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# The Effects of Storage on Turbine Engine Fuels

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## Abstract

Modern aviation requires reliable and safe sources of fuel which means fuel is frequently stored for extended periods. In addition, as fuel is used, new fuel is added which is not always compatible with the fuel in the tank. The incompatibility and long-term storage leads to a number of problems that will be addressed in this chapter. Some of the possible changes over time include formation of biofilms, deposit formation, water incorporation and additive depletion. The chemistry and biochemistry of each of these areas will be discussed along with how they might be prevented. New areas of research on low temperature oxidation of trace fuel components and the prevention of bacterial growth will be presented. Other problems are related to the reaction of trace components in the fuel which can lead to oxidation and deposit formation. Trace components also vary based on fuel source and lead to problems in compatibility of different fuels. In addition some of the reactions of fuel additives will be discussed.

**Keywords:** fuel additive depletion, oxidation, biofilm formation, polar component, deposits

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## 1. Introduction

The needs of modern aviation for a safe and reliable source of fuel are without question. Safe fuels must among other things, be able to be stored for periods of time and be compatible with similar fuels from other sources. For commercial uses, long-term storage is not normally required, since most fuel is used within a few months of refining although longer periods may be required at smaller airports. The military, however maintains much larger stockpiles of fuel in reserve for use in case of emergencies.

The composition of jet fuel can vary significantly depending on the refining process and the source of crude oil. Compatibility can be an issue, since storage tanks are normally refilled when they reach a certain level, and fuels from different suppliers are mixed, even though

compatibility issues are possible. Other aspects of storage standards require that the fuel remain free of contaminants, including surfactants, other petroleum products, microorganisms and dyes. All of these types of contaminants can arise from many sources, but careful storage can minimize the hazards associated with some.

The storage and delivery of aviation fuels is carefully regulated and must meet certain standards Including maintaining the purity of the fuel and safety of the aircraft and ground crew [1]. In this chapter, the contamination of fuel from only a few sources will be considered; in particular water contamination, contamination with solids formed by reaction to the fuel with oxygen and contamination due to microorganisms. Finally, some of the challenges associated with the transition to alternate fuels will be discussed.

2. Properties of jet fuel

Turbine engine fuel for aviation uses is a petroleum based fuel similar in properties to kerosene, although newer biofuels and synthetic fuels are under development. Liquid hydrocarbon based fuels are considered ideal for transportation use because they are more easily handled than solids and have a higher energy density than gasses. In most cases, fuel for aviation purposes is of a higher quality than fuels for heating or road transportation purposes. The higher quality requires a greater degree of refining to significantly reduce the level of sulfur, nitrogen and oxygen containing components. It is still thought that the heteroatom containing compounds are responsible for many of the issues of deposit formation and low temperature oxidation.

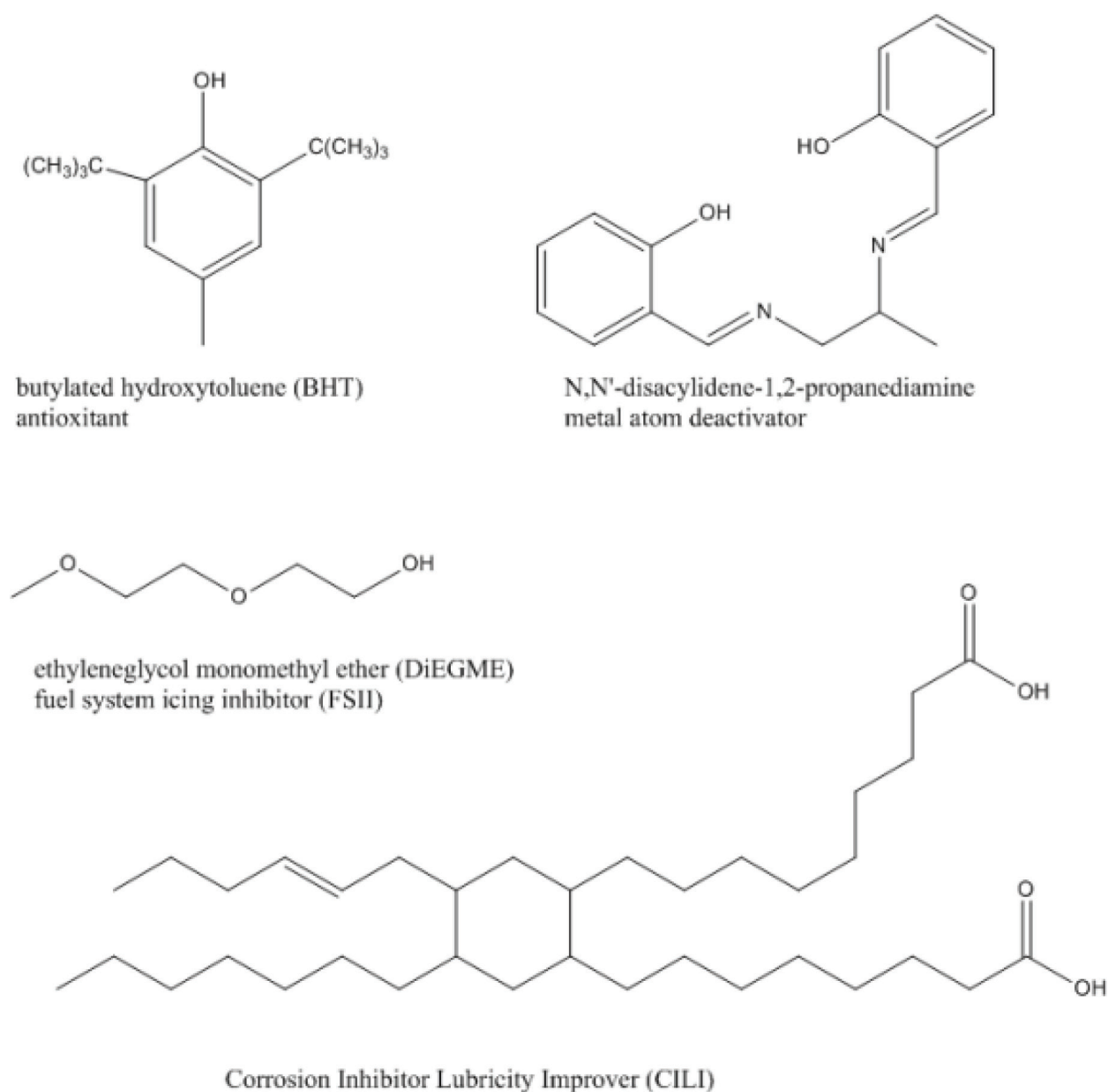
Fuel for turbine engines is produced meeting one of several specifications. Early turbine engines ran on kerosene based fuel. Over time, a wide cut fuel incorporating gasoline and kerosene was developed for use by the US military, because it was thought availability would be better. It was found, however to increase casualties and evaporation of fuel. It is still currently used in cold regions under the Jet B specification. In the rest of the world, commercial aviation has used a kerosene based fuel under the specification Jet A, Jet A-1 [2] or TS-1. Some

