Insight into Liquid Interactions with Fibrous Absorbent Filter Media using Low-Field NMR Relaxometry. Prospective Application to Water/Jet Fuel Filter-Coalescence

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ABSTRACT

We describe a low-field NMR relaxometry study of water and aviation turbine fuel (jet fuel) in contact with samples of fibrous media removed from an unused aviation fuel filter cartridge. This media was studied both in its as-received state and after modifying its wettability. The interaction of liquid droplets with fibers is the basis for fibrous coalescence widely used industrially to separate different types of liquid-liquid dispersion. Here, we are specifically concerned with interactions that potentially occur during the removal of entrained water from jet fuels, an application that is of particular importance on safety grounds, primarily to prevent ice formation in aircraft fuel tanks which could otherwise lead to fuel-line filter blockage and fuel starvation to the engines. Jet fuel is treated using various filtration systems, including cartridge-type microfilters and filter-coalescers, at different points between refinery and aircraft fuel tank in order to remove dirt (particulates) and water and ensure that contamination levels always meet the required specifications. The main objective of the present study was to apply proton NMR relaxometry to provide insight into the water coalescence process, specifically by probing water environments on fibrous media. On the basis of T_2 (spin-spin) relaxation distributions, it has been confirmed that the water environments depend on the media wettability, with three environments being identified: fiber surface adsorbed water; inter-fiber absorbed water; and unassociated (largely bulk) water. The use of such NMR techniques may therefore offer potential for monitoring or improving filter-coalescer performance.

INTRODUCTION

Fibrous media have been used extensively for many years in the commercial separation of flowing emulsions, both water-in-oil and oil-in-water.¹⁻⁹ In the case of “secondary emulsions”, comprising $<5\ \mu\text{m}$ diameter droplets, optimisation of the respective interactions between the solid (fibers), water and oil is essential for effective collection and coalescence of the disperse phase in order to enhance gravity separation.¹⁰ The role of solid wettability and surface energy on the efficiency of coalescence achieved in porous media and isolated fibers has been the subject of attention over the years.¹¹⁻¹⁵ As an example, when a water-in-oil emulsion containing fine water droplets is passed through predominantly hydrophilic fibrous media, water droplets attach to the fibers or to droplets already attached to the fibers.¹³ This restricts their flow with respect to the continuous oil phase.¹⁶ The water droplets attached to the fibers then coalesce with further incoming droplets, thereby growing and finally emerging from the filter media as enlarged drops which separate more easily from the oil under gravity.¹⁶

Our focus in the present study is the investigation of interactions leading to water droplet coalescence during the fibrous filtration/coalescence of aviation jet fuels. The daily global consumption of jet fuel is more than 8 million liters, all of which will have been subject to several filtration/coalescence processes by the time it reaches the aircraft. In view of the diversity of petroleum source and refinery processing (e.g., straight-run, hydroprocessed, Merox-treated), the compositional complexity of jet fuels is considerable, and it is therefore important that the methods to mitigate contamination, including filtration/coalescence, are as effective as possible. Moreover, post-production additization is often necessary for jet fuels to meet international specifications. This includes adding, for example, lubricity improver, antioxidant, electrical conductivity improver, metal deactivator and icing inhibitor, most of which exhibit some activity at fuel-water and fuel-solid interfaces.^{16,17}

Water separation from jet fuels. The presence of water in jet fuel is potentially detrimental to the safe operation of aircraft.¹⁸ Water-contaminated jet fuel at freezing temperatures can result in ice being formed in the fuel systems, which on very rare occasions, with extreme levels of contamination, can result in engine failure.¹⁹ Water exists in jet fuel in three different forms: (i) soluble water which is dissolved in the fuel and is therefore considered to be a constituent of the fuel; (ii) emulsified water present as suspended micron-sized droplets, often producing a hazy appearance;²⁰ and (iii) free water, which more readily

separates into a layer at the bottom of storage or aircraft fuel tanks.²¹ The latter two forms are considered contaminants and are strictly regulated in jet fuel specifications.²² The solubility of water in a given jet fuel is in the general range 50-100 ppm, but is thermodynamically and compositionally controlled, and so varies with partial pressure of water above the fuel and temperature.²³ If the concentration of water in the jet fuel exceeds the solubility limit of the fuel, for example as a result of a reduction in temperature, it will phase separate as an emulsion or a bulk (free) water phase.²⁴

