Study the Effect of Using Microwave Radiation and H-Donors on Improving Heavy Oil

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Abstract
The present research has investigated the effect of microwave energy on improving the flow properties of heavy crude oil. The fragmentation of crude oil molecules was carried out with and without using 1 and 10 wt. % concentration of various types of H-donors like tetralin, cyclohexane, and naphtha. Microwave power of 320, 385, and 540 W and radiation time 1-9 min, and temperature were studied. The kinematic viscosity and asphaltene content were measured for evaluation the improving of heavy crude oil.

Results show that viscosity of crude oil decreased with increase H-donor concentration, a maximum percentage of viscosity reduction was 10.63 % for tetralin at 6 min radiation time, while 8.67%, and 7.34% for cyclohexane and naphtha at 4 min respectively. The high H-donor polarity is the high viscosity reduction.

The asphaltenes content of crude oil was decreased during microwave treatment process, a maximum percentage of reduction was 39.73% for tetralin at 6 min radiation time, while 34.40% and 46.29 % for cyclohexane and naphtha at 4 min respectively. The viscosity of crude oil was decreased with asphaltenes content decrease.

The temperature of a crude oil was varied during the microwave treatment and it was depended on radiation time and radiation power and H-donor type.

The best reduction of crude oil viscosity and asphaltenes content was achieved at a moderate radiation power 385 W.

Key words: microwave heating, heavy crude oil, H-Donors.

Introduction
The continuous depletion of conventional light crude oil led to increasing interest in the upgrading of heavy crude oil and residue, which considered a huge resource of energy [1, 2].

On the other hand, heavy oils and bitumens contain a number of high molecular weight components and an aggregate that was require more processing steps in order to be converted into useful finished products.

The characterization of these components is high viscosity values, high asphaltenes content, high metals (e.g., Ni, V, and Fe), high heteratom (e.g., S, N, and O) and low API gravity [3].
The US department of Energy classified: heavy oil as whose API gravity between 10° and 20°. Bitumen and extra heavy oil with API less than 10° [4, 5] , which make them difficult to process compared with light crude oil , and that cause challenges for upgrading such oil. These challenges impact producing, transporting and refining heavy oil [6, 2].

Heavy crude oil can be upgrade to lighter oil using several techniques. However, current methods (conventional) usually require high temperature, long reaction duration, high costs, and cause serious environmental pollution, with and without using catalysts. These techniques include Thermal processes, hydroprocesses, Separation Processes etc.

Therefore, many new technologies (unconventional) used for upgrading heavy oil involve the use of electric field, ultrasonic energy, magnetic field, and Biological processing [7, 8, 9]. The technology used is microwave energy, and is represents an alternative to the conventional methods which it has many benefits. These benefits include are fast, clean eco-friendly, economic and selective heating [10, 11].

This technique based on electromagnetic waves which that pass through the material cause its molecules to oscillate, molecules try to orient themselves with the field and generating heat [11]. However, materials exposure to electromagnetic waves dependent on dielectric properties that interact strongly with polar materials and weakly with others [12, 13].

It is preferred to use H-donor in the upgrading process assisted by microwave oven because of the hydrogen formed from dehydrogenation of hydrogen donors helps to stabilize generated free radical that are formed during cracking reaction, to narrow the molecular weight distribution of the product [14, 3].

Several researches worked on Sharky Baghdad Heavy Crude Oil to upgrading as Hussain et al., 2011[15], used distillation and solvent extraction to get the deasphaltened oil (DAO), they were observed that API of DAO increased twice the API of reduced crude oil while sulfur and metals content decreased 20% and 50% respectively. Mohammed, 2013[6], used different types of hydrocarbon and oxygenated polar solvents such as toluene, methanol, mix xylenes, and reformate, and different types of dispersants to reduce its viscosity from break down asphaltene agglomerates, results show that the high solvent polarity is high viscosity reduction and high asphaltenes content reduction.

