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Complexities associated with nucleation of water and ice from jet fuel in aircraft fuel systems: A Critical Review

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ABSTRACT

The contamination and behaviour of water in aircraft fuel systems remains a significant global research interest following several aircraft incidents. To engineer a solution to the problem of icing in jet fuel, it is crucial to precisely identify the conditions and features that may exacerbate this phenomenon. This review will aid prospective researchers to identify work that has been done and work that is yet to be available for future study.

In this review, conclusive data integrating a wide range of literature and also providing an in-depth description of the factors that influence the behaviour of trace water, ice formation in jet fuels was carefully summarised. On investigational studies, it was discovered that no work is available that studies the impact of sustainable jet fuel and its

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blends on ice formation, size and frequency distribution of dispersed water droplets in aircraft fuel systems. Findings from comparative studies also reveal that surfaces will have an essential role in the growth pattern of ice in aircraft fuel systems. Furthermore, findings show that supercooled water droplets with sizes greater than or equal to 5 µm can induce ice accretion.

This review identified a common problem with the prominent methods of reporting results as a graphically fitted plot. Subsequently, it proposed that authors of any original technical work provide raw data as supplementary information to allow comprehensibility. The study further offers a system that could help manage the nature of ice in aircraft fuel tank systems—making it readily available and accessible.

Keywords: Ice accretion, Fuel systems, Aviation fuel, alternative fuel, water-solubility, sustainable aviation fuel, synthetic aviation fuel

1. INTRODUCTION

The issue of water and particulate contamination in jet fuel has long been recognised for the associated problems affecting an aircraft fuel system and causing maintenance downtime. It is accepted that the presence of water in jet fuel is undesirable and potentially hazardous [1][2][3]. The presence of free water can assist the growth of microbiologic cultures, which have the potential to form biofilms in aircraft fuel tanks [4][5]. Thus, the free water content has to be maintained below a certain level, typically below 15 ppm at the time of fuelling [6]. Coalescing technology is employed to keep the amount of free water to a minimum value. At about 21 °C, a saturated fuel usually contains about 40 to 80 parts per million (ppm) of dissolved water [7]. In icy conditions, dissolved water may precipitate from the solution; this free water in the fuel can form ice. Also, ice crystals can form in the presence of particulates at temperatures below 0 ºC in the cooler parts of the wing tank [8]. For example, the observation from the investigation conducted by the Air Accidents Investigation Branch (AAIB) indicated that ice accumulation in fuel systems is often inconsistent, as shown in figure 1 [1][9]. From figure 1 it can be seen that the critical icing temperatures were identified as being between -9 ℃ and -11 ℃ [1]. At these critical icing temperatures, agglomeration of ice crystal occurs, and this can potentially lead to blockage or restrictions in the fuel feed system, particularly if accreted ice is dislodged or released in a snow shower or transient ice event. However, on reducing the temperature below -18 ℃ the ice crystals tend to stick to itself and not the surfaces. Therefore, becoming larger on size. from this study the sticky range (range of temperature where ice sticks more to its surrounding rather than itself) was identified to be between -5 ℃ and -20 ℃.

The behaviour of water and ice has been studied from different angles, as summarised in tables 2-3 [10][11][12]. Also, studies have emphasised that the growth of ice on surfaces depends on the hydrophobic or hydrophilic nature of those surfaces [11][13][14][15][16]. Therefore, it can be concluded that surfaces play an important role in the nature and degree of ice formation.

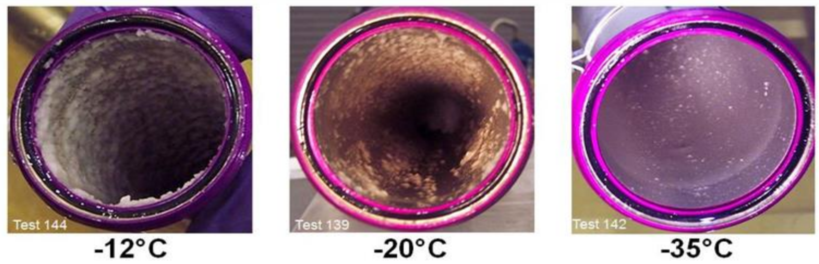


Figure 1. Photos from an ice accumulation testing of jet fuel through cold fuel feed pipes showing that more ice accumulated at the critical icing temperatures (-12 ℃) [8]

Trace contaminants may be present in jet fuel from many sources, for example, from the crude oil or synthetic feedstock, manufacturing process or entrained during distribution. Trace water is inherently present and has safety implications on how it affects aircraft fuel systems. However, the most recent reviewed paper related to this topic was by Baena in 2013, but the review focuses on the behaviour of water in conventional jet fuel only and nothing on synthesised aviation fuel and its effect on ice formation in aircraft fuel systems dissolved

Understanding the properties of this synthetic aviation fuel, along with the changing properties of existing fuel types, is required to understand their impact on aircraft fuel systems. Water solubility, settling rate, droplet size distribution ice formation/accretion, amongst others, is one such property of interest as it is a known problem within the aviation industry. Even though understanding the properties of these sustainable fuels and the changing properties of existing fuel types is required to understand their impact on aircraft fuel systems, there is very limited data available in the literature related to this topic. Unfortunately, most of the data available are related to ice formation in conventional jet fuel pipes only. A large body of work on adhesion testing on ice does not demonstrate how sustainable aviation fuel may affect it. Despite this, no research experiment has been conducted to fill these knowledge gaps. This could be because of the difficulty for potential researchers trying to identify work that has been done and work that is yet to be available.

The purpose of this review is to collect a great amount of data and compare and analyse the recent advances and technologies in the literature on this subject. This review paper also describes some complexities associated with jet fuel chemistry, knowledge gaps, systematic hypothesis, and recommendation for future development. The study further proposes a system that could possibly help manage the nature in which ice forms in aircraft fuel tank systems. Making it readily available and accessible to those wanting to obtain data in this area. Over one hundred and twenty articles from scientific papers have been examined. The sources came from journals, books, and conference proceedings, to cover a broad range of studies and views regarding the water and icing phenomenon. Data were collected from several papers and plotted in a scatter graph or bar chart for the purpose of comparison. Most of the key information extracted from the literature was discussed, making it easier to find and comprehend.

2. OVERVIEW OF JET FUEL

Jet fuels are intended to power gas-turbine engines for aviation purposes. The two major classes of jet fuel are the civil grades (Jet A, Jet A-1 and similar specifications), and military grades (JP-5, JP-8, AVTUR/FSII, AVCAT, F-24, and similar specifications). The military grades differ from the civil grades based on the type of additives used [7][17]. Jet fuel does not have a particular chemical composition but is a complex mixture that is mainly specified by physical characterisation [18][19][20][21][22][23][24][25][26][27] [28]. Studies have shown that jet fuel is based on numerous constituents, which contribute towards providing appropriate thermal output, clean combustion characteristics, and oxidation stability [7][29][30][31][32] [33]. Blends of over a hundred species exist in jet fuel, and the blends or mixtures are mainly hydrocarbons with the number of carbon molecules ranging from eight to sixteen. The major categories of hydrocarbon found in jet fuel are alkanes (also referred to as paraffin), cycloalkanes (also referred to as naphthenes), and aromatics [34][35]. The main difference between the different categories is the connection of the carbon atoms and their bonds Paraffins and naphthenes are the dominant components found in jet fuel. In comparison to naphthenes, paraffin has a high hydrogen-to-carbon ratio, high heat release per unit of mass and a cleaner burn characteristic. In comparison, naphthenes have a slightly lower hydrogen-to-carbon ratio, which consequently lowers the heat released per unit of mass but increases the fuel's density [31]. Aromatic hydrocarbons are good energy sources; however, their maximum acceptable levels in jet fuels are restricted to about 20-25%. Lack of aromatics yield fuels that are below minimum density and can also lead to shrinkage of elastomers; however, when in excess can lead to swelling of the elastomers, more soot production as a result of incomplete combustion and so must be restricted [36]. Finally, alkenes also known as olefins are unsaturated hydrocarbons with lower hydrogen to carbon ratios. The maximum acceptable levels are restricted to less than 1% by volume [7][37]. Traces of other elements like sulphur and sulphur compounds can also be found in aviation fuels. Their presence in aviation fuel can be beneficial in some aspects and not beneficial to others [38][39]. Furthermore, jet fuel may contain additives that are determined by the specific uses of the fuel [40][41]. These additives may be added to the fuel to help improve its performance.

Jet fuel has specialised features, properties and characteristics, which make it different from other fuel [42]. Some of these features are its low freezing point temperature (-40 °C for Jet A and -47 °C for Jet A-1), good combustion properties, high specific energy, density and thermal stability.

In order to maintain a uniform supply of jet fuel worldwide, a group of companies formed the Joint Inspection Group (JIG) and proposed the Aviation Fuel Quality Requirements for Jointly Operated Systems (AFQRJOS) [43][44][45]. The checklist contains the most rigorously binding requirements from the defence standards and the ASTM international specifications for jet fuels [7][46][47][48][49][50]. Although conventional fuel still accounts for a vast majority of aviation fuels, sole dependency on petroleum-derived fuels poses an increase in environmental concerns and price fluctuations [51][52]. Due to the rapid increase in global energy demand and large consumption of oil by the aviation sector, novel technologies to help optimize the use of sustainable aviation fuel source is now a significant area of global research interest. This is because the use of SAF is featured to have the potential to decrease the life-cycle of greenhouse-gas emissions [28][23][24][53][54][55]. These fuels are derived from renewable sources, or biomass so they can therefore reduce the contribution of GHG emission to the global climate. According to several authors, alternate jet fuels could be adopted in order to reduce the impact of the aviation industry on air quality [46][56]. It is important to note that a certified fuel must meet the basic aviation fuel criteria's for safety purposes [32][56][57]. Currently, the D7566 focuses is the standard specification for aviation turbine fuel containing synthesized hydrocarbons (HC) [32].