Exposure to water can potentially occur during transportation and storage of the fuel¹⁸ and stringent precautions are therefore taken to remove contamination before reaching the aircraft fuel tanks. As such, procedures have been developed over the years to remove water from jet fuel, including coalescence using filter/water separators.²⁵ Passing oil-water emulsions through fibrous beds is used to coalesce the smallest suspended water droplets into larger drops, which can be more easily separated from the fuel.²⁴ However, the effectiveness of fibers to coalesce water decreases with time in service, with increases in either hydrophobic or hydrophilic character arguably being detrimental to performance.^{16,18,24}

Jet fuel filtration/coalescence systems often use non-woven glass microfiber media bonded with organic resin, and the coalescence mechanism involves the capture of dispersed water droplets by exposed hydrophilic fiber surfaces.²⁶ Fiber wettability and the distribution of hydrophilic sites are therefore important factors for successful operation, for which it is important to achieve a balance of capture and release; too hydrophilic and the droplets could be retained within the fibrous network, which could become saturated,^{27,28} but too hydrophobic and the droplets will not be captured or coalesced efficiently and pass straight through.^{29,30} However, the large volumes of fuel passing through commercial filter-coalescers lead to changes in media structure and properties through the accumulation of surfactants and solids. In practice, this leads to “disarming”, characterised by a reduction in coalescence efficiency, with consequent detrimental effects on water separation and hence fuel quality.²⁴

The effect of fiber wettability on the efficiency of fibrous coalescers has been the subject of a number of studies over the years, dealing with both oil droplet separation from water and water droplet separation from oil. Previously, Shin and Chase¹⁴ observed that even though there is a general consensus that wettability affects coalescence mechanisms in porous

media, the relationship between the surface properties of the media and coalescer performance is unclear, and this still largely remains the case today.

Here, we consider the nature of interactions occurring within the fibrous media relating to wettability, and are keen to establish the feasibility of proton NMR relaxometry as a means of monitoring the role of wettability in water/jet fuel/fiber systems. In particular, the response of the T_2 (transverse or spin-spin) relaxation times of water and fuel protons has been determined when the liquids are in contact with untreated fibrous media and media made more hydrophilic or more hydrophobic by pre-treatment with appropriate reagents.

As far as we are aware, there has been no previous attempt to determine NMR relaxation times for liquids in contact with this type of fibrous filter material. In related studies, however, Bortolotti et al.³¹ studied the water porosity and water absorption kinetics of Lecce stone using NMR T_2 relaxation time distributions, and were able to identify the progressive uptake of water within the different pore structures. More recently, Zheng et al. reported the use of ^1H NMR relaxometry to determine water migration in tobacco, identifying two separate mechanisms involving inter- and intra-layer migration.³² Using similar considerations, we envisage that different environments within the fibrous media could be identified during liquid ingress.

Low-field NMR Relaxometry. Unlike high-field, frequency-domain, ^1H NMR spectroscopy which is used mainly for chemical analysis, low-field, time domain, techniques predominantly provide physical information about a system containing hydrogen nuclei, and attracts particular interests for industrial process monitoring.³³ Low-field NMR is used widely in the petroleum industry to determine oil/water ratios,³⁴ predict oil viscosity,³⁵⁻³⁷ as well as correlating with other physical and compositional properties of petroleum fractions.³⁸ This is performed with the use of specific pulse sequences enabling the determination of relaxation times of proton environments.^{35,37,39}

Hydrogen atoms in a molecule possess a nuclear spin, and in the absence of a magnetic field, the spin orientations are random. The application of a directional magnetic field, B_0 , however, causes most of the spins to align in a direction parallel to B_0 . This causes a net magnetization, M_z , to precess around the field.⁴⁰

The subsequent application of a radiofrequency pulse, B_1 , then rotates M_z by 90° into the xy plane. M_{xy} will then decay exponentially with time via two mechanisms, involving spin-

lattice or spin-spin relaxation. Spin-lattice relaxation returns the net magnetization to M_z with a longitudinal, or T_1 relaxation time. On the other hand, spin-spin relaxation leads to T_2 relaxation times, as determined herein, are caused by the net magnetisation de-phasing in the xy plane.⁴⁰

The value of T_2 is obtained by measuring the time taken for the magnetic signal to decay to $1/e$ of its starting value. T_2 values reflect the physico-chemical environments experienced by the protons such that free water, for example, will be expected to have different T_2 relaxation times compared to emulsified or adsorbed water.⁴⁰

Work done by Barbosa et al.^{35,41} and Muhammad and de Vasconcellos Azeredo³⁶ involved low-field NMR measurements to predict physical properties of petroleum fractions, including viscosity, American Petroleum Institute (API) gravity, acid number and refractive index. The results show that the predictions from the low-field NMR technique show clear correlations with standard ASTM methods, and they suggest that such NMR techniques can be used for routine analysis of petroleum. As well as this, the NMR method is comparatively low-cost and non-destructive to the sample being analysed.

