# Behavior of Heavy Oils

Yang Zhang <sup>a‡</sup>, Mohamed Adam <sup>b‡</sup>, Abarasi Hart <sup>c</sup>, Joseph Wood <sup>c</sup>, Sean P. Rigby <sup>b</sup>, John P.

Robinson <sup>b\*</sup>

<sup>a</sup> Institute of Petroleum Processing, East China University of Science and Technology, Shanghai,
China

<sup>b</sup> Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK

<sup>c</sup> School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

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## **ABSTRACT**

Electromagnetic heating techniques have recently received significant attention as alternatives to conventional heating methods for thermal processing of viscous and heavy oils. One of the benefits of electromagnetic heating is that the electromagnetic field can penetrate the viscous oil and the rock matrix, allowing heating to take place a significant distance away from the electromagnetic source. Opportunities exist for electromagnetic heating in overcoming the heat-transfer limitations within viscous oils, and potentially as a down-hole or in-situ heating technique to raise the

temperature within a reservoir. The fundamental interaction of electromagnetic energy with viscous and heavy oils and their constituent components is poorly-understood, and this study enhances the understanding of these interactions at microwave frequencies by establishing the effect of temperature on the dielectric properties of heavy oil and its SARA fractions. The dielectric properties of two heavy oils were studied at temperatures up to 300 °C and frequencies from 900 MHz to 3.0 GHz. The loss factor of both oils was found to increase significantly with temperature, which was linked to a corresponding reduction in viscosity. It is shown for the first time, contrary to previous assertions in the literature, that aromatics and resins are the main contributors towards dielectric loss in heavy oils, whereas saturates and asphaltenes were found to have a negligible influence on the loss factor of the oil. Thus, it will be seen that, at higher temperatures or where there is a high abundance of aromatics and resins, the oils are more susceptible to being heated directly with microwaves, opening up new opportunities for microwave processing of oils in refinery and field settings without a need for microwave-absorbing additives.

## **INTRODUCTION**

Despite the encouraging growth in renewable energy, oil and gas are projected to be needed to satisfy up to 55% of the world's energy demand in 2040, compared to 17% for renewables<sup>1</sup>. In addition to their use as an energy source, oil and natural gas are considered the main raw materials for about 95% of chemicals produced worldwide<sup>2</sup>. With the decline in light oil reserves attention has been shifting towards unconventional oil such as heavy oils and bitumen, which can contribute towards future demands whilst the necessary investment and technology development takes place in renewable energy. The world total oil reserves are currently estimated at around 9-13 trillion barrels, of which 70% are heavy oils and bitumen<sup>3</sup>.

Unlike conventional oil, heavy oils and bitumen have little or no mobility under reservoir conditions, with a viscosity greater than 0.1 Pa·s and a specific gravity less than 20 °API. Such properties make it difficult for heavy oils to be produced using the same technologies employed for conventional light oils. Over recent decades advanced recovery methods have been developed to facilitate the extraction and transportation of heavy oils. Thermal enhanced oil recovery (EOR) methods such as steam flooding, steam assisted gravity drainage (SAGD), cyclic steam stimulation (CSS) and in-situ combustion (ISC) are among the most widely used recovery methods. Advanced thermal EOR processes such as Toe-to-Heel Air Injection (THAI) and its catalytic add-on (THAI-CAPRI, CAtalytic upgrading PRocess in-situ) have received significant attention recently <sup>4,5,6</sup>. A comprehensive review of the existing and emerging recovery technologies for heavy oils can be found elsewhere <sup>7,8</sup>.

In the thermal EOR processes, heat is crucial for reservoir operation. Conventionally, heat is transferred to the reservoir either by injecting steam such as in the SAGD process, or by burning part of the oil as in the in the case of ISC and THAI. A novel method for heating heavy oils in the reservoir is through high-frequency electromagnetic energy, specifically microwave and radio frequency (RF). Electromagnetic heating techniques provide selective and volumetric heating instead of the heating via conventional conductive and convective mechanisms. Heating is achieved instantaneously as a result of the interaction of the electromagnetic field with the material at the molecular level. As a result, the material can be heated rapidly, delivering advantages in energy efficiency and processing time<sup>9</sup>. In downhole applications the electromagnetic field can penetrate the rock matrix, allowing heating to take place a significant distance away from the electromagnetic source.