2.1 Water and its behaviour in Jet Fuel

Water in jet fuel has been a significant area of research following several notable aircraft incidents [1][58][59]. One such scenario is the case of a British Airways Boeing 777-200ER engine that faced an un-commanded thrust as a result of ice blocking the face of the fuel-oil heat exchanger. Water in jet fuel is undesirable and may be hazardous because it can lead to corrosion problems, microbiological growth, and may precipitate out as ice [6][45][50][60]. These problems are significant and can increase aircraft operating/maintenance costs. However, water is always present and cannot be eliminated. Therefore, the water content should be kept to a minimal level [61]. Typically, a water-saturated fuel contains between 40 and 80 ppm dissolved water at ambient temperature (about 21 °C) [8].

Water may exist in fuel in the form of dissolved water, suspended/entrained water and free water [2][5][62][63][64][65]. This water may be introduced into fuel by various causes during fuel distribution, condensation, and equipment failure. However, the ability of a fuel to attract water vapour from the air depends largely on the chemical composition and temperature [66]. Carpenter et al. conducted research on how water behaves in aviation fuels at low temperatures [62]. In this work, Carpenter et al. explored three different model hydrocarbon types, including aromatics, alkanes, and cycloalkanes. Their results showed that on cooling to about -44 °C, visible ice crystals were formed in the aromatic model fuel. However, no ice crystals were observed in the model alkane and cycloalkane fuels, even at temperatures as low as -44 °C [62].

2.1.1 Water Solubility/Settling in Jet Fuel

It has been suggested by different authors that water solubility in jet fuel predominantly depends on the temperature and composition of the fuel [42][64][67][68]. When an aircraft is cruising at a high altitude, the fuel in the wing tank becomes cold, causing water to separate into a second phase. This has the appearance of a cloud or fog in the fuel [61][69][70]. As seen in figure 2, previous studies on this topic found that the solubility of water in hydrocarbons increases with an increase in temperature [61][62][63][66][69][70][71][42][72][67][68].

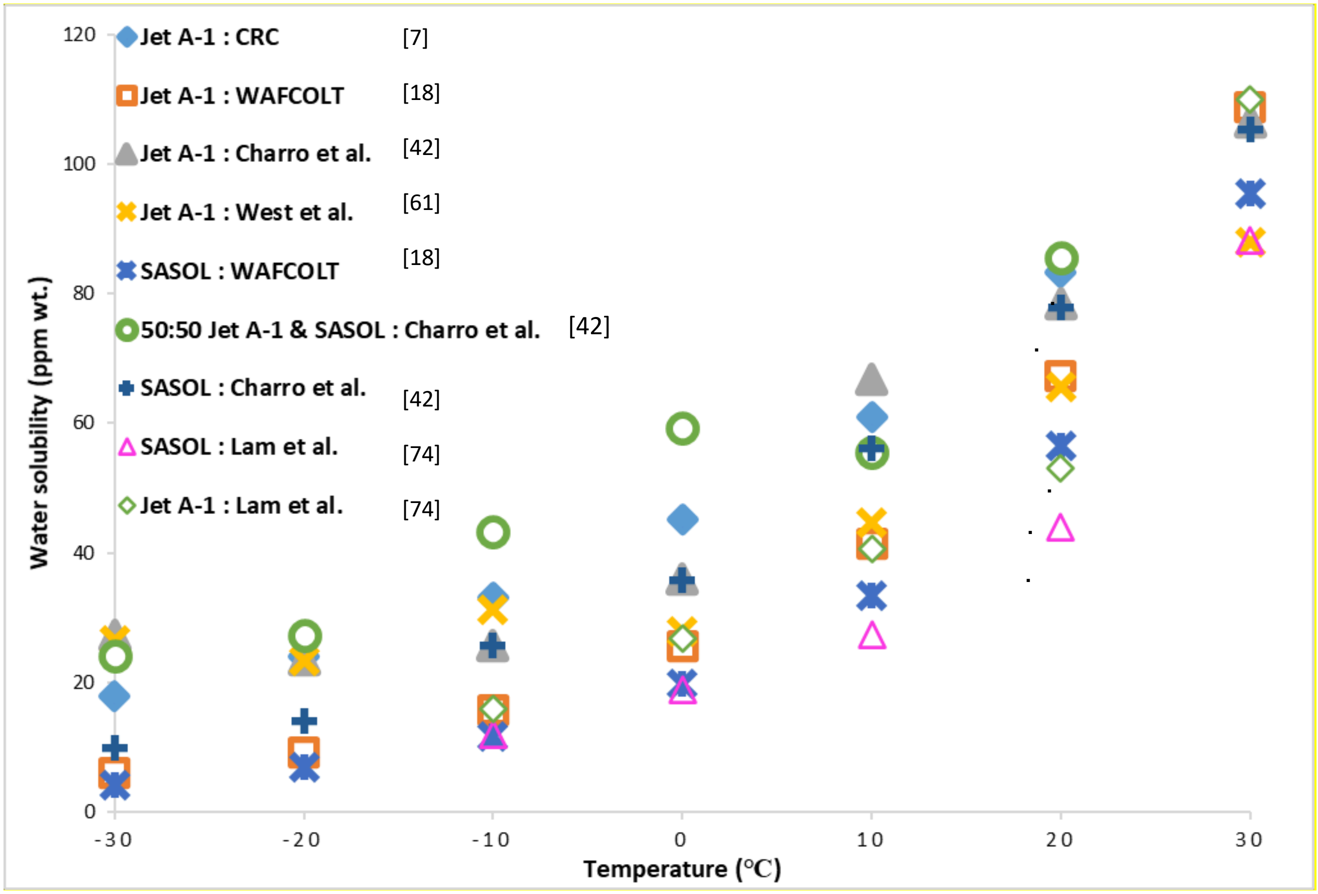


Figure 2. Compilation of results from the literature on the water solubility versus temperature profile for various jet fuels

An experiment analysing how the concentration of anti-icing agents, temperature and aromatic content will affect the water content of China No.3 jet fuel was conducted [73]. It was concluded that anti-icing agent has no effect on the water content of jet fuel; however, temperature and aromaticity play a key role in the fuel water solubility. From figure 3, it was demonstrated that pure aromatic fuels like toluene, as seen in figure 3, has a higher affinity for water and could contain seven times more dissolved water compared to fuels with similar carbon contents but containing only alkanes or cycloalkanes [62].

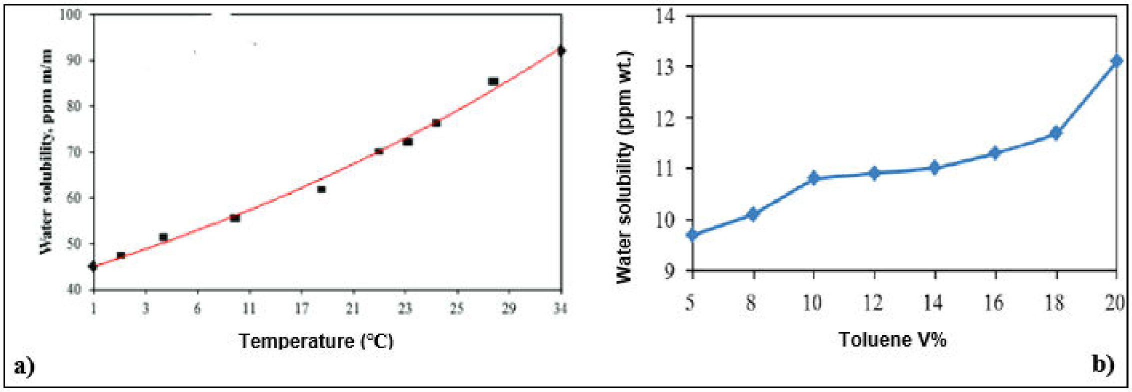


Figure 3. Effects of temperature/chemical composition on the water solubility of jet fuel showing; a) Water solubility increasing with an increase in temperature and b) an increase in aromatic content.

Another study by Carpenter et al. shows that as the aromatic content in the fuel increases, the water solubility increases. able of forming hydrogen bonds with water [66][74]. Lam et al. This is because aromatics have extended delocalised π electron clouds that are cap evaluated five different kerosene fuels and one wide-cut fuel at temperatures between -5 °C and 25 °C. The work conducted by Lam et al. proposed an exponential function that can predict the water solubility of fuels with a known flashpoint and aromatic content [74]. The results of the evaluation indicated that icing problems might be greatest in fuels with high aromatic contents as a result of their high affinity for water. The results from work by Lam et al. is in good agreement with work carried out by Marche et al., Wu et al., and Carpenter et al. that showed high aromatic content in jet fuel governing the increase in water solubility. For this reason, it can be concluded that the higher the amount of water that is likely to precipitate out of the solution, the more ice is likely to form. Furthermore, experiments that involved additives shows that it can play a key role in water uptake. For example, a study that explores the effects of static dissipator additive (SDA) suggested that it was likely to increase water uptake in fuels [75]. Also, according to Repetto et al., a fuel dehydrating icing inhibitor can help protect jet fuels against water contamination [76]. Repetto et al. proposed a dual-action strategy using a fuel-soluble water scavenger that mitigates against the effects of water crystallisation [76]. Although additives can play a key role in water uptake, the result of another experiment conducted by Carpenter et al. established this claim but noticed no significant difference in the water content in the presence or absence of the SDA [62].

Zherebtsov et al. carried out a study on naphthenic-based kerosene fuel and concluded that oxidation of jet fuel plays a key role in the solubility of water in fuels [77][78]. Goebel et al. suggested that an increase in water solubility could be attributed to the increase in natural surfactant-oxidation products, which in turn increases the number of polar molecules [77].

