

Impact of Oil Composition on Microwave Heating Behavior of Heavy Oils

Zhang, Yang; Adam, Mohamed; Hart, Abarasi; Wood, Joseph; Rigby, Sean P.; Robinson, John P.

DOI:

[10.1021/acs.energyfuels.7b03675](https://doi.org/10.1021/acs.energyfuels.7b03675)

License:

Other (please specify with Rights Statement)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Zhang, Y, Adam, M, Hart, A, Wood, J, Rigby, SP & Robinson, JP 2018, 'Impact of Oil Composition on Microwave Heating Behavior of Heavy Oils', *Energy and Fuels*, vol. 32, no. 2, pp. 1592-1599. <https://doi.org/10.1021/acs.energyfuels.7b03675>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in *Energy & Fuels*, copyright © American Chemical Society after peer review. To access the final edited and published work see [10.1021/acs.energyfuels.7b03675](https://doi.org/10.1021/acs.energyfuels.7b03675)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Impact of Oil Composition on Microwave Heating Behavior of Heavy Oils

Mohamed Adam ^{a‡}, Yang Zhang ^{b‡}, Abarasi Hart ^c, Joseph Wood ^c, Sean P. Rigby ^a, John P.

Robinson ^{a}*

^a Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK

^b Institute of Petroleum Processing, East China University of Science and Technology, Shanghai,
China

^c School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

Keywords: Heavy oil recovery, dielectric properties, electromagnetic heating, microwave dipolar relaxation

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 renewables¹. 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 worldwide². 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 bitumen³.

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^{4,5}. Advanced thermal EOR processes such as Toe-to-Heel Air Injection (THAI) and its catalytic add-on (THAI-CAPRI, CAlytic upgrading PRocess in-situ) have received significant attention recently ^{6,7,8}.

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 time⁹. 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^{9,10}. 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. ¹⁴ 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 (ϵ') and dielectric loss factor (ϵ''). 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. ¹⁵ 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. ¹⁴ 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. ¹⁵ and Porch, et al. ¹⁴ 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 ¹⁶. They are the most polar fractions due to the presence of strong electronegative heteroatoms such

as N and O. Asphaltenes have a much larger molecular size and weight and, unlike resins, they are insoluble in normal alkanes such as *n*-pentane and *n*-heptane¹⁶.

In cases where dipolar loss dominates the dielectric properties can be represented by Debye's equations¹⁷:

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

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

where ε_s and ε_{∞} represent the dielectric constant at d.c (static) and very high frequency respectively; ω is the angular frequency; τ is the relaxation time, which is the time required for the dipole to revert back to a random orientation when the applied field is removed¹⁸. The relaxation time is related to the size of the molecule and the intermolecular forces¹⁹. The mathematical form of Debye's equation is shown graphically in Figure 1, which shows that the dielectric constant has a constant high value, ε_s , at static and very low frequencies and a constant low value, ε_{∞} , 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, ω_o . The relaxation frequency is the reciprocal of the relaxation time ($\omega_o = 1/\tau$).

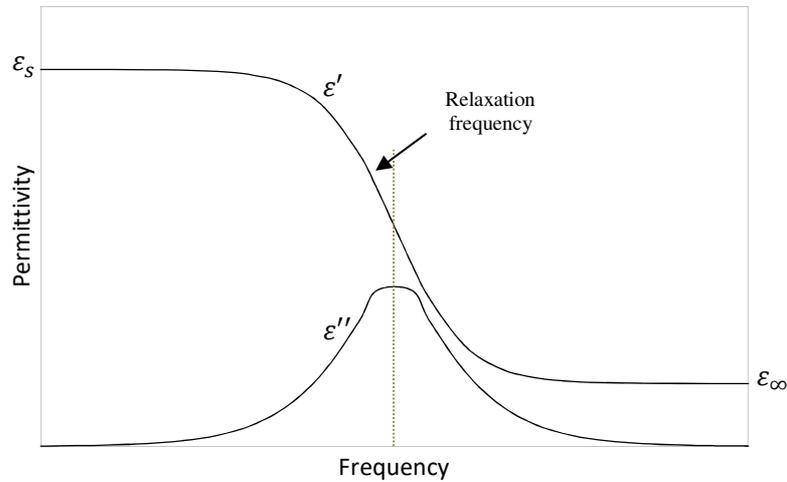


Figure 1. Typical graphical representation of the permittivity for polar materials following Debye's formula ¹⁷.