In the present paper, we also assess NMR relaxometry to study the effect of bi-liquid (water + jet fuel) systems on fibrous media.

EXPERIMENTAL SECTION

Materials. Filter media samples were removed from an unused microfilter element from a major filter manufacturer in order to evaluate responses to water and jet fuel addition. This material was found by optical microscopy to comprise glass micro-fibers, the diameter of the majority being $\sim 10\ \mu\text{m}$ with a minor contribution from $\sim 1\ \mu\text{m}$ fibers, as shown in Fig. 1. Attenuated total reflectance-infrared spectroscopic analysis confirmed their composition. The dry density was determined gravimetrically as $0.21 \pm 0.02\ \text{g/cm}^3$, by weighing several samples of media of known area and thickness (micrometer). This density corresponds to a fiber packing volume of $\sim 10\%$. Since this was obtained from a micro-filter, it is reasonably assumed, and confirmed from the absence of C-H or C-F bands in the infrared spectrum shown in Fig. 1, that no treatment had been applied to alter its surface chemistry, allowing us to modify the wettability as part of this study.

Deionized water (resistivity = 18.2 MΩ.cm) was from a Millipore Direct-Q unit. A stock jet fuel sample (density = 0.781 g/mL at 20 °C) conforming to UK MoD Defence Standard 91-91 (now DefStan 90-091)⁵¹ was originally supplied by QinetiQ Ltd., now Intertek Fuels and Lubricants Centre, Farnborough, UK. Petronate® L, an oil-soluble sodium petroleum sulfonate anionic surfactant, was obtained from Sonneborn Refined Products B.V., Amsterdam, The Netherlands. *n*-Heptane and dichlorodimethylsilane (DCDMS) were purchased from Sigma-Aldrich Ltd., Poole, UK.

Figure 1. (a) Opto-digital micrographs of the filter material glass fibers used in this study showing diameters ~ 1 and ~ 10 μm . (b) The infrared spectrum of the filter material, showing absorption bands characteristic of glass (assignments indicated).

Methods. Modification of media wettability. The wettability of samples of the as-received filter media was modified in one of two ways. Firstly, to increase hydrophilicity, the anionic surfactant Petronate® L, a sodium petroleum sulfonate, was used. Weighed samples of filter media were saturated with 100, 1000 or 10000 ppm solutions of Petronate® L in *n*-heptane. Excess solution was allowed to drain and was immediately re-weighed to determine the mass of solution retained by the filter material, prior to leaving the solvent to evaporate in a fume-hood. This enabled the mass of Petronate® L retained by the test samples to be calculated. The second wettability modification was made to increase the hydrophobicity of the filter media. Samples were prepared in a similar way to that described for hydrophilic samples, but this time the weighed filter media was saturated with a solution containing 10000 ppm dichlorodimethylsilane (DCDMS) in *n*-heptane. As before, the sample was allowed to drain before being re-weighed and allowed to dry. Prepared in this way, the fibrous media retains a volume of (7.36 ± 0.58) mL heptane/g filter, determined gravimetrically, which allows the concentration (in ppm m/m) to be determined for a given media sample mass.

Sample preparation for NMR. The NMR analysis involved the addition of water and/or jet fuel to small weighed strips of filter media (in the range ~0.01-0.02 g) which were placed in clean, dry 8 mm NMR tubes. Known volumes of the particular liquid were then carefully applied onto the strips (sequentially, when both liquids were involved) using a 10 µL microsyringe, ensuring that all the added liquid was placed in direct contact with the samples.

NMR measurements. The low-field NMR measurements were made using a 20 MHz Maran benchtop instrument from Oxford Instruments which was controlled by a Kea-2 spectrometer from Magritek and which operated at a sample temperature of 29.5 °C. The T_2 relaxation times were measured using a standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence^{42,43} using the parameters given in Table 1. Slight changes were made to the pulse amplitudes (see range used in Table 1) to optimize the signal/noise ratio for each measurement.

Table 1. Parameters used for the CPMG pulse sequence.