Marche et al. developed an apparatus that measures the mutual solubility of water and hydrocarbons for toluene and some alkyl cyclohexanes. Their results show that water solubility increases with the number of carbons in the alkyl cyclohexane and, as expected, an increase with temperature (ranging from 30 °C to 180 °C) [63]. The data reported by Marche et al. agrees with other literature published to date [63][64] [67]. Even though the composition of Jet fuel varies considerably, depending on the production process, parent source, or physical characterization, minimal data is available in the literature for synthetic jet fuels. An extensive assessment of the water solubility characteristics of six drop-ins/synthesised jet fuel blends was conducted by Charro et al. [42]. This study suggested that the water solubility of SAF/synthetic fuels behave differently from that of conventional jet fuels. A graph of water solubility ppm weight by weight (ppm w/w) versus temperature (°C) fits a polynomial trend for SAF/synthetic fuels, whereas conventional fuels fit an exponential trend. This effect is unphysical as it is unlikely to have a decrease in solubility at higher temperatures. Another drawback of the study carried out by Charro et al. was that the experiments were not replicated, and conclusions were drawn from a set of single experiments, therefore, are likely to not be physical [42]. Replicating the experiments for each temperature explored will provide a more precise judgment by either refuting or corroborating the trends from the experiment. A major comparative study by West et al. further analysed the water solubility trends with respect to temperature for thirty-six drop-in aviation fuel and model solvents samples (conventionally refined and synthetic aviation fuels) [61]. This work indicated that two out of thirty-six samples analysed had high water solubility because of their high aromatic content. Figure 4 shows the water solubility versus temperature graphs for two different sets of experiments conducted by West et al., and Charro et al., for comparison.

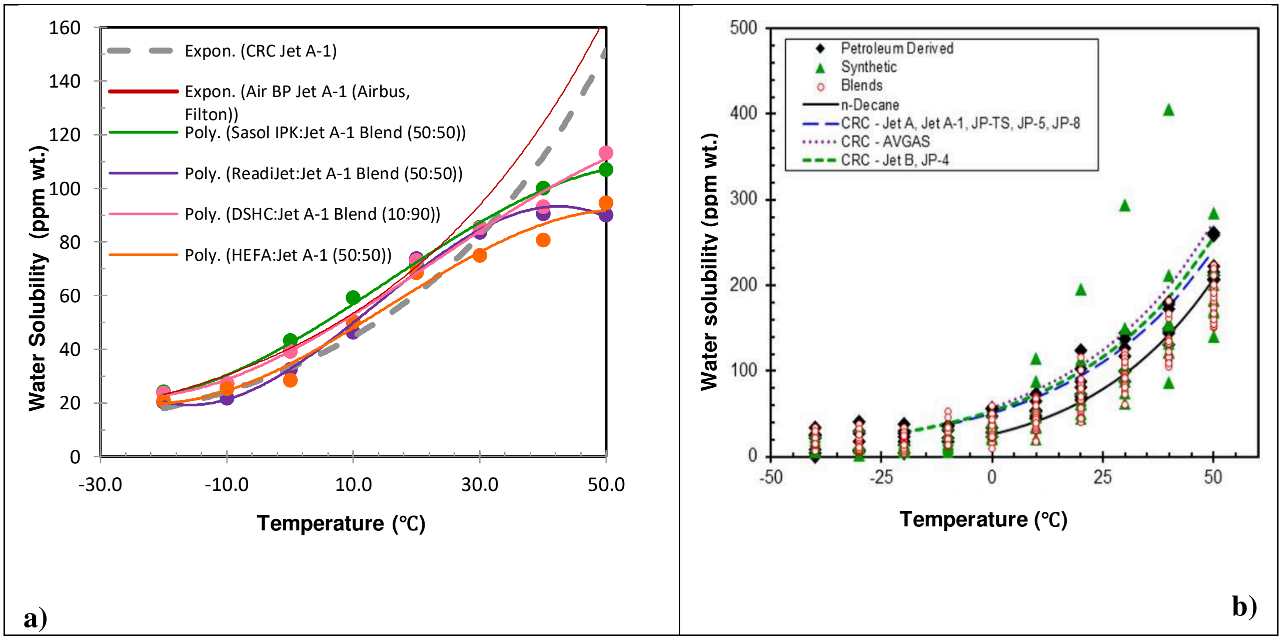


Figure 4. Graphs of water solubility vs temperature **4a.** results by Charro et al., fitting a polynomial trend for synthesised fuels, whereas conventional fuels fit an exponential trend (*replotted from raw data*) **4b.** result by West et al., fitting an exponential trend, and no form of limit was noticed above 30 °C [42][61].

From figure 4, the water solubility curve has been established as an exponential function by CRC; hence the decrease in solubility at high temperature in figure 4a deviates from the physical expectation. Water solubilities in alternative fuels in work reported by West et al. all fit an exponential trend as reported by CRC in figure 4a), and no form of limit was noticed above 30 ºC as reported by Charro et al. [42][61]. Even though both authors adopted the same approach of water introduction (equilibrium jacketed cell- achieving the saturation limit of water maintained at a 100% relative humidity vapour space in each test fluid), the trend observed by West et al. agrees with that observed by another group of authors Zherebtsov and Peganova as seen in figure 5 [71][61].

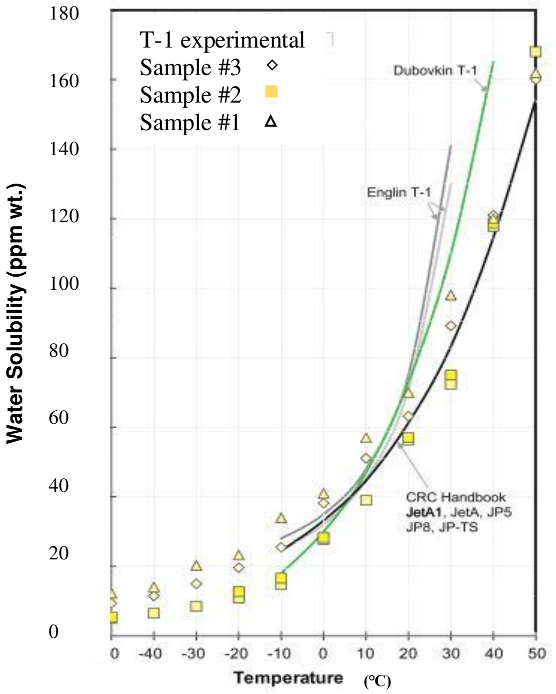


Figure 5. Graphs of water solubility vs temperature; result by Zherebtsov and Peganova showing that the water solubility data fits an exponential trend [71]

It is unsure if the difference observed by Charro et al. is as a result of the water content level used, fuel composition or merely because conclusions were drawn from the set of experiments conducted [42]. For this reason, it will be advantageous to replicate the set of experiments conducted by Charro et al. for result verification. Zherebtsov and Peganova experimented on water contamination in three different batches of Russian fuel TS-1. They reported that the linear regression for the logarithm of water solubility versus the inverse of temperature has different inclination, and this was attributed to the slight differences in fuel batches [71]. However, the reason for this discrepancy may be due to the experimental technique adopted by the authors. A note of caution is due here since all the authors used Karl Fischer analysis for the water content determination. In observational studies from the literature, there is still a potential for bias regarding the most widely used method for water content determination; several authors have also concluded that the Karl Fischer analysis is not a completely reliable technique [64[79][80][81]67]. Kang et al. showed that even after using a glove box for the Karl Fischer experiment, ambient moisture was still absorbed, limiting the accuracy and yielding high results [83]. Although the glove boxes are not hermetically sealed, the differences in results from work in this area cannot be ignored. Unfortunately, due to many of such differences, these findings are rather difficult to interpret. This explains the need to benchmark this procedure to see if there is any consistent offset to set a correction factor in place. This leads to the need to validate the trends observed by West et al., Zherebtsov et al. and Charro et al. This can simply be done by using a single experimental technique to explore the trends for conventional and synthesised fuels at different test conditions (e.g., different water content levels) with repeat tests.

The water settling rates in conventional and alternative fuels has been investigated by West et al. and Ugbeh et al. employing the Karl Fisher coulometer for water determination [61][84]. Whilst Ugbeh et al. focused on 1000 ppm by volume (ppmV) and a longer time interval. West et al. presented results for 10,000 ppmV, a relatively high concentration unlikely to represent an aircraft fuel system scenario. This concentration is not representative because, in a real scenario, water content must be kept within a tolerable limit, typically below 90 to 260 ppmV for normal and emergency system operations. Also, a fuel containing 10,000 ppm of water will likely appear cloudy and hence will probably fail the clear and bright test which is required before fuel can be used in an aircraft. Nonetheless, the results of both experiments followed a similar pattern, as shown in figure 6. It was concluded that the rate of free water settlement, assuming droplets are perfectly spherical, is a function of the droplet size in accordance with Stokes law (however, this is only true for perfectly spherical droplets) [61][84]. According to Ugbeh et al., the governing

Stokes law equation, as seen in equation one is mainly based on the size of a water droplet and the viscosity of the fuel. According to the author, water droplets will fall through jet fuel under the effect of gravity since water has a higher density than jet fuel.

$$\mathrm{v} = \frac{\mathrm{g} \cdot \mathrm{D}^2 (\rho_\mathrm{w} - \rho_\mathrm{f})}{18 \cdot \eta_\mathrm{f} \cdot \rho_\mathrm{f}} \text{ .... (equation1)}$$

Where:

ρ_w = density of water (kg/m^3)

ρ_f = density of fuel (kg/m^3)

g = acceleration due to gravity (m/s^2)

η_f = kinematic viscosity of the fuel (m^2/s)

V = terminal velocity of the water droplet (m)

D = Water droplet diameter (m)

