

The Development of Novel Fuel Dehydrating Icing Inhibitors

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ABSTRACT

Dissolved water is a normal component of jet fuel which is vapourised during combustion; however, free water is a contaminant that can starve engines, freeze to form ice crystals capable of blocking fuel feeds, support microbial growth, and contribute towards corrosion.

Jet fuel may be protected from the potentially hazardous effects of free-water using biocides and icing/corrosion inhibitors. This investigation seeks to identify novel chemical approaches to the dual management of both water contamination and ice formation in jet fuel.

The strategy of using organic molecules as dehydrating agents remains a relatively neglected approach perhaps because of the complexity of the physical organic chemistry involved in developing and refining these systems. However, organic molecules with well characterised dehydrating properties - such as ortho esters, acetals, hemiacetals, ketals, and hemiketals - present themselves as an excellent starting-point for the development and optimisation of novel Fuel Dehydrating Icing Inhibitors (FDII).

This paper describes our systematic approach towards the development of jet fuel additives which are kinetically fast, selective, lipophilic water scavengers that produce, upon hydrolysis, a hydrophilic ice inhibitor. A brief human and environmental toxicological screening of candidates is described. We anticipate that this class of FDII represents a novel approach towards protecting jet fuel against the effects of water contamination.

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INTRODUCTION

Solubility of water in this context refers to the maximum water concentration which can dissolve in any given amount of fuel at a specific temperature and air humidity; this is strongly dependent upon the chemical composition of the fuel itself [1,2].

Aviation turbine fuels are largely straight-run distillates of crude oil and their composition comprises, by volume, between 99-99.5% hydrocarbons, with the remaining fraction of heterorganic components containing the elements sulfur, oxygen and nitrogen. Jet fuel is a mixture of many different hydrocarbons; most of them can be grouped into three broad classes: paraffins (or alkanes), naphthenes (or cycloalkanes) and aromatics (or alkylbenzenes) [1,3,4]. The proportions of these three classes varies depending upon the source of the crude oil from which the fuel is derived and the refining

process. The aromatic content is limited to 25% v/v [5]. The formation of attractive electrostatic interactions between water and π -aromatic systems would account for the enhanced solubility of water in aromatics relative to both paraffins and naphthenes [4].

The aviation industry uses both mechanical and quality control approaches to protect jet fuel from water contamination [1]. However, even if jet fuel enters the fuel tank without free water, this does not prevent its formation.

Indeed, dissolved water present in fuel will precipitate out of solution in the form of micro droplets as the fuel temperature drops through diurnal cycles or during operation as the aircraft climbs to altitude [6,7]. Water solubility in the fuel decreases by approximately 2 ppm v/v per 1°C. For example, a temperature change from 20 → -10°C creates ca. 29 ppm v/v of dissolved water to be liberated as free water, which in 100 tons of fuel amounts to 3.62 L of free water [1].

A second source of free water in fuel tanks derives from the condensation of atmospheric moisture. As fuel is consumed, 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 [8]. Free water can starve engines, support microbial growth, contribute towards corrosion and furthermore freeze, risking plugging filters in the aircraft. The industry has developed equipment and procedures to mitigate these problems, but challenges remain [1,3].

Current Approaches

The aviation industry uses a variety of additives to counter the detrimental effects of free water. Biocides are added to prevent microbial growth, corrosion inhibitors are used to protect uncoated aluminium tanks and pipelines from corrosion and improve the lubricity of fuels, and Fuel System Icing Inhibitors (FSII) are added to inhibit ice formation.

Since ethylene glycol monomethyl ether (EGME) was banned because of its toxicity to humans and the environment, the only FSII currently approved for Jet A, Jet A-1, and military fuels is di-ethylene glycol monomethylether (di-EGME) [1,5,9]. FSII are hydrophilic substances, dissolving in any free water that forms, disrupting hydrogen-bonding networks responsible for molecular ordering - thereby lowering the freezing point of the liquid by preventing crystallisation [3]. The concentration of di-EGME must be in the range 0.07 - 0.15% v/v [1,5,9]. At these concentrations, Trohalaki *et al.* found that water (70 ppm v/v) in jet fuel freezes below -34°C [10]. Di-EGME has also proved to be an effective deterrent to microbial growth [1].

Drawbacks of FSII

The aviation industry has identified several problems related to the interaction of FSII and “wet” fuel, which can actually undermine fuel protection.