Property	Jet A	Jet A-1	Jet B
Place of use	United States	Western Europe	Parts of Canada and Alaska
Type of fuel	Kerosene	Kerosene	Wide cut
Density	0.775–0.840 g/cm <sup>3</sup>	0.775–0.840 g/cm <sup>3</sup>	0.750–0.801 g/cm <sup>3</sup>
Flash point	38°C	38°C	28°C
Freezing point	–40°C	–47°C	–51°C
Energy content	42.8 MJ/kg	42.8 MJ/kg	42.8 MJ/kg
Aromatics	25%	25%	25%

Table 1. Physical properties of some common jet fuels.

properties of each of the commercial jet fuels are shown in **Table 1**. The US military also has a number of different fuel designations; although JP-5 and JP-8 are the most commonly used and are kerosene based fuels.

While these properties can be met by a number of different fuel sources, the composition of the fuels can be quite different. In many cases, it is the trace heteroatom containing compounds that negatively affect the chemistry of the fuel, especially under storage conditions. In many instances, additives are included in the fuel in order to reduce the reactivity of the heteroatom containing compounds, but the additives themselves may contribute to the reactivity of the fuel. Several of the common additives found in jet fuels are described in **Figure 1** and **Table 2** [3].



**Figure 1.** Chemical structures of some common additives found in fuels.

Additive type	Jet A	Jet A-1	JP-4	JP-5	JP-8
Antioxidant	Allowed	Required	Required	Required	Required
Metal deactivator	Allowed	Allowed	Agreement	Agreement	Agreement
Corrosion inhibitor/lubricity improver (CILI)	Agreement	Allowed	Required	Required	Required
Fuel system icing inhibitor (FSII)	Agreement	Agreement	Required	Required	Required

Table 2. Some common additives found in jet fuel.

### 3. Incorporation of water

#### 3.1. Sources of water in fuels

Water is a very common contaminant in all fuels. The most common ways in which water is incorporated into fuel is through contact with air, condensation of water in the air on cold tank surfaces, leaks in floating cover storage tanks and hatches left open. In most cases, liquid water will drip through the fuel with a small amount dissolving in the fuel. Simple contact with air will cause surface layers of the fuel incorporate water based on the solubility of the water in the fuel, the relative humidity of the air and the temperature. Fuel typically arrives from the refinery saturated with water, which makes reducing the dissolved water in fuel impossible to eliminate. Through mixing, water reaches the entire storage tank. Since the temperature and humidity of the air is constantly changing, the amount of water in the fuel never reaches a steady state.

Kerosene based fuels will dissolve between 40 and 80 ppm water at 20°C. The solubility rises with increasing temperature and varies considerably with the composition of the fuel. Fuels with a high aromatic content can dissolve much more water than those with little aromatic content [4]. Single ringed aromatic compounds, for example dissolve 5–10 times more water than similar saturated compounds. Mixing fuels changes the solubility of water, which can lead to water depositing out of the fuel after mixing.

In addition to dissolved water in jet fuel, there is frequently also free water and emulsified water. Free water is water that sinks to the bottom of the storage tank. Since water is significantly more dense than fuel, if through changes in temperature or fuel composition the fuel exceeds its saturation point water droplets will form and sink to the bottom of the storage tank. As the seasons change is repeated, it is possible for a significant amount of water to settle to the bottom of the tank.

