

Dual Action Additives for Jet A-1: Fuel Dehydrating Icing Inhibitors

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Abstract

A novel approach for protecting jet fuel against the effects of water contamination based upon Fuel Dehydrating Icing Inhibitors (FDII) is presented. This dual-action strategy is predicated on the addition of a fuel-soluble water scavenger that undergoes a kinetically-fast hydrolysis reaction with free water to produce a hydrophilic ice inhibitor, thereby further militating against the effects of water crystallisation. Criteria for an optimum FDII were identified then used to screen a range of potential water-scavenging agents, which led to a closer examination of systems based upon *exo/endo*-cyclic ketals, and both *endo*- and *exo*-cyclic ortho esters. The ice inhibition properties of the subsequent products of the hydrolysis reaction in Jet A-1 were screened by differential scanning calorimetry. The hydrolysis products of 2-methoxy-2-methyl-1,3-dioxolane demonstrates similar ice inhibition performance to DiEGME over a range of blend levels. The calorific values for the products of hydrolysis were also investigated and it is clear that there would be a significant fuel saving on use of

the additive over current fuel system icing inhibitors. Finally, three promising candidates, 2-methoxy-2-methyl-1,3-dioxolane, 2-methoxy-2-methyl-1,3-dioxane and 2-methoxy-2,4,5-trimethyl-1,3-dioxolane were shown to effectively dehydrate Jet A-1 at room temperature over a two hour period.

1. Introduction

Jet fuel comprises between 99-99.5% hydrocarbons, grouped into three broad classes: paraffins, naphthenes and aromatics [1, 2]. Aromatics are limited to monocyclic and bicyclic compounds by the distillation process, and are regulated to a maximum of 25% v/v and an industry accepted minimum of 8% v/v [2]. The remainder of the non-hydrocarbon fraction is composed of hetero-organic compounds containing sulphur, nitrogen and oxygen. One of the most common contaminants of jet fuel are the naphthenic acids, a mixture of cyclopentyl and cyclohexyl carboxylic acids [3,4]. Dissolved water is also a normal component of jet fuel, though the concentration depends on the chemical composition of the fuel, the temperature, and the air humidity. Free water can starve engines, support microbial growth, contribute towards corrosion and furthermore freeze, risking blockages in aircraft filters [5]. The SAE Aerospace Recommended Practice (APR) 1401B covers a brief discussion of the icing problem in aircraft fuel systems and recommends standardised procedures for aircraft fuel systems or components icing tests [6]. The APR recommends using fuel with 90 ppm v/v of water for “Continuous System Operation” icing tests and fuel with 288 ppm v/v of water for “Emergency System Operation” icing tests. The aviation industry uses both mechanical and quality control approaches to protect jet fuel from water contamination. However, even if jet fuel enters the fuel tank without free water, this does not prevent its formation during flight [1,2]. Dissolved water present in fuel will precipitate out of solution in the form of micro droplets as the fuel temperature drops when the aircraft climbs to altitude [7,8]. Water solubility in the fuel decreases by approximately 2 ppm v/v for every 1°C drop in temperature. Jet A-1 containing higher concentrations of aromatics is also found to have a higher affinity towards water, and tends to shed the greatest quantity of water as the temperature decreases [9,10]. Another source of free water in the fuel tanks derives from the condensation of atmospheric moisture. As the aircraft is descending from cruise

altitude, air is drawn into the fuel tanks through the vent system; the moisture in the air condenses as it comes in contact with the cold fuel and tank surfaces at the end of a long flight [11].

A variety of additives have therefore been developed to counter the detrimental effects of free water, including biocides, corrosion inhibitors, and Fuel System Icing Inhibitors (FSII); the latter are hydrophilic substances which lower the freezing point of water by disrupting the hydrogen-bonding networks responsible for molecular ordering, thereby inhibiting crystallisation [12]. Currently there is only one FSII approved for this purpose – diethylene glycol monomethyl ether (DiEGME). At the approved concentrations of DiEGME (0.07-0.15% v/v), Trohalaki *et al.* [13] found that water (0.007% v/v) present in jet fuel only began to crystallise below -33°C. DiEGME has also proved to be an effective deterrent to microbial growth at high concentrations [2]. Unfortunately DiEGME is hygroscopic, which leads to an elevated uptake of atmospheric water during blending. DiEGME also has a high water-fuel partitioning ratio, which means that it preferentially dissolves in the water phase. This leads to denser water layers separating under gravity with up to 40-50% m/m of DiEGME. Unless replenished, the jet fuel is essentially stripped of its protection against icing. In addition, the presence of DiEGME in the water contained within the fuel alters interfacial properties, and can impair the performance of filters. Particularly, the separation efficiency of filters/coalescers can be compromised [11]. DiEGME is also toxic at the concentrations required for effective de-icing. Water drained from sumps of storage tanks and fuel systems inevitably contain higher concentrations of DiEGME, creating concerns about the handling and disposal of these waste materials [13].

Recently, we reported a highly promising class of compounds that could act as dehydrating agents for fuel [14]. This strategy employs an additive which preferentially partitions into the surrogate fuel layer and consumes water through a fast hydrolysis reaction. We reasoned that such a water scavenging agent would offer dual protection by affording as the product of hydrolysis, an ice inhibitor which would preferentially partition into residual water. To develop a solution to such a complex cascade of processes, the following fundamental criteria were identified as being vital for a successful additive: selectivity towards water, combustibility, atom economy, catalysed by jet fuel,

dual-action, fuel/water partitioning, kinetically fast, cheap and easy to synthesise and environmentally benign [14]. Geminal ethers (*i.e.* acetals, ketals, orthoesters, and orthocarbonates) appear to possess the appropriate levels of selectivity and stability for our purposes. The use of acetals and ketals derived from the sugar mannose has been explored previously by Mushrush and co-workers [16]. These compounds were proven to exhibit comparable ice inhibitor characteristics to DiEGME, were stable in jet fuel for up to two years, and importantly were found to be environmentally benign and relatively nontoxic at the necessary concentration [16]. We further demonstrated that acyclic orthoesters are effective dehydrating agents under acidic conditions [14]. In a recent study [17], we reported the dehydrating properties of a range of acyclic and cyclic geminal ethers (*i.e.*, **1-16**; Figure 1) using a model fuel system, along with the absolute rates for the hydrolysis reactions. Here, we report on the experimentally determined de-icing properties of the hydrolysis products (denoted with the prefix *P*) of selected cyclic geminal ethers (*i.e.*, **P1-16** – see supporting information for structures), and finally describe a proof of concept study which illustrates how the inherent acidity of fuel may catalyse the dehydration reaction of these compounds.