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.

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[®] 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^{20,21}. A schematic of the measurement setup is shown in Figure 2. The system consists of a TM_{0n0} 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.

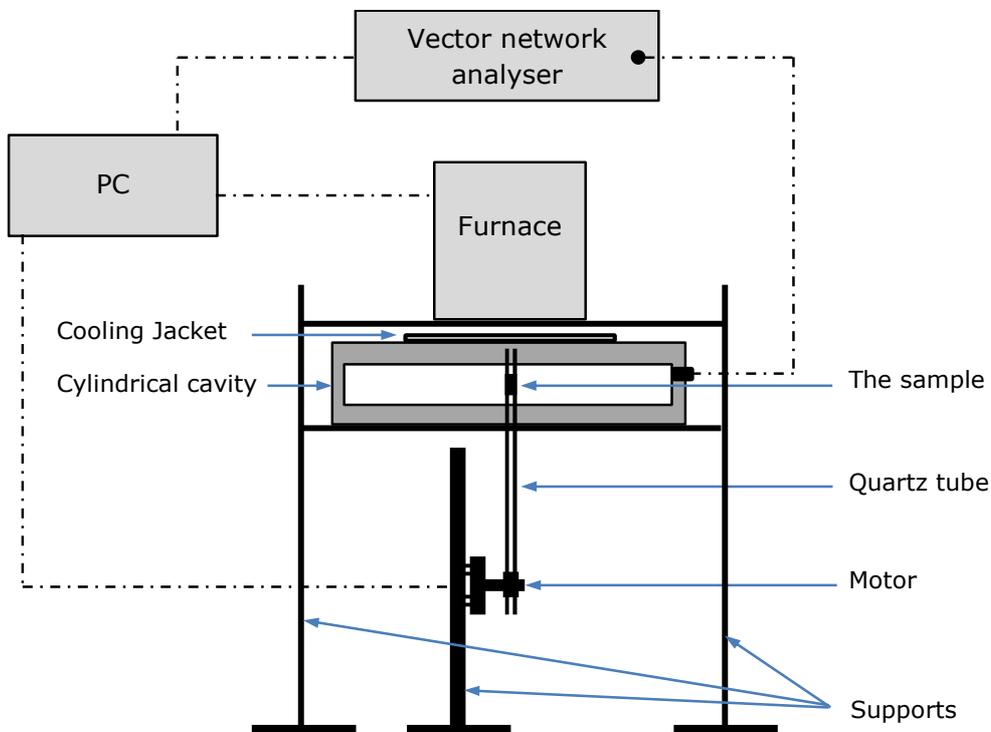


Figure 2. A schematic diagram of the dielectric properties measurement system

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^{22,23}. 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 evaporation²⁴. 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 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 (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 ± 0.40	32.34 ± 0.34
Aromatics	45.97 ± 2.68	33.19 ± 1.77
Resins	23.51 ± 3.41	15.86 ± 0.44
Asphaltenes	14.78 ± 0.73	7.91 ± 0.40
Total	97.49 ± 2.53	89.30 ± 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 continues to increase with temperature up to 300 °C. The dielectric constant of both oils does not change significantly (<15%) over the studied temperature range.

