Chemistry of Jet Fuel Instability

Thermal stability is a very important jet fuel property (*see page 5*). Instability involves the formation of peroxides and hydroperoxides, soluble gums, and, most critically, insoluble material that may either coat surfaces or form particulates.

Our knowledge about the details of the instability reactions is incomplete, although this is an area of ongoing research. They are believed to be multi-step reactions, some of which – perhaps including the initiating ones – are oxidation reactions. The reactants are believed to be certain nitrogen- and/or sulfur-containing compounds, organic acids, and reactive olefins. They are present at concentrations so low – parts per million at most – that identification by current analytical techniques is virtually impossible. Contaminants can also play a role. Oxidation reactions are accelerated by the presence of certain dissolved metals, especially copper, that function as catalysts.

Failure of the thermal stability test (*see page 6*) involves the formation of higher molecular weight compounds with limited fuel solubility. The development of insolubles depends on both trace and bulk fuel properties. The chemistries and molecular weights of the reaction products are determined by the reactants, which are present only in trace amounts. But once the reaction products have formed, it is the solvency of the fuel, which is a function of its bulk composition, that determines whether the products will be soluble or insoluble.

Contrary to intuition, two fuels, that by themselves are stable, can be less stable when combined. Each fuel may contain some, but not all, of the reactants required to form insolubles. Only when the fuels are mixed are all the reactants present, enabling the conversion to proceed. The solvency of the blend may also play a role.

Water in Jet Fuel

Water can occur in three different forms in jet fuel: dissolved in the fuel, as a separate liquid phase (*free water*), and as a fuel-water emulsion. Some amount of dissolved water is present in all fuels. This dissolved water is not a problem; free water or a water emulsion are potentially hazardous and must be avoided.

Dissolved Water

Water is very slightly soluble in jet fuel, and conversely, jet fuel is very slightly soluble in water. The amount of water that jet fuel can dissolve increases with the aromatics content[2] of the fuel and temperature.

Fuel in contact with free water is saturated with water, i.e., the fuel has dissolved all the water it can hold. A typical water-saturated kerosine-type fuel contains between 40 and 80 ppm dissolved water at 21°C (70°F). If the temperature of the fuel increases, it can dissolve more water. Conversely,

2 Water is more soluble in benzene than in any other hydrocarbon. Monoaromatics will dissolve five to ten times more water than saturates of the same carbon number.

if the temperature of water-saturated fuel decreases, some of the water dissolved in the fuel will separate as free water.

In the absence of free water, jet fuel can pick up water from the air. The amount depends on the *relative humidity*[3] of the air. Fuel in contact with air with a relative humidity of 50 percent will contain only half as much water as water-saturated fuel at that temperature.

The above statements assume that the fuel is in equilibrium with free water or moist air. Fuel close to a fuel-water or fuel-air interface will reach water equilibrium in a matter of minutes. However, if the volume of fuel is large and the area of the interface is limited – conditions that exist in a large fuel storage tank – some of the fuel will be many feet from the interface. In the absence of mixing, it will take a lot longer for this portion to reach water equilibrium. In fact, fuel in a large tank may never come to complete water equilibrium since ambient temperature and relative humidity are constantly changing.

Free Water

In jet fuel, free water exists as a separate liquid phase. Since water is denser than jet fuel, free water, under the influence of gravity, forms a lower layer and the jet fuel an upper layer. If jet fuel and water are mixed, normally they will quickly separate again. The speed of the separation and the sharpness of the fuel-water interface are indications of the fuel's *water separability*.

As mentioned above, when water-saturated jet fuel cools, free water separates out, taking the form of many very small droplets sometimes called *dispersed water*. Even if they are not stabilized by surfactants (*see below*), the droplets coalesce slowly because of their small size. The suspended droplets give the fuel a hazy appearance. The haze will disappear if the fuel is warmed enough to redissolve the water.

Emulsion

An emulsion is a mixture of two immiscible liquids in which very small droplets of one – less than 100 micrometers in diameter – are dispersed in the continuous phase of the other. An everyday emulsion is mayonnaise, a mixture of egg yolk (droplet) in oil (continuous phase). But here, it is emulsions of water (droplet) in jet fuel (continuous phase) that are of interest.

While immiscible liquids normally separate if they have different densities and/or surface tensions, an emulsion can persist for a long time. The mixture is stabilized by surfactants that congregate at the surface of the droplets, preventing them from coalescing.

Liquids that are immiscible have very different polarities. In the case of water and jet fuel, water is polar[4] and jet fuel is non-polar. Some molecules contain both a polar group (polar head) and a

3 Relative humidity is the percentage of water vapor present in air, relative to the maximum amount the air can hold at the same temperature.
4 When used to describe molecules, polarity refers to the distribution of electric charge in the molecules.Molecules with an even distribution, such as hydrocarbons, are non-polar.Molecules with a partial separation of charge, with one portion slightly positive and another portion slightly negative, are polar. Polar molecules found in jet fuel typically contain sulfur, nitrogen, or oxygen atoms in addition to carbon and hydrogen.

non-polar group within the same molecule. This duality causes the molecule to migrate to the interface between a pair of immiscible liquids, with the polar group interacting with the polar liquid and the non-polar group interacting with the non-polar liquid. These molecules are called surfactants (a contraction of *surf*ace *act*ive *a*ge*nts*) because they are active at the surface between the immiscible liquids. And because they work at the interface, not in the bulk liquid, trace amounts can affect the properties of a large volume of liquid.

Some surfactants found in jet fuel occur naturally in crude oil, such as naphthenic acids and phenols. Others may be introduced in the refining process, such as sulfonic acids. Still others may be introduced through contamination in the fuel distribution system. The amount of contamination need not be large because, as noted above, surfactants are effective in trace amounts. Surfactants are commonly removed from jet fuel by passing the fuel through clay (*clay treating*).

Surfactants can cause problems even if they don't lead to the formation of a fuel-water emulsion. They can impair the ability of a filter/separator to remove free water from jet fuel (*see page 81*). In this situation, the surfactants are said to "disarm the coalescer." Since it is imperative that only clean, dry fuel is delivered to aircraft, tests have been developed to detect the presence of surfactants in jet fuel through their ability to stabilize emulsions.

Additives

Additives are fuel-soluble chemicals added in small amounts to enhance or maintain properties important to fuel performance or fuel handling. Typically, additives are derived from petroleum based raw materials and their function and chemistry are highly specialized. They produce the desired effect in the parts per million (ppm) concentration range. (One ppm is 0.0001 mass percent.)

Additives are used in varying degrees in all petroleum derived fuels, but the situation with aviation fuels is unique in that only those additives specifically approved may be added to jet fuel. All jet fuel specifications list approved additives along with allowed concentrations. Some approved additives are required to be added, some are optional, and others are approved for use only by agreement between buyer and seller. Figure 4.6 lists additives approved for use in some of the major jet fuel specifications.

Before an additive can be approved for use in aviation fuel, it must undergo extensive testing to show both that it is effective and that it does no harm to any other fuel properties. To guard against harmful additive interactions, an additive must be tested at four times its maximum dosage in the presence of other additives before it is approved.

Use of additives is the principal difference between commercial and military jet fuels. U.S. military jet fuels will contain three or more additives. International Jet A-1 contains a static dissipator additive and may also have an antioxidant. Jet A in the United States usually contains no additives at all, or perhaps only an antioxidant.