An emulsion is formed when one liquid forms tiny droplets of less than 100 microns that are suspended in another liquid. Many emulsions will spontaneously separate if given enough time, but some will remain suspended indefinitely. Emulsions can form with changes in

temperature which can lower the solubility below the saturation point. The can also form when new fuel is added rapidly, dispersing free water into the bulk of the fuel as tiny droplets. Naturally occurring surfactants and surfactants formed during the refining process are known to stabilize water emulsions in jet fuel. These surfactants include naphthenic acids and sulfonic acids and they can cause an emulsion to be stable indefinitely [5].

### 3.2. Effects of water on fuels

Water can be present in fuel as either dissolved water, emulsified water or free water. Free water is water that is collected at the bottom of the tanks. In a well-designed storage system, the free water collects in well-defined places where it can be periodically drained. The dominant problem with free water that remains in the tank is it forms an interface for microbiological growth, which will be discussed in Section 5. Emulsified water, while it may eventually settle is a more difficult problem since it cannot be conveniently drained and can clog filters and forms a nucleus for ice formation. Typically, emulsified water and free water in the tanks of aircraft are picked up with the fuel and fed to the engine [6].

Dissolved water can be a significant problem since there is no physical way to remove it from the fuel. It is simply pumped into the aircraft. In flight aircraft fuels can experience a wide range of temperatures which certainly change the solubility of water in the fuel. As the temperature of the fuel decreases due to the low temperatures observed at high altitude small droplets of water form. Depending on conditions at low temperature, ice crystals can form and remain suspended in the fuel [7]. In order to reduce the possibility of ice formation fuel system icing inhibitors (FSIIs) have been developed and are required in military jet fuels. Diethylene glycol monomethyl ether (DiEGME) and triethylene glycol monomethyl ether (TriEGME) are two common FSII additives that act by stabilizing water in the fuel, reducing the formation of droplets, which decreases the temperature at which ice can form. A second approach under development is the use of a water reactive compound as an additive to completely remove the water from the fuel system. These compounds are either ketals or ortho esters which spontaneously react with water to form alcohols and either ketones or esters. The products of the reaction with water also act as icing inhibitors [8]. The mechanism of one such additive is shown in **Figure 2** below.

The effect of water on the usability of jet fuel depends greatly on the form of the water. Free water tends to settle to the bottom of the tank in pools. Ribbed tanks are frequently used so that the water will collect in predetermined areas and can be drained from the tank. A problem that can arise from the presence of free water is additive depletion. Some additives such as DiEGME and to a lesser extent TriEGME are much more soluble in water than they are in the fuel and will move from the fuel into the free water resulting in significant or complete additive depletion. Typical fuel systems use a filter or separator to ensure that free water is not pumped into the tank of an aircraft. There is still the possibility of free water depositing from the fuel due to changes in temperature and also changes in fuel source.

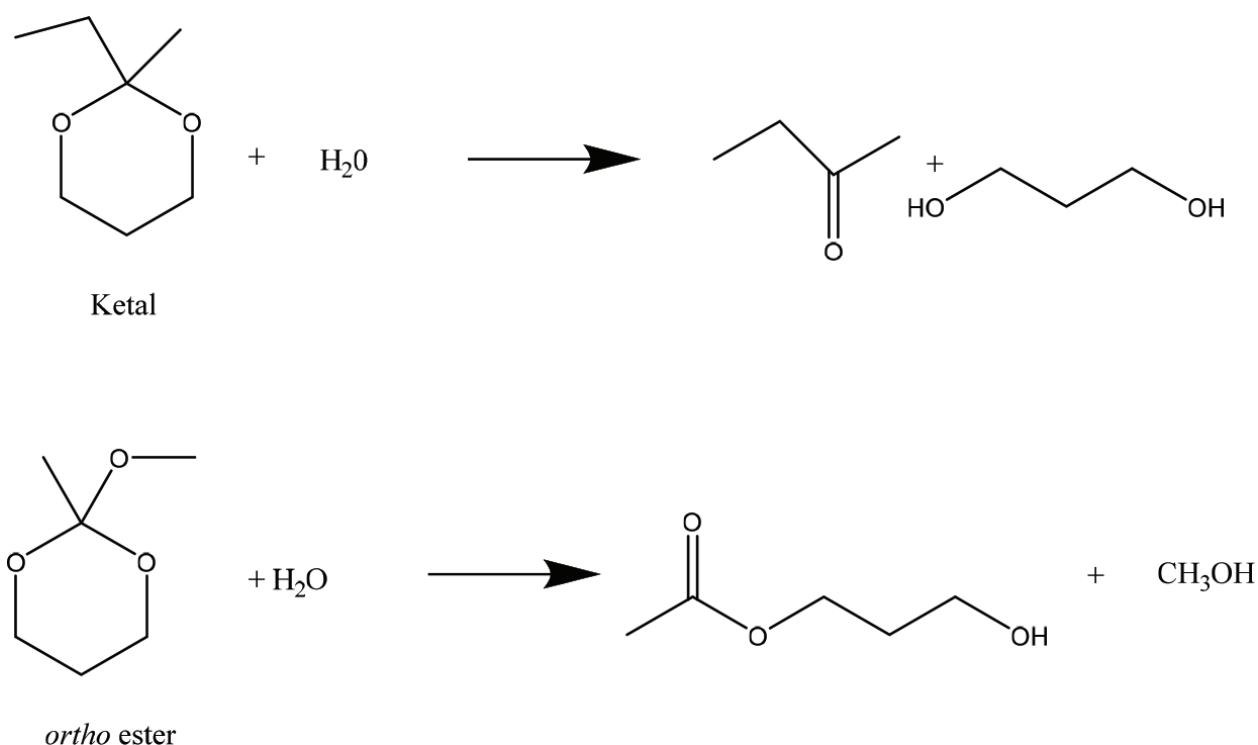


Figure 2. Reaction of a ketal and an orthoester with water.