Several studies have been conducted on the use of microwave heating for recovery and upgrading of heavy oils and a number of reviews have already been published<sup>9,10</sup>. The majority of the work in this area has been focused on the use of electromagnetic heating for catalytic upgrading of heavy oil. It is widely believed that heavy oils are poor microwave absorbers and, thus, they need to be mixed with a microwave susceptor in order to heat the oil to the desired temperature. Jeon, et al. 11 used silicon carbide (SiC) coated catalyst to heat bitumen samples up to 430°C to investigate microwave-assisted catalytic upgrading. The experiments were conducted in a modified domestic microwave oven and the silicon carbide was used as a microwave-absorbing susceptor. An increase of up to 14° in the oil API was reported. Li, et al. 12 showed that heating heavy oil mixed with carbon nanoparticles and a hydrogen donor (Tetralin) in a domestic microwave oven leads to significant viscosity reduction. The carbon nanoparticles were believed to allow thermal cracking to be achieved at a bulk oil temperature of only 150 °C. Hu, et al. 13 investigated a combined microwave heating and solvent-assisted gravity drainage process for heavy oil recovery. This was carried out at laboratory scale, and used water as a microwave susceptor to provide faster heating and improved oil recovery.

The majority of previous studies have concluded that microwave heating can be used for enhanced oil recovery by indirect means, i.e. via the use of a microwave susceptors, due to the relatively low microwave-absorbing ability of the oils themselves. Contrary to this, Porch, et al. <sup>14</sup> showed using simulation of the electromagnetic interactions that microwave heating devices for heavy oil processing could be designed and optimized to provide relatively high microwave absorption efficiencies without the need for added susceptors. The design and optimization of a microwave heating cavity requires knowledge of the fundamental interactions between the electromagnetic field and the materials being heated, which are defined by the dielectric constant

 $(\epsilon')$  and dielectric loss factor  $(\epsilon'')$ . The dielectric constant is related to the ability of a material to be polarized and to store electromagnetic energy, whilst the loss factor determines the ability of a material to convert electromagnetic energy into heat.

A number of studies have been made to understand the dielectric properties of heavy oils. Tjomsland, et al. <sup>15</sup> measured the dielectric properties of three crude oils and four distillation fractions at room temperature and frequencies from 1.0 kHz to 10 GHz. They found that the dielectric constant of the heavier fractions was higher than that of their lighter counterparts, which was attributed to the higher content of polar compounds, mainly asphaltenes and resins, in the heavier fractions. The dielectric loss factor was found to peak at lower frequencies for the heavier fractions and at higher frequencies for the lighter fractions, which was linked to the effect of viscosity. Porch, et al. <sup>14</sup> studied the dielectric properties of two types of heavy oil. They found that heavy oils generally have a low loss factor, and suggested that variations in loss factor between different types of heavy oil were due to the different concentrations of polar compounds.

Both, Tjomsland, et al. <sup>15</sup> and Porch, et al. <sup>14</sup> have suggested that the loss in heavy oils was due to the presence of polar compounds, although neither study was able to clearly identify these polar compounds. Moreover, the dielectric properties of materials are highly temperature-dependent, and previous studies have been limited by measurements carried out at room temperature only. The aim of this work is to measure the dielectric properties of heavy oils and their constituent components at temperatures up to 300 °C, identify microwave-absorbing phases and establish the opportunities and limitations for heavy oil processing. This work will show that temperature has a significant effect on the loss factor of heavy oils. It will also show that, contrary to previous work, the aromatics and resins fractions have the greatest influence on the loss factor. This will have the impact of that at higher temperatures or where there is a high abundance of aromatics and resins

the oils could be heated directly with microwaves without a need for microwave-absorbing additives.

## **THEORY**

The most common heating mechanisms for liquids in the microwave and RF frequency ranges are dipolar loss and conductive (or ionic) loss. Dipolar loss occurs due to the resistance to molecular movement, with the movement being induced via a dipole moment created by the electric field component of the electromagnetic wave. The dipole can occur through polarization of the molecule due to the presence of the electric field, or can be a permanent dipole, as arises in polar compounds such as water and alcohols. When an alternating electromagnetic field is applied the dipoles try to align themselves in response to the oscillating field, which results in molecular motion. Energy is then dissipated as heat as a result of the resistance to this induced molecular motion. Conductive loss can occur when free ions are present within a liquid. Ions move in response to the alternating electric field, and the resistance to this movement generates heat. Aqueous solutions will therefore typically exhibit both dipolar and ionic conduction heating mechanisms, and will have large dielectric loss factor values.

