**Ultrasonic modification of the viscosity of vegetable, mineral and synthetic oils — effects of nucleating agents and free-radical scavengers**

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ABSTRACT

We describe the ultrasonic initiated modification of four types of oil; sunflower oil, transformer oil, cable oil and silicone oil. Ultrasound is effective in initiating and driving reactions of the three hydrocarbon oils but ineffective in the case of silicone oil. The hydrocarbon oils showed noticeable reductions in viscosity after sonication; this reduction can be enhanced by incorporating nucleating agents such as particulate carbon. The viscosity loss is not permanent without using stabilisers and with time the viscosity approaches its initial value. The ultrasonic reaction is thought to be free radical in nature, since incorporation of a radical scavenger before sonication prevents any viscosity loss, whereas incorporation after sonication stabilises the drop in viscosity. Oxygen is proposed to be involved since purging with nitrogen diminishes any viscosity drop observed, and selected ion flow tube MS analysis of volatiles from the oils after sonication indicates an increase in the number and quantity of oxidised products.

**INTRODUCTION**

Sonication has been widely used for many years as a chemical processing method, e.g. for aiding dissolution of solids into solution, facilitating extraction procedures or aiding the mixing process in the formation of emulsions [1,2]. However, there is increasing interest in using ultrasound itself to initiate or facilitate chemical reactions. Liquid ultrasonic irradiation is useful for many chemical reactions at high energy through cavitation, a physical phenomenon that involves the formation, growth and implosive collapse of micro-bubbles. This phenomenon generates very extreme temperatures (1000–5000 K) and pressures (200 -5000 atm) for a very short time (<10 ms) at millions of localised places simultaneously, defined as ‘Hot Spots’ [1-5]. These high temperatures catalyse chemical reactions and radical formation. As well as this, strong shear gradients are also developed within the liquid and are responsible for the mechanical effects induced by cavitation [6].

Sound waves are longitudinal in nature, in which particle movement in the medium is parallel to the wave’s direction of travel. The acoustic impulse, generated by the oscillating body, compresses the particles in the medium (high pressure), although this compression is limited by the elasticity of the medium itself, which creates a rarefaction (low pressure). Compression and rarefaction alternate till the oscillation reaches its end and the medium goes back to equilibrium. When ultrasound is used on homogeneous liquid phase systems—including aqueous and non-aqueous organic solvents—the cavitational collapse leads to

the formation of highly reactive free-radical species (such as hydroxyl, hydrogen or organic radicals). These radicals — which can be formed both from molecular fragmentation, caused by the dissociation of vapours that fill the micro-bubbles, and from chemical bonds breaking due to shear forces of the liquid filling the cavity — are responsible for the catalysing effect on chemical reactions and their propagation under ambient conditions [2,7]. For homogeneous liquid systems, there is a strong correlation between the frequency of the ultrasound and the reaction sites, which influences the kind of chemical reaction that is

driven by cavitation. With low-frequency ultrasound (20–100 kHz), the growth of the micro-bubble requires many cycles during which volatile solutes and solvent vapours flow into the internal gas phase, and this inhibits the mass transfer from inside to outside the micro-bubble. This allows chemical reactions to take place within the micro-bubbles or at the interface between the micro-bubble and the surrounding liquid with the process primarily affecting hydrophobic solutes. When using medium-frequency ultrasound (300–1000 kHz), the growing and the collapse of the micro-bubbles are rapid, leading to a high energy release in the surrounding liquid, which in turn catalyses oxidation processes in the bulk solution [2]. The use of ultrasound to initiate chemical reactions in alkanes has been described previously.8 Ultrasonication of n-decane under oxygen-free conditions produced a number of products including hydrogen and short-chain alkanes and alkenes. A mechanism was proposed where hydrogen atoms are abstracted from carbon atoms, especially secondary and tertiary atoms to give free radicals. Adventitious oxygen in such system can then react with the hydrogen radical to give an unstable peroxy radical. This can then decompose or undergo further free-radical reactions such as hydrogen abstraction or combination with other radicals, which can lead to the scission of C–C bonds. The overall effect is that long alkane chains are cleaved by this mechanism. The presence of free radicals was confirmed by using ‘traps’, such as diphenylpicrylhydrazyl. Sonication in the presence of oxygen also led to the formation of carbon monoxide and dioxide [8]. Sonication has also been used in polymer chemistry, with ultrasound being shown to be capable of initiating polymerisation of monomers or cleaving preformed polymers to give lower molecular weight materials. [8–10].