## 4. Formation of chemical deposits

Chemical changes in the composition of fuels upon storage are a significant source of contamination and can result in the formation of particulates, slimes and other types of deposits in the fuel. The deposits can clog filters at the fueling stations, or if they pass through the filters cause operational problems in the aircraft. The changes in composition can be the result of the variable composition of fuels, low temperature oxidation of fuel components or other possible reactions of various fuel components. The reaction products are frequently insoluble in the fuel, resulting in their separation as a solid or film. The different types of reactions will be discussed separately in the sections below.

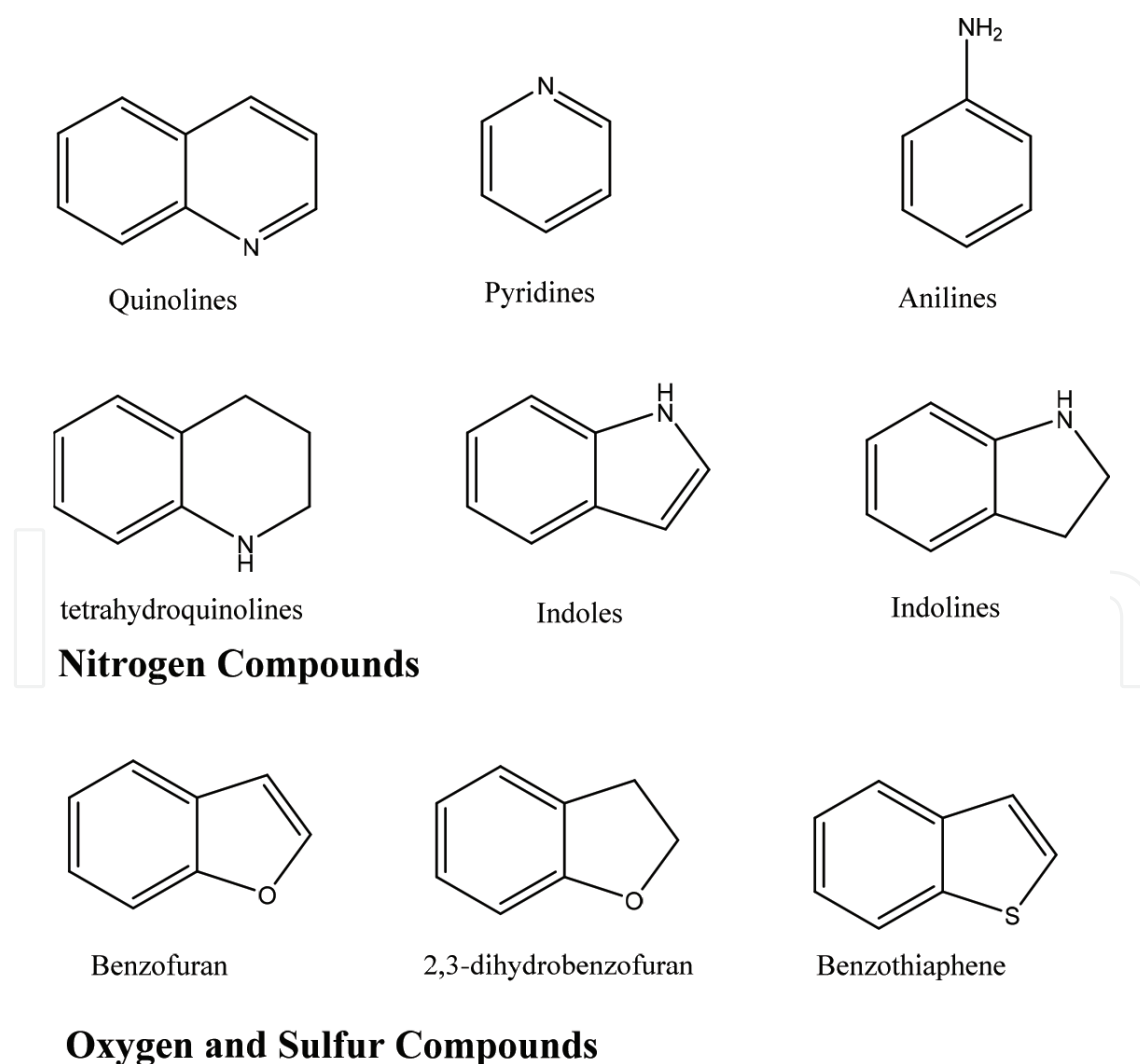
### 4.1. Low temperature oxidation of fuel components

The oxidation chemistry of jet fuel is normally divided into two distinct regions, with different mechanisms. The auto oxidation mechanism becomes important at about 140°C and the pyrolytic mechanism becomes important at about 300°C. Neither of these regions would appear to be operating at the normal storage temperatures of fuels. Studies of these mechanisms however focused on the chemistry of the hydrocarbon components of the fuel. They indicated that aromatic and cyclic hydrocarbons were substantially more reactive than the paraffinic compounds in the fuels [9]. It is known that free radical autoxidation of hydrocarbons occurs readily at temperatures between 30 and 60°C. The process is thought to be a radical chain reaction initiated by peroxides which abstract a hydrogen atom forming a free radical [10]. It has been shown that a number of factors are involved, but it is often the termination reaction



in the radical chain mechanism that leads to the formation of deposits. A startling observation was that the less stable fuels formed less deposit [11]. This observation is likely due to the less stable fuels reacting more quickly, but not through a mechanism that leads to the formation of solid deposits. A series of steps, after the formation of the radical; leads to the formation of oxygenated products, such as primary alcohols [12]. The alcohols further react to form more complex oxygenated products such as dihydrofuranones [13].