Heavy oils are believed to follow the dipolar loss mechanism because of the absence of free ions. They are composed of four main fractions: saturates, aromatics, resins, and asphaltenes. Saturates are non-polar aliphatic hydrocarbon groups including normal and branched alkanes and cycloalkanes. Aromatics include cyclic compounds that contain one or more benzene rings with or without alkyl side chains. Resins and asphaltenes are the heaviest fractions and they consist of polycyclic aromatic molecules containing alkyl side chains, heteroatoms, and/or trace metals <sup>16</sup>. They are the most polar fractions due to the presence of strong electronegative heteroatoms such as Nitrogen and Oxygen in small fractions. Asphaltenes have a much larger molecular size and

weight than resins and, unlike resins, they are insoluble in normal alkanes such as n-pentane and n-heptane<sup>16</sup>. Asphaltene molecules may consist of one central polycyclic aromatic hydrocarbon (PAH) core with peripheral alkane chains or multiple distinct PAHs connected by a single bond <sup>17,18</sup>. The presence of asphaltenes has a significant impact on increasing the oil viscosity<sup>19</sup>. The large size and high molecular weight of asphaltenes together with their high polarity add to the intermolecular interactions which results in an increase in the viscosity.

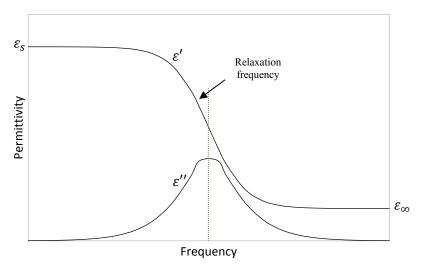
In cases where dipolar loss dominates the dielectric properties can be represented by Debye's equations<sup>20</sup>:

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_{s} - \varepsilon_{\infty}}{1 + (\omega \tau)^{2}}$$
, Equation 1

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} \qquad , \qquad \text{Equation 2}$$

where  $\varepsilon_s$  and  $\varepsilon_\infty$  represent the dielectric constant at d.c (static) and very high frequency respectively;  $\omega$  is the angular frequency;  $\tau$  is the relaxation time, which is the time required for the dipole to revert back to a random orientation when the applied field is removed<sup>21</sup>. The relaxation time is related to the size of the molecule and the intermolecular forces<sup>22</sup>. The mathematical form of Debye's equation is shown graphically in Figure 1, which shows that the dielectric constant has a constant high value,  $\varepsilon_s$ , at static and very low frequencies and a constant low value,  $\varepsilon_\infty$ , at very high frequencies. The drop in the dielectric constant at high frequency is because the molecules are no longer able to rotate significantly before the alternating field is reversed. The loss factor has a value of zero at very low and very high frequencies with a peak at an intermediate frequency called the relaxation frequency,  $\omega_o$ . The relaxation frequency is the reciprocal of the relaxation time ( $\omega_o = 1/\tau$ ).

The Debye formula has been shown to be applicable to small polar compounds that exhibit a single relaxation time, such as water and simple alcohols. In this study, Debye's theory will be used to understand the dielectric behavior of heavy oils and their SARA fractions by studying the influence of both temperature and frequency on the loss factor.



**Figure 1.** Typical graphical representation of the permittivity for polar materials following Debye's formula <sup>20</sup>.

## **EXPERIMENTAL**

Two types of heavy oil were used in this study. The first is heavy oil produced through Toe-to-Heel Air Injection (THAI) technology provided by Touchstone Exploration Inc. Canada. The second heavy oil is Vacuum Distillation Residue (VDR) supplied by Sinopec China. The properties of both heavy oils are shown in Table 1. The specific gravity was determined using glass pycnometers according to ASTM D5355-95 and ASTM D70-09 standards for the THAI oil and VDR respectively. The API gravity was calculated accordingly. The viscosity was measured using a dynamic viscometer (Brookfield DV-II pro manufactured by Brookfield Engineering Laboratories Inc., MA, USA). The viscosity of THAI was measured at 20 °C and 20 rpm. Because of its immobility at room temperature, VDR's viscosity was measured at 100 °C and 12 rpm. The

sulfur content was measured using a calibrated EDXRF (PANalytical Epsilon 3 manufactured by PANalytical B.V, Almelo, Netherlands) following ASTM D4294-16.

