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Behaviour of Water in Jet Fuel
A Literature Review

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Abstract

This review gives a detailed account of the different types of water contaminated fuel and the conditions that bring about each form of contamination. It also considers studies that have been done to date that investigate the physics behind the behaviour of water in different hydrocarbons and jet fuel at low temperatures.

Keywords:
Aviation fuel, Jet A-1, low temperatures, water, ice, hydrocarbons, fuel system.

Nomenclature

μ	Viscosity
ρ	Density
d	Diameter

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g Gravity Acceleration

v Velocity

1. Introduction

It is commonly accepted throughout the aviation industry that a mixture of water and jet fuel in any form is undesirable and potentially hazardous. Although jet engines are capable of burning a mixture of fuel and water, the water content must be kept below tolerable levels. Entrained or generated water in the fuel system, when combined with very low temperatures, may result in ice formation within the aircraft fuel system.

There are a number of systems in place to prevent the adherence of ice to the fuel system surfaces. Civil aircraft prevent ice build-up on fuel filters within the engine frame using fuel-oil or fuel-air heat exchangers. Aircraft feed pumps have protective pump mesh strainers with bypasses, that ensure uninterrupted fuel flow to the engine in the event of ice build-up and mesh strainer blockage. Pipes and tanks in the fuel feeding system of some aircraft use electric fuel line heaters. If conditions are extremely cold, anti-icing additives are mixed with the jet fuel in small quantities to prevent the formation of ice in the fuel.

These techniques effectively address the problem, but neglect the root cause. When a Boeing 777 crash landed at Heathrow airport in January 2008, the Air Accident Investigation Branch (AAIB) final report [1] raised concerns about the lack of understanding of the nature and behaviour of wa-

ter in jet fuel. Hence a number of research programmes, considered in this review, have been initiated to further understand the behaviour of water at low temperatures in different hydrocarbons and jet fuels.

In Section 2 the reader can find a general overview of jet fuels currently utilised in the civil aviation industry. Section 3 explains the different forms of water contamination in jet fuel. A detailed study of the effects of temperature and humidity on the hygroscopicity of jet fuel is included in Section 4. Section 5 is the result of an extensive literature search carried out to review the current understanding of water dropout and nucleation (i.e. ice formation) in aviation fuels. Section 6 gives a brief overview of ice accretion on metal surfaces and fuel systems.

2. Kerosene Jet Fuel

There are many different kerosene based jet fuels used in the aviation industry [2]. The current specifications [3–5] and designations for conventional jet-engined commercial aircraft are illustrated in Table 1. These specifications are alike in most respects, but differ significantly in the lower freezing point, flash point, and viscosity. Such characteristics are set to endure the low temperatures encountered in different countries.

Fuel Grade	Country/Region	Specification
Jet A	USA	ASTM D1655
Jet A-1	Worlwide	ASTM D1655, DEF STAN 91-91
TS-1	*Russia**	GOST 10227
Jet Fuel no.3	China	GB 6537
Jet A-1	Canada	CAN/CGSB-3.23

Table 1: Worldwide Petroleum Based Civil Jet Fuel Grades and Specifications (*Russia** and former Soviet Union countries)

2.1. Petroleum Based Kerosene Jet Fuel

Petroleum-based jet kerosene fuels are derived from crude oil, and consists of blends of different hydrocarbons. The kerosenes are colourless mixtures of non-volatile petroleum fractions with carbon chained components ranging from C_9 to C_{14}. It is this composition that determines the properties of kerosene which has a high molecular weight in comparison to many other fuels [6].

Petroleum from different oil fields, and even sometimes from different wells in the same field, vary greatly in the proportions of the many types of hydrocarbons and individual hydrocarbons present in them [7]. Hence the properties of the same type of kerosene based jet fuel are dependent on the nature of the crude oil from which they are obtained.

The composition of petroleum-based jet fuel comprises (by volume) between 99% to 99.5% pure hydrocarbons namely paraffins, naphthenes, olefins,

and aromatics. It is the latter group that is thought to have an effect on the solubility of water in jet fuel, as discussed in Section 4.3.2.

Approximately 0.5% to 1% of petroleum-based jet fuel consist of non-hydrocarbon components such as naphthenic acids and compounds of sulphur, sodium, lead and bromine [6]. Raw kerosene must meet the limits of non-hydrocarbon components set by the Defence Standard (DEF STAN) 91-91 (or equivalent, Table 1) [3, 4]. In most cases the kerosene has to be treated in the refinery (by hydrotreating or Merox-Processing) to meet these targets. The resulting chemical composition of jet fuel varies slightly with the different treatments, and this was thought to have an impact on the fuel hygroscopicity. However, recent studies have shown that the different treatments do not have a significant effect on the amount of water absorbed by the fuel [8].

2.2. Gas to Liquid Synthetic Kerosene Jet Fuel

Synthetic paraffinic kerosene (SPK) jet fuel is currently being derived from natural gas using the gas to liquid (GTL) Fischer-Tropsch (FT) process [9] followed by downstream processing [10]. Coal (CTL) and biomass (BTL) are also less widely used alternatives to natural gas.

The FT process creates mainly straight chain hydrocarbons [11]. The lack of aromatics and cyclo-paraffins in synthetic kerosenes yields fuels that are below the minimum density specification requirement set at $775\,\mathrm{kg\,m^{-3}}$ [12]. Aromatics are also responsible for swelling elastomers used in aircraft

fuel systems. Hence the lack of aromatics in the fuel may cause some of these elastomers to shrink, which may lead to fuel leaks [11].

The disadvantages discussed cease to exist if FT SPK fuels are blended with conventional jet fuels. Specific approved FT SPK fuels are currently being used in some commercial flights as a 50/50 blend with petroleum derived jet fuels, with at least 8% of aromatics (by volume) in the final blend [3, 4, 13]. The blend with petroleum derived jet fuel is termed semi-synthetic jet fuel (SSJF).