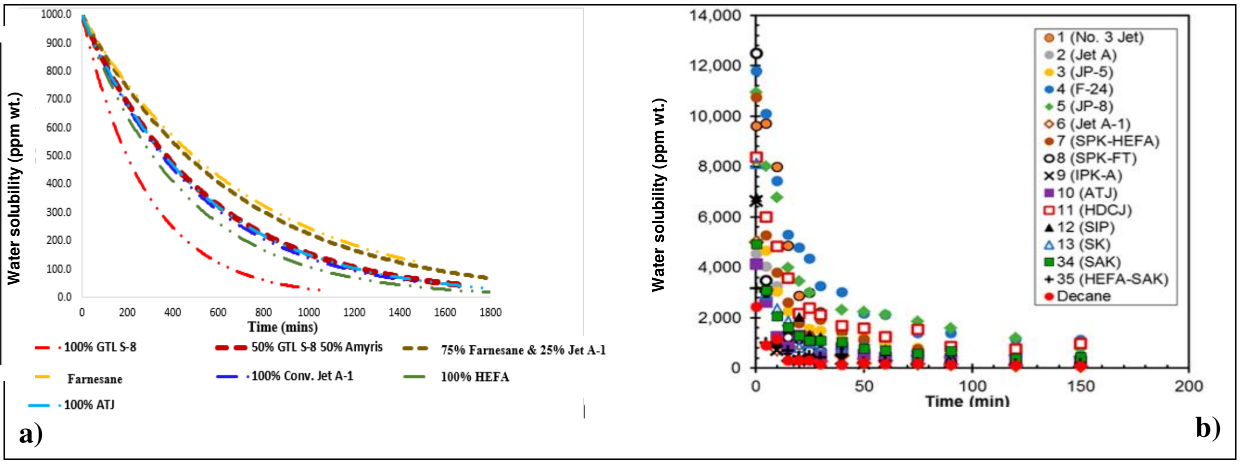


Figure 6. Average water settling rates for **6a.** 1,000 ppm [84] and **6b.** 10,000 ppm nominal water addition [61]

Literature has established that the water droplet in fuel is dependent on the form in which the water is present in the fuel. For example, dissolved water droplets are often regarded as a constituent of jet fuel as they are very tiny droplets that are naked to the eye [66]. Lam et al. reported suspended water droplets to be between 5 to 13 µm, with the latter dropping out as free water, whilst Clarke et al. reported free water droplet diameter to be within a range of 20 to 30 µm [18][5]. However, it is essential to note that sizes below 30 µm could negatively affect performance by impeding flow through filters and causing other safety issues [85][61].

2.1.1.2 Water Content Determination

Traditionally, water is detected by taking a fuel sample and looking to see if it is clear and bright. However, this method can detect only high-water concentrations and many operating conditions need to be considered, like the operators' interpretation, quality of vision and sunlight. Meanwhile, a clear and bright test (appearance test) is still considered the most basic test carried out to check for water in fuels. Additionally, different industries employ several techniques for the determination of water content in samples. There is many physical, drying, separation, radiochemical and chemical methods available [86][87][88]. Water is a significant contaminant in fuel, and this explains why water monitoring techniques must be accurate, repeatable, and reproducible so that any increase in water content can be rectified [89].

Water in fuel has been one of the significant issues facing the aviation industry [90]. Its presence can be potentially detrimental and lead to fatal consequences. It has been reiterated by several authors [66][83] that keeping the jet fuel free from water contamination is important, as its inclusion can negatively affect its performance. An overview of the methods for the determination of water content is tabulated in table 1.

Table 1 Overview of the available methods for the determination of water content

Method	Principle	Disadvantage	Measurement Range	Measurement Accuracy
Infrared & Halogen Drying	Uses direct infrared, halogen radiation and absorbed energy causes the heating of the sample	Water and some other volatile substances might vaporize	0.5-99%	0.1-0.5%
	Differential weighing	It might not be suitable for samples with a small amount of moisture		
Karl Fischer Titration	Involves the oxidation of Sulphur-di-oxide (SO_2) by iodine (I_2) in methanol.	Can form side reactions if the analyte contains species that interacts with the KFR		-
	Coulometric titration involves the electrochemical oxidation of iodide until it detects a trace of unreacted iodine	Variables can affect the end point (Temperature, lightening and atmospheric variations)		0.0001-1%
		Contamination of sample/syringe during introduction into the KF cell		
		Its PH sensitivity might		

		affect the endpoint. (Optimum PH value for water determination is between 5 & 8) Additional water might form if the PH does not fall within the range of accepted values. This can be attributed to side reactions as reactions tend to proceed at a faster or slower rate (Except the sample is buffered)		
Nuclear Magnetic Resonance Spectroscopy (NMR)	Measurement of the spin of a proton (hydrogen atom) determines the number of water nuclei in the sample.	Determines all nuclear properties of the H- atoms in the sample being analysd. Rather than the properties of the water molecule itself	0-15%	0.1%
IR- Infrared Spectroscopy	Irradiation of a sample with Infrared beam through an optical fibre transmitting energy at a particular wavelength (0.7 to 2.4 µm for water)	Variations in temperature can affect the result Band for water is not precise	1-80%	0.3-1%
Headspace	Involves the use of a high	Adsorption on the		

Gas Chromatography	polarity ionic liquid-based GC column and a pressurized loop headspace injection system. This technique is believed not to be affected by side reactions or other volatile constituents/contaminants	stationary phase is seen as poor peak shapes due to its consistent exposure to water. Therefore, producing unpredictable results On direct injection, volatile compounds tend to interfere with water peaks. This can lead to column deterioration.	0.1-1%	0.01%

Compiled from: [80][81][82][83][88][91][89][92][93][94].

2.1.1.2.1 Karl Fischer Analysis

Karl Fischer analysis is a method that helps to numerically measure the content of moisture in the matter, which is in the form of liquid or solid [86]. Karl Fischer analysis is an analytical method that involves an oxidation reaction where the iodine oxidises sulphur dioxide with consumption of water [93]. Volumetric and coulometric analyses are the two different Karl Fischer titration techniques employed to determine water content in a particular sample. The selection of a suitable approach depends on the measured water content required for sampling [92]. The volumetric Karl Fischer titration is ideal for samples where water is present as a major component (5 ppm to 100%) [93][95]. In contrast, coulometric analysis is suitable for trace water determination level, usually from 1 ppm to 5% [96]. These explains why the coulometric Karl Fischer titration is often employed for water content determination in jet fuels, as it contains typically 40 to 80 ppm of water at room temperature [8].

Karl Fisher reagent (KFR) usually contains sulphur dioxide and iodine [97]. The iodine is ionized, and due to the presence of this iodide ion, current flow begins [92]. Based on stoichiometry, the amount of water in a particular sample is equivalent to the amount of current flow or iodine used up. There will be no more usage of the current flow only when the entire water content in the sample has completely receded with the iodine. The coulometric Karl Fischer cell has two separate compartments known as the cathode and the anode. The anodic compartment is where the iodine is coulometrically generated, and based on stoichiometry, 1ml of iodine reacts with 1mol of water. Thus, the end point of the coulometric titration is determined as soon as the current detect unreacted iodine [98].

Various experimentalists using the Karl Fischer method have determined water content in fuels. However, a group of authors revealed that the Karl Fischer analysis method was not as effective as the thermometric titration method [99]. According to this author, the thermometric titration method provides more accuracy, rapidity, automation, convenience and applicability [99]. Another group of authors suggested the thermometric titration method be divided into two different groups [100]. The authors suggested water content be determined by using Karl Fischer analysis firstly and secondly by the exothermic heat of reaction measuring temperature pulse caused by the reaction of water and the KFR using a thermistor Wheatstone bridge system [100]. The total amount of water capable of reacting with the KFR represents the temperature increment.

Thermometric titration is an analytical method that measures the content of a particular substance because of an enthalpy change [101]. In this method, the titrant is added continuously into the reactant. The maximum temperature reached signifies the endpoint of the titration. In other work, the water content is based on an endothermic reaction between the titrant and the water [99].

A method of water content determination that a group of scientists claim is more sensitive, rapid, and convenient than the use of the coulometric Karl Fischer titration is the F-NMR with a combination of reagents like anhydrous fluoride salts (like tetrabutylammonium fluoride (TBAF) and iodobenzene diacetate ($PhI(OAc)_2$) [89]. The authors stated that handling errors were larger in the Karl Fischer analysis than that in the F-NMR because the sample preparation for the NMR method could be done in a glovebox [89].

2.1.1.2.2 Limitations to Accuracy for Use If Karl Fischer

As depicted in table 1, using Karl Fisher Coulometer creates hurdles in the evaluation of water content because some samples undergo side reactions, and acidic samples can influence the pH value during the water content determination. The presence of sulfur can lead to the acidity of jet fuels [102]. In the same way, variables can affect the endpoint (temperature, sunlight and humidity variations). Also, possible contamination of sample/syringe during introduction into the KF cell can affect the result. The limitation to the accuracy of using the KF cell was elaborated in table 1.

2.1.2 Complexities Associated with Water in Jet Fuel at High Altitude

Aircraft are equipped with vents that allow air into the tank and allow for changes in atmospheric temperature and pressure [68][103]. This explains why factors like relative humidity, temperature and altitude are considered in the level of water gain/loss in aviation fuels. It has been hypothesised by Goertz et al. that temperature influences the formation of ice in hydrocarbon fuel like diesel [104]. Similarly, a study on the morphogenesis of ice by Libbrecht et al. shows that temperature and supersaturation (humidity) influences ice growth [105]. The research by Libberrecht et al. reviewed earlier studies on ice growth and concluded that ice grows into different shapes and sizes. Therefore, this shows that the appearance, shape and morphology of the ice that is likely to form in fuel sensitively depends on the level of supersaturation and temperature of the fuel. This theorem can also be related to work carried out by the AAIB that indicated the ice sticky range temperature to be between -10 ºC to -20 ºC.

According to the Coordinating Research Council (CRC) handbook for aviation fuels, extensive studies conducted by both Boeing and Bristol in the 1950s showed that fuel tank temperatures could reduce to -40 °C when cruising at a low speed after about 4 hours while the tank temperature drops to -29 °C at a speed of Mach 0.82 [7]. The conclusion from these studies suggested that fuels with a maximum freezing point of -50 °C would be beneficial for civil aviation purposes to manage risks of wax formation. At such low temperatures, it should be noted that fuel viscosity will also increase, promoting entrainment of the wax and free water crystals formed, perpetuating hazards of filter blockage and engine fuel starvation. As discussed, work to investigate the behaviour of water in jet fuel has been done; however, it has been mainly based on conventionally refined fuel, and very few SAF and synthetic aviation fuels have been tested. Several authors also reported that the CRC handbook for aviation fuels contains data for only petroleum-derived fuel [7][42][106].