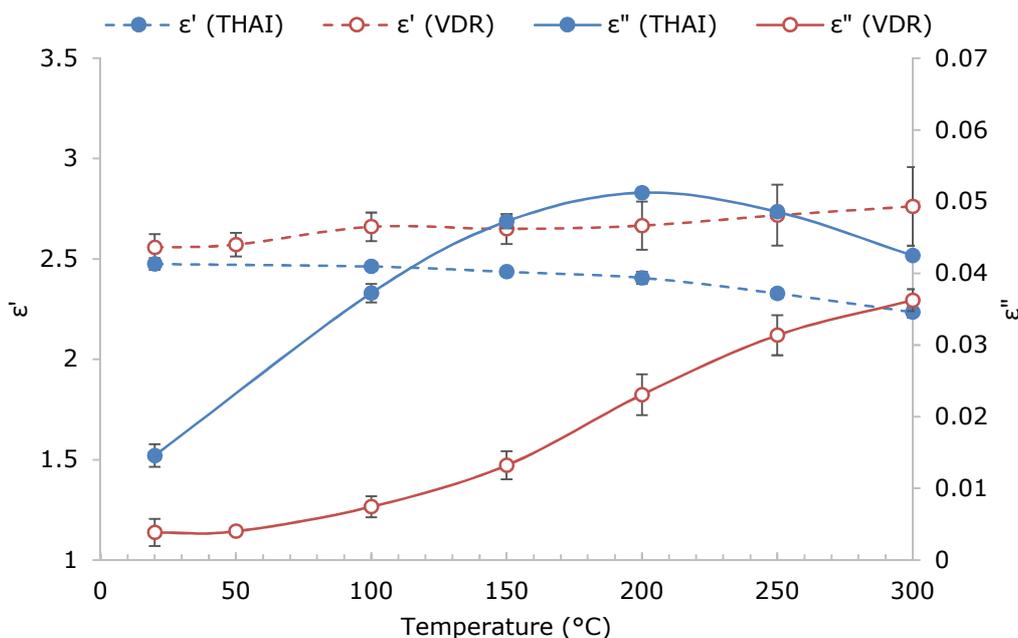


Figure 3. Dielectric constant (ϵ') and loss factor (ϵ'') of the heavy oils as functions of temperature at 2.45 GHz.

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 microwaves²⁵. 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. 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.

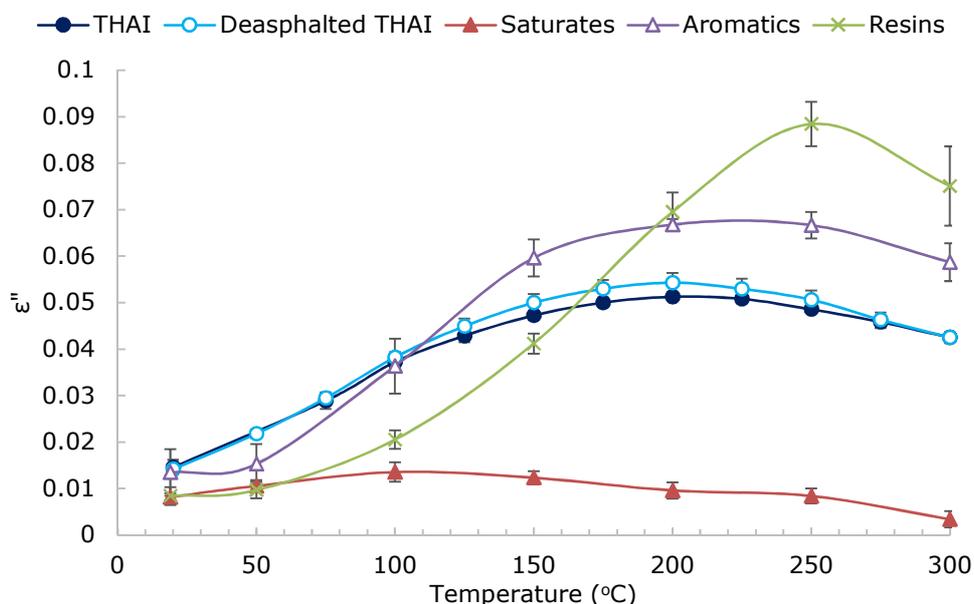


Figure 4. Loss factor of THAI oil and its fractions as a function of temperature at 2.45 GHz