- In addition to being hydrophilic, di-EGME is also hygroscopic - this additional characteristic leads to an uptake of atmospheric water during blending operations which affects its solubility in fuel.
- Di-EGME has a very high water-fuel partitioning ratio: it preferentially dissolves in water. This leads to denser water layers separating under gravity with up to 40-50% wt of di-EGME. Unless replenished, the jet-fuel is essentially “stripped” of its protection against icing.
- The presence of di-EGME in the water contained within the fuel alters interfacial properties, and can impair the performance of filters. Particularly, the separation efficiency of filter/coalescers can be compromised [8].

In addition, FSII are toxic at the concentrations required for effective de-icing. Sump water drained from sumps of storage tanks and fuel systems inevitably contain higher concentration of di-EGME, creating concerns about the handling and disposal of these wastes [11]. FSII are only mildly irritating, but they are rapidly absorbed by the skin.

Vapours can cause irritation to the eyes and the respiratory system. Long term effects include damage to the central nervous system, blood, skin, eyes, and kidneys [12]. Di-EGME is biodegradable in wastewater treatment system; however concentrations found in sumps water could be high enough to disrupt the microbiological process. In the environment, the high oxygen demand required for decomposition results in less available oxygen for aquatic organisms [13].

Smart Scavengers

In order to address these and other problems, we seek to develop a solution which meets most, if not all of the criteria delineated below.

Selectivity

Jet fuel is a mixture of thousands of organic compounds; it is therefore critical that the scavenger of choice reacts exclusively with water, a notoriously weak nucleophile. We have identified the alcohol-addition products of aldehydes and ketones (*i.e.*, acetals, hemiacetals, ketals, hemiketals, and orthoester) as possessing the appropriate levels of selectivity and stability for our purposes.

Combustibility

An important consideration as both scavenger and by-products must be readily combustible and leave no solid residues.

Atom economy

Because water is a relatively small molecule (molecular mass $\text{MM} = 18\text{g/mol}$), a relatively large number of reacting moles of scavenger - assuming a 1:1 reaction stoichiometry - are required to dehydrate the jet fuel. In the example mentioned above, 3.62 L of free water requires *ca.* 200 mol of scavenger. It is important therefore to ensure that the MM of a candidate scavenger is as low as possible, or possesses multiple reactive sites (higher reaction stoichiometry).

Switchable

A selective scavenger which is switchable (*i.e.* on/off) can be stored without degradation (off mode), and yet be activated (on mode) when mixed with fuel. This is best achieved by choosing a process that is catalysed by mild acid, a particular consideration when one recognises that Jet A-1 is mildly acidic.

Dual action

The products of reacting one mole of the scavenger with water would ideally produce one equivalent of FSII for optimum fuel protection. Although in principle, it is possible to design an acyclic scavenger which generates up to three equivalents of FSII upon hydrolysis; this would impact upon atom economy. We require then a functional group which can be incorporated into a cyclic system which - post hydrolysis -

affords an acyclic alcohol, thereby conserving atom economy.

Fuel/Water partitioning

A water scavenger must be sufficiently hydrophobic to be soluble in, and therefore protect jet fuel - yet the product of the reaction with water must be sufficiently hydrophilic to preferentially partition into residual water to act as an effective FSII.

Cheap & easy to synthesise

The production of the water scavenger should be a viable business for manufacturers and sustainable for the environment.

Environmentally benign

The use of acetals and ketals derived from sugar mannose for FSII has been explored by Mushrush and co-workers. These compounds prove to be stable (up to 2 years in jet fuel) and effective as icing inhibitors, and importantly were found to be environmentally benign and relatively nontoxic at the necessary concentration [11, 14].

Kinetically fast

Unlike an icing inhibitor, a water scavenger must undergo a *chemical reaction* at the very low operating temperatures (*T*) commonly encountered in an aircraft. Such low temperatures can dramatically reduce the kinetic energy of participating molecules, to the point that a chemical reaction slows down or effectively stops. It is necessary then to ensure that the energy barrier to reaction (*E_a*) - is small. This ensures a fast reaction even at low temperatures, which corresponds to a high rate constant (*k*). The relationship between temperature, energy of activation and reaction rate is expressed in the Arrhenius equation (I) [15].

$$k = Ae^{\frac{-E_a}{RT}} \quad (I)$$

By examining the rate constants for a range of candidate scavengers (*i.e.*, acetals, ketals, and ortho esters) with water, one may conclude clear correlations between molecular structure, and the barrier to reaction, *E_a* (Fig. 1). Hydration rates for acetals increase a thousand fold with the replacement of a single hydrogen atom at the functional carbon atom with an alkyl group (1→2 Fig. 1). A ten thousand fold rate increase accompanies progression to the related ketal (2→3 Fig. 1), and an extra 10 fold to the related ortho ester (3→4 Fig. 1). This important increase in relative rate is readily explained by a steric decompression factor as the tetrahedral intermediate collapses to the trigonal counterpart during the hydrolysis reaction, or by the fact that the rate increase corresponds with the stability of the corresponding dialkoxy carbenium intermediate (see later - Scheme 2) [16].