There is also potential for utilising ultrasound within the oil industry. For example, current typical processes for upgrading heavy gas oil involve such reactions as catalytic hydrotreating which requires expensive catalysts and high temperatures and/or pressures. Ultrasonication has been used [7] for upgrading heavy gas oil at atmospheric pressure without additives. A 5% decrease in viscosity and reductions in the levels of problematic nitrogen and sulfur compounds were obtained. Others workers have also utilised ultrasound to facilitate the oxidative removal of sulfur compounds from oil produced from tyre pyrolysis [11] and to produce ultra-low sulfur diesel [12].

Ultrasonication can be utilised in the food industry as a method for emulsification or other

processes; however, this sometimes can lead to degradation in food quality, especially in foods with high lipid content [13]. Often, a rancid odour can be noted, indicating that volatile compounds are being produced. Studies on fatty acids or olive oil indicated that sonication could produce these rancid odours and gas chromatography/mass spectrometry (MS) studies demonstrated that oxidation of the substrates was occurring [14]. In another study, sunflower oil was ultrasonicated, and the presence of compounds such as hexanal or limonene detected by gas chromatography/MS in the volatiles released from the ultrasonicated oil [15]. Also, after storage for 24 h, the oil became cloudy, indicating that further reactions such as polymerisation may be occurring. More in-depth work by the same group showed that again oxidation took place — and they also utilised electron paramagnetic resonance spectroscopy along with a spin-trap species to demonstrate increases in free-radical concentration after sonication. The signals obtained from the spin trap showed that the free radicals were oxygen-based such as superoxide or hydroxyl radicals [16]. Low levels of radicals were also detected in non-sonicated sunflower oil, although these were lower than in the sonicated samples, indicating that transient radicals form spontaneously even in untreated samples [16].

The rationale for this research programme was to investigate the use of ultrasonication to modify the physical properties of common oils without the need for high temperatures, pressure or precious metal catalysts. One possibility is to use the presence of small particles as nucleating agents to increase cavitational events and improve the efficiency of ultrasonic initiation. Also, since previous work indicated that reactions such as polymerisation continue after sonication has ceased, [15] we investigated whether the oils could be stabilised by the addition of a free-radical scavenger. A range of four oils with differing chemical structures were studied, the first being sunflower oil, which is a triglyceride where the sidechains are a mixture of linoleate, oleate, palmitate and stearate units. Transformer oil is a highly refined mineral oil consisting of alkyl chains of different lengths; cable oil is a synthetic mixture of a series of alkyl benzene compounds with aliphatic chains between 12 and 22 carbon atoms in length [17,18] and silicone oil (common synthetic oil based on an -Si(CH3)2-O- repeat unit).

**MATERIALS AND METHOD**

***Equipment and general procedure***

Sunflower oil (Flora, Princes Ltd., UK) was purchased from a local supermarket. Cable and

transformer oils were obtained from the National Tray Transco (UK), while silicone oil was purchased from Dow Corning (Barry, UK). Carbon powder (code 484164), glyceryl trilinoleate, glyceryl trioleate, ammonium acetate and sodium acetate were obtained from Sigma-Aldrich (Gillingham, UK). Carbon nanotubes were provided from the School of Engineering (Cranfield University, UK), while carbon plasma black was supplied by Gasplas (University of East Anglia, UK). Acetone and 4-tert-butylphenol were supplied by Acros Organics (Geel, Belgium). Isopropanol and methanol were supplied by Fisher Scientific (Loughborough, UK). Acetic acid and glass spheres (2.4 mm diameter) were purchased from BDH (Poole, UK).