2 Materials and Methods

2.1 Materials

The Jet A-1 fuel used throughout this study was obtained from Air BP, batch number BIS/HAL/12/035K, possessing an aromatic content of 17.1% v/v, and acidity of 0.01 mg KOH/g. All other materials were purchased from Sigma Aldrich (Dorset, UK) to the highest level of purity and used without further purification.

2.2 Synthesis

The synthesis of **1-16** (FDII) has been described previously [17]. 2-Hydroxyethyl acetate (**P5**), 3-hydroxypropyl acetate (**P8**), 3-hydroxybutan-2-yl acetate (**P10/11/14**), and 2-hydroxyethyl-3,3-dimethylbutanoate (**P16**) were prepared *via* the acid catalysed monoesterification of the corresponding diol using the appropriate carboxylic acid according to a method adapted from the literature [18].

2-Hydroxyethyl acetate (**P5**) was prepared by dissolving freshly distilled ethylene glycol (9.75 mL, 0.175 mol) in glacial acetic acid (10 mL, 0.175 mol), with a catalytic amount of concentrated H₂SO₄

(0.1 mL, 2 mmol). The reaction mixture was left refluxing for 2 hours at 105 °C, then allowed to cool to room temperature. The crude reaction mixture was washed with saturated aqueous Na₂CO₃ solution (20 mL) and extracted with diethyl ether (3 x 10 mL). The combined ethereal extracts were dried (MgSO₄), filtered, concentrated *in vacuo*, and purified by column chromatography to afford a clear colourless liquid characterised as 2-hydroxyethyl acetate (6.5 g, 36%); δ_{H} (400 MHz, CDCl₃) 2.07 (s, 3H), 2.51 (broad s, 1H), 3.79 (m, 2H), 4.17 (m, 2H). ¹H NMR data are in accord with the literature [19].

P8 - Synthesis as above; 1,3-propanediol (6.368 g, 0.084 mol) with glacial acetic acid (4.80 mL, 0.0840 mol) and concentrated sulphuric acid (0.05 mL, 0.00084 mol) afforded a clear colourless liquid characterised as 3-hydroxypropyl acetate; δ_{H} (400 MHz, CDCl₃) 1.84 (q, 2H), 2.04 (s, 3H), 2.42 (broad s, 1H), 3.66 (t, 2H), 4.19 (t, 2H). ¹H NMR data are in accord with the literature [20].

P10/11/14 - Synthesis as above; 2,3-butanediol (9.87 mL, 0.11 mol) with glacial acetic acid (6.30 mL, 0.11 mol) and concentrated sulphuric acid (0.06 mL, 0.0011 mol) afforded a mixture of 2,3-butanediol monoacetate diastereoisomers; δ_{H} (400 MHz, CDCl₃) 1.15 (d, 3H), 1.18 (d, 3H), 1.19 (d, 3H), 1.21 (d, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 3.73 (m, 1H), 3.88 (m, 1H), 4.74 (m, 1H), 4.85 (m, 1H). ¹H NMR data are in accord with the literature [21].

P16 - Synthesis as above; ethylene glycol (8.76 mL, 0.157 mol) with 3,3-dimethylbutanoic acid (20 mL, 0.157 mol) and concentrated sulphuric acid (0.09 mL, 0.0016 mol). In this case the reaction mixture was refluxed at 135°C for 6 h to afford a clear colourless liquid characterised as (2'-hydroxyethyl)-3,3-dimethylbutanoate; δ_{H} (400 MHz, CDCl₃) 1.02 (s, 9H), 2.23 (s, 2H), 2.27 (broad s, 1H), 3.80 (m, 2H), 4.18 (m, 2H).

Methyl 5-hydroxypentanoate (**P15**) was synthesised by reacting δ -valerolactone (15 g, 0.150 mol) and methanol (300 mL), in the presence of H₂SO₄ catalyst (0.8 mL, 0.015 mol) [22]. The reaction mixture was stirred and refluxed at 105 °C for 21 hours. Solid NaHCO₃ (2.52 g, 0.03 mol) was added, and the solution filtered and partially concentrated *in vacuo*. The reaction mixture was washed with water, extracted with diethyl ether (3 x 20 mL), dried (MgSO₄), filtered, and concentrated *in vacuo*. The ester was purified by column chromatography to afford a colourless liquid characterised as **P15** (8 g, 40%);

δ_{H} (400 MHz, CDCl_3) 1.52 (m, 2H), 1.64 (m, 2H), 2.30 (t, 2H), 2.75 (broad s, 1H), 3.57 (t, 2H), 3.61 (s, 3H). ^1H NMR data are in accord with the literature [22].

2.2 Calculated partitioning co-efficient (LogK_{ow})

LogK_{ow} values at 25°C were calculated using two well established computational methods; KOWWINTM from the EPI suite of the US Environmental Protection Agency [23], and LogP (AB/LogP v2.0) from the ACD/I-Lab of the National Chemical Database Service [24]. Both computational methods predict the log octanol-water partition coefficient by using an atom/fragment contribution method which can estimate logK_{ow} within ± 0.8 log units for over 96% of an experimental dataset of >8000 compounds [25]. The values reported are the average of the two results.