Parameter	Value
No. of echoes	256
Echo time, ms	20
Number of scans	64
90° Pulse duration, μ s (amplitude, dB)	5.5 (-6.6 to -7.2)
180° Pulse duration, μ s (amplitude, dB)	5.5 (-2.2 to -2.8)
Dwell time, μ s	1
Number of echo points	16

An inverse Laplace transform (ILT) was then applied to the relatively small echo decay signals from the measurements (examples of which are given in Supporting Information, Fig. S1) using with a Matlab code. The ILT allowed NMR T_2 relaxation time distributions to be determined, from which geometric mean relaxation times, T_{2gm} , were calculated according to

$$T_{2gm} = \exp\left(\frac{\sum_1^n A_i \ln T_{2i}}{\sum_1^n A_i}\right) \quad (1)$$

where A_i represents the amplitude at a given T_2 value, T_{2i} .⁴⁴ T_{2gm} values provide a weighted measure of proton environments which we had previously shown to be a useful measure of wettability changes with time.⁴⁴

Integration of the ILT-generated T_2 relaxation distributions enabled the area of the total distribution as well as the different contributing peak areas to be determined, and it is these areas that are subsequently referred to in this paper. The area of each contributing peak (A_1 , $A_2, \dots$) was obtained by integrating the log-normal plots of amplitude (A_{T_2}) versus $\ln(\text{relaxation time})$ between relevant T_2 limits using EasyPlot software (Spiral Software, Bethesda, MD, USA), i.e., eq 3.

$$A_i = \int_{T_2(1)}^{T_2(2)} A_{T_2} \cdot d\ln T_2 \quad (3)$$

Where necessary, deconvolution of the relaxation time distributions was also performed, again using EasyPlot, to obtain T_2 and amplitude values for overlapping peaks, by fitting the data to multiple log-normal distributions, i.e.,

$$f(T_2) = \sum_{j=1}^{j=m} \left[\frac{A(\max)_j}{T_2 \sigma \sqrt{2\pi}} \exp \left(-\frac{(\ln T_2 - \ln T_2(\max)_j)^2}{2\sigma^2} \right) \right] \quad (2)$$

where m is the number of peaks in the T_2 relaxation distribution, and $A(\max)_j$ and $T_2(\max)_j$ are the respective amplitude and relaxation times corresponding to peak j .

RESULTS AND DISCUSSION

After an initial evaluation of the baseline T_2 relaxation distributions for jet fuel and water as bulk liquids and singly- and co-imbibed into the media, further sets of experiments were conducted to evaluate: (i) water addition to dry untreated filter media; (ii) jet fuel addition to dry untreated filter media; (iii) jet fuel addition to water-wetted filter media; (iv) water addition to jet fuel-wetted filter media; (v) water addition to hydrophilic filter media; and (vi) water addition to hydrophobic media. The addition of jet fuel to the hydrophilic and hydrophobic media has not been considered here, partly because these situations are unlikely to arise in practice, and partly because the low surface energy of hydrocarbons will reduce differentiation between treated and untreated surfaces.

Water and jet fuel addition to untreated filter media. As can be seen in Fig. 2(a), the 20 MHz relaxation distributions of bulk water and jet fuel are characterized by one and two peaks, respectively. For bulk water, a T_2 relaxation time of 1.77 s is typical, reported values being in the range ~1.5-3 s (e.g., refs. 45-48). For the bimodal jet fuel relaxation distribution, we tentatively assign the peaks at 0.212 s and 0.932 s to aromatic (J1) and aliphatic (J2) fuel components, respectively, based on their relative magnitudes and recognizing that aromatic protons exhibit shorter relaxation times than aliphatic protons.⁴⁶ Generally, aromatic hydrocarbons constitute the smaller fraction of jet fuels, since they are considered undesirable as far as thermal oxidation stability,⁴⁹ particulate emissions⁵⁰ and energy density are concerned. Consequently, a maximum total aromatics content of 26.5 vol% is currently specified for aviation turbine fuels.⁵¹ The composition of the present jet fuel sample is confirmed by the high resolution 500 MHz NMR spectrum shown in Fig. 2(b), which indicates that the constituent aromatic protons (either directly bonded to the aromatic rings

(δ 6.8-7.4 ppm) or ring-substituted alkyl groups (δ 2.0-2.7 ppm)),⁵² correspond (via the integrals) to 11.3% of the total proton content of the fuel. For comparison, a value of 18.5% is obtained by integrating the time-domain relaxation distribution for the bulk sample in Fig. 2(a).

Fig. 2(c) shows T_2 relaxation distributions for jet fuel and water (30 μ L aliquots), added individually and in combination to the filter media. The relaxation distributions for the individual liquids are now both seen to be bimodal. For jet fuel, changes are seen in the positions of the original J1 and J2 peaks, as well as in their relative amplitudes.