The solubility of water in SSJFs is approximately 25% to 30% lower compared with conventional Jet A and Jet A-1 fuels [12]. The solubility of water in SSJFs fuels is dependent on the conventional jet fuel used in the blend.

The FT SPK contain no heteroatoms, aromatics nor any other polar compounds [12]. As discussed in detail in Section 4, such compounds are believed to increase water solubility in petroleum based jet fuels. However, research is still required to determine the behaviour of water in synthetic jet fuels.

2.3. Biokerosene Jet Fuel

Biokerosenes are hydroprocessed esters and fatty acids (HEFA) derived from plant oils and animal fats [14]. During the complex process of turning biomass into fuel, plant oils and animal fats are turned into a paraffin wax that is later submitted to the FT process. As a result, HEFA SPK is almost identical to FT SPK.

Biokerosenes were approved in the summer of 2011 [3, 4, 13]. As with FT SPK, aromatics are not found in biokerosenes. Hence for the reasons discussed in Section 2.2, biomass kerosenes are also being blended with conventional commercial jet fuel. Specific approved biokerosenes, namely BTL SPK and HEFA SPK, have been introduced in commercial aircraft as a 50/50 blend with petroleum derived jet fuels [15].

The solubility of water in both HEFA and BTL SPK fuels may be comparable to FT SPK, and is dependent on the conventional jet fuel used in the blend. Nonetheless, the hygroscopicity of biokerosenes needs further research.

3. Forms of Water Contamination in Jet Fuel

Water can be present in fuel in three forms: dissolved in the fuel, suspended in fuel as water-in-fuel emulsions, or free water. Dissolved water is invisible to the naked eye, and is considered a constituent of jet fuel that vaporises during combustion [6]. Suspended water appears as a dull, hazy, or cloudy appearance that takes time to coalesce or settle down. Free water, being denser than fuel, forms a separate layer at the bottom of fuel tanks. Water-in-fuel emulsions and free water are regarded as fuel contaminants, and are managed through rigorous Quality Control (QC) measures [16].

Water in aviation fuel comes from numerous different sources. Each year, a large amount of fuel is moved globally via pipeline networks, rail, ship,

road or a combination of these methods [7]. Even if the jet fuel is dry as it leaves the refinery, it may pick up free water during its transit and storage through the transport network [6].

Means of water contamination of jet fuel include [17]:

- Rain water entering through the seals in poorly maintained floating-roof tanks
- Rain water entering through hatches of fuel storage tanks
- Water left behind after cleaning operations in tanks or transport vehicles due to poor personnel procedures
- Condensation of water from moist air to the tank walls in vented fixed roof storage tanks
- At low temperatures, precipitation of dissolved water from the fuel itself, as discussed in Section 4.

3.1. Dissolved Water

Water is not soluble in jet fuel. A fuel is said to be saturated with water when it has dissolved all the H_2O molecules it can hold under certain conditions. For example, at 21 °C and atmospheric pressure, a saturated kerosene based fuel contains approximately 40 to 80 (water) parts per million, (ppm) [2].

Like many other components in fuel, dissolved water is regarded as another fuel constituent, and is not considered a contaminant as long as it is

maintained in a dissolved state [2]. Dissolved water cannot be removed by any mechanical process such as settling, filtering or separation and so any attempt to dry jet fuel in these ways is futile.

3.2. Free Water and Water-in-Fuel Emulsions

Water is sparingly miscible with hydrocarbon fuel and since water is denser than fuel, any free water within the fuel forms a lower layer separated from the jet fuel upper layer. If jet fuel and water are mixed, they will separate back to the two layers.

An emulsion is a mixture of two or more immiscible liquids where one is dispersed as droplets, of microscopic or ultra-microscopic size (in this case, 0.1 μm to 100 μm water droplets), in the continuous phase of the other (jet fuel).

Emulsions of water droplets in jet fuel are formed by a) dissolution of water from the fuel (fully explained in Section 4.5) and b) mechanical means such as agitation as jet fuel passes through different components in the fuel system. When jet fuel goes through pumps in the aircraft, free water in the fuel is separated into a very fine dispersion of droplets of different sizes that lie in the range of 50 μm down to 5 μm [7].

The rate of settling of finely dispersed water from fuel is subject to Stoke's Law; giving the movement of water droplets a direct proportionality to their diameter, and an inverse proportionality to the fuel's density and viscosity

[7], as seen in Equation 1, Figure 1.

$$v = \frac{(\rho_w - \rho_f)\, g\, d^2}{18\, \mu_f} \tag{1}$$

Water in fuel emulsions can be removed from fuel by passing it through water separators and filter units. These components contain fibres with a hydrophilic surface that combines water droplets into larger drops (Figure 2). Larger droplets of water are not usually held back for long in the fuel, forming unstable emulsions that are easily broken down [18].

Stoke's law should be applied to emulsions with caution. Substances such as naphthenic acids, phenols (both natural contents of crude oil) and sulphonic acids (introduced during refining) that are present in jet fuel have an effect on the coalesce and settling of water droplets. These substances act as surfactants by congregating at the surface of the dispersed water droplets, forming a protective film around them that prevents the coalescence of the droplets into coarser ones, hence delaying the breakdown of the emulsion [6].

Stable fuel emulsions are also formed by the development of static charges on the water droplets [18]. Under the influence of charges of equal sign, the droplets are repelled by each other hence avoiding their coalescence and causing the breakdown of the emulsion.