2.3 De-icing properties

Differential Scanning Calorimetry (DSC) was used to determine the freeze points of aqueous solutions of the products of FDII hydrolysis at various concentrations, and these were compared to the corresponding DiEGME solutions in order to characterise relative de-icing performance. A TA Q20-2160 differential scanning calorimeter equipped with a liquid cooling accessory was used. Firstly, aqueous solutions of the hydroxyester ranging in concentration from 0-50% v/v were examined, and then equimolar aqueous solutions of the hydrolysis products (i.e. hydroxyester/ethanol) ranging from 0-50% v/v were examined. Standard solutions were prepared at 10% v/v intervals prior to testing to avoid sample degradation. For each analysis, approximately 20 mg of standard solution was weighed into a Tzero open aluminium pan and referenced against an empty aluminium pan. The temperature program used for this analysis consisted of a cooling rate of $10^\circ\text{C}/\text{min}$ to -70°C , followed by heating at $1^\circ\text{C}/\text{min}$. The primary purpose of the cooling portion of the cycle was to solidify the aqueous mixture rather than estimate the freeze point, due to potential undercooling effects [26]. The low ramp rate during warming was used to provide the most accurate estimate of the temperature for the solid-to-liquid phase transition [27,28]. Since the ASTM definition of freeze point is the temperature at which the last solid crystal melts upon heating, the temperature at the maximum value of the measured endotherm was taken as the freeze point [29,30]. The results obtained using DSC were

reproducible to within ± 0.2 °C, based on triplicate runs, despite supercooling being observed during cooling of the samples.

2.4 Energy density

Bomb calorimetry was used to obtain the gravimetric energy density of the FDII hydrolysis products. This is the method of choice for measuring heat of combustion values of fuels and additives as shown by ASTM D 4809 [31]. An IKA C1 bomb calorimeter was used to obtain calorific values of the additive products. Each sample was weighed in a metal crucible (0.5 g) and promptly analysed.

2.5 Fuel surrogate/water equilibrium partition coefficients

The fuel surrogate used to mimic Jet A-1 throughout this study (*i.e.*, aromatic content of 17% v/v) was prepared by mixing 83% v/v dodecane and 17% v/v toluene. The amount of dissolved water in the fuel surrogate was initially determined via Karl Fischer titration using a Mettler DL37 KF Coulometer and was found to be in accord with the amount of water dissolved in Jet A-1 (*i.e.*, 60 ppm v/v in fuel surrogate, and 59 ppm v/v in Jet A-1). Mixtures of fuel surrogate (20 mL) and FDII hydrolysis products at the appropriate concentrations were prepared, vortexed for 15 sec and allowed to achieve equilibrium at the specific temperature for 2 hours prior to being analysed via GC-FID to establish the initial concentration of p in the fuel surrogate (*i.e.*, $[p]_{\text{Fuel}}^i$). The required free water was added to the mixture, the sample vortexed for further 15 secs and allowed to achieve equilibrium at the specific temperature for a minimum of 3 hours. The fuel surrogate phase was then analysed by GC-FID to establish the final equilibrium concentration of product in the fuel surrogate $[p]_{\text{Fuel}}^f$. The partition coefficient of the products of hydrolysis between free water and the fuel surrogate $\log K_{FW}$ are readily calculated using $\log\{[p]_{\text{Fuel}}^f/[p]_{\text{Water}}\}$, given that $[p]_{\text{water}} = [p]_{\text{Fuel}}^i - [\text{prod}]_{\text{Fuel}}^f$.

2.6 Dehydration of jet fuel

To quantify the additive products, and assess the extent of dehydration, GC-FID was used. The full GC-FID experimental procedure is reported elsewhere [14]. The analyses were performed using a Varian CP-3800 GC equipped with a flame ionisation detector, and a CP-Sil 8CB column. The methodology has been developed to minimise the analysis time whilst ensuring that the alcohol formed during hydrolysis and the internal standard (3-methyl pentane) both elute before the jet fuel

component. Water (500 ppm v/v) was dispersed in 2 mL of Jet A-1 by 3 min of sonication and the additive was added immediately after with stirring at 800 rpm at room temperature. Measurements were taken after 2 hours from the addition of the additive. Karl Fischer titration was also performed concurrently, using a Mettler DL37 KF Coulometer.

3 Results and Discussion

3.1 FDII additive selection

In principle cyclic acetals, ketals, ortho esters, and ortho carbonates may be considered suitable as dual action de-icing additives as the products of hydrolysis resemble the FSII DiEGME, possessing *both* hydrogen bond donors, and acceptors within an aliphatic backbone. A review of the structural characteristics of cyclic acetals, ketals, ortho esters, and ortho carbonates, along with anticipated hydrolysis products, suggests that the *exo/endo*-cyclic ketals, and both *endo*- and *exo*-cyclic ortho esters, present themselves as promising candidates for a dual purpose additive, meeting the criteria outlined earlier (Figure 2).

Acetals were excluded for further consideration as they afford an aldehyde upon hydrolysis, which may be converted to the corresponding carboxylic acid under oxidising conditions. Whilst carboxylic acids can be expected to increase the rate of the hydrolysis reactions, they are undesirable from the perspective of corrosion. The *endo*-cyclic ketal affords glycols, which are notoriously toxic to the environment, whereas *exo*-cyclic ketals are expected to afford cyclic ketones which are expected to be poor de-icers because they possess a single site for hydrogen bonding. Hydrolysis of ortho-carbonates leads to cyclic carbonates, which may spontaneously decompose to afford ethylene glycol, water and carbon dioxide.