Carpenter et al. experimented on the behaviour of water uptake in three batches of jet fuels and model hydrocarbons at temperatures above -60 ºC [62]. The fast/slow heating and cooling method of testing was employed for the analysis, and from the result of the analysis, there was no evidence of ice crystals even at −44 ºC for some of the fuels explored [62]. This disagrees with other reports that supercooled tiny water droplets (≥50 µm) freeze homogenously in fuel at temperatures between -32 ºC to -44 ºC [107][108]. However, the results of all these experiments were obtained through laboratory-based experiments only. According to Tascón et al., ‘even though experimental results are in good agreement with simulation results, simulations can help to easily perform an in-depth and a ''what if'' analysis that is unexpected and beyond limits of applicability [109]. Also, a recent study by Fitzner et al. suggested that although computational efficiency has some limitations, it can help conceive a large breadth of study with sufficient data diversity [110]. Consequently, it is highly recommended that due to the complexity of this analysis, an advanced and reliable data analytics computer-based tool capable of capturing fuel-related effects be employed for future work to accurately reflect the randomness and interdependence present in real-world systems.

Research is currently ongoing by the jet fuel screening and optimisation platform (JETSCREEN) design tool that is capable of predicting jet fuel properties using a machine-learning algorithm "Gaussian process regressor'' (GauProReg) [111][112]. So far, the result from the work has suggested that the GauProReg is probably fit for predicting traditional jet fuel properties but lacks clarity for new fuels with unfamiliar compositions. It is recommended that the future models from this work be tested and validated on experimental measurements. Additionally, it is essential to note that fuel/air temperature will vary depending on weather conditions [66]. The effectiveness of the experiment related to the water in jet fuel mentioned by Zherebtsov and Peganova argued that the relationship between water solubility and temperature behaves differently at temperatures below and above 0 °C [71]. Zherebtsov and Peganova attributed this to discontinuous and continuous change in enthalpy and entropy during the phase separation of water/ice. A discontinuity in the water solubility line is possible if there is a discontinuity in entropy during the transition through 0 °C. Several authors suggested that at higher altitudes as aircraft meets lower pressure (extreme cold conditions), the fuel in the aircraft wing tanks becomes cold [113][108]; this decrease in temperature is likely to decrease fuel water solubility.

Lao et al. explored the behaviour of water in a simulated fuel tank. The result of the analysis found that water solubility in the fuel decreases as the temperature decreases, thereby leading to a fog regime (dissolved water that appears in the form of a cloud of fine water droplets) [114]. Lao et al. further revealed that at temperatures below -10 ºC, a hexagonal type of ice crystal would form in areas with sharp surfaces like edges growing at the expense of ice of the cubic of ice crystal [62][114][115]. The lowest temperature simulated by Lao et al. was -17.3 ºC. In a comparative study by West et al., conditions that more closely replicate actual aircraft system operation (temperature of -47 °C) were simulated. However, the study concentrated on the quantification of equilibrium partitioning of fuel system icing inhibitor (FSII) [116]. Furthermore, from work carried out by the AAIB, a fuel temperature of -35 ºC was estimated with water content between 35 and 40 ppm [1]. However, the results experienced were unusual. From this study, it was observed that the rate of ice accumulation increased in the critical icing temperature (-5 ºC to -20 ºC) and reduced as soon as the temperature dropped from -20 ºC to -34 ºC. This suggests the need to run experiments that will involve exploring from sub-zero temperatures to ambient temperatures and vice versa whilst varying the added water content level. The trends from the result of this analysis will give a better understanding of the growth of ice in aviation fuel. Lam et al. took a step further by studying the ice growth in jet fuels [106]. From this work, some hexagonal ice crystals were observed. However, it was noticed that the larger ice crystals tend to grow at the expense of metastable ice particles near them. This is similar to results obtained from more recent studies by Moon et al. that metastable ice crystals helps with growth of hexagonal type if ice crystals [9]. Moon et al. further classified shapes of ice crystals obtained in a fluid static condition into three different types (plate/spherical shapes, columnar shapes, and irregular shapes) [9].

A study conducted by the AAIB observed that ice crystals tend to stick to surface surroundings and other ice crystals near them at the critical icing temperature (also called the ‘sticky’ range) between -5 ºC and -20 ºC [1]. This scenario can be attributed to the Ostwald ripening process [67]. Jiao et al. further explain that the rate of the ripening process can differ depending on the composition of the fuel/nature of surfactant present [117]- [118][119]. The uncertainty as to how water behaves in jet fuel is still a challenge faced by the aviation industry to date. Several authors state that water will remain in its supercooled state and will not form ice even below its freezing point as long as it is a homogenous mixture [108][113][120]. Furthermore, freezing occurs in the presence of particulates for a heterogeneous mixture [121].

Soria et al., emphasised that ice formation in jet fuel is an important issue that cannot be overlooked as it is capable of leading to fatal consequences [122]. Thus, it is rather difficult to determine the severity of atmospheric temperature so that excessive formation of ice, and its accumulation could be prevented. Campbell et al. argued that researchers must have sufficient information on the chemical compositions of jet fuel. However, due to its complexity, it is difficult to develop a theory about the behaviour of ice in fuel [123]. To date, the behaviour of ice has been studied through different angles, whereas no study in the literature has provided a complete description of all the factors that influence the behaviour of ice in jet fuels. Table 2 summarises some key information discussed in this section.

Table 2 Summary of key elements discussed in section 2: Water in Jet Fuel

Topic	Analysis/Comment	References
Water Solubility	Depends on the temperature and composition of the fuel - water solubility decreases with a decrease in temperature	[63][64][71][42][67][68][114]
	An increase in water solubility could be attributed to an increase in natural surfactant-oxidation products	[77]

Fuel Aromaticity	The higher the aromatic content, the higher the water solubility and dissolved water concentration	[18][61][62][66][74][73]
	Lack of aromatics yield fuels that is below minimum density and can also lead to shrinkage of elastomers; however, when in excess, can lead to swelling of the elastomers, more soot production as a result of incomplete combustion and so must be restricted	[36]
Water Shedding	The rate of free water settling is a function of the water droplet size following Stokes law	[7][61][84]
Surfactants	An increase in water solubility could be attributed to an increase in natural surfactant	[77][78]
	Ostwald ripening rate reduces with increasing	[117][119][124]

	surfactant concentration	
	Surfactants can reduce water droplet size and consequently, reduce its settling velocity	[12][124]
Additives	Anti-icing agents: Water content may increase with an increase in the concentration of anti-icing agents	[73]
	Static dissipator additive is likely to increase water uptake	[62][75]
Homogenous Mixture	Water may remain in its liquid state even below its freezing point	[107][108][113][120]
Heterogeneous Mixture	At cold temperatures, freezing occurs in the presence of particulates	[107][121]
Karl Fisher Analysis (KFA)	As with all measurement techniques, a consensus has it that the limit to the accuracy	[64][79][80][81]

	of using the KFA is the tendency of forming side reactions

2.2 Ice and its Behaviour in Jet Fuel

Gibbs free energy (energy associated with a chemical reaction that is available to do useful work) must be overcome for ice to be formed from water. Hence nucleation is simply the birth of a new thermodynamic phase (crystal in this case) [125][126]. Water content, droplet size, surface type and ambient conditions have been identified as having an influence on the process of ice formation in jet fuel [48]. One of the most important factors impacting the ice formation in jet fuel is the presence of supercooled water droplets [127]. According to Schmitz et al., ice formation is a result of fine water droplets that have precipitated out and solidified into ice crystals [10]. Also, Baena et al. state that the ratio or extent of supercooled water droplets influences the rate of accretion or growth of the ice [3]. Furthermore, the accretion of ice on a subcooled surface that is immersed in fuels was examined by Lam et al. [18]. The strength of the accreted ice was evaluated, and it was deduced that the amount of ice accretion (which is a process in which a film of ice forms/builds up on a solid surface exposed to freezing precipitation) increased as the subcooled surface temperature was lowered [18]. Similarly, previous work conducted by Baena et al. suggests that low temperature dispersed water can lead to ice crystals within the aircraft fuel systems [2]. The results of the experiment conducted show that the amount of ice accretion increases with higher cooling rates.

Analysis of the formation of ice in fuels contaminated with particulates was conducted by Murray et al. [107]. From their experiments, it was observed that ice is more likely to form when the fuel is contaminated with particulates. Water tends to remain in its supercooled liquid state as long as there is no contact with any particulates until it gets to its homogenous freezing point of about -36 ºC [107]. However, particulates are always present in jet fuel, so an ideal situation is impossible. Lam et al. carried out an experimental study on ice growth in fuels; a visual representation can be seen in figure 7 [18]. In this study, they observed that ice formed homogenously and was detected between -32 ºC and -36 ºC, which compares well with the temperature of -36 ºC that has been observed by Murray et al. as the homogenous freezing point [107][113].