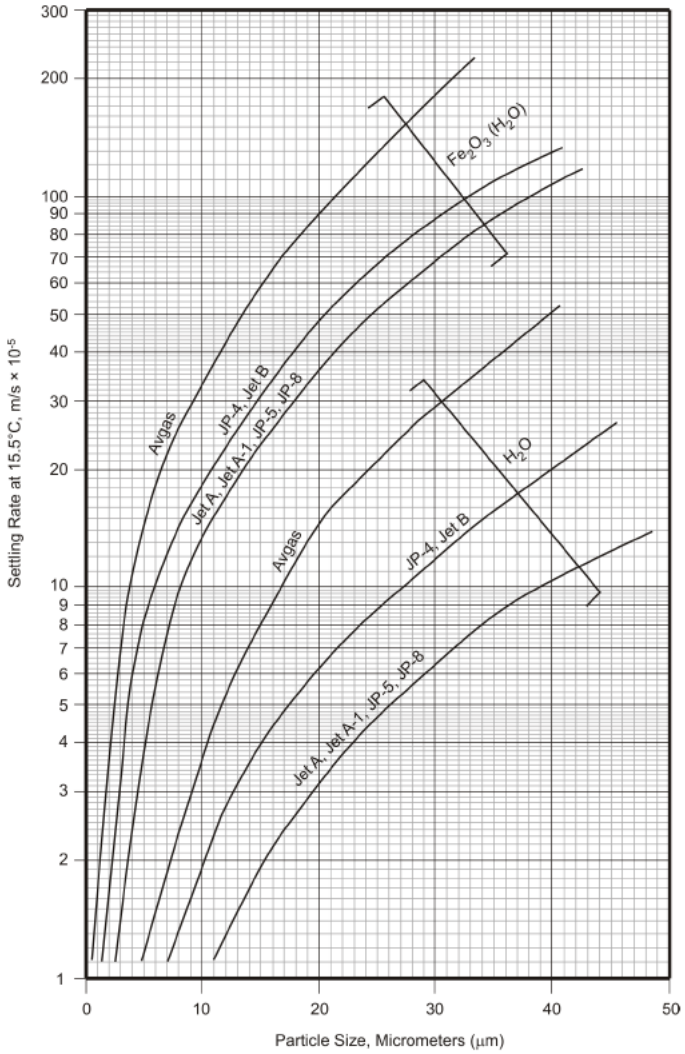


Figure 1: Settling times of water droplets (and rust particles $Fe_2O_3(H_2O)$) in different types of jet fuel [2]

Certain molecules or materials, such as surfactants or solid particles, can be added to the fuel to encourage coalescence, making emulsions kinetically unstable. These additives usually provide electrostatic attraction, or steric

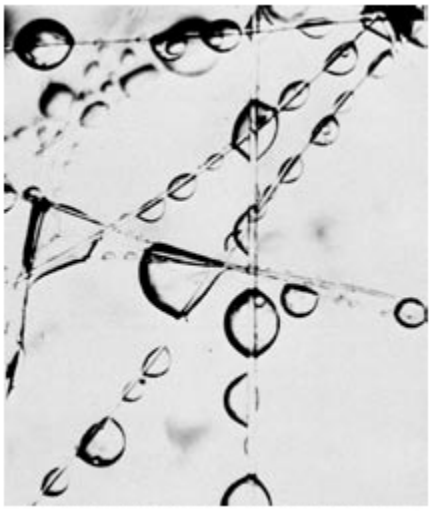


Figure 2: Photomicrograph of coalescing process inside fibreglass media [19]

attraction between water droplets in the emulsion, or weakens the interfacial layer of the droplets, making coalescence easier. However in the aviation industry, it is imperative to deliver the fuel to the aircraft in as clean a state as possible, thereby reducing the need for the addition of enhancing additives.

Several corrective measures are used in the fuel industry to minimise the action of surfactants or static charges. Under aircraft operating conditions, the standard procedure is to allow the fuel to stand for for a period of time. Emulsions are then allowed to settle at the bottom of the fuel tanks, which are comprised of ribs and spars that promote its accumulation as free water at desired pooling points.

Depending upon the nature of water-in-fuel emulsions, it may take minutes, hours or weeks to coalesce and settle down. Unfortunately, maintaining

an aircraft for weeks or even hours on tarmac is not cost-effective in today's civil aviation industry, where turnarounds can be as short as 30 minutes for smaller commercial aircraft. Hence the pooled, free water is routinely picked up and fed to the engine in a mixture with the fuel. This is part of current commonly adopted water management and is achieved using scavenging jet pumps. Free water in pooling points is also drained on the ground during routine maintenance.

4. Hygroscopicity of Jet Fuel

The hygroscopic nature of jet fuel refers to its ability to attract moisture from the air and surroundings. The reversible hygroscopicity of jet fuel strongly depends on atmospheric conditions such as the temperature and relative humidity to which the jet fuel is subjected. Any variation in these conditions will cause phase transitions of the water contained in the fuel.

It is important to understand the difference between solubility and hygroscopicity. The solubility of water in fuel refers to the degree to which water dissolves in fuel to make a solution, and is dependent upon the chemical composition of the fuel. Once the hygroscopic nature of jet fuel attracts moist air to its surface, the water molecules in direct contact with the hydrocarbon based fuel go into solution.

4.1. Effect of Relative Humidity in the Solubility of Water in Jet Fuel

The amount of water generated in fuel depends on the relative humidity (RH) of the air above the fuel. When the fuel is not in equilibrium with the atmosphere above its surface, and its RH is lower than the RH of the air in the ullage, jet fuel absorbs moisture from the air to regain a state of equilibrium according to the surrounding conditions [7]. This process is reversible, and the dissolved water is taken out of solution when the RH of the air above the fuel decreases, i.e. becomes lower than the RH of the fuel.

To have an idea of the effect of moist air within a fuel tank, fuel in direct contact with air with a RH of 50% contains only half as much water as water-saturated fuel at that temperature, however fuel tends to enter the tanks of the aircraft already saturated due to its contamination during transport from the refinery [20].