Analysis of saturates, aromatics, resins and asphaltenes content (SARA analysis) of the heavy oils was performed in accordance to ASTM D2007. Asphaltenes were first separated by mixing 1.0 g of heavy oil in 40 mL n-heptane for 4 hours with stirring. Asphaltene precipitants were left to settle for 24 hours before separation with a filter paper (Whatman<sup>®</sup> grade 1). The filter paper with its content was left to dry overnight, and the asphaltenes were then collected and weighed. The de-asphalted liquid was separated from the n-heptane in a rotary vacuum evaporator, before being further separated into saturates, aromatics and resins in a chromatography column (1.2 cm ID and 90 cm height) packed with activated alumina (40 g) and maintain at 50 °C. The alumina bed was first wetted by adding 30 mL n-heptane at the top of the column. The de-asphalted oil was placed on top of the alumina bed. The column was then washed with solvents in stages to separate the fractions starting with 80 mL n-heptane to separate saturates, then 80 mL toluene to separate aromatics. Resins were washed by passing 40 mL toluene and ethanol mixture (50:50), then 40 mL toluene and finally 40 mL ethanol. The solvents were separated from the oil fractions in a rotary vacuum evaporator followed by oven drying at 120 °C. The oil fractions were then weighed separately to complete the SARA analysis.

The dielectric properties of the heavy oils and their fractions were measured using the cavity perturbation technique. Heavy oils, in general, have a low dielectric loss. The cavity perturbation technique is widely used for measuring dielectric properties of low loss materials<sup>23,24</sup>. A schematic of the measurement setup is shown in Figure 2. The system consists of a TM<sub>0n0</sub> cylindrical cavity, vector network analyzer (Agilent E5062A), tube furnace, 3 mm i.d. quartz tube, tube holder

connected to a step-motor, and a computer with software to control the system and record the results.

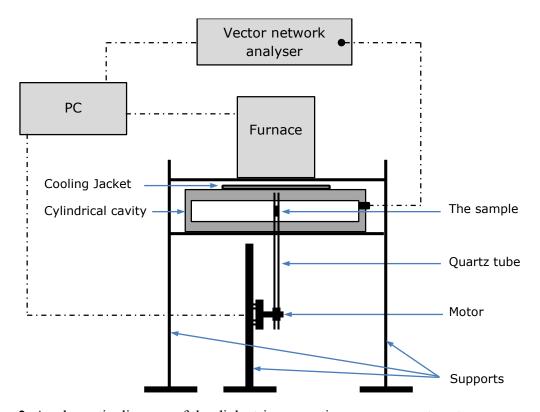


Figure 2. A schematic diagram of the dielectric properties measurement system

In the cavity perturbation method the network analyzer produces and sends electromagnetic signals to the cavity and measures the resultant resonant frequency and quality factor of the cavity. This is done before and after inserting the sample inside the cavity, and the difference in the resonant frequency and quality factor are used to calculate the dielectric constant and the loss factor<sup>25</sup>, <sup>26</sup>. The dielectric properties were measured at temperatures from 20 °C to 300 °C and frequencies from 900 MHz to 3 GHz. THAI oil was loaded into the measuring tube using a syringe, while VDR, which is immobile at room temperature, was loaded into tube in the form of small solid pieces cut using a knife. Before measurements were conducted the VDR samples were heated to 100 °C while in the tube to gain mobility and take the shape of the tube, thereby occupying a comparable volume to the THAI oil. Prior to the dielectric property measurements the tube was

purged with nitrogen and closed at the top with a silicone cap to ensure that measurements were made within an inert atmosphere.

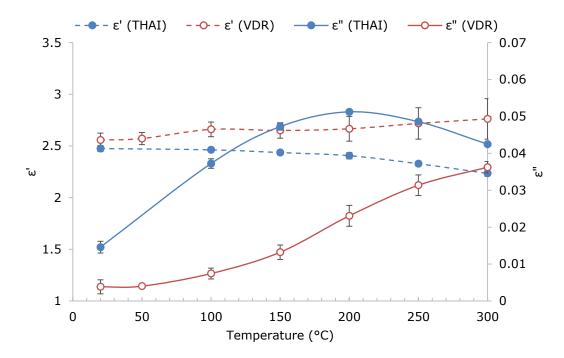
## **RESULTS AND DISCUSSION**

The SARA analysis of the two oils involved in this study is shown in Table 1 together with the density, viscosity and sulfur content. The sum of the SARA fractions is less than 100%, and this is a common occurrence that can be attributed primarily to losses of saturates and aromatics through evaporation<sup>27</sup>. As can be seen in Table 1, VDR has a smaller API gravity and a greater viscosity than the THAI oil even though the viscosity of VDR was measured at a higher temperature. The SARA analysis shows also that VDR has higher aromatics, resins and asphaltenes content compared to THAI oil, while THAI oil has a higher saturates content. The higher asphaltenes and resins content of VDR compared to THAI is reflected in its high viscosity and high sulfur content.