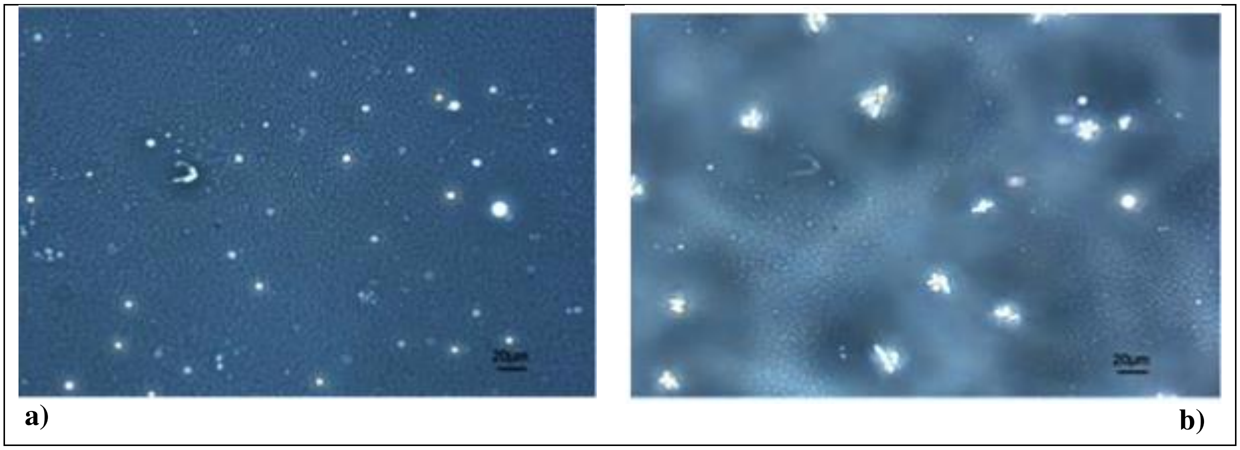


Figure 7. Water droplet formation from jet A-1 fuel with dissolved water **7a.** on cooling down to -3.8 ºC **7b.** Ice crystals are seen on holding the temperature of the fuel at -34 ºC [18]

In addition to that, several authors have acknowledged that that ice nucleation rates are size-dependent [128]. supercooled water droplet with sizes greater than or equal to 5 µm can induce the accretion of ice [15][18][127][129][130]. At temperatures below 0 ºC, water droplets can exist in a supercooled metastable state depending on its size [90]. Other authors carried out experiments using micro and nanometre-size droplets to investigate ice nucleation [131][132]. It was concluded from one of the studies by Laksmono et al. on micrometer-sized (microsize) water droplets that there is a slower nucleation rate increase as the temperature decreases. The authors also observed that microsize droplets (between 3−12 µm diameter) do not form ice crystals at temperatures below -41 ºC [132]. Baena et al. took a step further to analyse the effects of these ice crystals on a mesh strainer [3]. They designed a test rig, and experiments were conducted at -12 °C and -15 ° C. From the experiments, it was concluded that both the amount of water in fuel and temperature of the fuel play vital roles in the thickness of ice layers on mesh strainers. They concluded that the amount of ice accretion in the fuel is related to the quantity of water in the fuel. A summary table of ice in jet fuel is shown in table 3.

Table 3 Ice in Jet fuel Summary Table

Topic	Analysis/Comment	References
Ice Nucleation	The contact angle is an essential factor that governs ice nucleation	[12]
	Gibbs free energy has to be overcome for ice (the critical nucleus) to form from the liquid	[125][126] [132]
Ice Accretion	The amount of ice accretion increases with a decrease in temperature (until it reaches the critical icing temperature between -5 °C to -20 °C) and an increase in nucleation sites.	[10][12][18][2]

	Size of supercooled water droplets greater than or equal to 5 µm can induce the accretion of ice	[15][18][127][129][130]
	Ice accretion is dependent on the amount of water in the fuel and the temperature of the fuel	[125]
	Fuel flow rates of between 0.2 and 0.6 m/s favour ice accretion	[1]
	Ice accumulation can be quantified by differential pressure measurements that occur as a result of fuel flow restriction	[12]
Sticky Range	Ice crystals tend to adhere to surface surroundings and other ice crystals near them	[1][81]

Additives	According to Zabarnick et al., cold flow improving additives: Alters the ice crystal structure/size in jet fuel at low temperature	[133]
	A strategy that involved the use of fuel dehydrating icing inhibitor (FDII) alongside a fuel-soluble water scavenger to aid in protecting jet fuel against the effects of water contamination was predicted by Repetto et al	[76][134]
	Although di-ethylene glycol monomethyl ether aids in preventing water solidification at low temperatures, it is less efficient than FDII when used	[76]

	in low concentrations	
Ice Adhesion	Ice adhesion strength increases with an increase in the hydrophobicity of the surface	[12][135][16][136][137]
	Ice adhesion depends on the nature of the surface	[14][15][135][138][16][139][140][141]
	Key parameters affecting ice adhesion are temperature and roughness of a surface	[16][137]
Nature of Ice	Soft, fluffy and snowflake-like ice with high porosity and little adhesion strength (Ice formed from dissolved water)	[10][11][12][1][62]
	Hard ice with more adhesion strength (Ice formed from free	[12]

	water)	
	Crystalline, spherical ice particles of cubic and hexagonal habit (Ice formed from dissolved water)	[18][107][114]
High Altitudes	A decrease in temperature is likely to decrease water solubility	[113][108][105]

3. Effect of Material/ Surfaces on Nucleation of Ice

Aluminium is the most widely used material in the aviation industry, from the fuselage to main engine components, however, just like other metals, it is susceptible to corrosion under adverse conditions and biofilm contamination in the presence of microbial growths [114][142][143]. Figure 8 shows the trend of ice growth with time on an aluminium surface blasted with glass beads on cooling from 0 ºC to -18 ºC [10]. Schmitz et al. evaluated the effect of surface roughness and surface types on ice accretion in flowing fuel to help gain a better understanding of the ice accretion process in flowing fuel. As seen from the result in figure 8, the ice thickness increases steadily with time [10].

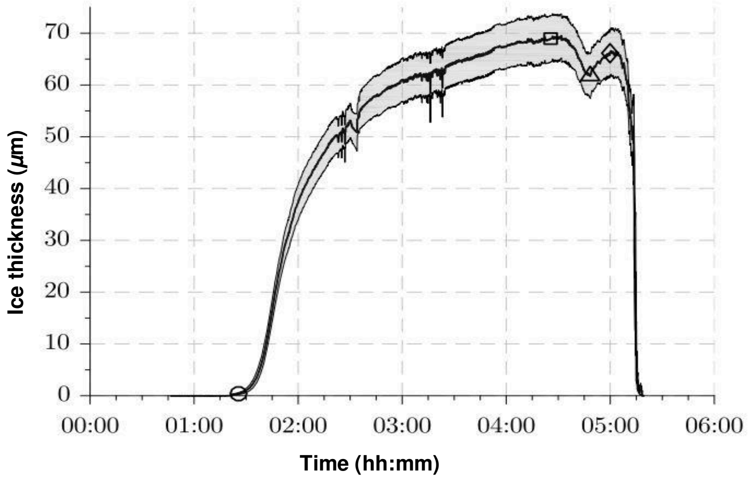


Figure 8. The trend of average ice thickness on an aluminium surface blasted with glass beads against time on cooling from 0 ºC to -18 ºC Reproduced from Schmitz et al. [10]

The dip seen at time 04:26 in figure 8 is due to the gradual increase of the volume flow rate by the authors Schmitz et al., thereby making part of the accreted ice shed off then reducing its thickness.

The effect of wettability (a measure of the water contact angle and sliding angle) and roughness on hydrophobic, hydrophilic, and superhydrophobic surfaces has been explored by Bharathidasan et al. [135]. This work deduced that silicone-based hydrophobic surfaces manifested an ice adhesion strength that is approximately forty-three times lower than the adhesion strength of bare aluminium alloy [135]. This was followed up in 2018 by Zhang et al. fabricating a superhydrophobic surface (with a water contact angle >150 °) on an aluminium surface to enhance its application [14]. Figure 9 compares the result of experiments conducted by several authors on this topic.

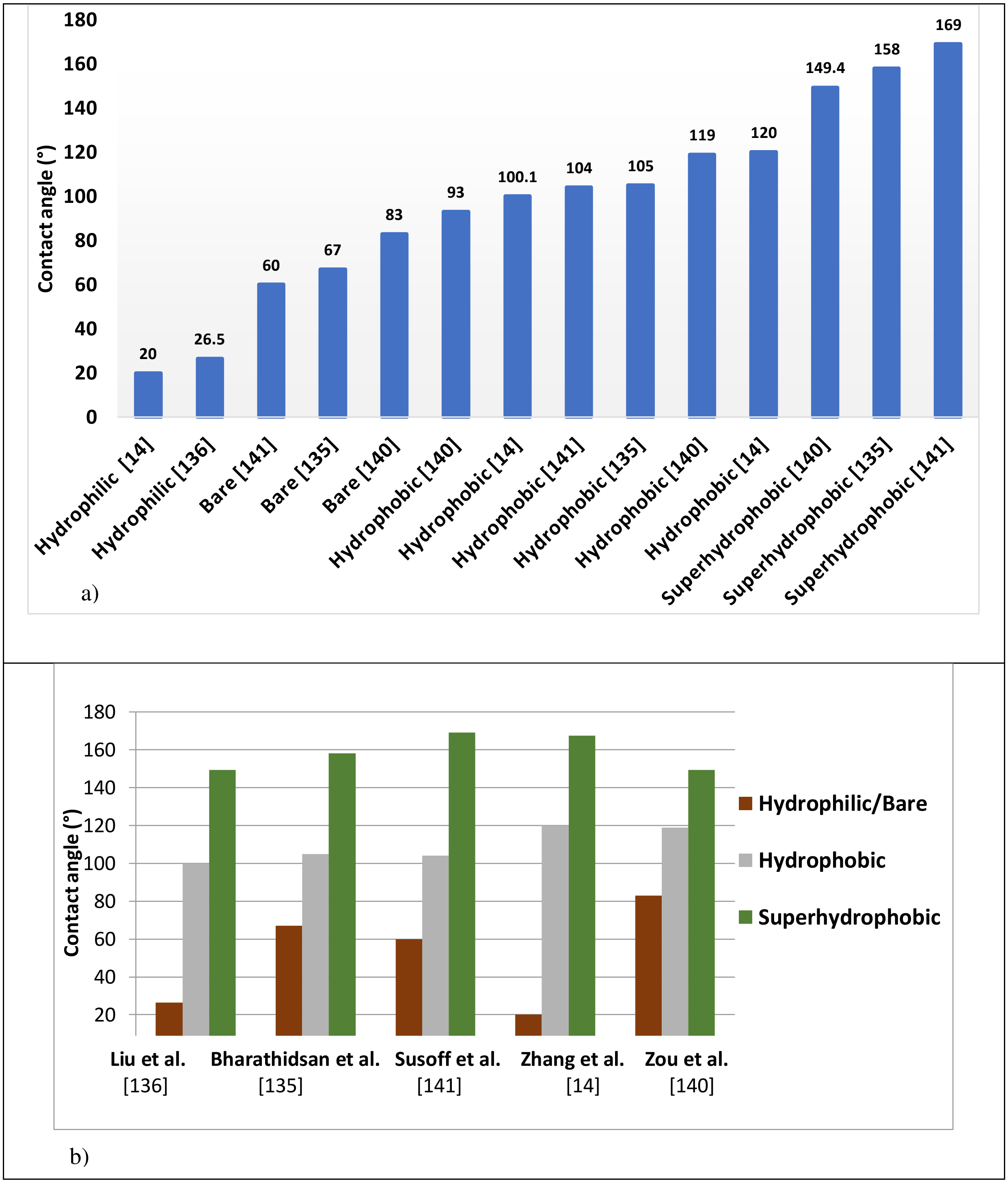
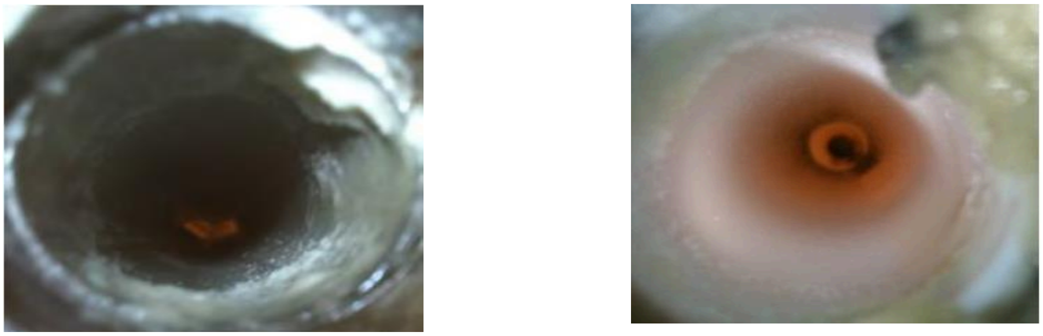