The amount of free water generated in fuel storage tanks can be significant if the tanks are located in humid climates. Smith [7] argues that daily temperature changes in countries with such climates are fairly small and the water released at night, is then re-absorbed during the day, i.e. it is "self-compensating". However, more recently Oreshenkov [21] has demonstrated that over a period of a few months, cyclic temperature changes produce a significant amount of water accumulation in fuel tanks.

4.2. Effect of Temperature in the Solubility of Water in Jet Fuel

As shown in Figure 4, there is a connection between solubility of water in fuel and temperature. The greater the solubility of H_2O in the fuel, the higher the temperature at which dissociation of water particles and hydrocarbon components takes place (i.e. reversible hygroscopicity).



(a) t = 0 min

(b) t = 14 min



(c) t = 30 min



(d) t = 58 min

Figure 3: Water dispersed in Jet A-1 fuel [22]

Water released from fuel appears as a fine cloud of minute droplets. Lao *et al.* [22] measured the relative transparency of 20 L of water saturated Jet

A-1 fuel as a function of temperature. It was observed that at temperatures above 14 °C the water was completely dissolved and the fuel had a clear appearance. As seen in Figure 3, at temperatures below 14 °C, excess water precipitated out forming a fog phenomena, hence reducing the transparency of the fuel. Measured data was in agreement with the solubility of water in fuel depicted in Figure 4.

4.3. Effects of Different Hydrocarbons in the Solubility of Water in Jet Fuel

Hydrocarbons are organic compounds formed of carbon and hydrogen atoms. As discussed in Section 2, there are three main types of hydrocarbons in jet fuel; paraffins ($\approx 60\%$), naphthenes ($\approx 20\%$), and aromatics ($\approx 20\%$).

The main difference between each class of hydrocarbons is the way in which the carbon atoms are connected to each other (as depicted in Figure 5), which dictates the ratio of hydrogen to carbon atoms within the molecule. This determines the physical and chemical properties of the fuel, including water solubility [6].

4.3.1. Paraffins & Naphthenes

Paraffins and naphthenes - also known as alkanes - are the major components of aviation fuels [6]. They consist of singly bonded carbon chains or rings in which each atom is fully saturated with hydrogen (i.e. saturated

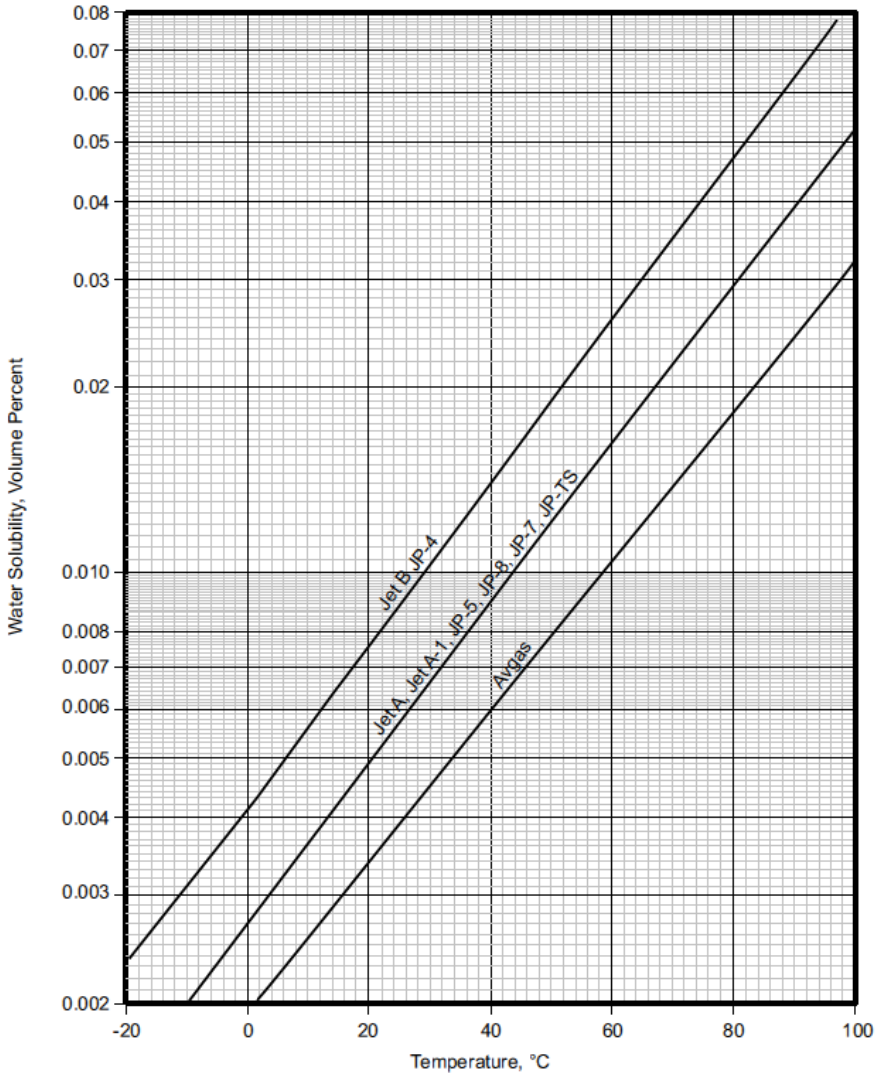
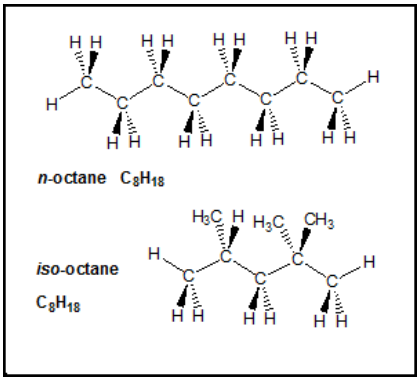