For water, the peak W1 is characterized by the shortest T_2 and is found at ~ 0.1 s, which is in the region customarily assigned to surface-bound (immobile) water.⁴⁶ The second new peak (labelled W2) in the T_2 range 0.1-1 s, is too short for bulk (free) water, seen in Fig. 2(a) at 1.77 s (and referred to herein as peak W3), and is therefore considered to be due to water of lower mobility, for example held within the fibrous structure.

Also shown in Fig. 2(c) is the T_2 relaxation distribution for equal volumes of water and jet fuel (30 μ L of each) on the fibrous media, from which it is seen that the co-addition of the two liquids produces a relaxation distribution containing only two discernible peaks in almost identical positions to the water-only distribution. However, the peak integrals agree remarkably well: adding 30 μ L of water or jet fuel separately to the fibrous media, the respective total integrals (in arbitrary units) are 1.19×10^{-3} and 1.71×10^{-3} , respectively. Surprisingly, co-addition of the same volumes of the two liquids yields the additive result, 2.90×10^{-3} , suggesting that a combination of the relaxation peaks occurs for the supported liquids which, in this case, is coincident with the water relaxation.

Figure 2. (a) T_2 relaxation distributions (at 20 MHz) for bulk samples of water (peak labelled W3) and jet fuel (peaks labelled J1 and J2). (b) 500 MHz ^1H NMR spectrum of the jet fuel sample. (c) T_2 relaxation distributions for 30 μL water (continuous line), 30 μL jet fuel (dashed line) and co-applied water (30 μL) immediately followed by jet fuel (30 μL) supported on the media. Additional water peaks are labelled W1 and W2.

Jet fuel addition to untreated fibrous media. Fig. 3 shows the effect of adding increasing volumes of jet fuel (JF) to the media. The appearance of the two JF peaks in Fig. 3(a) is seen to change as more JF is added to the media and approach the bulk J1 and J2 positions shown in Fig. 2(a). Thus, in Fig. 3(a) it can be seen that, relative to the bulk JF, the intensities of the J1 and J2 peaks are apparently inverted, with the shorter T_2 peak, which we assigned above to the less abundant aromatic components, being larger. It is to be noted, that for the smallest JF volumes added to the media, the J1 peak in the distributions is close to the experimental echo time of 20 ms, which would influence the signal in this region, possibly making J1 quantification less reliable and explaining the apparent peak intensity inversion. With further JF additions, however, there are improvements in signal/noise ratio, as well as an increase in J1. Thus, following the addition of $\sim 60\text{--}80\ \mu\text{L}$, the relative intensities of J1 and J2 are seen to approach those found for the bulk liquid (Fig. 2(a)).

In Fig. 4, increasing JF addition is seen to result in a steady transition between peak positions for imbibed and bulk states. Linear extrapolation of the lines in Fig. 4 indicates that the

limiting ‘imbibed’ J1 and J2 T_2 relaxation times are ~ 0.03 and ~ 0.10 s, respectively, and that the bulk JF distribution is attained upon the addition of 300 μL JF.

Figure 3. (a) T_2 relaxation distributions (at 20 MHz) for incremental addition of JF to the fibrous media; (b) distribution peak areas, $A_t = \int A_{T_2} \cdot d\ln T_2$, as a function of the volume of JF added (error bars are obtained from EasyPlot non-linear regression of the relaxation distribution peaks); and (c) geometric mean T_2 relaxation times, T_{2gm} , as a function of the volume of JF added. All lines are drawn to guide the eye.

Figure 4. The positions of the J1 (circles) and J2 (squares) peaks shown as a function of the volume of jet fuel added to the fibrous media.

However, the concentration dependence of each component is different. The suppression of the aliphatic peak is apparently strongest at low concentrations on the media, such that it is overshadowed by the aromatic signal when surface effects are important. When ~60 μL JF had been added to the media, the aliphatic signal apparently becomes more dominant in the relaxation distribution, as the aromatic peak approaches a limiting contribution to the total area. Thereafter, further additions show up mainly as contributions to the aliphatic peak.

Notwithstanding these uncertainties in the individual contributions from the J1 and J2 peaks in Fig. 3(a) and plotted as integrated area contributions in Fig. 3(b), it is also evident in Fig. 3(b) that the *total* integrated area of each relaxation distribution correlates linearly with the volume of JF added to the media.

The T_{2gm} values, as shown in Fig. 3(c), have been found previously to be a good indicator of the overall proton environment.⁴⁴ Here, it is apparent from Fig. 3(c) that, together with the total area, this parameter also correlates linearly with the volume of jet fuel added to the media.

Water addition to untreated media. On adding increasing volumes of water to the fibrous media, the two initial water peaks mentioned above change their positions and relative intensities, each gradually moving to longer relaxation times. This is shown in Fig. 5 for two different experiments in which different incremental water volumes are added to the media.