Figure 9a. Column chart showing the effect of surface wettability on contact angles **9b.** Comparative compilation of data from the literature, showing the effect of surfaces on

the nature of ice formed

Figure 9 shows the impact of a surface's wettability on the contact angle; the contact angle between a hydrophobic surface and ice crystals, formed in-situ, is larger than the contact angle for ice crystals that grow on hydrophilic surfaces. Table 3 summarises the different substrates evaluated in reported contact angle experiments.

The nature and morphology of ice can be very dynamic [144][105]. Experiments on the behaviour of interfacial shear strength of accreted ice on subcooled surfaces immersed in jet fuels showed the accreted ice formed to be soft and fluffy [11][114][145]. No differences in adhesive strength were noted between the ice deposits formed on three different surface materials (aluminium, painted aluminium and carbon fibre) that were explored by Lam et al. [11]. On the other hand, a study carried out by Maloney et al. showed that a given material surface is not only influenced by the size and quantity of supercooled water droplets but it is also affected by the flow rate, Reynolds number (A dimensionless quantity that is a function of the flow velocity, pipe diameter and fluid viscosity), quality and nature of the material used [12][85]. Maloney et al. explained that stainless steel accumulated more ice than roughened aluminium and Teflon, as seen in figure 10 [12]. Similarly, a recent study by Airbus on the ice accretion/release test in a large scale flowing fuel system indicated the non-uniformity of ice thickness and porosity and suggested that it is a result of water injection/mixing method [146]. Therefore, it can be concluded that the variation in reported data throughout the literature can be attributed to different testing conditions and experimental techniques.



Stainless steel (Reynolds number = 5975)

Teflon (Reynolds number = 2024)

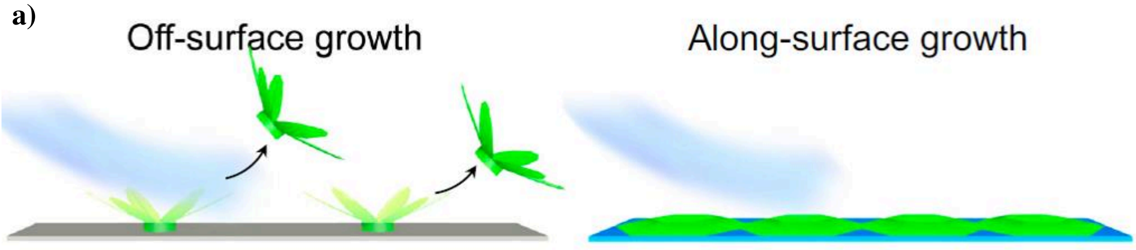
Scratched aluminum Reynolds number = 5975

Stainless steel (Reynolds number = 2024)

Figure 10. Pipe configuration variations showing that stainless steel accumulates more ice than scratched aluminium [12]

Maloney et al. assessed the ice accumulation along the test pipes by employing detachable test pipe sections for easy examination and measuring the pressure drop across the pipes [12][85]. As shown in figure 10, the layer of ice accumulation decreases with an increase in Reynolds number and an increase in hydrophobicity. In this line, a study by Cox et al. stated that an efficient nucleating agent should not bind water too strongly, while a strongly adsorbing surface is detrimental to ice nucleation as a result of a higher water coverage [108]. Experiments conducted on different surfaces (silicon, mica, and glass) showed that water drops freeze near the homogeneous temperature limit. This homogenous temperature limit was said to be unaffected by roughening the surface with diamond powders of different size distribution [123]. This is further supported by Elliott et al., emphasising that the growth of ice on surfaces solely depends on the hydrophobic or hydrophilic nature of the surface [15]. Additionally, an earlier study conducted by Antonini et al. suggested that alongside a de-icing strategy, a hydrophobic/superhydrophobic coating strategy should also be implemented for anti-icing systems [13]. Fitzner suggested that ice crystals are birthed from the mobility of water molecules adopting their lattice position [147]. Then, Thompson et al. postulated that fuel tank systems coated with hydrophobic substances reduce the size of water droplets and simultaneously increase the migration speed of the water droplets to the sump once in motion [148]. This system might help manage how ice forms or accumulates in aircraft fuel tank systems because the amount of ice accretion is related to the quantity of water in the fuel, as stated in section 2.3 [3].

A relationship between ice adhesion and surface roughness has been recently developed [14][135][138][16][139][140][141]. Elliott et al. explored a liquid droplet's behaviour on rough/smooth surfaces, and the results showed that the roughness of a surface influences ice formation [15]. Elliott et al. stated that the reason for this rapid liquid adhesion on a rough solid surface is the number of potential nucleation sites for bonding [15]. This is because the rough surface has stronger surface energy than the surface tension of water; therefore, the surface energy will overpower the surface tension of water, leading to a lower contact angle. Hence, roughness increases the probability of interaction between water droplets and the surface, therefore leading to a faster rate of nucleation. Susoff et al. screened different coatings and the influence roughness has on the surfaces; they observed that surface roughness increases the ice adhesion strength and [93]. Also, Zou et al. investigated the effects of surface roughness on the ice adhesion strength and found that a decrease in the ice adhesion strength on surfaces with similar roughness was related to the water contact angle [140]. A comprehensive study by Work et al. compared data in the literature and concluded that the key parameters affecting ice adhesion to a solid substrate are temperature and roughness [16][149][150]. A nearly linear increase in adhesion strength with decreasing temperature from 0 to -20 was noticed. Other studies by Liu et al. and Alizadeh et al. illustrated that water-repelling surfaces ease the removal of ice [136][137]. Ice crystals appear to grow at right angles on a hydrophobic surface and grow across a hydrophilic surface, as seen in Figure 11. The important questions are: is it better to have a multitude of ice crystals floating in the fuel tank? Or a large thickness of ice in the wall of the fuel tank? This is difficult to measure because either scenario can potentially have safety implications. For example, ice might not accumulate in the fuel tank but will adhere to the inner walls of the aircraft fuel distribution pipework. The second scenario is that the multitude of ice crystal could form a big snowball and potentially block the fuel distribution pipework. These questions will need to be answered as the ice crystals from both scenarios can potentially block the fuel distribution pipework. The reason for this, as per the first scenario, is that the large thickness of ice that adheres to the inner walls might eventually slide (where there is a slight increase in temperature) and still lead to potential blockage. To answer these questions, experiments must be conducted in a simulated aircraft wing tank comparing the behaviour of ice when the pipe's inner walls are made of a superhydrophobic or hydrophilic material.



b)

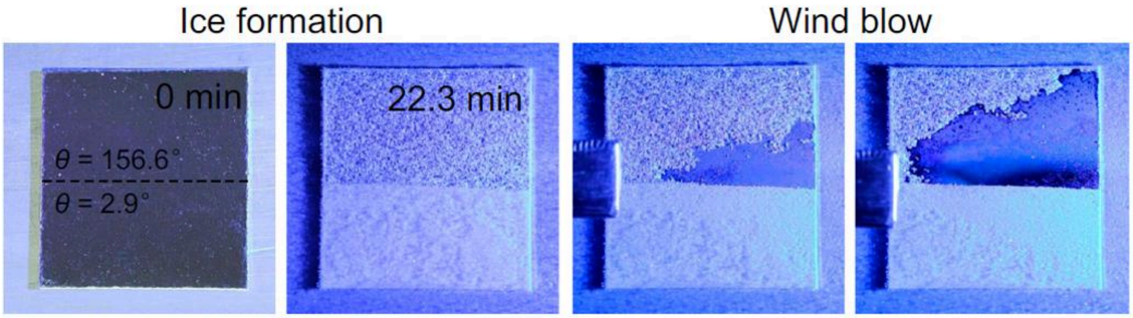


Figure 11a. Schematic showing that off-surface Ice growth (OSG) does not adhere firmly to the surface and can be dislodged easily. Along-surface ice growth (ASG) remains bonded to the surface; therefore, it cannot be displaced readily by fluid flow. **11b.** Test panels cooled to −20.2 °C prepared with adjacent coatings; with a water-repelling surface (of high contact angle of 156.6°) and water-loving surface (low contact angle of 2.9°) to illustrate that water-repelling surfaces ease the removal of ice after blowing with a gush of wind. Surfaces [94].