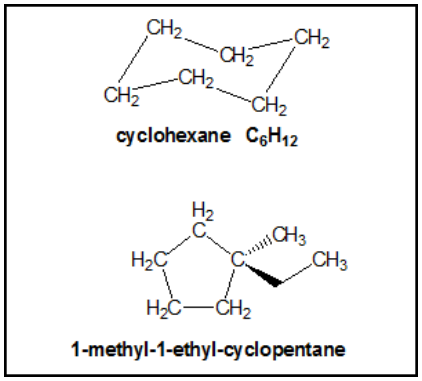
Figure 4: Water solubility vs. temperature for aircraft fuel, at 100% RH [2]

hydrocarbons). Paraffins can either be linear or branched chain molecules, and the naphthenes have at least one saturated carbon ring. The carbon-carbon and carbon-hydrogen bonds in these molecules do not possess strong permanent dipoles [23]; therefore this class of molecules interact with each

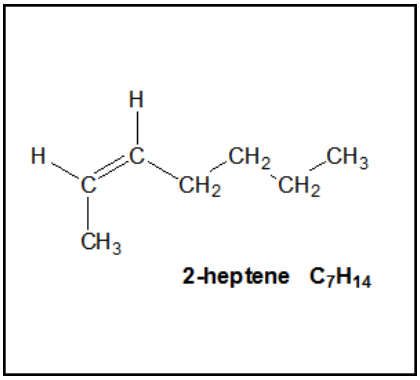
other via the weakest of intermolecular forces, resulting from the temporary movement of electrons (London dispersion forces).



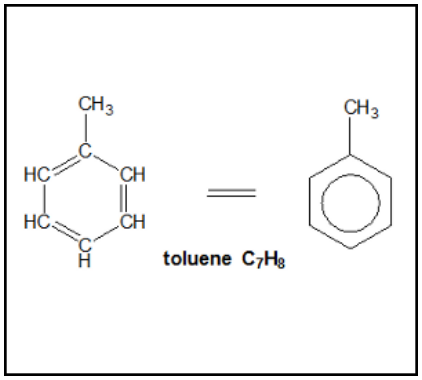
(a) Paraffins



(b) Nephthenes



(c) Olefins



(d) Aromatics

Figure 5: Examples of hydrocarbons commonly found in jet fuel

4.3.2. Olefins & Aromatics

Olefins and aromatics (Figure 5) are unsaturated hydrocarbons because they contain fewer hydrogen atoms than the corresponding alkanes, and carbon-carbon double bonds, called π bonds.

The aromatics in particular have a characteristic ring of six carbon atoms (benzene), about which the π electron cloud is evenly distributed. The quantity of aromatic compounds in Jet A/A1 is limited to a maximum of 25% by volume, because of their tendency to form coke deposits on combustor surfaces, to create smoke when burned, and to contribute to high-luminosity flames [3, 4].

4.4. Water Solubility in Jet Fuel

The hygroscopic capacity of jet fuel is determined by the water solubility of the individual hydrocarbon components. Because water is sparingly soluble in hydrocarbons, accurate determinations are difficult to achieve, and remains an active and challenging area of research [24].

Water possesses a strong permanent dipole because of the difference in electronegativity that exists between the hydrogen and oxygen atoms. Therefore, relatively strong attractive interactions exist between adjacent water molecules, leading to extended hydrogen bonding networks. Experimental observations of water dissolution in hydrocarbons have led to a variety of theoretical models which all require, as a first step, the disruption of these hydrogen bonding networks [24–31].

The energy associated with dissolving water - enthalpy of solution - in a range of unbranched alkanes has only a weak dependence on the number of carbon atoms present (i.e. $C_7 - C_{12} = 34.9 \pm 1.1\,\mathrm{kJ\ mol^{-1}}$ at 298 K) [28]. The magnitude of the enthalpy of solution is comparable to the hydrogen bond energy, suggesting that the dissolution of n water molecules requires the breaking of n hydrogen bonds [31].

The enthalpy of solution of water in both alkylbenzenes and alkenes decreases by approximately 11 and 2 kJ $\mathrm{mol^{-1}}$, respectively. The energetic cost of disrupting the hydrogen bond network of water is offset by attractive electrostatic interactions with these hydrocarbons. It has long been recognised that extended π electron systems, such as those encountered within alkylbenzenes, form hydrogen bonds with water [29, 32, 33]. A weaker form of that interaction, between water and the π bond of an alkene, may account for the $\sim 2\,\mathrm{kJ\ mol^{-1}}$ enthalpy reduction [30].

The formation of attractive electrostatic interactions between water and π-aromatic systems would account for the enhanced solubility of water in alkylbenzenes, relative to both paraffins and naphthenes.

There are a number of studies that compare the solubility of water in different hydrocarbons [8, 22, 24–39]. Most recently, Carpenter *et al.* [8] showed that aromatic hydrocarbons absorb up to seven times more dissolved water than the alkane or cycloalkane with a comparable number of carbon

atoms.

As depicted in Figure 6, water solubility increases with the proportion of aromatic hydrocarbons, but not in a linear fashion. Figure 6 also reflects the behaviour of water solubility in hydrocarbons in general, suggesting that this physical property is non-colligative i.e. not simply dependent upon the number of molecules [29, 38].

