHT were constant at 8 and 10 min and declined around 50% with continued heating time. Under CHT, the aromatic components declined from 15.712 wt% at 12 min to 10.734 wt% at 14 min. Of the aromatic components of the MHT samples, C9 and C10 had the highest percentage weight on average; but of the aromatic components of the CHT samples, C6 and C8 had the highest percentage weight. The iso-para components (C5–C12) under MHT declined over 10 min and then showed an increasing trend, reaching their highest value (32.364 wt%) at 14 min. Under CHT this value varied with heating time from 28.543 wt% to 35.694 wt%. Among the iso-paraffins on average the highest weight under CHT was for C6 (7.994 wt% at 14 min), and under MHT process was for C9 (6.805 wt% at 14 min). The naphthene components (C6–C12) showed no significant change with heating time under MHT, with the only change being a decline from 15.557 wt% to 14.441 wt% at 14 min. Under CHT, the naphthene components were mostly constant with heating time, although they showed an increase of 3.046 wt% at 14 min. Most naphthene compounds under CHT and MHT were C6 and C7. The olefin components under both CHT and MHT declined with heating time. Of the olefin components, C4 values increased with heating time under MHT, albeit to only a low value. Nevertheless, its value was much higher than under CHT, and almost constant. The oxygenate (C5) components under MHT were very low compared with CHT and showed no consistent changes. Under CHT, the oxygenate components declined to one-third with heating time. The para components (C4–C15) increased with heating time under MHT, varying from 35.513 wt% at 8 min to 42.214 wt% at 14 min. Under CHT, the para components increased with heating time to around 3.183 wt%
in 14 min. Generally, under MHT, low carbon numbers increased gradually with heating time, while under CHT these results were reversed. As Table 2 shows, the sulfur content under CHT was very low. Under MHT, no regular change in sulfur content was observed, with values fluctuating over heating time: at 10 min we observed an increasing trend (+0.069 wt%), at 12 min we observed a declining trend (−0.056 wt%), and at 14 min we again observed a rising trend (+0.106 wt%).

3.4. SARA compounds

Results of SARA analysis on the crude oil sample and heated samples under MHT are shown in Fig. 7. SARA results for CHT revealed that at time intervals of 2 and 4 min no significant alteration occurred in SARA components, and that as heating time extended past 8 min, saturate components declined, diminishing to 5.61 wt% at 14 min. Therefore, only the graphs related to MHT are given. Resin and asphaltene are the most prevalent polar compounds in crude oil [24]. The coefficient absorption of some components in crude oil is higher than

![Fig. 8. Structure and EDS of crude asphaltene particle.](image)
others, causing more coupling interaction under MHT. Resin and asphaltene have higher sensitivity to microwave irradiation and play a key role in heating by electromagnetic field because of their S, N and O compounds. The heating in these materials is caused by the rotation of polar molecules as they align themselves in an alternate electromagnetic field. These compounds can greatly improve microwave absorption and have a large impact on the upgrading of crude oil, as their dielectric properties mean that the molecules’ polarity aligns them with the microwave field pole. At 2 and 4 min, asphaltene content declined. At 4 min, the greatest reduction in asphaltene content (26%) was observed. At 4 min, the asphaltene content began to increase, finally reaching 11.87 mass% at 14 min. It should be noted that the trends of resin and asphaltene were in inverse proportion to each other. The highest amount of resin was at 6 min (56% increase), and the lowest
amount at 14 min (55% reduction), with the greatest reduction occurring at 8 min. The components of asphaltene, including sulfur as well as nitrogen and oxygen, caused the asphaltene to show a high potential for absorbing microwaves.

Asphaltene particles were separated from the crude oil using IP-143 testing. SEM and EDS images of asphaltene particles before and after 14 min microwave heating are shown in Figs. 8 and 9, respectively. As the figures show, microwaves not only changed the structure of the asphaltene particles but also caused changes in the CSNO components. The amounts of these components at various time durations are given in Table 3. The greatest reduction can be seen in sulfur content, which declined with heating time under MHT to approach one-third of its initial value. Nitrogen, unlike oxygen, showed a decrease at the start of MHT, and in 14 min had fallen to around 56%. The oxygen amount was almost constant up to 8 min; at 10 min it began to decrease, finally reaching 25% of its initial value at 14 min. The vanadium value of asphaltene was constant at all time ranges under MHT. According to the observed alterations in asphaltene elements, sulfur has the largest potential to absorb microwaves, followed by nitrogen. Oxygen has the least capability to absorb microwaves.

4. Conclusions

The main conclusions for this study are summarized below:

- Heating time is a critical factor in MHT, because unlike under CHT the trend of changes in heavy crude is clear and predictable; at different time durations we observed various changes which were not generally predictable.
- Under CHT, $C_{20+}$ components increased with heating time, and light components left the sample during the heating process. Under MHT, the $C_1-C_{10}$ and $C_{11}-C_{19}$ components in the oil sample increased with heating time. In MHT, when the sample temperature exceeds normal evaporation, volatile matter cannot leave the oil sample in the form of vapor and approaches a superheated state, which traps them in the oil sample until the heating time and temperature of the sample increase further. In this sample, this phenomenon took place after 8 min and the components started to leave the sample. GC results of produced gases under CHT and MHT show that CHT yields a greater amount of light components. Under MHT, early in the heating process lower amounts of light components escaped, but these amounts increased with heating time. In contrast, $C_{2+}$ components of gas produced under MHT showed a declining trend. This is consistent with the carbonic components of crude sample. Light components rose at initially time in the crude sample, after which they decreased. The composition of the gas produced earlier in the heating process contained insignificant amounts of light components; later, these amounts increased. The analysis of produced condensate components showed that paraffinic and iso-paraffinic components were emitted in the highest percentage, which increased with heating time.

- The sulfur that exists in heavy crude oil has a higher capacity to absorb microwaves than other crude-oil components, which can cause the sulfur to be expelled during the cracking process; this assists in the upgrading of heavy crude oil. This phenomenon is not observed under CHT because all components are uniformly heated. GC showed that the gases produced under MHT during cracking of the crude sample contained $H_2S$ and $SO_2$, which constitute two ways sulfur can leave heavy crude oil. $H_2S$ is produced at the initial stage of heating under MHT and rises with heating time. $SO_2$ is produced later in the heating process; in this special case its production commences at 6 min and increases with radiation time. In contrast, under CHT the values for $H_2S$ and $SO_2$ are zero. The condensate produced under MHT contains some sulfur; with heating time the amount increases.
- Among the SARA components of crude oil, asphaltene components have the highest potential to absorb microwaves under MHT at initial time ranges, as they contain SNO matter that creates hot zones in crude oil under MHT. SEM images of asphaltene show that microwaves disturbed the structure of these particles. EDS results for these particles also demonstrated that sulfur had the highest potential to absorb microwaves, followed by nitrogen and oxygen.

References