**Table 1.** Properties and SARA analysis of the heavy oils involved in this study.

	VDR	THAI
Specific gravity (20 °C)	1.0247	0.9706
API gravity (20 °C)	6.59	14.29
Viscosity (cP)	2360 (100 °C)	1360 (20 °C)
Sulfur content (wt. %)	4.0	3.2
SARA (wt. %)		
Saturates	$13.23 \pm 0.40$	$32.34 \pm 0.34$
Aromatics	$45.97 \pm 2.68$	$33.19 \pm 1.77$
Resins	$23.51 \pm 3.41$	$15.86 \pm 0.44$
Asphaltenes	$14.78 \pm 0.73$	$7.91 \pm 0.40$
Total	$97.49 \pm 2.53$	$89.30 \pm 2.11$

The dielectric properties of the two heavy oils and their fractions were measured at temperatures up to 300 °C in an inert atmosphere. Figure 3 shows the change in the dielectric constant and loss factor of THAI oil and VDR with temperature at 2.45 GHz. Both heavy oils have low loss at room temperature (about 0.015 and 0.004 for THAI and VDR respectively). However, it can be seen from Figure 3 that the loss factor of both THAI and VDR increases with temperature. THAI reaches a peak at around 200 °C before it starts to decline while VDR continuous to increase with temperature up to 300 °C. The dielectric constant of both oils does not change significantly (<15%) over the studied temperature range.



**Figure 3.** Dielectric constant ( $\epsilon$ ') and loss factor ( $\epsilon$ '') of the heavy oils as functions of temperature at 2.45 GHz.

Whilst the loss factor values of both oils are low compared to substances such as water and ethanol, they are still appreciably higher than smaller hydrocarbon molecules. For example, n-hexane exhibits loss factors <0.001 at temperatures up to its normal boiling point and is considered

to be effectively transparent to microwaves<sup>28</sup>. The heavier VDR and THAI oils have a greater degree of microwave absorbing ability, particularly at higher temperatures, and this presents opportunities for microwave heating at industrial and field-scales that will be discussed later.

The dielectric properties of the SARA fractions were measured in order to investigate which fractions of the heavy oils are most responsive to the microwaves. Figure 4 shows the loss factor of THAI and its fractions at temperatures up to 300 °C. It also includes data for de-asphalted THAI, which is a sample taken after separating asphaltenes but before the chromatography separation. The loss factors of the original THAI and the de-asphalted THAI are very similar, which suggests that asphaltenes do not have a significant effect on the loss factor of the THAI oil over this range of temperature and frequency. Similar behavior is observed with VDR as shown in Figure 5.

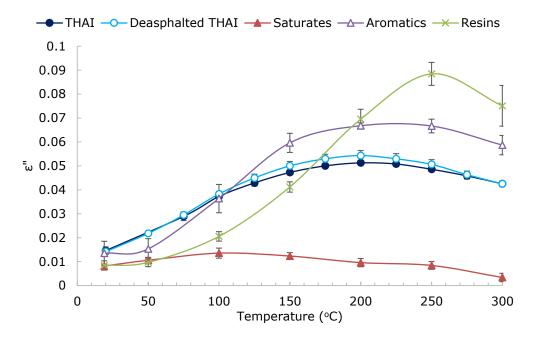
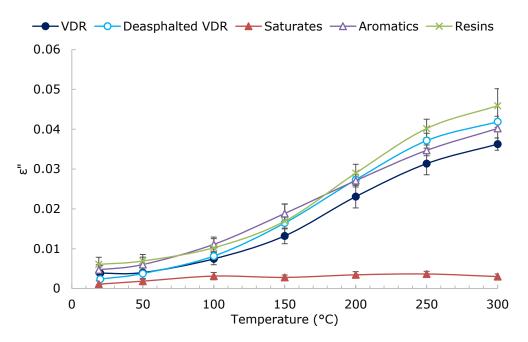


Figure 4. Loss factor of THAI oil and its fractions as a function of temperature at 2.45 GHz



**Figure 5.** Loss factor of VDR and its fractions as a function of temperature at 2.45 GHz.

Saturates have an extremely low loss factor for both THAI and VDR as can be seen in Figure 4 and Figure 5 respectively, so the two components that contribute to the overall microwave absorbing ability of the oil are the aromatic and resin fractions. It can be noted that the de-asphalted oils have even higher loss factors than those of the original oils which can be seen more clearly in the case of VDR. This can be attributed to the increase in the fraction of the molecules with stronger microwave absorbing ability after eliminating the asphaltenes fraction.