Also, many attempts used microwave heating with and absence H-donors in crude oil treatment such as, Britten et al., 2005[12], used heavy petroleum samples with or without hydrogen donor addition using microwave energy process. They were observed with longer radiation time asphaltenes increased due to recombination reaction which is associated with high temperature. The maximum reduction percentage of asphaltenes content was 18.60% for Kerrbert heavy crude oil, while the reduction percentage of asphaltenes content was 28.57% when using 55wt. % naphtha at the same radiation time 2 min.

Miadonye A. & Macdonald B., 2014[10], studied the performance of microwave irradiation for upgrading heavy crude oil and Bitumen by inducing petroleum visbreaking, and used di-Ethanolamine DEA as hydrogen donor with different sensitizer (Activated charcoal, serpentine).
The results indicate that the reductions of viscosity crude oil at the same radiation time were 73.10% for 10 wt. % DEA with crude oil and 77.93 wt. % for 10 wt. % DEA and activated charcoal with crude oil.

Mohammed et al., 2011[16], used microwave oven and atmospheric distillation to upgrading heavy petroleum without any addition of chemicals or additives, and studied different of power and exposure time for irradiation microwave and from distillation results show that low power rates was very effective and gave a higher products yield due to fragmentation reaction.

The objective of present research is improving properties of Iraqi heavy oil by hydrogen donor assisted by microwave heating. This technology is based on the reduction of viscosity and asphaltenes content of heavy oil due to maximum break-up in asphaltene molecules. The upgrading of heavy oil by microwave is come out at different conditions as follows: Crude oil (without addition), different types of hydrogen donors (Tetralin, Cyclohexane, Light Naphtha), and concentration (1 and 10 wt. %), and studying the influence of different power level, radiation period, and reaction temperature.

Experimental Work
Materials
1- The feed stock of heavy crude oil in this study was supplied from East Baghdad oil fields, well number 14, with physical properties in table 1.

Table 1, physical properties of Iraqi heavy crude oil

<table>
<thead>
<tr>
<th>Test</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic viscosity (cst.)</td>
<td>163</td>
</tr>
<tr>
<td>API at 60 F°</td>
<td>18.5</td>
</tr>
<tr>
<td>Density at 15 C°</td>
<td>0.9428</td>
</tr>
<tr>
<td>Asphaltenes content wt.%</td>
<td>7.27</td>
</tr>
<tr>
<td>Sulfur content wt.%</td>
<td>4.81</td>
</tr>
</tbody>
</table>

2- Hydrogen donors used for treatment crude oil in this study were:
   a. Tetralin with 0.97 specific gravity and (206-208) °C boiling point supplied by Kunshan Yolong Trading Company (china).
   b. Cyclohexane with 0.78 specific gravity and 81°C boiling point supplied by Ridel-Dehaen agseelze company (Germany).
   c. Light Naphtha, with 0.77 specific gravity and (30-90) °C boiling point supplied from Al-Doura Refinery.

Microwave Treatment Unit for Crude Oil
1- Microwave set up
This consists from the followings: microwave oven supplied by china with (MM717CPJ) model, and power range (17L - 700) watt. Thermocouple with (M4012) model manufactured by (BBC-UNIVERSAL) Germany guard read temperature from (-30 – 700) °C. Q.V.F crucible tube with 2.5 inch diameter and 14 cm length. Teflon tube, Rubber stopper, Teflon stopper, Thermal isolator shield, Di-electromagnetic flange as shown in figure1.
2- Microwave treatment procedure

In case without addition: 40 gram of crude oil was used directed to run. In other hand, In case adding of H-donor was 40 gram crude oil and H-donor (1&10 wt. % base of crude oil) mixed using mechanical mixer for 10 min and 400 rpm.