What is frequently not accounted for in studies of the autoxidation mechanism of fuels is the presence of trace polar components in the fuel and the presence of catalytic metal ions in the fuel. Polar components have been shown to be correlated to deposit formation, with phenols, indoles and carbazoles showing the largest effect [14]. Some common classes of polar compounds are shown in **Figure 3**. It is well known that nitrogen containing compounds are oxidized much more rapidly than typical hydrocarbons. The enhanced reactivity of the polar compounds then leads to a wide range of new reactions that eventually result in the formation of particulates and films.



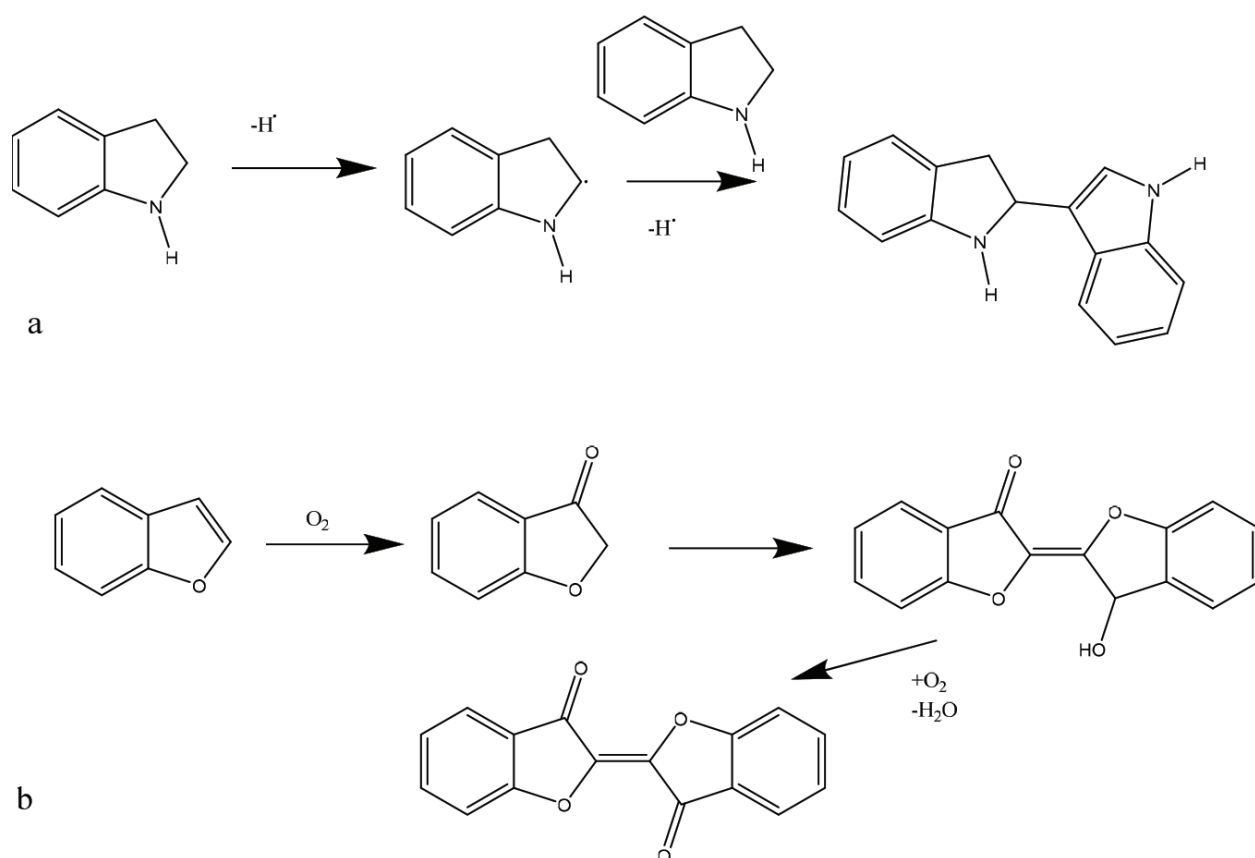
**Figure 3.** Classes of polar compounds found in jet fuel.



The oxidative addition reactions of a number of nitrogen, oxygen and sulfur containing compounds have been studied at 130°C. Considering that these compounds react completely in a few hours at this temperature, the mechanism could be valid at lower temperatures over a longer period of time. The oxidative addition reaction of several nitrogen and oxygen containing polar compounds are shown in **Figure 4**. It has been shown that the rates of oxidative addition depend greatly on the hetero atom present with  $N > O \gg S$  [15].