***Ultrasonic reaction and characterisation***

For the viscosity investigation experiments, two ultrasonic water baths were used: either a Camlab Transsonic T460 (Camlab, Cambridge, UK) at 35 kHz frequency and 85 W power output or an Ultrawave U100 (Ultrawave Ltd., Cardiff, UK) at 44 kHz frequency and 35 W power output. These baths are relatively similar and were used to determine whether small differences in bath power/frequency can have major effects on the results of sonication. Samples of the oils (30 ml) were sonicated in 50 ml glass beakers, and for each experiment, three separate samples of the oil were sonicated simultaneously unless detailed otherwise. For all the viscosity measurements, a dropping ball viscometer was used (Figure 1). This type of viscometer is based upon Stokes’ Law for flows around submerged objects [19]. According to this law, the forces that act on a sphere settling through a fluid are the force of gravity, the drag forces and the buoyant force; when the drag forces acting on the sphere become equal to the gravity force, the sphere falls at a constant velocity termed terminal velocity (equation (1)):



where V is the terminal velocity of the sphere (m s-1), D is the diameter of the sphere, (m), g is the gravitational acceleration (9.8 ms2), ρS is the density of the sphere (kgm-3), ρF is the density of the fluid through which the sphere is settling (kgm3), μ is the viscosity of the fluid (Pa s). By rearranging this equation, it is possible to determine the viscosity of a fluid by measuring the terminal velocity of the sphere (equation (2)). For simplicity, all the viscosity values are here reported in cP with 1 cP = 0.001 Pa s (dynamic viscosity).



The terminal velocity of the sphere was recorded with the aid of a video camera, and the videos were analysed with a free video analysis and modelling software (TRACKER 4.50 — Open Source Physics). Glass spheres were used as the balls in this experiment, three different spheres of 2.4 mm diameter were used, and 10 measurements of terminal velocity were made with each sphere (a total of 30measurements). The sonication process was found to raise the temperature of the oils by up to 20°C. Since the temperature of the oil will affect its viscosity, oil viscosity was measured 30 min after sonication ceased. A detailed investigation of the change in temperature with time was not undertaken, but after 15–20 min, the oils had all returned to within a degree of room temperature, so 30 min was used, as this time interval is in excess of that required to allow any heating effects caused by the sonic bath to dissipate, and the oils returned to room temperature (23°C). Samples were stored under dark conditions (to prevent any light-initiated reactions) at room temperature.

***Spectroscopic studies on oils***

Fourier transform infrared spectroscopy was carried out with an Equinox 55 (Bruker Optik GmbH, Ettlingen, Germany) in the attenuated total reflection mode using a zinc selenide prism mounted on a Specac Gateway Multi-Reflection ATR (Specac Ltd., Slough, UK). NMR analysis was carried out using a JEOL ECX 400 MHz NMR, oil samples were measured in CDCl3. Examination of the nucleating agent nanostructures (1.5 nm resolution) was carried out with a high-resolution FEI XL30 SFEG analytical scanning electron microscope (SEM). Liquid chromatography-MS (LC/MS) analyses were performed using an Agilent HPLC 1290 Infinity—6540 UHD (Ultra High Definition) coupled with an accurate-mass quadrupole time-of-flight MS detector. A Zorbax Eclipse Plus C18 (50 mm) column at 30°C was used with an elution solvent of 18% isopropanol in methanol with the addition of 0.1% acetic acid, 0.05% ammonium acetate and 0.001% sodium acetate, at a flow rate of 0.25 ml min1 as described elsewhere.20 Standards and samples were injected at a concentration of 100 μgm-1 in 50%acetone, 41% methanol and 9% isopropanol. The gas temperature and the drying gas temperature were 325°C, the fragment voltage was +150 V and the capillary voltage was +4000 V.

The selected ion flow tube MS (SIFT-MS) analysis of the volatiles was performed using a Profile 3 SIFT-MS (Trans Spectra — Instrument Science, Crewe, UK). Liquid samples were injected into polyethylene terephthalate bags, which were then filled with zero grade air. The bags were allowed to equilibrate at 30°C for 15 min before the analysis and were then linked to the apparatus, and the headspace volatiles were collected at a flow rate of 0.62 torr -1 flow rate for 30 s via a heated calibrated capillary, with the same temperature being maintained during the collection. The analysis was performed in full scan mode in the mass-to-charge ratio (m/z) range between 10 and 200 m/z. The products identified in the samples were then normalised to the products identified from the analysis of a control bag of zero grade air.