Then, the prepared feed was put in Q.V.F crucible tube. Rubber stopper used to prevent escape of hydrocarbon vapor during microwave heating, and subsequently losses of the lighter molecules could be reduced. Then, the sample was placed at the center of the microwave oven, then the microwave was switched on a certain power level (320, 385, and 540 watts), the radiation time for heating sample at different radiation period (1- 9 min), the reaction temperature of sample was measured through Thermocouple. Then the sample was removed from microwave oven and it was left to cool to ambient temperature in sealed container for 1 day to allow all volatiles to condense and reconstitute a liquid phase.

Test of Feed Stock and Products

1- Kinematic viscosity

The kinematic viscosity of crude oil was measured by ASTM D 446 at 40 °C using Canon-Fenske, Routine viscometer, (300 and 350) size number.

2- Asphaltenes content wt. %

Asphaltenes content of crude oil samples were measured as following procedure: taken 1 gram of crude oil.

Then, 30 ml of n-heptane was added to crude oil in a 250 ml conical flask and mixed well using magnetic stirrer with 500 rpm for 15 min at ambient temperature. Then, the flask was covered and left for 48 hr. The mixture was then filtered using vacuum filtration unit and medium size of filter paper (no. 105). The precipitate asphaltene on filter paper was washed (2-4) times with 20 ml of n-heptane each time and filtration was continued at steady rate until washing are colorless.

Then, the precipitate (asphaltene) was dried in an oven over night at 100 °C. Finally, the asphaltenes weighted to find the asphaltene content.

Results and Discussions

Effect of microwave radiation time on properties of crude oil

1- Kinematic Viscosity

Figure 2 shows comparison of kinematic viscosity of crude oil between heavy crude oil with and without using different types of H-donors at 10 wt. % concentration at 385 W. It is obvious that the kinematic viscosity response is unstable with radiation time, and there is a transference behavior.

The viscosity heavy crude oil of thermally microwave was increased at radiation time from 1 to 2 min in spite of molecules fragmentation is occurred, due to the generation of light hydrocarbon molecules less than C$_5$ at short radiation time [12], which could not retain in crude oil.

Then, viscosity began decreasing at 3 min radiation time and continued until 4 min. The percentages of viscosity reduction were 1.22% and 2.45% at time 3 and 4 min respectively. This decreasing in viscosity was due to the fragmentation of high molecular weight hydrocarbon molecules and especially the asphaltenes to a condensable hydrocarbon (C$_5$-C$_{20}$) [12].

Then, the viscosity increased dramatically with increasing of radiation time from 5 to 9 min, due to increase of temperature led to the initiation of recombination reaction for fragmented molecules [13].
While, it is clear that the viscosity change behavior affected by radiation time is relevant to the type of H-donor. In general, the kinematic viscosity at 1 min radiation time was increased for all types of H-donors. Then, viscosity began to decrease until 3 min radiation time where zero-time viscosity was approximately reached. Beyond, a sharp decline in the viscosity was observed, and the maximum viscosity reduction was obtained 8.67% and 7.34% for cyclohexane and light naphtha respectively at 4 min radiation time, but except the tetralin, where the maximum viscosity reduction 10.63% was obtained at 6 min radiation time.

The results indicated that tetralin gave the higher percentage of viscosity reduction compared with cyclohexane and light naphtha, and this occurred due to the disparity in the solvents polarity (tetralin > cyclohexane > light naphtha). Also, tetralin give a better microwave absorption characteristic for the crude oil at low temperature, and this in agreement with Miadonye, 2014 [10]. After that time, the kinematic viscosity increased gradually with radiation time due to increase of temperature led to the initiation of recombination reaction for fragmented molecules [13].

Figure 3 shows comparison of kinematic viscosity of crude oil between heavy crude oil with and without using different types of H-donors at 1 wt. % concentration. It could be recognized that viscosity increased during first two minutes radiation time. It is worth mentioning that the viscosity response was approximately similar for all H-donors and crude oil without addition at 1 wt. %, while a diverse in behavior between the H-donors types and crude oil without addition was clear at 10 wt. %.