The observation that the oxidative addition reaction produces molecules of significantly higher molecular weight and that those molecules can react further suggests that the problems would eventually become insoluble in the jet fuels, resulting in the formation of solid particles or oligomeric films.

A fundamental understanding of the mechanism of deposit formation under both thermal autoxidation and typical storage conditions has been a long-term goal. One possible mechanism that leads to the formation of high molecular weight products involves the oxidation of hydrogen containing heteroatomic aromatic compounds to form electrophilic quinone-like species. The quinone-like species reacts with nucleophile present in the fuels to eventually form soluble macromolecular oxidatively reactive species (SMORS) [16]. The initial step of the SMORS mechanism is the reaction of phenol with a peroxy radical to abstract a hydrogen atom. A similar reaction would also be possible with anilines and thiophenols that may



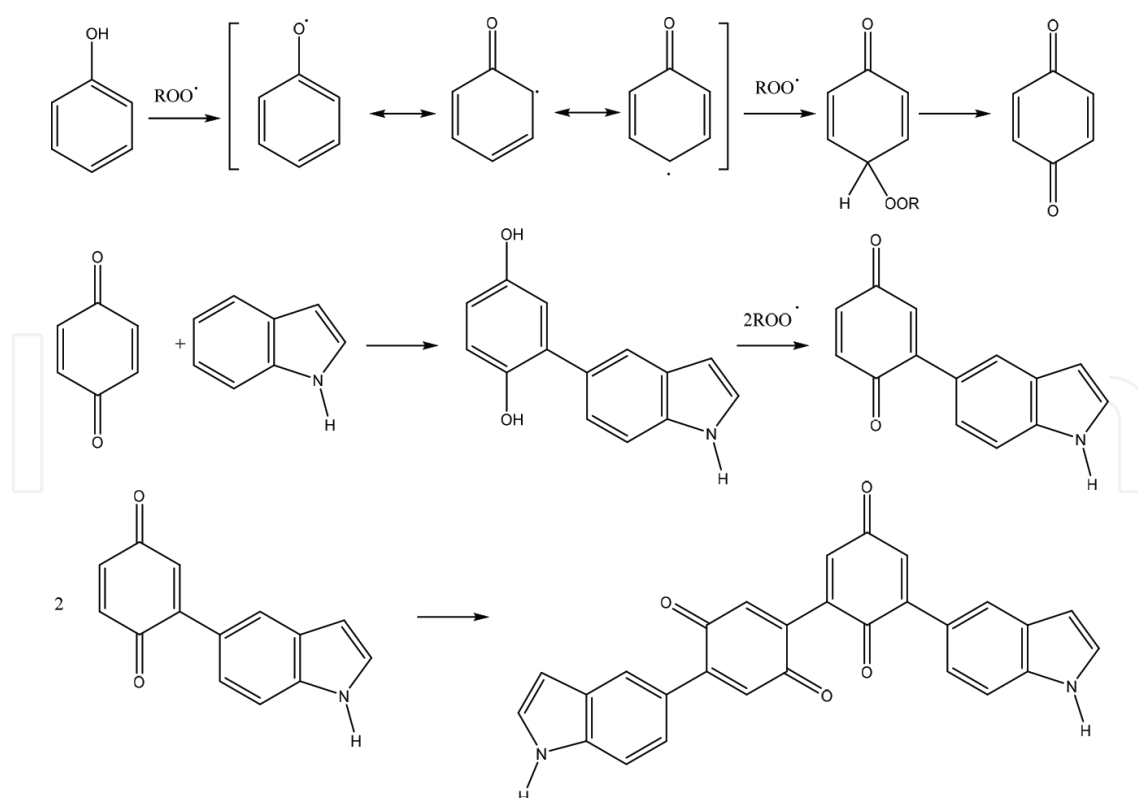
**Figure 4.** Reactions of polar compounds in jet fuel. (a) Reaction of 2,3-dehydroindole to form higher molecular weight products and (b) reaction of benzofuran to form higher molecular weight products.

also be present [17]. The importance of the phenol has been demonstrated by conversion of active hydrogen containing species to silyl ethers which resulted in a dramatic decrease in deposit formation [18]. The phenoxy radical rapidly reacts to form an electrophilic quinone which then reacts with a nucleophilic aromatic heterocyclic compounds, such as pyroles, indoles, and carbazoles (see **Figure 5**). Further reactions lead to the formation of SMORS which can then react further to form insoluble deposits [19]. The understanding of this mechanism has led to some possible stabilizers which may improve the stability of stored fuel [20].

#### 4.2. Reactions between fuels with differing composition

Jet fuels obtained from different sources, refined in different ways have been shown to have somewhat different compositions. The differences are quite apparent when the classes of polar compounds from several different jet fuel samples are compared as is shown in **Table 3**.

The heteroatom containing components of the fuels are in large part responsible for the low temperature reactivity of the fuel [21]. This can be particularly problematic when a fuel that is high in basic nitrogen containing groups is added to a storage tank containing a fuel rich in acids or phenols. The product of the acid-base reaction is reasonably expected to form an insoluble film in the tank.



**Figure 5.** Mechanism for the formation of SMORS, and further reaction to form insoluble species. The figure shows the reaction of indole, however other nucleophilic heterocyclic compounds also react.