The fastest rate within the series of alcohol-addition products of carbonyl compounds is achieved with the ortho ester 4 (Fig. 1), which is readily hydrolysed because there are

three oxygen atoms with lone-pairs which may increase the basicity of the leaving group - ROH (see later - Scheme 2).

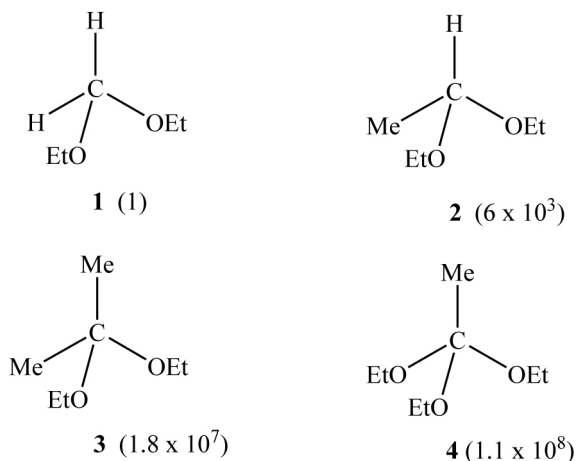


Figure 1. A comparison of the relative rate constants (in parentheses) for the hydration of acetals 1-2, ketal 3, and ortho ester 4.

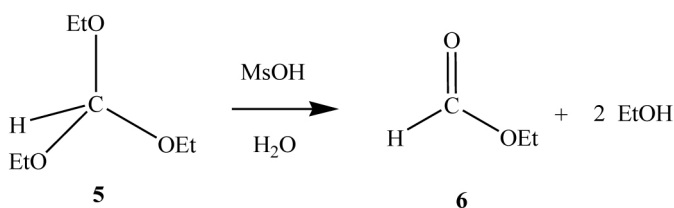
In conclusion, ortho esters appear to be the most promising candidate for a dual purpose additive meeting the criteria outlined above. The next step was to examine the feasibility of using the acid catalysed hydrolysis of a low molecular weight ortho ester to dehydrate jet fuel.

RESULTS & DISCUSSION

Removing Free Water from Jet Fuel: Proof of Concept

Gas chromatography is a convenient tool for the analysis of mixtures; in the case of Jet A-1 however, which contains thousands of components, the GC chromatogram can be expected to be correspondingly complex (Fig. 2). As shown, higher molecular weight components possess correspondingly higher retention times, and so for reasons associated with fuel volatility, there are few if any components which elute <2min under the conditions reported in the experimental section. We aimed therefore to develop an analytical technique which affords volatile “analytical markers” which elute during the initial two minutes of the GC chromatogram of Jet A-1 (Fig. 2). A careful choice of methodology was therefore necessary before work could be undertaken in order to demonstrate the feasibility of using ortho esters as a dehydrating agents for jet fuel.

Chen *et al.* developed a useful analytical approach for measuring the water content of a range of hydrophobic solvents such as decane; a reasonable surrogate for Jet A-1 [17]. The method relies upon the indirect determination of water *via* the GC measurement of ethanol (EtOH), a volatile side-product liberated *via* the acid-catalysed stoichiometric reaction of water with ortho ester 5 (Scheme 1).



Scheme 1. Hydrolysis of triethyl orthoformate (TEOF) 5 catalysed by methane sulfonic acid (MsOH).

The GC method was adapted for measuring water in jet fuel (see experimental). Importantly - and as confirmed by GC-MS - the products of the hydrolysis of **5** *i.e.*, the volatile analytical markers ethanol, ethyl formate **6**, and the internal standard (3-methylpentane), all elute before the components of jet fuel (Fig. 2). The retention times for ethanol and 3-methylpentane (internal standard) were 1.69 and 1.8 min, respectively.