We previously demonstrated that ortho esters are rapidly hydrolysed by dissociated acid catalysts (i.e., hydroxonium ions derived from naphthenic acid), whereas a much slower process occurs with an associated acid catalyst. The implications of this finding are that lipophilic ortho esters which preferentially partition into the fuel phase will hydrolyse much more slowly in the presence of dissolved water, whereas a rapid hydrolysis reaction is expected to occur at the interface with free

water [14]. Prior work saw the assembly of a library of potential FDII in which the geminal ethers **1-16** (Figure 1) were ranked according to their rate constants in their reaction with water (i.e., the hydroxonium catalytic coefficient = $\log k_{H^+}$) in a solvent system that mimics the water/fuel interface (water:acetonitrile = 1:4 v/v) [17]. The rate constants for structures **1-16** ($\log k_{H^+}$) are presented on the vertical ordinate of Figure 3 and the horizontal ordinate corresponds to $\log K_{ow}$ with zero representing the boundary between the H₂O and fuel surrogate phases. In this way, the balance between the lipophilicity/rate constants for water hydrolysis ($\log k_{H^+}$) of FDII, along with the hydrophobicity of the corresponding hydrolysis products may be viewed. Ideally, effective FDII are fast water scavengers (i.e., $\log k_{H^+} > 0$), are lipophilic (i.e., $\log K_{ow} > 0$), and the corresponding hydrolysis products are hydrophilic (i.e., $\log K_{ow} < 0$) with the capacity to disrupt water crystallisation [33].

The products of hydrolysis of FDII are an ester and an alcohol (Figure 2); the ester products are labelled with respect to their corresponding geminal ether using the prefix P. There will clearly be a tipping point for the ideal dual-action reagent as the lipophilicity of the fuel dehydrating agent, and hydrophilicity of the potential icing inhibitor are inextricably linked. The octanol-water (1:1 v/v) partition coefficient (K_{ow}) at 25 °C was used to calculate the lipophilic or hydrophilic properties of the molecules [34,35]. Since values range across many orders of magnitude, the logarithm was employed, i.e., $\log K_{ow}$ (x-axis, Figure 3). Assuming that octanol represents a reasonable surrogate for the lipophilic jet fuel phase, then a calculated value of $\log K_{ow} > 0$ indicates a propensity for a given molecule to partition preferentially in the fuel phase. Conversely, $\log K_{ow} < 0$ indicates a preference for preferential partitioning in the aqueous phase. Effective and well established fuel system icing inhibitors are known to possess $\log K_{ow}$ approximately equal to, or less than zero (DiEGME $\log K_{ow} = -0.68$ [36]), indicating a preference for aqueous solubility. All the fuel dehydrating agents considered in this study were predicted to partition preferentially into the fuel phase. On the basis of hydrolysis products possessing $\log K_{ow}$ less than zero, **1**, **2**, **5**, and **8** present themselves as promising candidates for further consideration. FDII additives **4**, **10**, **11**, **14** and **15** are also interesting candidates, since their corresponding hydrolysis products have calculated $\log K_{ow}$ close to zero (i.e., $\log K_{ow} \leq 0.20$). Importantly, much like DiEGME, candidates **P5**, **P8**, **P10**, **P11**, **P14**, and

P15 possess one H-bond donor, and two H-bond acceptors, indicating their potential as effective icing inhibitors.

Although sterically demanding substituents can increase the reaction rate of five-membered ring systems [17], the impact upon the lipophilicity of the hydrolysis products undermines the partitioning properties of the de-icer (*i.e.*, **P16**). We decided however, to continue to investigate candidate **16** because of the unusually high kinetic activity as water scavenger in the surrogate model (water:acetonitrile=1:4). FDII **13** was also considered for further investigation since it is a promising water scavenger that is also commercially available. Furthermore, the hydrolysis of the geminal ethers considered in this study will also produce either ethanol or methanol, depending on the starting material. The experimental $\log K_{ow}$ values for these alcohols are -0.31 and -0.74 , respectively, which indicates that they partition preferentially in the water phase.

3.2 Experimental determination of ice formation inhibition

Differential scanning calorimetry (DSC) was used to determine the ice inhibition properties of the hydrolysis products in water, since it is a thermal analysis technique that can provide information on phase transition temperatures [27]. It has been previously used to study the phase change characteristics of Fuel System Icing Inhibitors [37], and jet fuels with and without additives [30]. The freezing point of neat DiEGME is -70 °C [37].

The measured phase change for pure water begins just below 0 °C and is complete at 1.3 °C, affording a minimum freeze point of water (*i.e.*, 1.3 °C) within acceptable tolerance for the experimental methodology used. DiEGME significantly reduced the measured freeze point and broadened the temperature range over which the phase transition occurred. The broadening of the temperature range over which the melting occurred may indicate that the phase transition becomes less homogeneous with higher FSII content. A comparison of the temperature reduction of the phase transition of pure

water with 0-50 % v/v of DiEGME, EtOH, MeOH, and hydrolysis products of additives **1, 2, 4, 5, 8, 10/11/14, 13, 15, and 16** are presented in Figure 4a-c.

At low concentrations, the differential reductions from water are relatively small however they rapidly increase as the concentration approaches 50% v/v (Figure 4a). The relationship between freezing point depression as a function of concentration is non-linear, indicating that the freezing point of the solution does not depend solely on the concentration of the solute, indicating some non-bonded intermolecular interactions between water and the additive (*i.e.*, hydrogen bonding). The measured freezing point values as a function of FSII concentration obtained during these studies were in agreement with those previously reported [37].

As hydrolysis of FDII results in more than one product (*i.e.*, an ester and an alcohol - Figure 2), both products were examined for their freeze point depression activity. Depending on the FDII additive, the resulting alcohol will be either methanol or ethanol. Both alcohols were examined, and promisingly, they demonstrate superior de-icing capabilities than DiEGME within the 0-50% volume concentration, and since they also have a $\log K_{ow}$ value below zero, they constitute excellent de-icing agents. Methanol exhibits greater anti-icing performance than ethanol at very high concentrations though ethanol is less toxic [38,39].

The products of hydrolysis of **1, 2, 4, 5, 8, 10, 11, 13, 14, 15, and 16** were also analysed for their de-icing properties by DSC (Figure 4b-c). Hydrolysis of **1** affords 1,3-propane diol which is an excellent de-icer. Hydrolysis of **2** and **13** affords methyl formate and ethyl acetate respectively. These compounds are not particularly soluble in water, with corresponding water solubilities of 300 g/L and 83 g/L, respectively. They were therefore examined to the limit of their solubility. Even at the maximum solubility in water, methyl formate and ethyl acetate are poor de-icing agents.