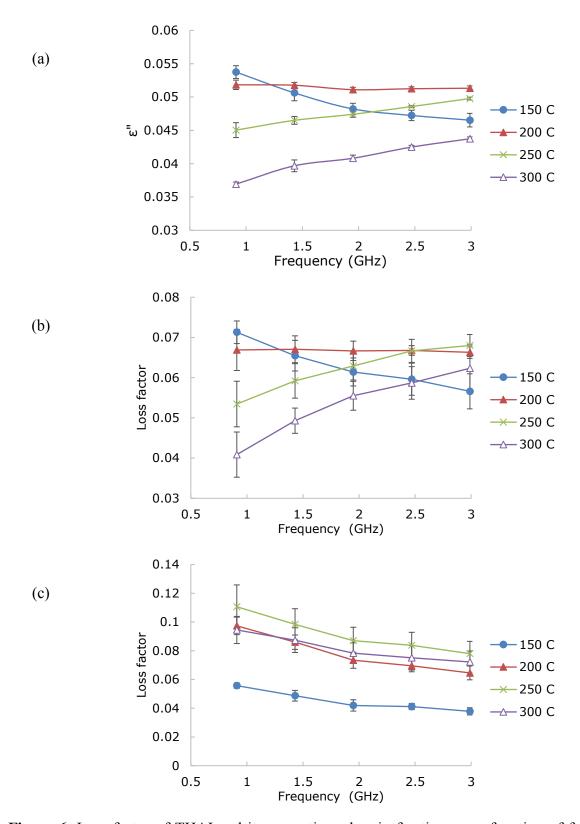
Saturates are mixtures of nonpolar compounds including linear, branched and cyclic saturated hydrocarbons. Thus, their low dielectric loss is understandable due to the lack of polar groups. Because of the presence of strong electronegative atoms within asphaltenes they can be considered as polar compounds, and it has been suggested that asphaltenes make a significant contribution towards the loss factor of heavy oils <sup>13</sup>. However, the results shown in Figure 4 and Figure 5 confirm that, contrary to previous work, asphaltenes do not have significant effect on the loss factor over the studied range of temperature and frequency. Instead, the smaller but less-polar

aromatics and resins appear to have a more dominant influence on the loss factor of the oils. Aromatics do not contain strong electronegative atoms as in the case of asphaltenes and resins, so cannot be considered as polar compounds. However, some aromatics exhibit polarity caused by their structural asymmetry. Toluene, for instance, has a dipole moment of about 0.36 D due to the structural asymmetry caused by the single methyl group. On the other hand, benzene and p-xylene have zero dipole moment because of their structural symmetry  $^{29}$ . The loss factor of toluene was measured at room temperature and 2.45 GHz and found to be 0.013 which is an order of magnitude greater than that of p-xylene (Figure 5). This structural asymmetry is believed to be the main cause for the relatively high loss in the aromatic fraction of heavy oil.

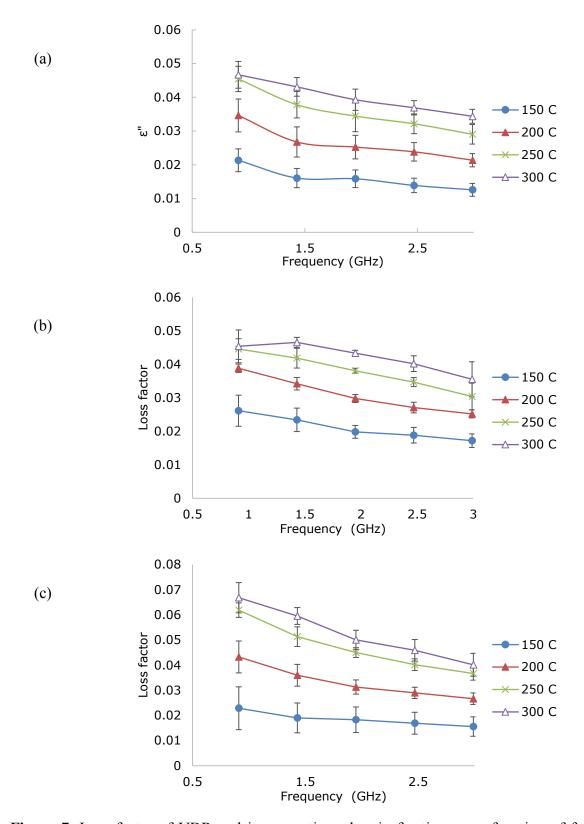
Oils with high concentrations of aromatics and resins are good candidates for microwave heating, allowing the oils to be heated without the use of microwave-absorbing additives. Oils that are high in saturates and asphaltenes will not undergo any significant microwave heating, and these substances require conventional heating or the use of high-loss additives if microwave heating is to be employed.