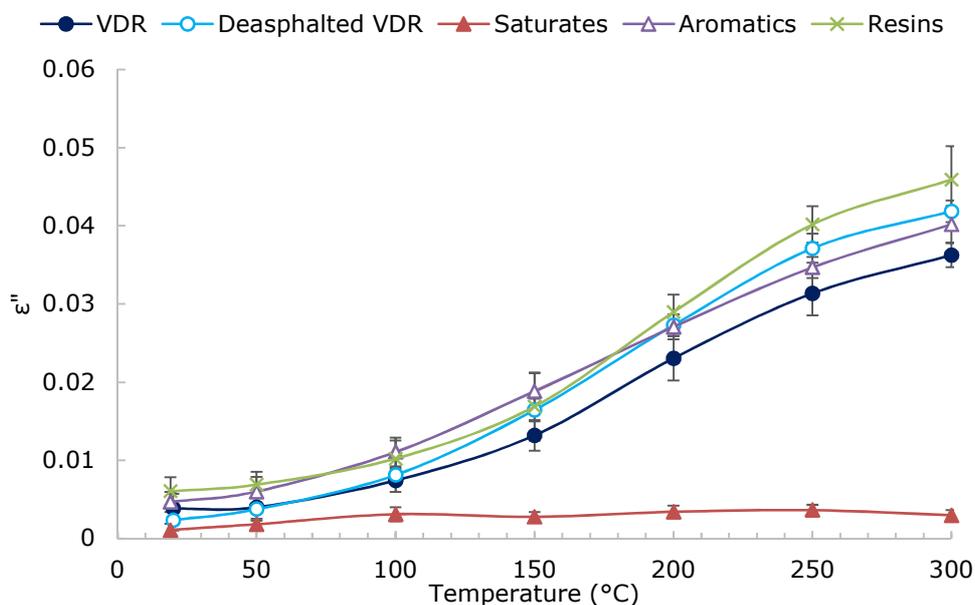


Figure 5. Loss factor of VDR and its fractions as a function of temperature at 2.45 GHz.

Saturates 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 oils¹³. However, the results shown in Figure 4 and Figure 5 confirm that asphaltenes do not affect 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 symmetry²⁶. 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.