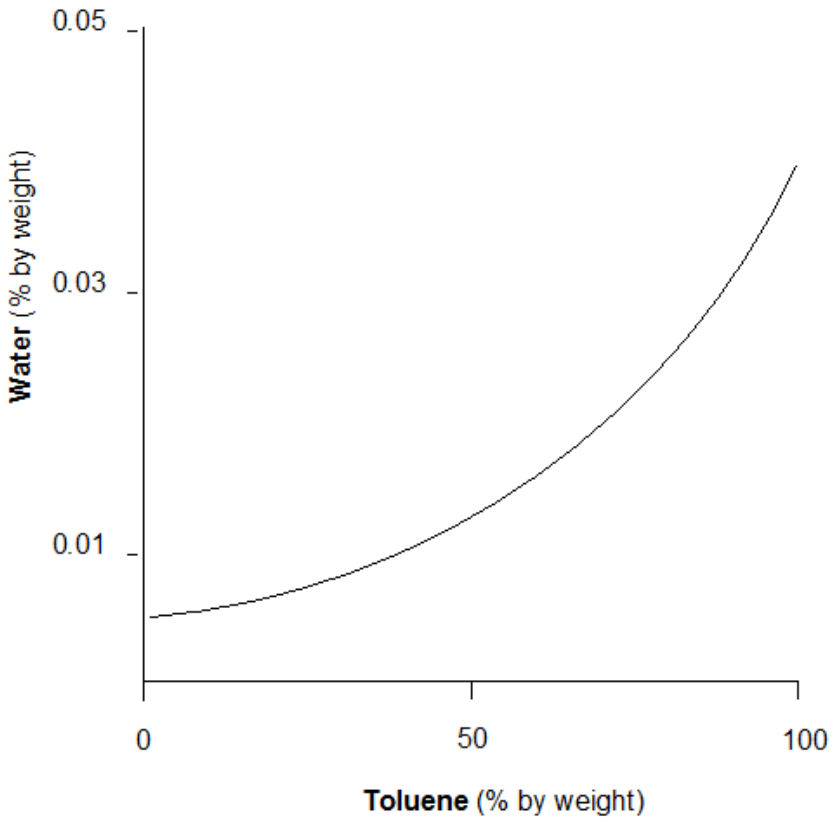


Figure 6: Water solubility in n-Octane/Toluene mixtures at 15.5°C

4.5. Water Cycles in Aircraft Fuel Tanks

Fuel in the aircraft system is subject to significant changes in temperature and exposure to humid air within the tanks. As a result of such variations and given the reversible hygroscopicity of fuel during flight, there is a continuous process of absorption and spontaneous liberation of the dissolved water [2].

At high altitudes and low temperatures, water from the fuel evaporates until its concentration in the fuel reaches equilibrium with the concentration of water in the air within the fuel tanks. This evaporation is followed by the condensation of the water in the ullage on the metal walls of the tanks as well as the cold surface of the fuel. A continuous process of evaporation from fuel and condensation of the surplus water vapour in the space above the kerosene is established. The evaporation process continues until the pressure of the water vapour above the jet fuel attains an equilibrium established by the humidity and temperature of the air [2, 18].

Separation of water molecules from fuel also takes place as an emulsion. If the fuel surfactants concentration is limited, the water droplets settle on the bottom of the tanks (as free water) in quiescent conditions, or remain suspended in the fuel otherwise [1, 18]. Below freezing temperatures, the small droplets turn into ice crystals within the fuel and the condensed water freezes on the walls or forms small ice particles on the surface of the fuel by the process of nucleation.

5. Water Nucleation in Fuels

Nucleation is the process by which nuclei are formed, usually in solution. The term *nucleus* as used in the stem of the word refers to the formation of a small, solid phase collection of atoms, molecules or ions during precipitation, capable of spontaneous growth.

The *metastable* state of a body or system, in this case hygroscopic water, refers to the condition of the water existing at an energy level in the liquid state which is above that of a more stable condition, i.e. ice. It would take a small amount of energy to induce a transition to the more stable state.

Metastable states of solutions or any liquid involve both supersaturated and supercooled solutions. Hygroscopic water in jet fuel can exist in a supercooled metastable phase, when supercooled water droplets prevail inside the crystalline domain of stability [40], i.e. at temperatures below its freezing point.

For a new phase to appear, an interface must be formed. The creation of ice crystals from supercooled water droplets may occur via a) germs, or crystallites of water molecules (homogeneous nucleation, Section 5.1) [41] or b) germs formed upon foreign particles such as dust, rust or dirt (heterogeneous nucleation, Section 5.2).

5.1. Homogeneous Nucleation of Water in Jet Fuel

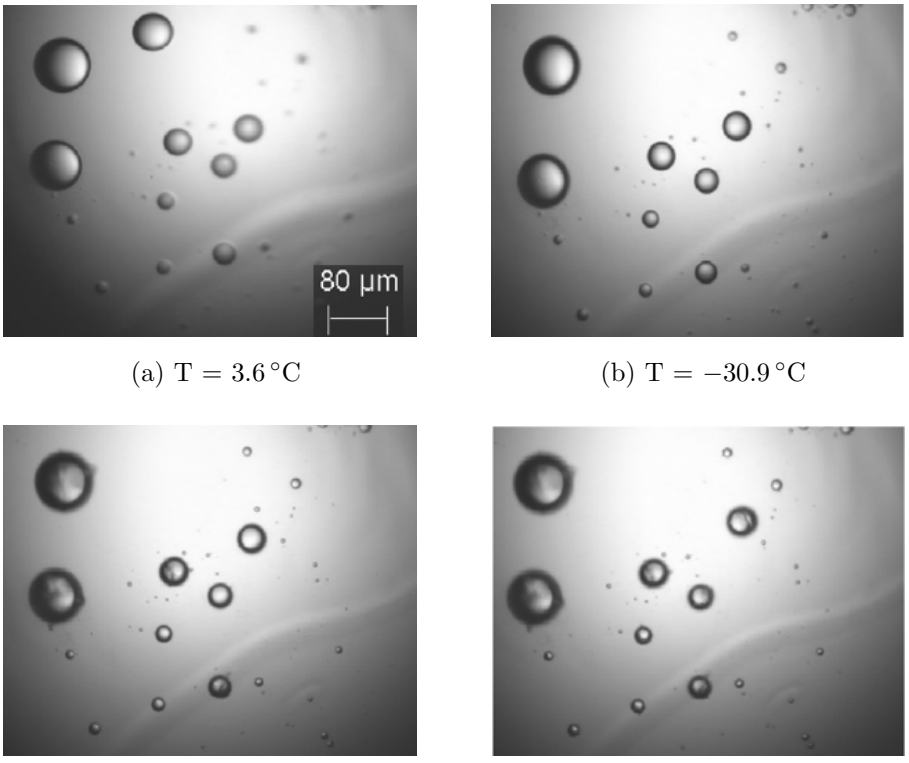
Classic Nucleation Theory (CNT) states that in the initial phase of homogeneous nucleation, embryos are formed as a result of spontaneous density or composition fluctuations [42, 43]. The critical- sized embryo is in unstable equilibrium and energy is required to form a particular cluster of molecules; embryos smaller than the critical size shrink spontaneously, releasing energy back into solution [42], while embryos larger than the critical size grow spontaneously.