## Understanding the heating mechanism

Given there are no ionic species present within VDR and THAI oils, heating will take place due to a dipolar loss mechanism. This is dependent on the size and shape of the oil molecules, and can be used in conjunction with the Debye theory to explain the phenomenon presented in Figures 3-5. Further insight can be gained by assessing the effect of frequency as well as temperature on the dielectric loss factor, and this data is shown in Figure 6 for THAI oil and Figure 7 for VDR.



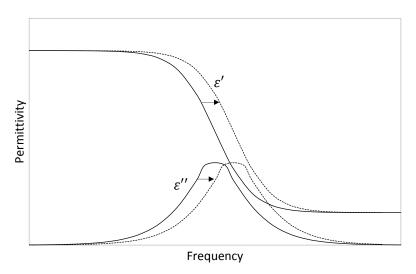
**Figure 6.** Loss factor of THAI and its aromatic and resin fractions as a function of frequency measured at 20 °C: (a) THAI oil; (b) THAI aromatics; (c) THAI resins



**Figure 7.** Loss factor of VDR and its aromatic and resin fractions as a function of frequency measured at 20 °C: (a) VDR; (b) VDR aromatics; (c) VDR resins.

For the VDR and its constituent components the loss factor increases with increasing temperature at all frequencies tested in the 0.9 - 3.0 GHz range. The behavior of THAI oil and its associated fractions is more complex. The oil and the aromatic components show a decrease in loss factor with increasing temperature at 0.9 GHz, but at 3.0 GHz the loss factor data exhibits a maximum around 200 - 250 °C. The resins behave differently to the bulk oil and the aromatics, with the loss factor increasing with temperature across the frequency range in a similar manner to the VDR. These variations in the effect of temperature and frequency on the loss factor can be explained through Debye model.

For substances that follow the Debye model the effect of frequency and temperature on the dielectric properties is illustrated in Figure 8.



**Figure 8.** Effect of temperature on permittivity of materials following Debye's formula. The dotted line represents a higher temperature.

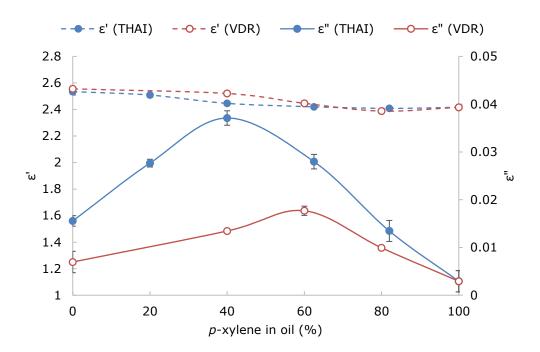
The peak in the loss factor shown in Figure 8 corresponds to the relaxation frequency, which increases with temperature. For VDR and its components the relaxation frequency is below the minimum frequency that was investigated in this study (0.9 GHz), as the increase in temperature leads to an increase in loss factor at all measured frequencies (Figure 7). With THAI oil and its

SARA fractions the relaxation frequency is much closer to the measured 0.9 - 3.0 GHz range, and in some cases within. For example, THAI oil and its aromatics fraction appear to exhibit a transition in the relaxation frequency at around 200 °C; at lower temperatures the loss factor decreases with increasing frequency whereas at higher temperatures there is an increase with frequency. The relaxation frequency in the case of THAI resins is below 0.9 GHz. This can be realized from the reduction in the loss factor with frequency with no indication of a shift in the relaxation frequency over the measured 0.9 - 3.0 GHz range.

The relaxation frequency depends, in-turn, on the size of the molecules and their intermolecular forces. Larger molecules tend to have smaller relaxation frequencies (long relaxation time) which explains why THAI resins have lower relaxation frequency than that of the aromatics. Temperature has an impact on the intermolecular forces and the relaxation frequency (Figure 8). Increasing the temperature of a viscous liquid leads to a reduction in its viscosity via the breaking of the intermolecular forces thereby giving the molecules more freedom to move/rotate under the influence of the applied electric field. This leads to an increase in the relaxation frequency and, hence, an increase in the loss factor with temperature as long as the operating frequency is lower than the relaxation frequency. When the relaxation frequency becomes greater than the operating frequency, increasing temperature results in a reduction in the loss factor with temperature. This is the case for the THAI oil, and its aromatics fraction, that were used in this study.