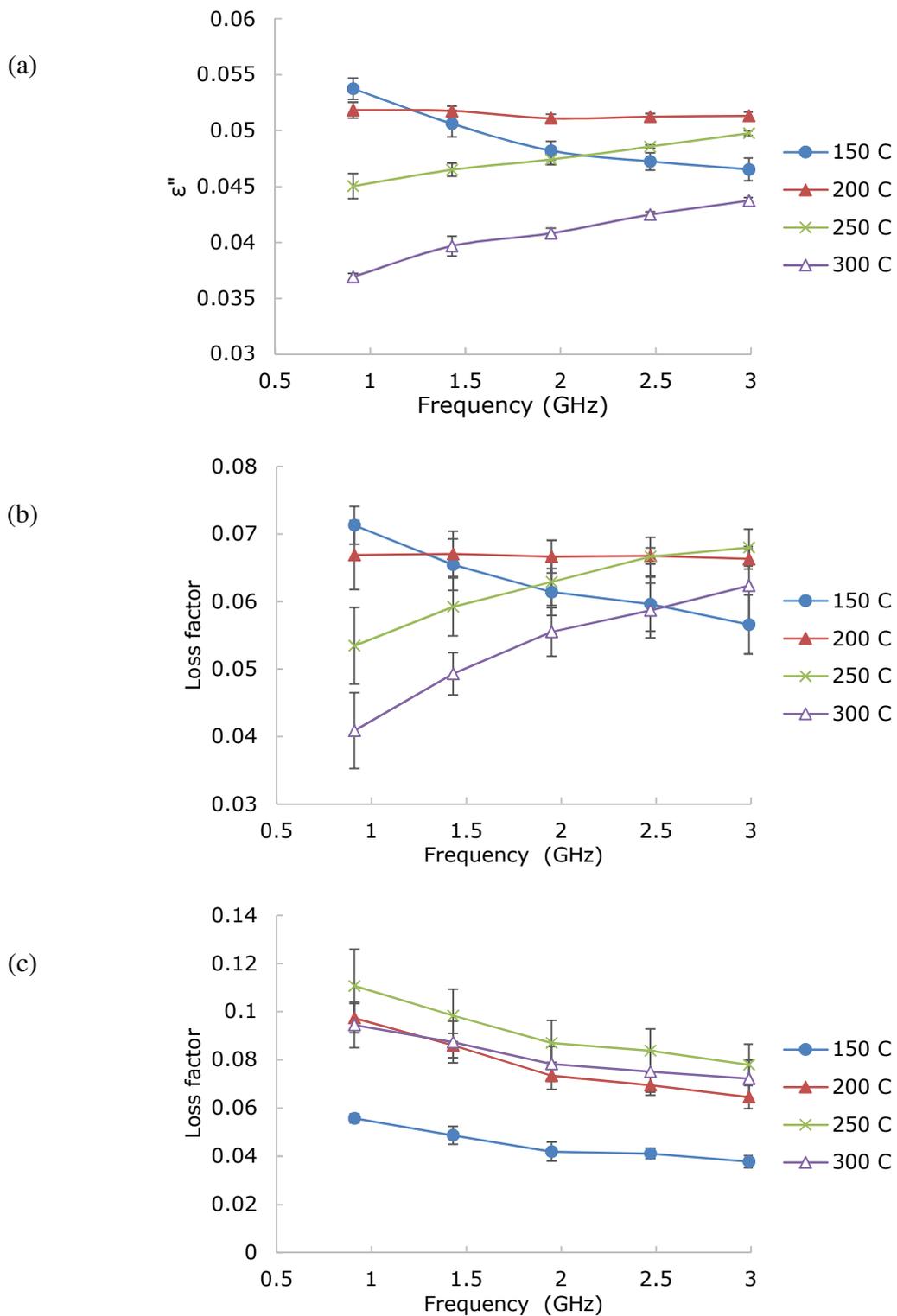


Figure 6. Loss factor of THAI and its aromatic and resin fractions as a function of frequency measured at 20 °C: (a) THAI oil; (b) THAI aromatics; (c) THAI resins