For a clean, uncontaminated water droplet to turn into ice, it must first overcome an energy barrier to form a critical nucleus. Hobbs [42] describe different studies on homogeneous water nucleation, establishing that for a droplet of radius of a few μm , homogeneous nucleation becomes significant in the range of $-10\,^{\circ}$C down to $-40\,^{\circ}$C.

Murray *et al.* [44] investigate water drops deposited on a glass slide surrounded by a matrix of Jet A-1 fuel. Water droplets of above $10\,\mu$m in diameter within the fuel are submitted to sub freezing temperatures. As the temperature is lowered at a rate of $10\,^{\circ}$C min^{-1}, most of the droplets freeze between $-36\,^{\circ}$C and $-39\,^{\circ}$C (illustrated in Figure 7), which is in good agreement with the results reported by Hobbs [42].

In a series of similar experiments, Carpenter *et al.* [8] investigate three different batches of Jet A-1 fuels as they are cooled down to $-70\,^{\circ}$C. At temperatures above $-44\,^{\circ}$C, there is no evidence of the water droplets (of

diameter $\leq 5\,\mu m$) changing to crystalline ice formations. However below $-44\,^{\circ}C$, some of the water droplets change to a different colour under the light of the microscope. This is explained as an indication of water freezing as spherical droplets. Results were in good agreement with the results reported by Murray *et al.* [44].



(a) T = 3.6 °C

(b) T = −30.9 °C

(c) T = −36.6 °C

(d) T = 39 °C

Figure 7: Pure water droplets in Jet A-1 fuel, cooled at 10 °C min^{-1} [44]

5.2. Heterogeneous Nucleation of Water in Jet Fuel

The germs of H_2O molecules have been regarded so far as isolated clusters dispersed in the liquid water, but in most cases such germs can be encouraged to turn into ice by seeding it with a grain of ice, or with a small particle of dust, rust or dirt [45]. This is the heterogeneous nucleation case, compared to the previously considered homogeneous case. Homogeneous nucleation requires a greater degree of metastability, i.e. supercooling or supersaturation, than heterogeneous nucleation.

Shaw *et al.* [45] examine the phenomenon of contact nucleation in a series of laboratory experiments, where a drop of pure water is surrounded by naphthenic oil and later by air. The study compares the efficiency of an ice nucleus in causing crystallisation when it is either immersed in the water droplet or when it is in contact with the droplet's surface. The result is an estimate of the most likely temperature at which droplets freeze.

The investigation concludes that, regardless of whether the water drop is surrounded by oil or air, the freezing temperature when the ice nucleus is in contact with the droplet is about 4 °C to 5 °C higher than when it is immersed in the droplet; therefore *contact nucleation* is a more effective mechanism than *immersion nucleation*.

In its series of monographs Ragozin [18] describes the different forms of ice encountered in jet fuel samples during a set of experiments:

- Minute, four-sided ice crystals; very common in undisturbed fuel

- Fluffy clumps of snow, of a dirty yellow colour or snowy mass of random form; after pumping or in supersaturated conditions
- One to four centimetre long broken crystals or cotton-like fluffy mass; when there are impurities in the fuel.

The introduction of foreign particles and external factors obscures and complicates the understanding of hygroscopic water nucleation in jet fuel. It adds many different parameters that are currently the subject of wide interest in many scientific studies as well as industry projects.

Aviation fuel in aircraft tanks may contain traces of foreign particulate matter such as dust or rust particles, microbiological mats or sludges, crystals of benzene or paraffin, filter fibres and other impurities [17] that may provide crystallisation nuclei for the nucleation of supercooled water droplets dispersed in the fuel. Rough surfaces and surface defects in the system may also provide nuclei sites for crystallisation to occur. The existence of nucleation sites in supercooled water tends to speed up the nucleation process, producing ice in jet fuel at temperatures higher than those discussed in Section 5.1.

Real aircraft feeding system components also add factors such as turbulent flow and agitation. The AAIB [1] final report reveals the formation of different forms of ice in the fuel similar to that described by Ragozin [18].

6. Ice Accretion on Metal Surfaces and Aircraft Fuel Systems

According to Hayashi et al. [46] the formation of frost can be divided in three stages, a) crystal growth period, b) frost layer growth period and c) frost layer full growth period. As the frost layer develops, it goes through these transformations. The frost thickness and surface temperature is gradually increased until the melting temperature of ice water is reached. Lüer and Beer [47] demonstrated in a series of experiments that the density and thickness of the frost surface layer depends on factors such as time, air temperature, air velocity, air humidity and surface temperature.

Lao et al. [22] observed deposition of water/ice on the surface of a sub-cooled aluminium block immersed in Jet A-1 fuel. The experiments were carried out in the cold tank depicted in Figure 3. The observed deposition formed a uniform thin layer of spherical droplets on the sub-cooled aluminium surface. The characteristics of the growth of this layer are analogous to that of the initial frost formation period described by Hayashi et al.[46]. However there was no evidence of frost layer growth on the sub-cooled aluminium surface. This may be due to the small and limited hygroscopic water contained in the test rig closed fuel system, compared with an open system (as in the atmosphere).