Figure 5. (a) T_2 relaxation distributions for incremental addition of water to the fibrous media (Run 1), with the three peak positions W1, W2 and W3 indicated; (b) T_2 relaxation distributions for larger incremental volume additions of water to the fibrous media (Run 2); (c) total relaxation distribution peak area as a function of the water volume added; and (d) geometric mean T_2 relaxation times, T_{2gm} , as a function of the water volume added. Lines are added to (c) and (d) to guide the eye.

In Figs. 5(a) and 5(b), peaks W1 and W2 apparently coalesce at ~ 100 - $120 \mu\text{L}$ water addition, the differences in the peaks in this concentration region reflecting inevitable variations in liquid distribution on the media. This region also closely corresponds to the appearance of the W3 peak, indicating saturation of the media. In these relaxation distributions, the position and intensity of W1 is found to be more variable than the other peaks, which, as above, most likely reflects echo time used, as suggested above for JF.

In Fig. 5(c), it can be seen that the slope of the drawn line for small water additions, comprising peaks W1 + W2, is approximately double that of the subsequent additions, leading to peaks W2 + W3. This finding is unexpected and arguably without physical foundation. However, by analogy to peak J1 in Fig. 3(a), we conjecture that the deviation is linked to the proximity of peak W1 to the echo time used producing an artefactual enhancement to the W1 signal. As with jet fuel addition (Fig. 3(c)), the T_{2gm} is also found to change linearly with the volume of water (Fig. 5(d)), with no features being evident in this parameter that can be related to the different water environments. The non-zero T_{2gm} values in the absence of either liquid may also be a consequence of the acquisition parameters used in these experiments.

A closer examination of the peak positions and relative areas for water on the media is shown in Fig. 6. Thus, Fig. 6(a) summarizes the changes seen in the relaxation distributions shown in Figs. 5(a) and (b). Here, the earlier comment regarding the sensitivity of peak W1 is seen in the scatter of the associated points, in contrast with W2 and W3. It is also clear that the loss of W1 coincides with the appearance of W3, presumably as the media becomes saturated with water, whereupon peaks W2 and W3 begin to dominate. Following higher levels of water addition, exchange between surface sites (W1) and inter-fiber sites (W2) may also occur, thereby causing the two peaks to become indistinguishable under the experimental conditions.

Fig. 6(b) complements the foregoing in many respects, and also provides additional quantification. It is clear, for example, that surface-associated water, producing W1, is only a very minor contributor to the total peak area, and is evident up to $\sim 100 \mu\text{L}$ addition. It is also confirmed that the W2 peak, arising, we suggest, from inter-fiber water, reaches a limiting level after approximately the same level of addition. This serves to indicate that water interacts with these two positions from its initial application to the media, and that exchange between the two positions is slow on the NMR timescale, consistent with the hydrophilic nature of the fibers. Only when the media is saturated, with respect to the sites responsible for the W2 peak, does the excess water peak W3 appear.

To summarize, therefore, as a very approximate guide, we consider that in the absence of a second liquid such as JF, we consider that fiber-bound water (region W1) relaxes within the range $0.01 \leq T_2 \leq 0.1$ s, interstitial water (region W2) relaxes within the range $0.1 \leq T_2 \leq 1$ s, and bulk water (unconstrained, region W3) relaxes for $T_2 > 1$ s. The respective relaxation

times reflect the increasing entropy of water molecules within the different regions, as seen in the peak positions in Fig. 6(a).

Figure 6. (a) T_2 positions for peaks W1, W2 and W3 as a function of the water volume added to the fibrous media. The dashed line is the bulk water relaxation T_2 . (b) Corresponding plots of the respective peak areas, with the dashed line representing the total peak area from Fig. 5(c). Solid lines on both plots are added to guide the eye. Error bars are obtained from non-linear curve-fits of the deconvoluted data.

Water addition to wettability-modified media. Fig. 7 contains a comparison of the effects of surface treatment on the water T_2 relaxation distributions. Increasing hydrophilicity introduced by treatment with 1000 ppm Petronate L solution is seen to result in the coalescence of peaks W1 and W2, possibly indicating an increased water exchange between these two environments, in contrast to the untreated media discussed above. For the hydrophobized media, however, distinct contributions from all three environments produce a trimodal (W1 + W2 + W3) relaxation distribution.