**RESULTS AND DISCUSSION**

***Effect of sonication on hydrocarbon oils***

Samples of sunflower, cable and transformer oil were all sonicated for a series of 1 h interval, and their viscosities were measured. After the final sonication, they were then stored for up to 7 days with the viscosity being measured at 24 h interval. Figure 2 shows the overall results for these experiments. For all three oils, there is a steady decrease in viscosity with increasing sonication time for at least 4 h. This is consistent with cleavage of the alkyl chains, lowering the overall molecular weight of the oils. Once sonication has ceased, the viscosity increases with storage over the next 3 days (Figure 2). Longer storage times (up to 7 days) only led to small further increases. Reductions of viscosity in the region of 25% could be obtained for all the oils.

In the case of sunflower oil, the sonication experiments were repeated using a second sonic bath supplied by Ultrawave. The resulting viscosity of the oils sonicated using this bath followed a very similar trend to those studied using the Camlab bath. For example, after 4 h the viscosity of the sunflower oil had been reduced by 23.4%, compared with 25.3% observed previously for the Camlab bath.

However, there are a number of different effects that may be competing with each other. The Ultrawave bath operates at a higher frequency (44 KHz) and lower power (35 W) than the Camlab bath (35 kHz, 85 W) as well as having a smaller tank volume (1.5 against 2.75 l). This means that it is difficult to determine how much ultrasonic energy is delivered directly to the sample, especially since it has to pass through the glass walls of the beakers containing the oil sample. The similarity of the results obtained however does indicate that, in this instance, any differences in volume, power applied and frequency are negated. There appears to be no significant difference between the two baths in terms of obtained results; however, for consistency, the 35 kHz Camlab bath was used for all further experiments.

***Utilisation of carbon nucleating agents***

Since ultrasonication reactions are caused, at least in part, by the formation of bubbles, attempts were made to see whether inclusion of small particulate matter would enhance nucleation of these bubbles and thus increase the efficiency of the ultrasonication process. Carbon was chosen as the nucleating agent since it is easily available in a variety of shapes and sizes, is relatively chemically inert and is hydrophobic, suggesting that it would mix with the oil sample. Three types of carbon, commercial carbon particles from Sigma, carbon nanotubes supplied in house and a commercial carbon plasma black, were utilised. The carbons were dispersed in water and then cast onto silicon wafers, allowed to dry and then examined by SEM.

**Structures of the nucleating agents.**

Figure S1a shows the structures of the Sigma carbon, which takes the form of regular spheres approximately 2–3 μm in diameter, some of which are fused together. The schematic for the material from the suppliers describes it as ‘glassy, spherical powder 2–12 μm’. Figure S1b shows a sample after it has been sonicated for 60 min before casting, as can be seen, sonication leads to the breaking up of some of the particles. Carbon plasma black was also dispersed in the same way and was examined. This material was shown to consist of carbon agglomerates in the range of 1–10 μm, formed by aggregation of smaller particles with sizes in the range of 20–200 nm (Figure S2). Sonication did not appear to have any effect on the structure of this carbon.

Finally, carbon nanotubes were also examined, and SEM studies showed them to have lengths in the range of 60–150 nm with widths between 15 and 20 nm (Figure S3). Unfortunately, the carbon nanotubes proved impossible to separate effectively from the oil after sonication, and it was impossible to obtain high-quality SEM.

***Effect of nucleating agent and sonication on viscosity.***

Initial experiments were performed using sunflower oil and carbon powder (Sigma). Samples of sunflower oil to which 0–2% (w/w) of carbon powder had been added were sonicated for 1 h at 35 kHz. The samples were then centrifuged at 4000 rpm for 15 min to remove the carbon. Viscosity measurements were taken before sonication, after the sonication (having allowed the samples to cool down to room temperature (23oC) — resting time 30 min) and then every 24 up till 120 h. As can be seen (Figure 3), sonication led to a decrease in measured viscosity in samples to which the nucleating agent was added, greater than that obtained for the control sample for the full time period examined herein. In these initial experiments, samples which had been stored for 24 h actually showed a further decrease in viscosity rather than the expected increase. Later examination of this process in greater detail by measurement of the viscosity every 6 h after sonication up to 48 h demonstrated that the measured viscosity reached a minimum after 24 h. After

this time, an increase could be seen in the viscosity values.