After that, the viscosity decreased until maximum reduction 3.58% and 2.70% for cyclohexane and light naphtha was achieved respectively at 4 min radiation time. On other hand, the maximum viscosity reduction 3.44% for tetralin was achieved at 6 min radiation time. Cyclohexane gave the maximum viscosity reduction at 1 wt. % among the other H-donors, and this situation agree well to the explanation by Hart, 2015 [3] Dehydrogenation of cyclohexane (CH) could liberate hydrogen for hydrocracking and hydrogenation reactions, if the partial pressure of hydrogen is high enough. After that time, viscosity increased gradually with increasing radiation time, and this back to recombination reaction.
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Fig. 3, effect of Radiation Time on kinematic viscosity of crude oil with and without various types of H-donors addition at 1 wt. % concentration and 385W

For comparison between figures 2 and 3, observed that the viscosity for 10wt. % H-donors gave higher percentages of reduction and response a diverse in behavior between the H-donors types different than 1wt. % in viscosity and this reasons beyond to the presence H-donors material and ability of hydrogen atoms transferring to the heavy hydrocarbon in the oil led to restrict and minimizing the polymerization of the molecules (heavy oil) via free radicals, and improving quality of the crude oil [17, 10].

Also, observed that the same behavior of effected radiation time on kinematic viscosity of crude oil where decreasing of kinematic viscosity due to the presence of light fractions at shorter radiation time and the strong possibility of the abundance of higher molecular weight hydrogen carbon due to increase the temperature at prolonged radiation time.

Figure 4 shows comparison of viscosity reduction percentage between crude oil without addition and H-donors types' addition, at 10wt. % and 1wt. % concentrations.

At high concentration 10wt. %, observed that the maximum kinematic viscosity reduction percentage for tetralin at 6 min, while both cyclohexane and light naphtha at 4min, and this situation agree well to the explanation by Vazquez, 2012 [17] described the importance of tetralin as hydrogen donor due to highly activated hydrogen atoms in the saturated ring adjacent to the aromatic ring.

Fig. 4, comparison between kinematic viscosity reduction percentages with and without various types of H-donors addition: (A) At 10 wt. concentration, and (B) at 1wt. % concentration
While, at low concentration 1wt. %, it is obvious that the kinematic viscosity reduction was Convergent in values between tetralin and cyclohexane at different radiation time 6min and 4min respectively, but light naphtha gave lower reduction percent in kinematic viscosity, and this occurred due to the disparity in the solvents polarity (tetralin > cyclohexane > light naphtha).

Also, observed that the percentage of viscosity reduction of crude oil without addition is 2.45% at 4min lower than when using H-donors.

2- Asphaltene Content

Figures 5 and 6 show the effect of radiation time on asphaltene content of crude oil at 385W with and without using different H-donors type at 10 wt. % and 1wt. % concentration respectively.

Figure 5 shows the comparison of asphaltenes content of heavy crude oil between heavy crude oil without addition and using different types of H-donors at 10 wt. % concentration.

The asphaltenes content has diverse respond with radiation time during microwave treatment. Where, asphaltenes content increased slightly from start to 1 min radiation time, caused by losing the light hydrocarbons (less than C5) produced by fragmentation which occur at short radiation time and led to concentrate the high molecular weight hydrocarbons (asphaltenes).

Beyond the 1 min radiation time, the asphaltenes content began to decline until 4 min where a maximum percentage of asphaltenes reduction 8.243% is achieved. While, the maximum percentage of asphaltenes content reduction was 34.30% and 46.29% for cyclohexane and light naphtha respectively at 4 min radiation time, while 39.73% for tetralin at 6 min.

This sharp decline is an evidence of asphaltenes molecules fragmentation to condensable distillates [12]. After that, the asphaltene content of heavy crude oil was increased due to increase of temperature at longer radiation period lead to recombination reaction [12].