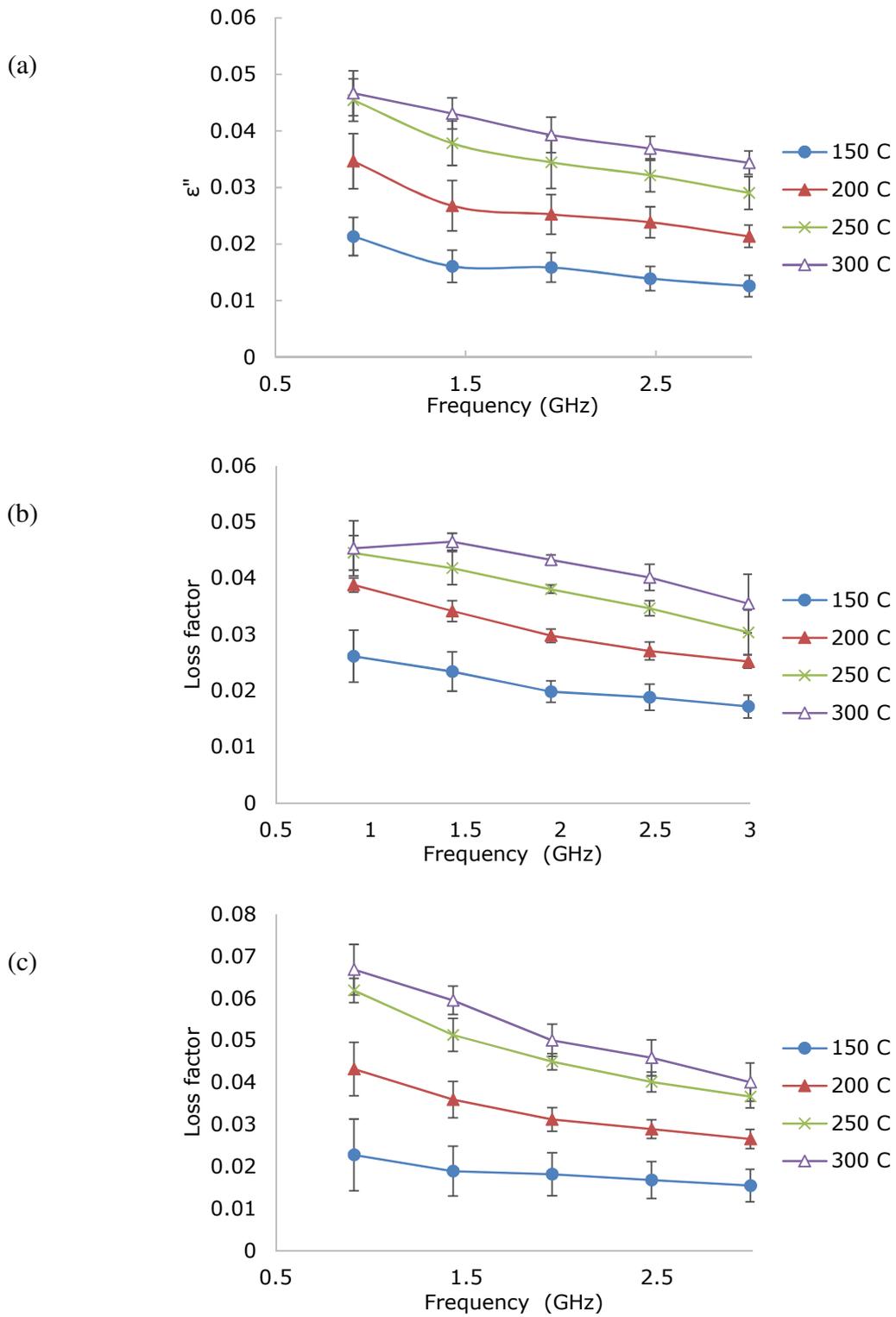


Figure 7. Loss factor of VDR and its aromatic and resin fractions as a function of frequency measured at 20 °C: (a) VDR; (b) VDR aromatics; (c) VDR resins.

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.

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

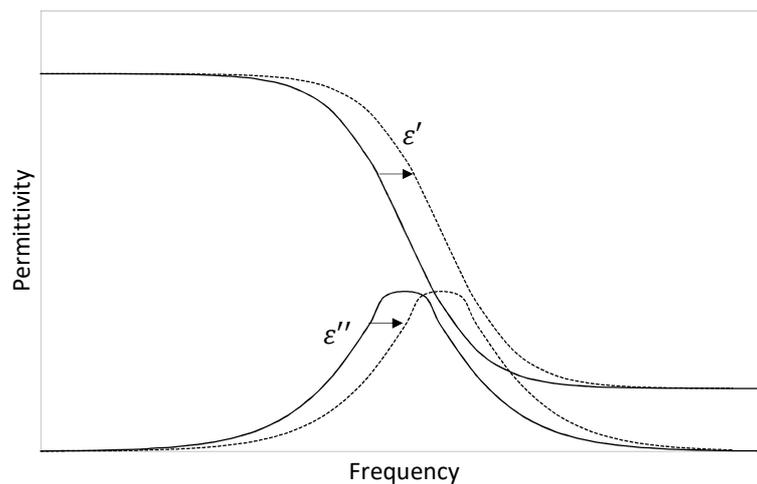


Figure 8. Effect of temperature on permittivity of materials following Debye's formula. The dotted line represents a higher temperature.

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. 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 depends in-turn on the size and mobility of the molecules within the liquid under study. Dielectric loss is a function of the extent to which molecules move under the influence of the applied electric field, and the viscosity of the liquid medium. Substances that contain large molecules, although they have a high viscosity, are unable to move to a significant degree and hence their loss factor is low. For these materials increasing temperature reduces their viscosity but enables greater molecular mobility, with the net effect being an increase in the loss factor. This is the case for the VDR and its fractions that were used in this study. When molecules are smaller the loss factor is not limited by mobility but by viscosity, so increasing temperature results in a decrease in loss factor due to the corresponding viscosity reduction.

To confirm the effect of viscosity on the dielectric properties, the heavy oils were mixed with *p*-xylene (Acros Organics™) 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.