As reported by Lao et al. [22], ice accretion on a sub-cooled surface is elucidated by the Bergeron process. This theory is confirmed with the observations made by Carpenter et al. [8]. Furthermore, observations during fuel system icing tests, have demonstrated that accreted ice on sub-cooled

surfaces have very little adhesion strength. It takes minor fluid disturbances near the accreted ice to dislodge it from the surface. It is reasonable to postulate that ice suspended in fuel in the aircraft fuel system may be the result of dislodged ice previously accreted on the system sub-cooled surfaces.

The findings from the AAIB [1] are in agreement with Lao et al. [22], where ice is deposited on sub-cooled surfaces through the Bergeron process. This occurs at higher temperatures than the homogeneous nucleation of water droplets, indicating that the nucleation and crystallization of water in the fuel may be heterogeneous.

The AAIB investigations [1] suggested that at fuel temperatures between $-5\,^{\circ}\mathrm{C}$ and $-20\,^{\circ}\mathrm{C}$ ice crystals tend to form in the fuel and adhere to fuel system components. Under certain conditions, a considerable amount of ice was found on the inner surfaces of the cold fuel test rig. A summary of significant temperatures found in their investigation is exhibited in Table 2. As seen on the fourth row, a "sticky region"of ice in fuel was observed between temperatures ranging from $-12\,^{\circ}\mathrm{C}$ to $-18\,^{\circ}\mathrm{C}$. The ice adhered to fuel lines, strainers, and tank walls.

The AAIB also observed that fuel velocity, fuel temperature and water concentration in the fuel, play an important part in the thickness fluctuations of ice layers within the fuel feed lines [1]. These factors are comparable to those that have an effect on the thickness and density of a frost layer [47].

Temperature Range	Water and Ice Behaviour Observations
$10\,^{\circ}\mathrm{C} \geq \mathrm{T} \geq 4\,^{\circ}\mathrm{C}$	Concentration of dissolved water begins to decrease
$-1\,^{\circ}\mathrm{C} \geq \mathrm{T} \geq -3\,^{\circ}\mathrm{C}$	Ice crystals begin to form
$-12\,^{\circ}\mathrm{C} \geq \mathrm{T} \geq -18\,^{\circ}\mathrm{C}$	Ice crystals begin to adhere to their surroundings in the form of ice
$\mathrm{T} \leq -18\,^{\circ}\mathrm{C}$	Crystals of large dimensions are formed

Table 2: Observations of water and ice behaviour in jet fuel at low temperatures [48, 49]

7. Summary

Water in jet fuel has been a topic of interest since the 1950s when turbine-powered aircraft started to replace piston-powered aircraft, and a new type of fuel was required. A number of incidents related to ice formation and accretion in aircraft fuel systems gave rise to research programmes, particularly in the United States and Russia, in order to investigate the behaviour of ice in jet fuel. The research was carried out by military entities and gradually became dormant as fuel icing inhibitors were added to military aircraft fuel, and fuel heaters were introduced in civil aircraft. As a result, there is little information about water and ice in jet fuel in the public domain.

Petroleum kerosene based fuels consist of three main types of hydrocarbons: paraffins, naphthenes and aromatics. Past and present research shows

that the solubility of water in individual hydrocarbons becomes more prominent in aromatics. The quantity of aromatic compounds in jet fuel is limited to a maximum of 25% by volume. In practice, the aromatic content is in the range 12% to 24%. Given the higher solubility of water in aromatic compounds, it is believed that fuels with a higher concentration of aromatics display a higher degree of hygroscopicity.

Synthetic kerosene fuels made from coal, natural gas, or other hydrocarbon feedstock have now been integrated, as a 50/50 blend with petroleum derived jet fuels, into commercial aircraft with little or no modification to current aircraft designs. The final blend must contain at least 8% of aromatics (by volume) in order to be used. The solubility of water in synthetic kerosene is dependent on the conventional jet fuel used in the final blend. Nonetheless, the hygroscopicity of synthetic kerosenes needs further research.

The hygroscopic nature of jet fuel refers to its ability to attract moisture from the air or surroundings. This ability strongly depends on the fuel temperature, with the Coordinated Research Council [2] reporting that for a temperature drop of 10 °C in water-saturated fuel, 15 to 25 ppm of undissolved water comes out of solution. This is not a significant amount on its own, but considering other sources of water contamination, fuel in a flying aircraft may produce enough water that, when turned into ice, it may be of concern for the safe operation of the aircraft fuel feeding system.

The type of nucleation of hygroscopic water as it slowly comes out of jet

fuel is an area of active interest in the research community. During experiments, droplets can be seen in jet fuel at 14 °C, although other sources bring this temperature down to 10 °C. The water droplets nucleate homogeneously at temperatures lower than −35 °C.

If the fuel is agitated, there seems to be a shift in the temperature of nucleation to temperatures just below the freezing point of water (0 °C). Ice crystals and even snowflakes can be seen in the fuel at this stage, and it is believed to be a case of heterogeneous nucleation.

A form of ice clusters that are prone to adhere to surfaces and to each other has been labelled by the AAIB [1, 50] as "sticky ice", and it is described as soft and porous snow. Sticky ice in fuel is observed between temperatures ranging from −12 °C to −18 °C. The ice tends to adhere to fuel lines, strainers, and tank walls.

Hygroscopic or "shed-out" water is not a threat to aircraft fuel systems. These systems have robustly designed scavenge systems that avoid the accumulation of water in remote corners in the aircraft tanks. There are also a number of bypasses and fuel heaters to prevent ice from interrupting fuel flow to the aircraft engines. Stringent QC measures are in place to deliver dry fuel to the aircraft, as well as good maintenance procedures at airports to sump any free water from aircraft tanks. However, the behaviour of water in jet fuel, particularly at low temperatures, is an interesting phenomenon that needs further understanding to reinforce design and certification require-

ments for future commercial aircraft.

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Behaviour of water in jet fuel: a literature review

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