Fuel	Type	Phenols	Quinoline/ aminonaphthalene	Indoline/ tetrahydroquinoline	Aniline/ pyridine	Pyrroles/satd. indoles
2747	Jet A	X	X	X	X	
2959	Jet A	X				
3656	Jet A	X	X	X	X	X
3658	Jet A	X	X	X	X	X
3773	JP-8	X	X	X	X	
4336	JP-8	X	X	X	X	X
4177	JP-8	X	X	X	X	
5098	JP-8	X	X	X	X	X

**Table 3.** Comparison of the classes of polar compounds found in various jet fuels.

5. Biological contamination and biofilm formation

Microbial contamination of fuels is a major problem that affects all types of fuels, however because of the demanding specifications and use requirements for jet fuel is a much more important type of contamination. Jet fuel is a very harsh environment; however, many different types of microorganisms have found ways to metabolized different components of the fuel. The paraffinic and some other hydrocarbons are a food source for bacteria but some aromatic compounds and most sulfur containing compounds are toxic to microorganisms [22]. Microorganisms are generally found at the water-fuel interface, indicating that water removal is always a part of microorganism control. The effects of microorganisms growing in fuel are quite diverse, from the filter clogs in the fueling system, to problems in flight, to biocorrosion problems in the tanks and associated fueling system components and hydrogen sulfide corrosion [23].

Microorganisms that can metabolize a wide range of aromatic and aliphatic hydrocarbons have been identified and studied. The metabolism of aromatic compounds involves initial attack on side chains to oxidize the compound at the benzylic position and in subsequent steps open the aromatic ring [24]. The metabolism of paraffinic hydrocarbon is known to occur under both aerobic and anaerobic conditions and there have been several mechanisms proposed [25]. All of the mechanisms appear to convert the hydrocarbons initially to fatty acids either through an oxidative mechanism or through a mechanism that begins with the addition of fumarate, followed by a series of steps to give carbon dioxide and fatty acids [26]. The various anaerobic bacteria depend upon either sulfate or nitrate as an oxidant in their metabolism.

In order to survive, microorganisms have mechanisms that protect them from the toxic compounds such as formation of biofilms, secretion of surfactants and regulation of efflux pumps [27]. Biological contamination, especially where colonies or films can clog filters, reduce fuel flow among other effects. Biological contamination also changes the composition of the fuel,

as the microorganisms metabolize their preferred hydrocarbons, typically paraffinic compounds, leaving the more difficult to metabolize. Some of the effects of microorganisms on fuel and fuel storage systems are shown in **Table 4**.

A number of different types of microorganisms have been isolated from air force fuel tanks, including *Micrococcus*, *Bacillus*, *Staphylococcus*, *Sphingomonas* and *Discosphaerina fagi* [28]. Microorganisms are typically present in fuels, but require the presence of water in order to grow. Regular removal of water and the use of biocides can minimize their growth [29]. Numerous types of microorganisms have been isolated from fuel systems, including moulds, bacteria, yeasts and fungi. The microorganisms require water for growth and they feed on nutrients in the fuel. Many microorganisms can metabolize the hydrocarbons, while others feed on partially degraded fuel, the trace heteroatom containing contaminants in the fuel and the additives in the fuel [30].

The types of microorganisms present in the fuel frequently depend on storage conditions and length of storage. Normally, aerobic microorganisms are dominant; since there is a constant supply of oxygen saturated fuel. During long-term fuel storage however, the oxygen is quickly used and anaerobic microorganisms flourish. In many cases, bacteria are able to use sulfate which results in the formation of hydrogen sulfide. This toxic and foul smelling gas attacks the steel of the bottom plate. Hydrogen sulfide also dissolves in the fuel and the fuel can become aggressive toward steel, silver and copper alloys [31]. Anaerobic bacteria are a particular problem in marine environments where salt water provides an abundant supply of sulfate that the anaerobic bacteria convert to hydrogen sulfide which leads to foul smelling and toxic fuel and significant biocorrosion of steel [32].

Problem	Microorganism type
Blockage of pipes, valves, filters and incorrect readings from fuel probes	Fungi; polymer producing bacteria
Increased water content	All
Sludge formation	All
Surfactant production, forming fuel/water emulsions and coalesce failure	Fungi and aerobic bacteria
Corrosion of storage tanks	Fungi and anaerobic bacteria
Production of suspended solids	All
Breakdown of hydrocarbons	Fungi and aerobic bacteria
Fouling of injectors	Fungi and aerobic bacteria
Penetration of protective linings	Fungi
Increased sulfur content in fuel	Sulfur-reducing bacteria
Health problems	Endotoxin producing bacteria, pathogens, sulfur reducing bacteria

**Table 4.** The effects of microorganisms on fuel system components.

Microorganisms have been shown to be highly adaptable in their ability to use different food sources. It has been shown that several adaptations are needed for *Pseudomonas aeruginosa* to metabolize jet fuel [33]. When jet fuel is the available carbon source, the bacteria alter their metabolism through transcriptional regulation to favor the use of paraffinic hydrocarbons of the  $C_{11}$ – $C_{13}$  length as a food source [34]. These same transcriptional changes require biofilm formation for bacterial growth.