Peak W1 for the hydrophobic surface, appears at a shorter relaxation time (0.040 s) than for the untreated surface (0.059 s), suggesting stronger water-surface interactions in the former case. However, the most significant effect is the greatly reduced W2 peak, and together with the appearance of a W3 peak suggests that water ingress is particularly restricted into the inter-fiber region (W2 peak) of the hydrophobized media. The treated media will be considered in more detail below, especially in relation to the mechanism of filtration-coalescence.

Figure 7. T_2 relaxation distributions for 40 μL water in contact with untreated fibrous media and media treated to increase the hydrophilic and hydrophobic character.

Hydrophobic media. With reference to Fig. 8, it appears that a significant proportion of the initial water (10 μL) becomes strongly bound to fiber surfaces, which are presumably areas of the media where the hydrophobic treatment may be incomplete. Unlike the usual

symmetrical log-normal appearance of ILT-generated relaxation peaks, the asymmetry observed in the W2 peaks in Fig. 8 suggests that water in this predominantly hydrophobic environment may be slow to equilibrate, an effect that is not seen in the untreated media.

Multiple T_2 relaxation distributions (Fig. S2, Supporting Information) were obtained following 40 μL water addition to the hydrophobic media in order to provide a measure of the repeatability of the method. Average values (in arbitrary units) for the areas under the three peak regions (with their standard deviations) for four replicates were $(9.38 \pm 1.24) \times 10^{-4}$ (W1), $(5.35 \pm 0.58) \times 10^{-4}$ (W2), and $(4.31 \pm 0.46) \times 10^{-4}$ (W3). On the basis of the standard deviations, we estimate the uncertainty in individual measurements to be approximately $\pm 10\%$.

Surprisingly, under these conditions approximately twice as much water is apparently associated with fiber surfaces than is retained within the fibrous structure itself. However, as discussed in connection with JF and water addition to untreated media, the intensity of the faster relaxing peaks, closer to the echo time used, may be subject to more uncertainty. In this case, this applies particularly to the addition of 10 μL water.

Figure 8. T_2 relaxation distributions for the addition of different volumes of water to a sample of hydrophobic media.

Hydrophilic media. The behavior of media treated with different concentrations of Petronate L is entirely different from the preceding hydrophobic situation. Indeed, the treated media

remain highly absorbent towards water and, as shown in Fig. 9, produce bimodal ($W_1 + W_2$) relaxation distributions for all Petronate L concentrations studied.

Figure 9. Bimodal T_2 relaxation distributions for the addition of water (20 μL (light gray) and 40 μL (dark gray)) to media treated with different amounts of Petronate L.

By comparing data given in Figs. 5, 7, 8 and 9, for 20 μL or 40 μL water additions to untreated, hydrophilic and hydrophobic media, the total integrated area data shown in Fig. 10 have been compiled. This comparison shows that the integrated areas are influenced by the media wettability, and decrease in the order hydrophilic > untreated > hydrophobic. For the media treated with Petronate L, it is also seen that the measured area is highest for 100 and 1000 ppm Petronate L coatings. These latter concentrations also correspond to a shift to shorter relaxation times for both 20 μL and 40 μL additions (Fig. 9), representing greater water affinity for the media, but also leading to greater uncertainty in the respective integrated area values.

Increased affinity for water in the presence of Petronate L has been seen previously, when water condensed and spread over similarly-treated coalescer fibers upon cooling in a saturated atmosphere inside an environmental scanning electron microscope.⁵³ By comparison, untreated media showed discrete water droplet formation which exhibited a wide range of contact angles on the fibers, typical of droplet-fiber contacts.⁵⁴

Figure 10. Total integrated areas for different wettability media in the presence of 20 µL and 40 µL water (hydrophilic – blue; hydrophobic – red; untreated - gray).

Liquid addition to pre-wetted media. *Water on jet fuel-wetted media.* In the practical situation of jet fuel filter-coalescence, the media will be principally wetted by the excess hydrocarbon phase. Dispersed water droplets must therefore interact with fiber surfaces through a jet fuel wetting layer. In Fig. 11 are shown T_2 relaxation distributions for the addition of water to media pre-wetted with jet fuel. Here, it can be seen that 5 and 20 µL water cause little effect on the magnitude and position of the jet fuel J1 and J2 peaks, the

only notable change being the appearance of the W3 excess water peak at ~ 1.6 s for the larger water volume. This indicates that a small volume of water remains associated with the inherently hydrophilic fibers, only slightly affecting the relaxation distribution which largely retains the JF characteristics, but suggests a slight increase in overall intensity. On the other hand, the further addition of 15 μL water results in the formation of a bulk water peak at ~ 1.6 s, indicating that it remains unassociated with the media which would otherwise be expected to produce the red distribution in Fig. 11.