To confirm the effect of viscosity on the dielectric properties, the heavy oils were mixed with pxylene (Acros Organics<sup>TM</sup>) to different volume fractions and the dielectric properties of the
mixtures were measured. p-xylene was chosen because it is a nonpolar liquid with a zero dipole
moment and consequently an extremely low loss factor (<0.005 at room temperature). It is an
organic solvent that is able to dissolve heavy oils, but has a viscosity of 0.65 cP at 20 °C, which is

about four orders of magnitude lower than that of heavy oils. Figure 9 shows that the dielectric constant and loss factor of the mixtures at 2.45 GHz against the volume fraction.



**Figure 9.** Dielectric constant and loss factor of different fractions of heavy oils in p-xylene measured at 20 °C and 2.45 GHz.

There is no significant change in the dielectric constant with the solvent fraction. The loss factor of the heavy oils increases with the addition of p-xylene fraction until a peak value is reached. For THAI oil the peak occurs at around 40% p-xylene and for VDR the peak occurs at 60% p-xylene. p-xylene does not absorb microwaves directly, but it acts to reduce the viscosity of the mixture by breaking the intermolecular forces giving greater freedom to the microwave absorbing molecules to move/rotate under the influence of the applied electromagnetic field. With the freedom of movement increased the dielectric loss factor increases, despite the increase in concentration of a microwave-transparent species. After the peak in loss factor, the molecules freedom is no longer the dominant factor that governs the size of the dielectric loss factor, which reduces toward that of pure p-xylene as the concentration is increased.

# **Industrial Implications**

Where oils were previously reported to be transparent to microwaves, this study has identified components of heavy oil that are microwave-absorbent, namely aromatic and resin fractions, and temperature/frequency ranges where the loss factor of oil increases. At higher temperatures or where there is a high abundance of aromatics and resins the oils are more amenable to be heated directly with microwaves, without the use of microwave-absorbing additives such as activated carbon and silicon carbide that have been widely used until now. Previous studies have used microwave-absorbent catalysts for oil upgrading due to the low dielectric loss of the oil, but this study has shown that a greater range of catalysts, including those that are microwave-transparent could be employed. Further work will build upon these findings to assess the opportunities and advantages of microwave heating for catalytic upgrading of oils in a refinery setting (visbreaking) and a field setting. One of the potential applications in a field setting is the THAI-CAPRI process where microwave heating can be used to raise the temperature around the catalyst bed from less than 300 °C which is the temperature of the mobile oil zone in the THAI process<sup>30</sup> to ~ 400 °C which is the minimum temperature needed for successful catalytic upgrading<sup>5</sup>.

## **CONCLUSIONS**

This study investigated the interactions between microwave energy and heavy oils. The dielectric properties of THAI Oil and Vacuum Distillation Residue were studied at temperatures up to 300 °C. It was found that both oils have a relatively low loss, and will be challenging to heat with microwaves at room temperature. The loss factor was found to increase with increasing temperature, making the oils more microwave absorbent under these conditions. This was attributed to an increase in molecular mobility due to the viscosity reduction associated with an increase in temperature. Among the four SARA fractions, aromatics and resins were found to have

the most significant effect on the loss factor in both heavy oils. In contrast to previous literature findings, saturates and asphaltenes were found to have a negligible influence on the loss factor. The loss in the aromatics was related to possible polarity caused by structural asymmetry. Although, both resins and asphaltenes are considered polar compounds, only the resins showed a significant contribution towards the loss factor of the heavy oils. Asphaltenes have been previously highlighted as a microwave-absorbing species within oils, however this study has shown that they do not contribute to the dielectric loss and this behavior is attributed to the molecular mobility being too low for the molecules to respond to the electromagnetic field at microwave frequencies. This study revealed that at higher temperatures or where there is a high abundance of aromatics and resins the oils are more amenable to be heated directly with microwaves opening up opportunities for microwave processing of oils in refinery and field settings without a need for microwave-absorbing additives.

#### **AUTHOR INFORMATION**

## **Corresponding Authors**

\* john.robinson@nottingham.ac.uk, Tel: +44 115 95 14092

<sup>‡</sup> These authors contributed equally

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from the Nottingham Transportation Engineering Centre (NTEC) with the viscosity measurement is also appreciated.

## **ABBREVIATIONS**

API, American Petroleum Institute; CAPRI, CAtalytic upgrading PRocess in-situ; CCS, Cyclic Steam Stimulation; EDXRF, Energy Dispersive X-ray Fluorescence; EOR, Enhanced Oil Recovery; ISC, In-Situ Combustion; PAH, Polycyclic Aromatic Hydrocarbon; RF, Radio Frequency; SAGD, Steam Assisted Gravity Drainage; SARA, Saturates Aromatics Resins Asphaltenes; THAI, Toe-to-Heel Air Injection; VDR, Vacuum Distillation Residue.

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