The introduction of ultralow sulfur and low sulfur fuels introduces new complexities in biofilm formation. It is known that sulfur compounds normally found in petroleum based fuels are natural lubricity improvers, antioxidants and antimicrobial agents [35]. Studies have shown that the removal of the sulfur compounds does not appear to alter the bio-corrosion properties of the fuel under anaerobic conditions [36], however microorganisms have also been shown to rapidly deplete the corrosion inhibitor/lubricity improver (CILI) additives from the fuel [22].

One approach to reduce microorganism growth in fuels is to incorporate biocides in the fuel formulation. There are very few biocides that have been approved for use in Jet A, but are not allowed in the military jet fuels JP-4, JP-5 and JP-8. In Jet A, the allowed biocides are Biobor™ and Kathon™. Kathon has a sulfur heterocyclic compound as the active ingredient [37] and Biobor has a boron containing compound [38].

## 6. Alternative or synthetic fuels

The aviation community uses huge amounts of fuel and requires a reliable source of high quality fuel. The uncertain markets for petroleum and the differences in fuel composition due to different crude oil feed stocks has led the industry to investigate alternate sources of fuel. In the United States, several alternative energy sources are possible, including natural gas, coal and biomass. Natural gas and coal are in abundant supply in the United States but are still non-renewable and have a large environmental footprint [39]. Biomass based sources, are potentially more environmentally friendly, although the life cycle analysis must certainly be taken into account [40, 41]. The United States military has estimated that at least 50% of its energy use would be from renewable sources by the year 2020 [42]. Several processes are under investigation, but considering current market conditions of low crude oil prices, prospects for widespread development are not promising [43].

Primary attention has been paid to processes which produce fuels that can serve as drop in replacements for petroleum based fuels requiring no modifications to the aircraft, and can be interchanged with conventional fuel depending upon local availability [44]. It is also important that the feedstock can be produced sustainably and are not either used in foods or raised on land that can also be used to raise food crops [45]. Two processes that are the most developed and can produce a synthetic fuel from a variety of feedstocks to provide an alternative fuel source are synthetic fuels through the Fisher-Tropsch process and hydroprocessed esters and fatty acids fuels.

The synthesis of liquid fuels from natural gas, coal or biological sources has been an important goal for many years. The primary industrial process that is used is the Fischer-Tropsch process that was initially developed in Germany in the early 1920s. The process takes carbon monoxide and hydrogen and converts them in the presence of a catalyst to paraffinic and branched chain hydrocarbons. The carbon monoxide and hydrogen can come either from coal, natural gas or renewable sources. Depending on the catalyst and reaction temperature different types of fuel can be prepared [46]. Fischer-Tropsch fuels have the advantage of containing no aromatic content, no metals and no heteroatom containing impurities. These fuels have been shown to be cleaner burning with reduced particulate emission than conventional fuels. Current specifications for aviation use state that synthetic fuels must either be mixed 50–50 by volume with petroleum based fuels for semi-synthetic jet fuel or be tested to ensure at least 8% aromatic content for a fully-synthetic jet fuel.

The aviation industry has shown an intense interest in developing fuels from renewable resources. Initial evaluation of fatty acid methyl esters similar to biodiesel showed the fuel did not have low temperature properties needed for aviation [47]. The need however for a renewable source of jet fuel, preferably from a non-food source led to the development of a hydrotreated renewable jet fuel (HRJ) from camelina. The hydrotreating process for jet fuel converts the typical esters into paraffins and isoparaffins by reaction with hydrogen in the presence of a catalyst. Camelina based HRJ and other isoparaffin-rich bioderived fuels are similar in composition to ultralow sulfur hydrocarbon fuels [48]. Isoparaffin rich fuels also have the advantage of lower exhaust emission of nitrogen oxides and particulate matter.

The storage stability of Fischer Tropsch fuels and hydrotreated renewable jet fuel will be likely enhanced by the reduced solubility of water in fuels that have no aromatic content. Since the heteroatoms are not present, many of the deposit formation reactions found in normal fuels should be absent. The primary concern would be the ability of microorganisms to metabolize the hydrocarbons that comprise the majority of the fuel. Microorganisms have been shown to metabolize synthetic paraffinic kerosene readily, since aromatics and sulfur containing compounds in conventional fuels are toxic to many of the microorganisms. The use of synthetic jet fuel has been limited to a partially synthetic 50:50 blend of the synthetic fuel with a petroleum jet fuel; with the exception of a fully-synthetic fuel produced by Sasol. The primary limitation is due to the lack of aromatics which can result in seal cracking. The added petroleum based jet fuel or additional treating in the SASOL product increases the aromatic content to 8% which is adequate to avoid seal shrinkage [49]. The increased aromatic content, however leads to an increase in oxidative addition reactions which are closely associated with the formation of deposits [50].

## 7. Conclusions

Civilian and military aviation requires an abundant, affordable, safe and storable source of fuel. The variable composition of fuel depending upon crude oil source and refining methods creates many challenges for fuel storage. Chemical deposit formation, which has been tied



to oxidation reactions, followed by addition mechanisms is one source of fuel degradation. Other problems in fuel storage are related to the presence of water, both from contamination through leaks in the storage tanks and the general solubility of water in jet fuel can create icing problems and also provide a growth medium for microorganisms. Good water management can provide added safety in the fuel storage system. Finally, the development of renewable and synthetic fuels will change the problems of fuel storage, due to the more predictable composition of the fuel and the lack of heteroatom containing impurities associated with the fuels.

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