Figure 11. T_2 relaxation distributions for the addition of water to media pre-soaked with jet fuel (180 μL): no water - solid black curve; 5 μL water – dashed blue curve; 20 μL water – solid blue curve. The relaxation distribution is also shown for 20 μL water on untreated media (red solid curve).

Jet fuel on water-wetted media. In contrast to the foregoing, in Fig. 2(c) it has already been seen that the effect of introducing jet fuel (30 μL) to the equivalent volume of water already present on the media is to increase the intensity of the existing water peaks W1 and W2. Thus, in Fig. 12, where the media had been pre-wetted with water to bring the media close to saturation, we also see no evidence for peaks J1 and J2 appearing on addition of jet fuel, the series of relaxation distributions mainly serving to illustrate the degree of variability of

individual T_2 measurements, perhaps arising from an uneven distribution of liquid phases on the media. However, the overall behavior is the opposite of that found when water was added to the media, and suggests that jet fuel is entering adsorbed and absorbed phase regions.

Figure 12. T_2 relaxation distributions for the addition of jet fuel to media pre-soaked with water (60 μL).

The results of these latter co-addition experiments seem to suggest that the initially-applied liquid dictates the effects of subsequently added liquids.

Implications for water coalescence. As we have already discussed to some extent, wettability is an important factor for the efficient removal of finely dispersed water droplets from hydrocarbons. In the present study, low-field NMR has been able to recognize surface (adsorbed) and inter-fiber (absorbed) sites for water. Excess liquids behave approximately as bulk materials.

477 Changing the wettability has been shown to cause a redistribution of water between the
478 different environments. In addition, the respective relaxation time distributions suggest that
479 the strength of the interactions may also change. These results provide some confirmation of
480 certain mechanistic aspects reported over the years. For example, the presence of petroleum
481 sulfonate surfactants has been shown by Hazlett to influence the release process from the
482 coalescer, such that so-called “graping” occurs, in which the water is released into the fuel
483 stream as very fine droplets.⁵⁵ This occurs through an excessive water spreading occurs
484 within the fibrous structure, rather than the existence of discrete (but enlarged) droplets.

485 On the other hand, the hydrophobic case described here showed evidence for a small residual
486 interaction with the fiber surfaces, but with much-reduced incorporation within the inter-
487 fiber absorption region. Excess water is identified as a bulk water peak. It thus appears that
488 the hydrophobizing treatment was not 100% effective, but in this regard, it fortuitously
489 provided evidence for the coalescence mechanism of media of this type. In particular, it
490 demonstrated that the hydrophobized media is able to retain water without becoming
491 saturated, which could offer advantages as a model coalescer. Future work could therefore
492 involve designing and evaluating the partial silanization of fibrous media as a practical
493 coalescer system.

495 CONCLUSIONS

496 In this work, the use of low-field NMR relaxometry has been shown to provide relevant
497 information relating to the behavior of water and jet fuel in contact with fibrous filtration
498 media. When the liquids are applied to such media, three relaxation environments are
499 discernible, each of which is characterised by a different T_2 relaxation time. Peaks exhibiting
500 the shortest relaxation times are characteristic of liquid molecules associated with fiber
501 surfaces. Slightly longer relaxation times are a result of liquid present within the fiber
502 network. The slowest relaxation times are due to bulk liquid that is external to the filter
503 medium.

504 Depending on factors such as media wettability, when liquids enter a particular region, the
505 corresponding peak will increase in amplitude (up to a saturation point). Additionally, when
506 the phase entered is the adsorbed phase, the corresponding peak has been observed to shift
507 to a slower relaxation time. When jet fuel is applied to media which has been pre-treated

with water, the corresponding peak is seen to decrease in amplitude; when the region is the fiber surface, the corresponding peak also shifts to a shorter relaxation time.

The use of fibrous filters as water coalescence media to separate water from oil gives additional significance to the observations in this study, for example in condition monitoring. Using this knowledge, it would be possible to observe changes in the relative amounts of water present in the filter media over time, since the relaxation distribution is sensitive to the amount of water present in different environments. It has thus been shown that there is evidence for saturation of the media, which in practice could represent a “disarmed” condition of a filter-coalescer. Undoubtedly, more work is necessary to explore fully the application being considered here in order to understand its relevance to wettability determination in filter/coalescer systems. This work should extend to the influence of the properties of the media itself, including the role of surface relaxation.

Additionally, the results of this study have suggested that filtration media could be modified by partial hydrophobization. In the past, other workers have used mixtures of mixed wettability fibers,⁵⁶ but controlled (partial) silanization may be a convenient route for certain applications.

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