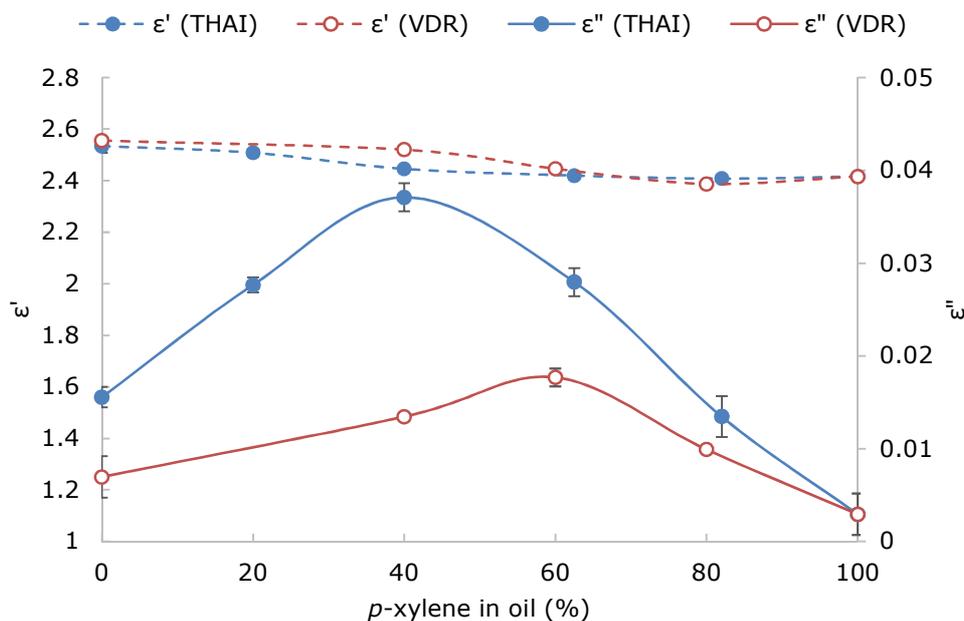


Figure 9. Dielectric constant and loss factor of different fractions of heavy oils in *p*-xylene measured at 20 °C and 2.45 GHz.

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 and increase the mobility of the larger oil molecules. With the mobility increased the dielectric loss factor increases, despite the increase in concentration of a microwave-transparent species. After the peak the mobility of the large molecules is no longer the dominant factor that governs 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 (microwave-assisted THAI process).

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 Author

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

‡ These authors contributed equally

ACKNOWLEDGMENTS

This research is funded by the Engineering and Physical Sciences Research Council (EPSRC) (grant number: EP/N032985/1). The authors would like also to thank Petrobank Energy and Resources, Ltd. (now Touchstone Exploration Inc.), Canada and PetroChina Company Ltd., China for supplying the oils used in this study. The assistance of Lawrence Pont from the Nottingham Transportation Engineering Centre (NTEC) with the viscosity measurement is also appreciated.

REFERENCES

1. EIA *International Energy Outlook 2017*; U.S. Department of Energy, Energy Information Administration September 14, 2017, 2017.
2. Koutinas, A. A.; Du, C.; Wang, R. H.; Webb, C., Production of Chemicals from Biomass. In *Introduction to Chemicals from Biomass*, John Wiley & Sons, Ltd: 2008; pp 77-101.
3. Zhang, H. Q.; Sarica, C.; Pereyra, E., Review of High-Viscosity Oil Multiphase Pipe Flow. *Energy & Fuels* **2012**, *26* (7), 3979-3985.