The decreases in viscosity that occur in the 24 h after sonication are unexpected. Previous work has shown that not only are radicals generated during sonication but also transient radicals form in untreated sunflower oil.16 Possibly, the presence of the carbon particles besides aiding cavitation also helps remove certain species from the oil, which cause recombination of the chains, perhaps by quenching the radicals after sonication ceases. One possibility is that ultrasonication is not involved at all in the carbon catalysis process and that the carbon particles are acting as simple chemical catalysts. However, control experiments where sunflower oil was mixed with carbon powder for 1 h without sonication and centrifugation showed no changes in viscosity.

Since there appears to be relatively small differences between the viscosity decrease obtained with the higher concentrations of carbon (1% and 2% w/w) and the lowest concentration (0.1% w/w), possibly due to an effective saturation of the solution, the 0.1% w/w concentration was therefore been chosen for following studies. The experiments were repeated with both the carbon plasma black and carbon nanotubes. Carbon plasma black showed behaviour very similar to carbon powder, the reduction in viscosity after 1 h sonication being practically identical. However, this material is proved to be much more difficult to remove from the oil by centrifugation, with some of the carbon particulates remaining in suspension. Carbon nanotubes were also briefly studied; however, these proved somewhat inferior, with the reduction in viscosity after 1 h sonication being only 60% that achieved with carbon powder. It should be noted that there are toxicological issues associated with working with carbon nanotubes. The Sigma carbon powder was therefore chosen as the best material for further experiments.

***Effect of radical scavenger***

Since previous work concludes that reactions in these systems are free-radical-based, we utilised a free-radical scavenger, 4-t-butyl phenol, to determine whether these reactions could be controlled. First, as a control, 0.1 mM of t-butyl phenol was added to samples of the three hydrocarbon oils, and their viscosity was measured. No changes in viscosity were observed, suggesting that at these levels, the scavenger does not directly affect the viscosity of the oil.

Batches (n = 6) of all three oils were then sonicated for 1 h at 35 kHz. After sonication, the

viscosities were measured, and then two samples from each oil had 0.1 mM t-butyl phenol added. After 24 h, the viscosities were measured again, and two more of the original samples had the scavenger added, with the final pair of samples remaining as a control. Figure 4 shows the behaviour of these oils; as can be seen, sonication as expected lowers the viscosity of all three sample types. The sample that has t-butyl phenol added immediately after sonication has its viscosity stabilised at that value. The other two samples increase in viscosity after 24 h. The sample that had t-butyl phenol added after this 24 h period is then again stabilised at that value—whereas the control continues to increase. This would indicate that the increase in viscosity is due to free-radical reactions, possibly due to the decomposition of unstable species formed during sonication or due to the transient radicals that occur in some oils [16].

Samples of all three oils containing 0.1% (w/w) of carbon powder were sonicated for 1 h and had their viscosity measured. Viscosity was measured again after 24 h, after which, 0.1 mM t-butyl phenol was added. The oils were then measured again at 24 h interval (for 9 days). Control samples without any carbon black or t-butyl phenol were also measured. Figure 5 shows similar behaviour for all three oils, i.e. a drop in viscosity after sonication followed by a further drop after 24 h. However, after this time there was no further increase in viscosity even after 9 days storage, indicating that the presence of the scavenger was preventing any further rearrangements.

Further experiments were made where the radical scavenger was added before sonication. Samples of all three oils, with or without 0.1% (w/w) carbon powder, all containing 0.1 mM t-butyl phenol, were sonicated at 35 Hz for 1 h. In all cases, no decrease in viscosity was seen, again demonstrating that the scavenger is quenching the free radicals formed during sonication.