Zhang et al. took a step further to analyse supercooled droplets of water on different superhydrophobic surfaces [14]. They suggested that at a high/low speed, smooth superhydrophobic surfaces with microscale and nanoscale roughness repel supercooled water droplets better than a rough superhydrophobic surface [14]. Mohammed et al., Zhang et al., and Chan et al. supported this work amongst many other authors that emphasised that superhydrophobic surfaces show high water repellence with both rough and smooth surfaces [14][135][138][148][151][152][153]. Also, a superhydrophobic surface tends to have a remarkable ice-phobicity (the high repellence ability of a solid surface), but its repellence on a rough surface can be controversial [14][120][150][153]. In comparison, a hydrophobic surface can repel impacting water droplets before ice nucleation occurs, but superhydrophobic surfaces were found effective in preventing ice formation instead of fighting its build-up [14][152].

Findings from different studies in the literature also reveal in Table 4 that surfaces will have an important role to play in the growth pattern of ice in aircraft fuel systems; it is not yet known if having a multitude of ice crystals floating is better than having a large thickness of ice in the wall of the fuel tank. Yet, no work has been carried out to evaluate the effect of surface types on ice accretion in synthetic aviation fuels for the basis of comparison with conventional jet fuel.

Table 4 Summary of Substrates Explored in the literature for Contact angle between ice crystals and different substrates

Author	Surface	Substrate	Contact Angle Θ
Liu et al. 2017 [136]	Hydrophilic Surface	Aluminum Surface	26.5° ± 1.2°
	Hydrophobic Surface	1H,1H,2H,2H-Perfluoromethyldecyltrimethoxysilane	100.1° ± 1.0°
Zhang et al. 2018 [14]	Super-hydrophobic Surface	Nano Silicon	149.4° ± 1.2°
		P_4S_3[a]	156.8° ± 1.6°
		SHS-Al[b]	167.4° ± 1.4°

Bharathidsan et al. 2014 [135]	Hydrophilic	Bare Aluminum Alloy	67.0° ± 2°
	Hydrophobic	RTV 11[c]	105° ± 1.5°
	Super-hydrophobic	RTV11-EH5[d]	158°
Upadhyay et al. [154]	Amphiphilic	Amphiphilic siloxane polyurethane (AmSiPU) coatings	90 - 110°
Susoff et al. [141]	Super-hydrophobic	Sol-gel fluorinated Aerosil,	169◦
	Hydrophilic	Sol-Gel PEG	10-60
	Hydrophobic	Siloxane modified polysiloxane	104◦

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a. Phosphorus sesquisulfide; superhydrophobic surfaces with micrometre-scale and submillimetre-scale posts fabricated on the solid surface using photolithography and etching of inductively coupled plasma on silicon surfaces.

b. Super-hydrophobic coating sprayed uniformly on an Aluminum surface (multi-surface aerosol, Rust-oleum Corporation).

c. RTV 11- Vulcanised silicone rubber hydrophobic coating (Cured at room temperature).

d. RTV11-EH5- a mixture of RTV 11 and toluene with ultrasonically dispersed cabosil EH5 and silica resin.

4. Conceptual problems and knowledge gaps identified from the literature

Many problems have been identified in the literature. With authors adopting different experimental techniques and conditions for testing, there exist some prominent methods that have emerged as favourites. One of which is the use of the Karl Fischer analysis, which is the most widely used method for water content determination. The second will be the water introduction method that involves adopting an equilibrium jacketed cell to achieve the saturation limit of water maintained at a 100% relative humidity vapour space in a test fluid. A classic example is an investigation of water solubility in jet fuels by three different authors [42][71][61]. Even though all three authors adopted the same water introduction and water analysis method, the trend observed by West et al. agrees only with that observed by Zherebtsov and Peganova [71][61]. It is unsure if the difference observed by Charro et al. is because conclusions were drawn merely from a set of single experiments or as a result of the experimental technique adopted by the authors**.** Although it is not possible to make a direct comparison as a result of the large number of variables that may exist, it may be possible that replicating the experiments for each temperature explored by Charro et al. will provide a more precise judgment by either refuting or corroborating the trends observed from the experiment [42]. Bias trends in the data could also be as a result of the water content determination test employed. Therefore, it is recommended that authors provide raw data as part of the supplementary information rather than just graphical plots with fitted curves. Curve fits can be obscure as the integrity of the result is usually unknown.

A primary problem that several authors in the literature have identified is that the Karl Fischer analysis is not a completely reliable technique as it has the potential to form side reactions and some other limitations to accuracy [64[79][80][81]67]. To reconcile these differences, the authors suggest benchmarking this procedure to see if there is any consistent offset to set a correction factor in place. Also, the authors suggest that a good homogenisation method be used for introducing water into the fuel, and also, water should be introduced at room temperature to achieve reliable conditioning of the fuel. This is because the KF analysis is only accurate for measuring dissolved water and unfortunately, free water never has a homogenous distribution[153].

The complexity of how water and ice behave in jet fuel is still extremely problematic, making it difficult to reach a definitive agreement. For example, comparing results from a study by Carpenter et al. on-ice formation in aviation jet fuel, it was observed from this study that ice formed homogenously at -44 ºC. However, this is a much lower temperature than the -36 ºC observed by Murray et al. as the homogenous freezing point [107][113]. Again, this may be due to the selected jet fuel composition, experimental technique or conditions adopted by the authors. Furthermore, findings from different studies in the literature reveal that surfaces have an important role in the growth pattern of ice in aircraft fuel systems. Yet, no work has been carried out to evaluate the effect of surface types on ice accretion in SAF/synthesised fuels for the basis of comparison with conventional jet fuel. Hence, it may be important to run tests investigating the role surface may play on ice accretion in flowing synthetic aviation fuel. An open question has been identified from section 3 on the discussion on ice crystals growing at right angles off a hydrophobic/superhydrophobic surface and growing across a hydrophilic surface. The important questions are: Is it better to have many ice crystals floating in the fuel tank? Or a large thickness of ice in the wall of the fuel tank? As discussed, this will be difficult to measure because either scenario can potentially have safety implications; for example, ice might not accumulate in the fuel tank but will adhere to the aircraft fuel distribution pipework's inner walls. The second scenario is that the multitude of ice crystal could form a giant snowball and potentially block the fuel distribution pipework. These questions will need to be answered as the ice crystals from both scenarios can potentially clog the fuel distribution pipework. The only way these questions can be answered is by conducting experiments comparing both scenarios at the same test conditions and variables.

It is noteworthy that minimal data exist in the literature on investigating some of the properties of existing synthetic aviation fuels and their impact on aircraft fuel systems. The bulk of data in the literature is from work done on conventionally refined jet fuel. However, available data in the literature focusing on this type of synthesised fuels explores the effect of water solubility and water settling rate only. The majority of this is on water solubility investigation and only one paper by West et al., exist on the effect of water settling rate in synthetic aviation fuels [61]. Unfortunately, the trends obtained will require verification as the results presented are for 10,000 ppmV which is unrealistic and a relatively high concentration unlikely to represent in-flight conditions.

5. Conclusion

This study has identified knowledge gaps in the literature that require to be filled in order to engineer a lasting solution to the problem of ice formation in jet fuel. To gain a better understanding and identify precisely the conditions and features that may exacerbate free water drop-out, ice accretion and formation in flowing fuel, a number of questions must be answered: Can the Karl Fischer analysis for water content determination be benchmarked? How will surface type on ice accretion be affected by synthetic aviation fuels in comparison to conventional jet fuel? How will jet fuel composition affect the frequency size distribution of dispersed water droplets? Does the theoretical assumption about droplet size/frequency distribution in jet fuel being governed by shearing conditions agree with experimental data? How will jet fuel composition influence the rate of water-shedding under realistic and representative test conditions? How will an increased blending portion with conventional jet fuel on the synthesised fuels approved by ASTM D7566 affect this water-shedding rate? Is it better to have a multitude of ice crystals floating in the fuel tank? Or a large thickness of ice in the wall of the fuel tank? Currently, there is very little to no information on any of the questions listed above. Therefore, further work is required to establish the viability of these experiments as this might help proffer a better understanding and help manage the nature in which ice forms in aircraft fuel tank systems. This study proposes implementing a hydrophobic/superhydrophobic coating strategy alongside a de-icing strategy in future aircraft fuel systems design. Thereby serving as a basis for design guidelines to minimise ice formation within an aircraft fuel system and finally suggest possible solutions to prevent future occurrence.

This review investigated over 150 papers and collected a significant amount of information for the basis of comparison and analysis with the recent advances and technologies in the literature. This study provides conclusive data providing a detailed description of the factors that influence the behaviour of water and ice in jet fuels. Furthermore, the study presents a detailed account of some complexities associated with jet fuel chemistry, knowledge gaps, systematic hypothesis, and future development recommendation. The authors of this work identified significant problems with the way results are reported and recommended that authors provide raw data rather than just graphically fitted plots as curve fits can be obscure due to the unknown veracity of the result

The literature summarises that the study of the behaviour of water and ice in jet fuel is rather complicated. Hence a computer-based tool for multivariable analysis and modelling is required to reflect the randomness and interdependence present in reality adequately. Furthermore, it is advised to make laboratory tests more representative by attempting to correlate this observation with what happens in in-service aircraft fuel tanks. Hence, in this work, it is proposed to develop a metric from an experiment that involves exploring sub-zero temperatures to ambient temperatures and vice versa.

In observational studies from the literature, there is still a potential for bias regarding the most widely used water content determination method. Several authors have concluded that Karl Fischer analysis is not entirely a reliable technique. Unfortunately, due to many discrepancies, there is a need to benchmark this procedure to see if there is any consistent offset to set a correction factor in place.

Credit authorship contribution statement

Judith Ugbeh Johnson: Writing - review & editing, Data curation, Resources, Conceptualization, Visualisation and Formal analysis. **Mark Carpenter:** Supervision, validation and editing. **Jean-François Pons and Colleen Williams:** review & editing. **Dan McLaren**: Validation

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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