The FDII containing a bulky substituent (**16**) also demonstrated poor freeze point depression behaviour because of its low water solubility. The freeze point temperature of **P4, P10/11/14, and**

P15 at low concentration ($\leq 20\%$ v/v) are similar to DiEGME; however they diverge at concentration $> 20\%$ v/v. At 50% v/v they afford a freeze point temperature range of $17\text{-}20\text{ }^\circ\text{C}$ higher than DiEGME. The additive **15**, depending on the pH, will afford a mixture of methyl 5-hydroxypentanoate (**P15**) and δ -valerolactone (**P15***) [40]; here an equimolar mixture of these products was examined. Both **P5** and **P8** appear to be the most promising de-icers with performance identical to, if not better than DiEGME at low concentrations ($\leq 20\%$ v/v). Both additives have slightly higher freezing point temperature at concentrations above 20% v/v, and at 50% v/v, they exhibited a freezing point of $11\text{ }^\circ\text{C}$ and $15\text{ }^\circ\text{C}$ higher than DiEGME.

Since the ester products will be produced concomitantly with the corresponding alcohol (excluding additive **1**), the phase transition temperatures of a mixture of the products and ethanol/methanol were investigated (Figure 5a-b). For the analysis, standard solutions of $10\text{-}50\%$ v/v of the products and alcohol in the correct molar ratio were prepared; this assumes an identical fuel-water partition coefficient for the products and the alcohol. The de-icing performance of **P1** decreases with the introduction of 2-butanone, with a comparatively large fall in performance compared to the neat solution at higher concentration (see Figure 4b). When **P2** or **P5** were present with the requisite amount of methanol, the freezing point of the mixture was comparable to DiEGME, with a positive increase at concentration $< 20\%$ v/v and a negative decrease at concentration $> 30\%$ v/v resulting in a difference of $8\text{ }^\circ\text{C}$ and $7\text{ }^\circ\text{C}$ at 50% v/v, respectively. The presence of methanol also enhanced the freeze point depression for **P4**, **P8**, **P10/11/14**, **P13**, **P15** and **P16**, but the performances above 30% v/v in concentration were between $10\text{-}70\%$ v/v that of DiEGME. Interestingly, **P5** possesses significantly greater de-icing performance than any other products at high concentrations; however in the presence of methanol, both **P2** and **P5** demonstrate performance comparable to DiEGME.

3.3 Energy density of the subsequent FDII additive products

One further persuasive factor in determining the suitability of an additive is the effect on the energy density and therefore range of an aircraft. Gravimetric energy density of the FDII's hydrolysis

products were determined experimentally by bomb calorimetry and compared to DiEGME (Figure 6). The energy densities of methanol and ethanol are 22.66 and 29.67 MJ/kg, respectively [41]. Ethanol has an additional methylene group (-CH₂-) compared to methanol; therefore it releases more energy per unit mass of fuel upon combustion. Furthermore, ethanol is preferable to methanol as it is more soluble in jet fuel and less toxic. The materials **P5**, **P8**, **P10/11/14** and **P13** have a lower energy density than DiEGME, whereas **P15** and **P16** have higher energy densities.

To understand the impact of the calorific value of the FDII hydrolysis products, simple calculations were performed by considering a total of 1 tonne of fuel. The impact of water contamination was then assessed by comparing Jet A-1 contaminated with water at a concentration of 260 ppm v/v and DiEGME (0.15 v/v), to 1 tonne of Jet A-1 with the products of hydrolysis of the additives present. In the case of FDII, the loading of the additive was calculated on the basis of the concentration of additive necessary to remove 260 ppm v/v water. The hydrolysis products of **15** are expected to be equally distributed between **P15** and **P15*** (methyl 5-hydroxypentanoate and δ -valerolactone, respectively). 1 tonne of pure Jet A-1 used in this study has an energy density of 45,870 MJ. 1 tonne of Jet A-1 with DiEGME and 260 ppm v/v of water has a reduced energy density of 45,820 MJ. Figure 6b illustrates the change in energy density for 1 tonne of Jet A1 containing the hydrolysis products of the additives. The addition of the additive to Jet A-1 leads to a gravimetric energy density approximately equivalent or higher than the DiEGME system. Though the energy density change is very modest compared to pure Jet A1; this demonstrates that a water management system based on these novel additives would not lead to a significant reduction in aircraft range or could potentially slightly increase the range of the aircraft opposed to a system using DiEGME.

Other key fuel properties could potentially be altered by the addition of the additive. For example, the flash point could be lowered due to the hydrolysis products ethanol and methanol. However, the loading of the additive should be insufficient to alter the properties of the fuel batch such that it falls out of specification. Thermal stability could also be improved in principle, though this would require extensive testing to assess the effects of the additive on actual fuel systems.

3.4 Fuel surrogate/water equilibrium partition coefficients

The equilibrium partition coefficients for fuel and aqueous phases provides a guide to the realistic concentrations of FDII hydrolysis products in the water phase, and therefore the de-icing potential. The complexity of jet fuel renders difficult the accurate determination of the concentration of FDII hydrolysis products, therefore an appropriate fuel surrogate composed of dodecane (83 % v/v) and toluene (17 % v/v) was used instead (Table 1). It has been established previously that FDII reacts very slowly with dissolved water, whereas reaction is rapid in the presence of free water [14]. For this reason, the water added to the fuel surrogate was in addition to the amount of water present in its dissolved form (i.e., 59 ppm).