Fig. 5, effect of Radiation Time on asphaltene content of crude oil with and without various types of H-donors addition at 10 wt. % concentration and 385W

Figure 6 shows the comparison of asphaltenes content of heavy crude oil between heavy crude oil without addition and using different types of H-donors at 1 wt. % concentration.

The asphaltene content at 1 and 2 min radiation time was increased slightly and convergent curves for all types of H-donors addition.

Then, the maximum percentages of asphaltene content reduction at the same radiation time when 10 wt. % were: 23.96% for tetralin, and 21.94% for cyclohexane, while 19.83% for light naphtha.

After that, the asphaltene content of heavy crude oil was increased with increasing radiation time, back to recombination reaction [12].
Fig. 6. Effect of Radiation Time on asphaltene content of crude oil with and without various types of H-donors addition at 1 wt. % concentration and 385W.

Figure 7 shows comparison of asphaltene content percentage between crude oil without addition and H-donors types’ addition, at 10 wt. % and 1 wt. % concentrations.

The asphaltenes content reduction of crude oil without addition is lower than when using different H-donors addition due to hydrogen transfer from solvent to the heavy hydrocarbons in oil [3].

The asphaltenes content reduction increase with increasing H-donor concentration in their reaction mixture. This situation agrees well to the explanation by Mohammed, 2012 [18] who reported for different concentration of H-donor with different type in reaction mixture.

At 10 wt. % of H-donor, observed that light naphtha gave the higher reduction in asphaltene content compared with tetralin and cyclohexane, due to low aromaticity of solvent and temperature effects leading to micellisation, agglomeration and precipitation of heavy molecules as asphaltenes, then these molecules step down of Q.V.F crucible tube, and when exposure to microwave radiation leading to possible breakup or reorientation of asphaltene molecules [12].

But, At 1 wt. % of H-donor observed that tetralin give the higher reduction in asphaltene content from both light naphtha and cyclohexane.

Fig. 7, comparison between asphaltene content reduction percentages with and without various types of H-donors addition: (A) At 10 wt. concentration, And (B) at 1 wt. % concentration.

3- The Temperature profile

Figures 8 and 9 show the effect of radiation time on the temperature measured during the microwave heating of crude oil at 385W with and without using for different H-donors type at 10 wt. % and 1 wt. % concentration respectively.

It is clear that the temperature measured is proportional to radiation time, and increased gradually with...
increasing of radiation time based on types of addition.

Also, It is clear that the temperature measured of crude oil without addition is lower than when using for different H-donors type at both concentration due to the poor microwave absorption characteristics of heavy crude oil which distinguished by several of researcher as [13, 14], and the measured temperature at 1 min radiation time was 35°C, and then continued increase until reached the 72°C at 9min.

The results of measured temperature against microwave radiation time agreed with results of section 1.1 and 1.2 of microwave treatment, the reaction of cracking is strong dependent on the radiation time and observed that only heavy oil given the lower temperature, lower viscosity reduction percent, and the viscosity proportional to asphaltenes content due to the lower degree of fragmentation and hydrogenation saturation of the fragments to produce lower boiling Fractions [10, 20].

Figure 8 shows the effect of radiation time on temperature measured at 10 wt. % concentration of H-donors, at the beginning of microwave radiation, all H-donors had nearly values of temperature. But it rose very rapidly to around 60 °C in just 4 min, and then within the radiation time from 5 min to 7 min each type had taken different trend. Thus, the curve of the 10 wt. % light naphtha and 10wt. % cyclohexane have had almost similar trends in such a way that their gradual temperature increase as function of radiation time had almost similar numerical values, within this period (4-7 min).

Then, the temperature increased with range from around 80 to more or less 90 °C for within 7 and 8 min respectively.

Figure 9 shows the effect of radiation time on temperature measured at 1 wt. % concentration of H- donors, at 1 min radiation time all H- donors had nearly values of temperature around 36 °C. It rose at radiation time between 1min to 6min where each type had taken different trend. Then, temperatures were 83, 82, and 79 for tetralin, cyclohexane, and light naphtha to achieve a maximum at 9 min.