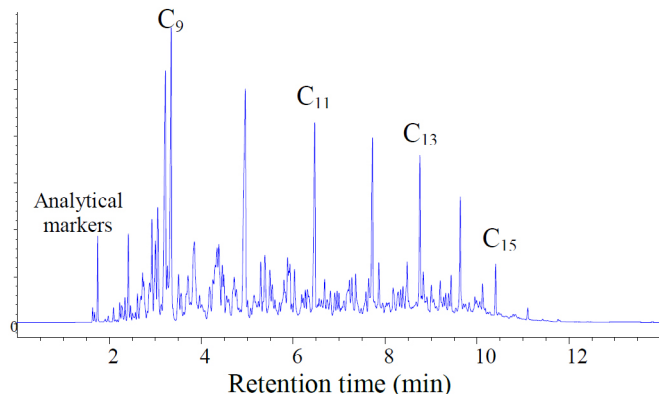


Figure 2. Typical chromatogram of GC analysis of Jet A-1.

For each water standard, the relative peak area (RPA) of ethanol was calculated by dividing the ethanol peak area by the internal standard peak area. To correct for atmospheric and residual water present in the reactant solution, the RPA of the reactant solution was subtracted from each ethanol RPA. A calibration curve was plotted, and is presented in Figure 3.

As can be seen, an excellent linear correlation ($R^2 = 0.9995$) exists between the ethanol RPA and water concentration in Jet A-1 in the concentration range examined (100 - 1250 ppm v/v). Importantly, the GC method reported here can be used to determine water concentrations in jet fuel beyond the accuracy of the industry standard - namely the Karl Fischer method [17].

In conclusion, the linearity of this relationship clearly illustrates the effectiveness of using triethyl orthoformate **5** as a dehydrating agent for Jet A-1.

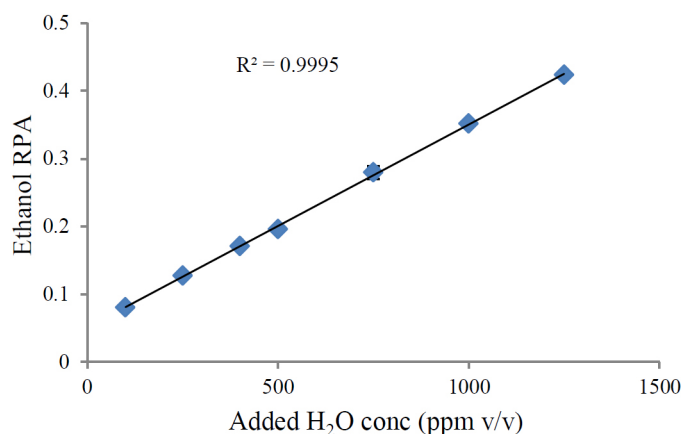


Figure 3. Calibration curve for the reaction of water in Jet A-1 with scavenger 5.

Jet fuel is mildly acidic because it contains mixtures of cyclohexyl and cyclopentyl carboxylic acids *i.e.*, naphthenic acids [1]. Indeed, the batch of Jet A-1 used for these analyses is reported to be 0.01 mg KOH/g by ASTM D3242 [18]. In order to examine the capacity of **5** to dehydrate jet fuel in the absence of added acid, the GC method described here was repeated without methane sulfonic acid. In the absence of an added acid catalyst - with only the inherent acidity of jet fuel to catalyse the process - the reaction was found to be 60-75% complete after 2 days at $T = 20^\circ\text{C}$, compared to 100% completion in 30 minutes using methane sulfonic acid at the same temperature.

Since a strong acid catalyst is undesirable inside the fuel tank of an aircraft, a kinetically faster process must be sought either through modifying the; (a) reaction conditions *i.e.*, the nature of the acid catalyst, or (b) molecular structure of the ortho ester. We report our preliminary findings upon the former herein.

The Nature of the Acid Catalyst, and its Relationship to the Rate of Hydrolysis

Although there is still much to be uncovered about the acid catalysed hydrolysis of ortho esters, it is generally accepted that the process can be divided into two stages; namely, the formation of the *water scavenging* dialkoxy carbenium ion **11** from ortho ester **7**, and the subsequent hydration of **11** and collapse of **12** to afford ester **13** (Scheme 2). The initial protonation of **7**, and the subsequent formation of **11** is considered to be slow - and therefore rate determining - whereas the hydration of **11** and all subsequent steps *en route* to **13**, are considered to be relatively fast [19,20].

The protonation of **7**, and the subsequent formation of **11** is subject to two clearly defined mechanisms; namely *general* (*via* undissociated acid HA) - and *specific* (*via* dissociated acid H^+) *acid catalysis* (Scheme 2) [19].