Table 1 clearly indicates that the products of FDII hydrolysis preferentially partition into water with the same order of magnitude as the DiEGME [11]. Most notably for the hydrolysis products of FDII's **5** and **8**, partitioning into lower concentrations of water (i.e., 90-500 ppm v/v) is two to three orders of magnitude more favourable than suggested in the calculation (Figure 3), which assumes a 1:1 ratio of water/fuel. Table 1 also clearly indicates that partitioning into the water phase increases as the temperature of the fuel decreases. Similarly, a higher water content leads to an increase in the partitioning of the products into the water phase. This demonstrates that the products will effectively partition into the water phase effectively reducing the freezing point of any remaining free water in the fuel tank.

3.5 Proof of concept study

Finally, a proof of concept experiment was undertaken to establish whether the additives could dehydrate a standard sample of Jet A-1 fuel, and whether the inherent acidity of the fuel was sufficient to catalyse the hydrolysis reaction of FDII. To this end, water (500 ppm v/v) was dispersed in Jet A-1 for 3 min via sonication, and the additive (0.5% v/v) was added immediately after this. Whilst this

represents a relatively high additive loading, the experiment affords an effectively constant concentration of FDII throughout the reaction (i.e., second order with respect to $[H_2O]$ and $[H^+]$), thereby illustrating the impact of the inherent acidity of Jet A-1 [14, 17]. The reaction was stirred for 2 hours and then analysed by *both* Karl Fischer titration (industry standard for determining residual water) and GC-FID (to determine product concentration; see Table 2, Figure 7).

Although **5** appears to be a more effective water scavenger, there is little statistical difference between the three candidates. Both Karl Fischer and Gas Chromatography results are in good accordance. Importantly, these preliminary studies confirmed that the inherent acidity of Jet A-1 is sufficient to catalyse the hydrolysis reactions of FDII. While the results from this preliminary proof-of-concept study are extremely promising, Jet fuels vary substantially in terms of acidity, water content and aromatic content, all of which may influence the rates of reaction and effectiveness of the FDII additives described here.

4. Conclusions

The criteria identified for an effective FDII led to a closer examination of water scavengers based upon *exo/endo*-cyclic ketals, and both *endo*- and *exo*-cyclic ortho esters. Although the rate of the hydrolysis reaction may be optimised through bulky substituents (i.e., **16**), the lipophilicity of the hydrolysis product (i.e., **P16**) reduces the effectiveness of their de-icing performance. The products of the hydrolysis reaction of FDII in Jet A-1 were screened for their ice inhibition capabilities by differential scanning calorimetry. Derivative **P5** possesses significantly greater de-icing properties than any other products at high concentrations. It should be noted that while DiEGME is a better de-icer at high concentrations, FDII would have already removed a significant amount of water and formed the corresponding ice-inhibitor. The calorific value of the products of hydrolysis demonstrated that the use of FDII would not lead to a reduction in energy density by substituting the presence of water and DiEGME in the fuel tank. Furthermore, proof of concept studies confirmed that the inherent acidity of Jet A-1 was sufficient to catalyse the hydrolysis reactions of ortho esters **5**,

8, and 10/11/14, at 0.5% v/v loading with a water concentration of 500 ppm v/v. Correspondingly FDII can be stored without degradation, and will only be activated when it comes into contact with jet fuel and water. While further work is necessary to determine the effectiveness of the additive over a range of loadings, FDII represent a potentially effective solution to the challenging issue of water contamination in fuel tanks.

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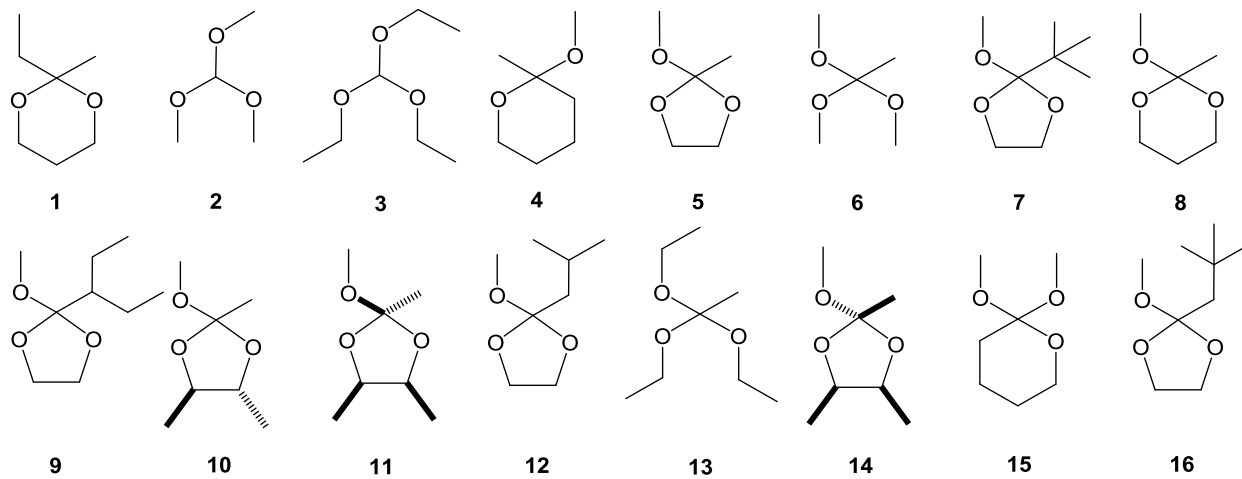


Figure 1.

Potential FDIIs examined in this study.