4. Shah, A.; Fishwick, R.; Wood, J.; Leeke, G.; Rigby, S.; Greaves, M., A review of novel techniques for heavy oil and bitumen extraction and upgrading. *Energy & Environmental Science* **2010**, *3* (6), 700-714.
5. Guo, K.; Li, H.; Yu, Z., In-situ heavy and extra-heavy oil recovery: A review. *Fuel* **2016**, *185*, 886-902.
6. Xia, T.; Greaves, M., 3-D Physical Model Studies of Downhole Catalytic Upgrading of Wolf Lake Heavy Oil Using THAI. In *Canadian International Petroleum Conference*, Petroleum Society of Canada: Alberta, Canada, 2001.
7. Shah, A.; Fishwick, R. P.; Leeke, G. A.; Wood, J.; Rigby, S. P.; Greaves, M., Experimental Optimization of Catalytic Process In Situ for Heavy-Oil and Bitumen Upgrading. *J Can Petrol Technol* **2011**, *50* (11-12), 33-47.
8. Greaves, M.; Dong, L. L.; Rigby, S. P., Simulation Study of the Toe-to-Heel Air Injection Three-Dimensional Combustion Cell Experiment and Effects in the Mobile Oil Zone. *Energy & Fuels* **2012**, *26* (3), 1656-1669.
9. Mutyala, S.; Fairbridge, C.; Paré, J. R. J.; Bélanger, J. M. R.; Ng, S.; Hawkins, R., Microwave applications to oil sands and petroleum: A review. *Fuel Processing Technology* **2010**, *91* (2), 127-135.
10. Bera, A.; Babadagli, T., Status of electromagnetic heating for enhanced heavy oil/bitumen recovery and future prospects: A review. *Applied Energy* **2015**, *151*, 206-226.
11. Jeon, S. G.; Kwak, N. S.; Rho, N. S.; Ko, C. H.; Na, J.-G.; Yi, K. B.; Park, S. B., Catalytic pyrolysis of Athabasca bitumen in H₂ atmosphere using microwave irradiation. *Chemical Engineering Research and Design* **2012**, *90* (9), 1292-1296.
12. Li, K.; Hou, B.; Wang, L.; Cui, Y., Application of Carbon Nanocatalysts in Upgrading Heavy Crude Oil Assisted with Microwave Heating. *Nano Letters* **2014**, *14* (6), 3002-3008.
13. Hu, L. X.; Li, H. A.; Babadagli, T.; Ahmadloo, M., Experimental investigation of combined electromagnetic heating and solvent-assisted gravity drainage for heavy oil recovery. *Journal of Petroleum Science and Engineering* **2017**, *154*, 589-601.
14. Porch, A.; Slocombe, D.; Beutler, J.; Edwards, P.; Aldawsari, A.; Xiao, T.; Kuznetsov, V.; Almegren, H.; Aldrees, S.; Almaqati, N., Microwave treatment in oil refining. *Applied Petrochemical Research* **2012**, *2* (1), 37-44.
15. Tjomsland, T.; Hilland, J.; Christy, A. A.; Sjoblom, J.; Riis, M.; Friiso, T.; Folgero, K., Comparison of infrared and impedance spectra of petroleum fractions. *Fuel* **1996**, *75* (3), 322-332.
16. Sieben, V. J.; Stickel, A. J.; Obiosa-Maife, C.; Rowbotham, J.; Memon, A.; Hamed, N.; Ratulowski, J.; Mostowfi, F., Optical Measurement of Saturates, Aromatics, Resins, And Asphaltenes in Crude Oil. *Energy & Fuels* **2017**, *31* (4), 3684-3697.
17. Metaxas, A. C.; Meredith, R. J., *Industrial microwave heating*. Peter Peregrinus Ltd.: London, 1983.
18. Nelson, S. O.; Trabelsi, S., Factors Influencing the Dielectric Properties of Agricultural and Food Products. *Journal of Microwave Power and Electromagnetic Energy* **2012**, *46* (2), 93-107.
19. Gabriel, C.; Gabriel, S.; H. Grant, E.; H. Grant, E.; S. J. Halstead, B.; Michael P. Mingos, D., Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews* **1998**, *27* (3), 213-224.
20. Clarke, R. N.; Gregory, A. P.; Cannell, D.; Patrick, M.; Wylie, S.; Youngs, I.; Hill, G. A *Guide to characterisation of dielectric materials at RF and microwave frequencies*; Institute of Measurement and Control / National Physical Laboratory: London, 2003.

21. Lester, E.; Kingman, S.; Dodds, C.; Patrick, J., The potential for rapid coke making using microwave energy. *Fuel* **2006**, *85* (14–15), 2057-2063.
22. Nakamura, E.; Furuichi, J., Measurement of Microwave Dielectric Constants of Ferroelectrics Part I. Dielectric Constants of BaTiO₃ Single Crystal at 3.3 KMc/s. *Journal of the Physical Society of Japan* **1960**, *15* (11), 1955-1960.
23. Smith, A. D.; Lester, E.; Thurecht, K. J.; El Harfi, J.; Dimitrakis, G.; Kingman, S. W.; Robinson, J. P.; Irvine, D. J., Dielectric Properties of Free-Radical Polymerizations: Molecularly Symmetrical Initiators during Thermal Decomposition. *Industrial & Engineering Chemistry Research* **2010**, *49* (4), 1703-1710.
24. Kharrat, A. M.; Zacharia, J.; Cherian, V. J.; Anyatonwu, A., Issues with Comparing SARA Methodologies. *Energy & Fuels* **2007**, *21* (6), 3618-3621.
25. Hermiz, N. A.; Hasted, J. B.; Rosenberg, C., Microwave dielectric losses of n-alkanes. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **1982**, *78* (1), 147-161.
26. Hurdis, E. C.; Smyth, C. P., Dipole Moments in the Vapor State and Resonance Effects in Some Substituted Benzenes. *Journal of the American Chemical Society* **1942**, *64* (9), 2212-2216.