***Effect of oxygen***

Two batches, each of three samples, of sunflower oil were sonicated in a bath sonicator at 35 kHz frequency for 60 min. Prior to sonication, one of the batches was bubbled with nitrogen (N2) for 30 min in order to de-oxygenate the sample. Bubbling with nitrogen was also continued during the sonication process. Viscosity measurements were undertaken before sonication (no attempt was made to prevent the ingress of oxygen during the viscosity measurements or storage), 30 min after the sonication and every 24 h after the sonication for 3 days. Results (Figure S4) show that the nitrogen-purged system had a lower drop in viscosity, approximately 75% of that of the control. After 72 h, the two samples had both increased in viscosity — and had essentially identical values.

***Spectroscopic and SIFT-MS measurements on sonicated hydrocarbon oils***

FTIR and 1H NMR studies. Amongst our earliest characterisation efforts were the measurement of the Fourier transform infrared spectroscopy and NMR spectra of the oil prior to and after sonication. Samples of sunflower, cable and transformer oil were sonicated for up to 4 h with and without 0.1% carbon black. In all cases, only minimal changes were seen for the oils (Figure S5a–S5c), indicating that as reported previously,14 16 only a fraction of the oil chains react, insufficient for the changes to be visible in the IR spectra. Samples of sunflower oil were also sonicated for 1 h and interrogated using NMR spectroscopy. As can be seen, there are no obvious changes to be seen, again indicating that only a fraction of the chains react (Figure S6a and S6b). Similar results were obtained for cable and transformer oil, but again, no differences could be detected.

***LC/MS analysis.***

The LC/MS analysis was performed on a sunflower oil sample and, since the oil is a

mixture of triglycerides, on a triglyceride found in the oil. Glyceryl trilinoleate was chosen as a reference standard since linoleic acid is a major component of the triglycerides of sunflower oil. One sample of sunflower oil and one sample of the standard were sonicated for 60 min. Following sonication, these samples and non-sonicated control samples were analysed using LC/MS.

The total ion chromatograms (TIC) of the non-sonicated and sonicated glyceryl trioleate

standard were obtained (Figure S7). As can be seen, sonication does not lead to any further peaks in the LC/MS chromatographs, indicating that any products of the sonication reaction are at levels too low to be detected by this method. The TIC of the sonicated glyceryl trilinoleate standard (Figure S8) is also shown, and again, only the single reagent peak for the trilinolate is obtained. Figure S9 shows the TIC for non-sonicated and sonicated sunflower oil samples. Each single peak in the TIC was analysed to determine the mass spectrum of each component. No differences are visible between the TIC of the oil and the standards before and after the sonication as well as on the pattern of the ions observed in the mass spectra. These results again suggest that the fraction of oil molecules undergoing structural changes is too small to be detected with this technique.

***SIFT analysis of the volatile fractions***

Selected ion flow tube MS analysis was performed on samples of sunflower, transformer and cable oil sonicated for 1 h and on non-sonicated (control) samples. Analyses were performed on 2.5 ml samples, which were allowed to equilibrate as previously described to allow the volatiles of the oils to disperse into the air-filled bags. A bag filled only with air (zero-air sample) was used as an internal control.

The principal volatiles identified before and after the ultrasound treatment of the oils are those listed in Figure 6. The composition of the volatiles potentially indicates an oxidative process taking place within the samples during sonication, but it could also be possible that the volatiles are formed from the smaller fragments of the chains broken by the ultrasound. SIFT-MS is a highly sensitive method that can quantify a wide range of volatiles. Only the most prevalent are shown here as a detailed examination of all of the volatiles present is outside the scope of this paper. We present an overview for each oils of the most prevalent volatiles detected. As can be seen, there are noticeable increases in many oxygen bearing species in the sonicated samples. For example, sunflower oil shows large increases in acetone and some alcohols. Transformer oil shows enhanced levels of formaldehyde and some alcohols after sonication. Cable oil appears to show less production of volatile by-products, although there are increases observed in both formaldehyde and acetone levels.

In the same manner, as described for the aforementioned hydrocarbons, samples of silicone oil were sonicated for up to 4 h, with and without 0.1% w/w carbon black. In all cases, no significant decrease in viscosity from the initial value of 68 cP was observed after sonication and after 24 h further storage. This particular behaviour can be explained by considering the different chemical structure of the core chain of silicone oil (Si–O chain) in contrast to the other oils considered within this work (C–C chains); these chains are characterised by different bond energies, C–C bonds having an energy of 346 kJ mol1 and Si–O bonds of 452 kJ mol-1.21 Moreover, the lower vapour pressure of silicone oil increases the tensile strength of the liquid, limiting the formation of the cavities and thus inhibiting the action of the ultrasound.22 It is also worth noting that the siloxane chain is relatively resistant to free radical attack — instead free radical reactions tend just to involve the methyl side groups.