As mentioned in the scope of these results indicated that increasing concentration led to increasing temperature, and specially 10 wt. % tetralin lead to increase degree of temperature due to polar nature of solvent that make it good absorption characteristics to microwave radiation[10].

These results for temperature agree with results of section 1 and 1 where increased the degree of fragmentation and hydrogenation saturation of the fragments to produce lowers boiling fractions increased when using H-donors.
Effect of Microwave Radiation Power On Properties Of Crude Oil

Figures 10 and 11 shows the effect of radiation power on kinematic viscosity and asphaltenes content respectively with and without using 10 wt. % concentrations of H-donors and different radiation time according to the best result in section 1.

Figure 10 shows the effect of radiation power on the kinematic viscosity of crude oil with and without using 10wt. % of H-donors. It is obvious that the kinematic viscosity has diverse respond with the variation in radiation power. The change in the microwave power at the same of radiation time led to change in temperature, degree of fragmentation, and recombination, and subsequently the variation in crude oil characteristics.

The percentage reduction of kinematic viscosity heavy crude oil without addition at 320 W and 385 W radiations power was increased from 1.226% to 2.453% respectively.

The percentages of viscosity reduction of crude oil for tetralin, cyclohexane, and light naphtha were 5.57%, 5.02%, and 3.95% respectively at 320 W radiation power.

While, at 385 W were 10.63%, 8.675%, and 6.21% for tetralin, cyclohexane, and light naphtha respectively.

But, the kinematic viscosity of crude oil increased at 540 W radiation powers due to recombination is the predominant at high microwave power capacities.

Thus, the optimum heating in microwave were at low power rates due to fragment of higher molecular weight and formation of free radicals, which seem to recombined at zero energy activation, producing smaller normal and branched carbon chains.

This is similar to results obtained by Mohammed, 2011 and Mohammed, 2012 [16, 18].

Also, observed that 385 W radiation power giving higher reduction in kinematic viscosity than 320 W, also from figure 10 observed that tetralin gave higher reduction in kinematic viscosity than both cyclohexane, and light naphtha.
Figure 11 shows the effect of radiation power on asphaltene content of heavy crude oil with and without using 10wt. % of H-donors. It is obvious that asphaltene content increased at 540W and decreased at both 320W and 385W radiation powers.

Thus, the percentage of asphaltene content reduction of heavy crude oil without addition was 4.729% and 8.243% at 320W and 385W radiation power respectively.

But, the percentages of asphaltene content reduction of heavy crude oil with using 10wt. % of H-donors at 320W were 20.36%, 25.87%, and 26.14% for tetralin, cyclohexane, and light naphtha respectively.

At 385W, it mentioned earlier were 39.37%, 34.30%, and 46.29% for tetralin, cyclohexane, and light naphtha respectively.

At these powers, the asphaltene content was reduced affected by fragmentation reaction due to the action of polar molecules and temperature caused permanent changes in petroleum rheology [19].

But, asphaltene content increased at higher radiation power 540W. Hence, increasing of asphaltene content is due to the circumstances of the microwave associated with high radiation power which encourage the recombination reactions, of light hydrocarbon molecules [9].

Conclusion

In general, the effect of radiation power, radiation time, and type of addition with concentration promotes two reactions (fragmentation and recombination) during upgrading heavy crude oil.

Crude oil viscosity was decreasing with increasing polar solvent concentration except light naphtha represented special case could arguably be attributed to either poor solvent system or a combination of solvent and temperature effects.

It was observed that the maximum viscosity reduction at 10 wt. % of H-donors was obtained 8.67% and 7.34% for cyclohexane and light naphtha respectively at 4min radiation time, but 10.63% for tetralin at 6min.

While the maximum percentage of asphaltene content reduction was 34.30% and 46.29% for cyclohexane and light naphtha respectively at 4 min, while 39.73% for tetralin at 6 min.
References
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