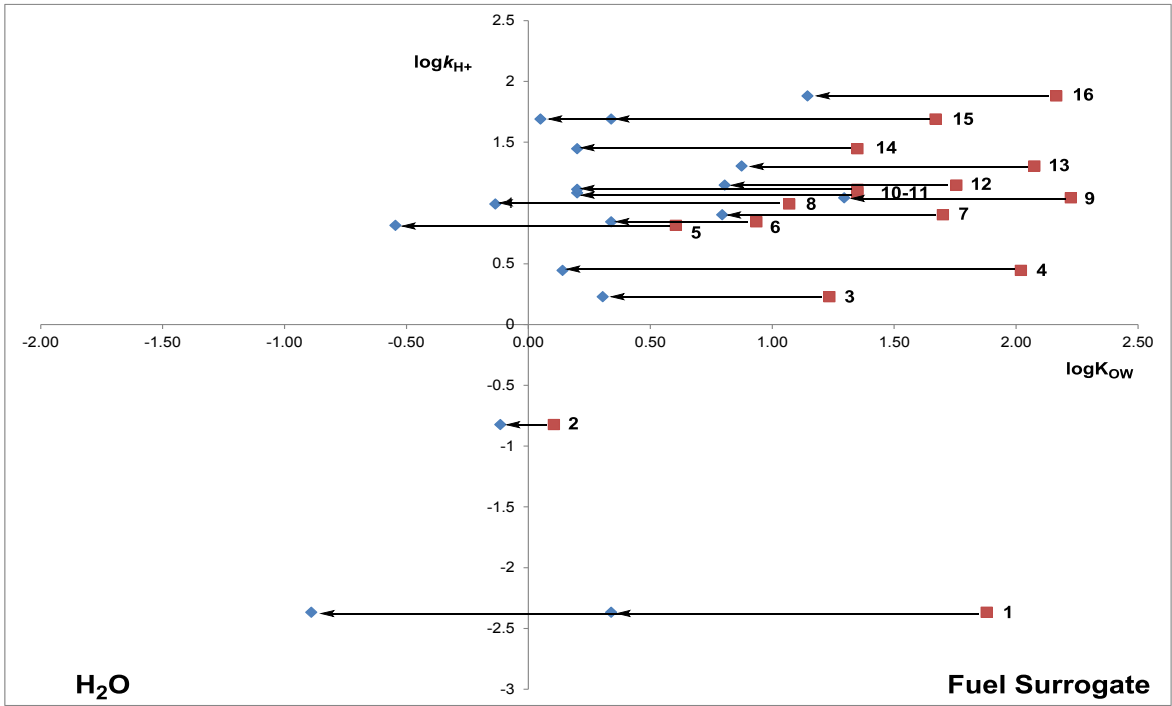


Figure 3. Graphical representation of $\log k_{H^+}$ and $\log K_{ow}$ for candidate FDII ■ and hydrolysis products ◆

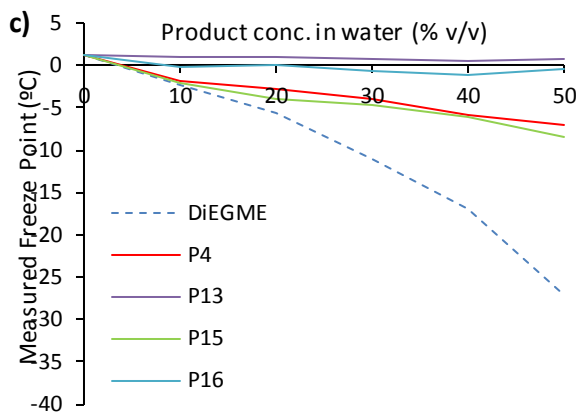
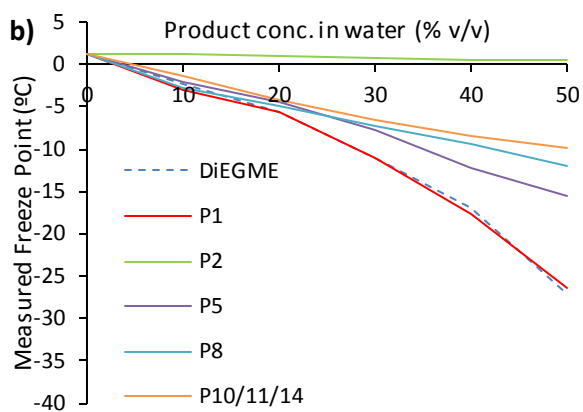
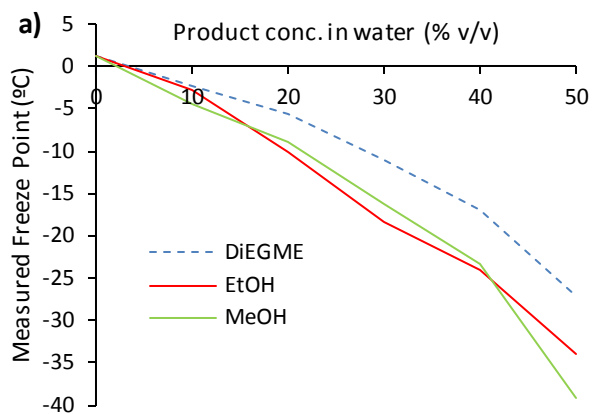


Figure 4. Comparison of the temperatures of the phase transition of pure water with 0-50 % v/v of (a) DiEGME, EtOH or MeOH, (b) DiEGME and hydrolysis products of additives **1,2,5,8,10/11/14**, (c) DiEGME, and hydrolysis products of additives **4, 13, 15, 16**.