**CONCLUSIONS**

This work has shown that ultrasound is effective in cleaving the chains of carbon-based oils. However, despite the success in carbon-based oils, this approach has proven to be ineffective on non-organic oils, such as silicone oil. This difference in behaviour is suggested to be due to the different bond energies between the C–C and Si–O bonds constituting the core chains of the oils. The proposed mechanism through which the ultrasound breaks the chains of the oils (thus leading to a drop in the viscosity) is based on the generation of radical species whose nature is either oxygen or non-oxygen related. After sonication is terminated, the generation of lower molecular weight species ceases, and the radicals or peroxides formed undergo further reactions thus leading to an increase in the viscosity. The efficiency of the ultrasound, in breaking the oils’ chains, was found to be increased by the addition of a nucleating agent, such as carbon black. To prevent the viscosity increasing after sonication, the addition of a radical scavenger has proven to be effective. Chemical analysis of the oils before and following sonication indicates that structural changes only occur for a fraction of the oil molecules during sonication. Analysis of the volatile by products indicates the potential of an oxidative process occurring within the samples and seems to confirm the hypothesis of the chain cleaving action of the ultrasound.

The present work has mainly investigated the effects of ultrasound at an operational frequency of 35 kHz, which was found to be effective in breaking the C–C bonds of carbon-based oils. Future work will investigate other frequencies of ultrasound to determine if higher or lower ultrasonic frequencies are able to break the chains of materials such as silicone oil. Application of ultrasound with lower frequency but higher power could possibly speed up the growth step of the cavitation phenomenon, thus having a stronger effect on the samples, potentially leading to a greater viscosity decrease for shorter exposure times. Although the falling ball viscometer can determine viscosity, there are a range of other techniques that could be used, which would have higher accuracy and allow more precise determination of the effects of ultrasound. Another issue is that within our work, we utilised glass beakers to contain the oil within the ultrasonic bath. This will of course attenuate the ultrasound and reduce its efficiency, in any application, it is more likely that ultrasound will be applied via a probe-type sonicator or possible a custom-designed vessel with integral sonicators. The use of additives such as oxygen or hydrogen peroxide to increase oxidation is also of interest. More exhaustive chemical analysis will allow determination of the products formed and the reaction mechanisms occurring. Vapour pressure osmometry could potentially be used to determine the effect of sonication of the average molecular weight of the oil, giving an estimate of chain scission. Other work will examine the combustion characteristics of the oils to see if they are improved as well as the scale-up of these processes.

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**Figures:**



**Figure 1.** Schematic representations of a falling ball viscometer and of the forces acting on the falling sphere.



**Figure 2.** Effect of sonication at 35 Hz and storage on the viscosity of (a) sunﬂower oil, (b) transformer oil or (c) cable oil. Results show viscosity at 1, 2, 3 and 4 h sonication, then after 24, 48 and 72 h storage. The measurements were performed in triplicate with the standard error being shown.



**Figure 3.** Effects of nucleating agents (Sigma carbon powder), sonication (1 h) and storage on the viscosity of sunﬂower oil.



**Figure 4.** Effects of the radical scavenger on oils. 4-tert-butylphenol (Ph) was added to two of the samples after 30 min from the sonication and after 24 h from the sonication. The measurements were performed in triplicate with the standard error being shown.



**Figure 5.** Effects of the radical scavenger on (a) sunﬂower oil, (b) transformer oil or (c) cable oil. 4-tert-butylphenol was added after 24 h from the sonication to the samples that were sonicated in the presence of carbon black (CP). The measurements were performed in triplicate with the standard error being shown.



**Figure 6.** Principal products identiﬁed from the selected ion ﬂow tube analysis of the headspace volatiles for (a) sunﬂower, (b) transformer and (c) cable oil before and after treatment with ultrasound. Amounts are expressed in parts per billions (ppb)