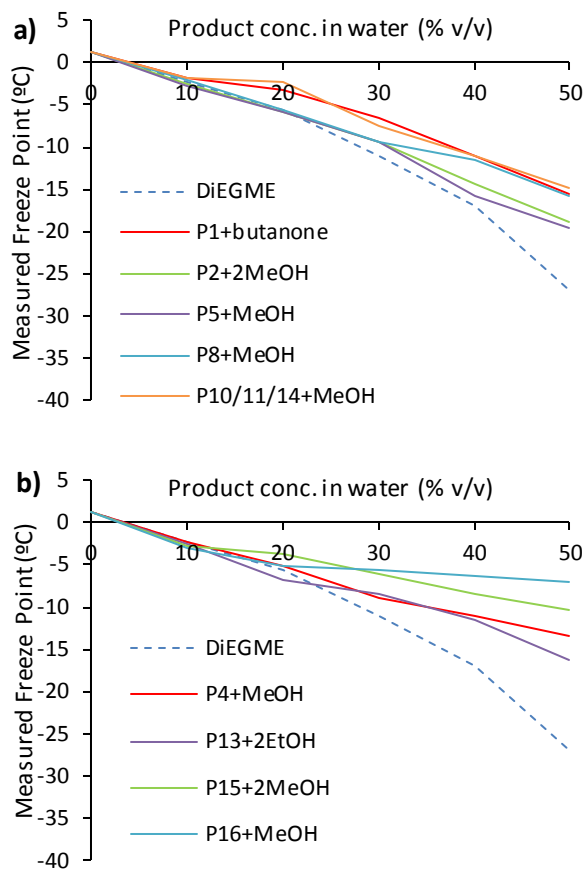


Figure 5. Comparison of the temperatures of the phase transition of pure water with 0-50 % v/v of: **(a)** DiEGME and the hydrolysis products of additives **1,2,5,8,10/11/14** with the requisite alcohol, **(b)** DiEGME and hydrolysis products of additives **4, 13, 15, 16** with requisite alcohol.

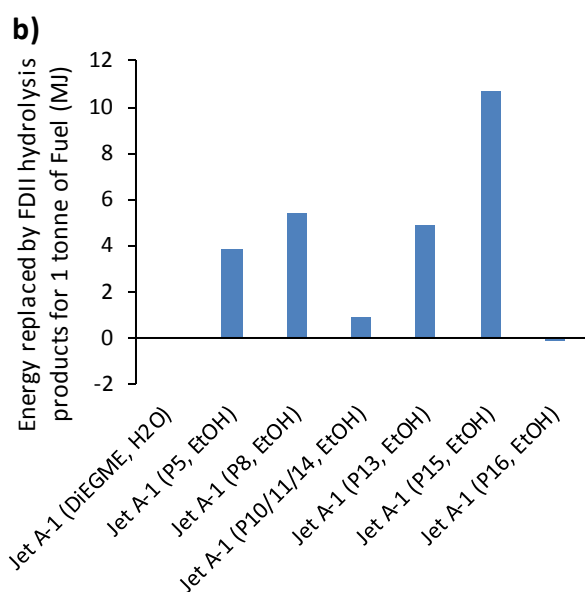
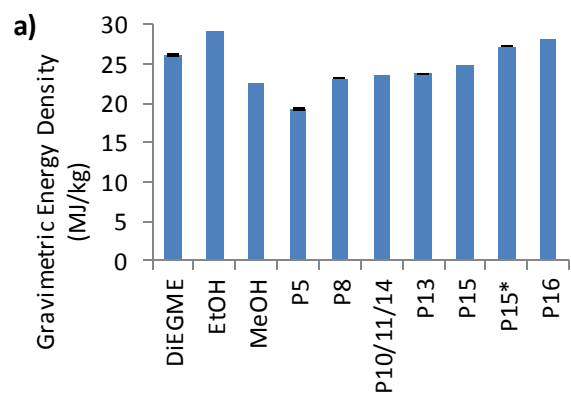


Figure 6. (a) Gravimetric energy densities obtained by bomb calorimetry of DiEGME, ethanol, methanol and hydrolysis products of additives **5, 8, 10/11/14, 13, 15, 16**, (b) The change in energy density of one tonne of Jet A-1 with the hydrolysis products of the additives **5, 8, 10/11/14, 13, 15, 16**, compared with 1 tonne of Jet A-1 with DiEGME (0.15 v/v) and water (260 ppm).

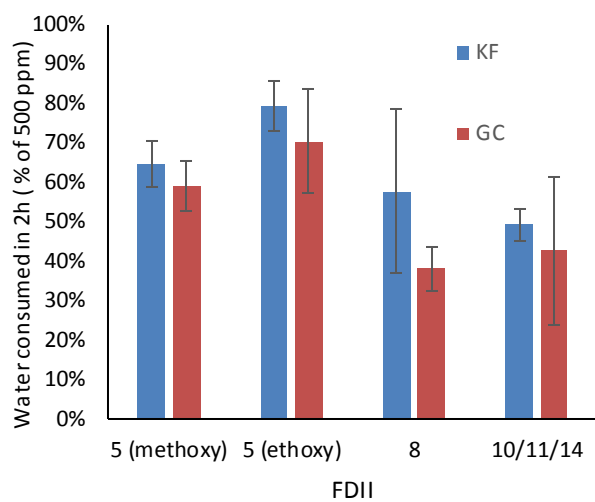


Figure 7. Water consumption after 2 h of candidate FDII (0.5 % v/v loading) in Jet A-1 at room temperature with an initial water concentration of 500 ppm v/v, water consumed calculated through Karl Fisher titration (KF) and a GC-FID method (GC)

Table 1. Partition coefficients [fuel surrogate/H₂O (LogK_{FW})] of FDII hydrolysis products, with varying added H₂O concentration (90, 260 and 500 ppmv/v) and temperature (5 and 25 °C). The water added is in addition to the amount of dissolved water present in the fuel (59 ppm).

FDII hydrolysis product,	H ₂ O (ppm v/v)	LogK _{FW} (5 °C)	LogK _{FW} (25 °C)
MeOH	90	-3.12	-1.22
EtOH		-2.65	-1.84
P5		-3.20	-2.41
P8		-2.37	-2.20
MeOH	260	-3.16	-2.64
EtOH		-2.87	-2.19
P5		-3.25	-2.68
P8		-2.98	-2.59
MeOH	500	-3.20	-2.92
EtOH		-2.89	-2.56
P5		-3.28	-2.98
P8		-3.03	-2.68

Table 2. Loading of additives in jet fuel, corresponding densities (*experimentally determined), and consequent theoretical maximum removal of water.

FDII	Loading (% v/v)	Specific Density	Molar amount (mmol)	Theoretical maximum water removal (ppm v/v)
Water	0.05	1	0.055	-
5	0.5	1.0424 [42]	0.088	792
8	0.5	1.0387 [43]	0.079	708
10/11/14	0.5	0.983*	0.067	606