

AUTOXIDATION OF AVIATION FUEL BLENDS

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INTRODUCTION

The use of aviation fuel to cool component systems in military aircraft creates conditions under which fuel containing dissolved O_2 is exposed to hot surfaces. Liquid-phase oxidation from fuel heating during this application can lead to fouling of critical fuel-line surfaces; problems associated with surface fouling are predicted to become more severe in future aircraft where additional heat dissipation will be required.¹ Low-cost additives including antioxidants have been successful in reducing such fouling in both automotive² and aviation³ fuels. A variation on the introduction of additives is the blending of two fuels. For example, adding a small amount of straight-run fuel which contains many natural antioxidants to a second fuel whose antioxidants have been reduced by refining techniques is equivalent to adding a small amount of antioxidant.⁴⁻⁶ In an effort to better understand autoxidation and changes resulting from antioxidants and blending, the depletion of dissolved O_2 has been monitored in aviation fuels and fuel blends under high-pressure and elevated-temperature conditions that simulate, to some extent, the thermal oxidative stress experienced in aviation fuel lines.

In the present study we tracked depletion of dissolved O_2 at 185°C in a series of eight aviation fuels and many of their 1:1 blends. The selected fuels, summarized in Table 1, include JPTS, JP-7, JP-8, and Jet-A examples covering a broad range of thermal stability. The fuels are numbered approximately in order of decreasing thermal stability, and a blend of Fuels 1 and 8 is designated (1/8). The total quantity of surface insolubles measured for these fuels under the current test conditions ranges from 0.1 to 5 $\mu\text{g/mL}$. In general, after 22 min of stressing under these reaction conditions, fuels with high thermal stability deposit < 1 $\mu\text{g/mL}$ of insolubles and fuels with low thermal stability deposit > 3 $\mu\text{g/mL}$.⁷ The complex oxidation behavior of each fuel and fuel blend was tracked; the time, t , required to deplete dissolved O_2 by 50% was interpolated from the data and used as a simple measure of oxidation time.

The overall goal of these efforts is the reduction of surface fouling. The specific goal of this study was twofold: first, to investigate whether knowledge of the oxidation behavior of two neat component fuels would be sufficient to predict the oxidation behavior of their 1:1 blend and, second, to identify cases in which blending causes significant delays in autoxidation and search for corresponding delays or reduction in surface fouling. Any method of slowing autoxidation has potential for reducing the extent of surface fouling.

EXPERIMENTAL

Blends are prepared by stirring together equal volumes of the component fuels. The amount of dissolved O_2 is assumed to be approximately the same for each fuel.⁸ The methodology used in this study has been described in detail previously.⁵ Oxidation and deposition reactions occur as fuel that is saturated with respect to air at room temperature passes through single-pass heat exchangers (NIFTR's) operated isothermally at 185°C. A system pressure of 2.3 MPa ensures a single reaction phase with no headspace. Fuel reaction time (residence time) in the 0.81-m tube (i.d. 0.216 cm) is varied by changing the flowrate. Dissolved O_2 in the stressed fuel is measured by the GC method developed by Rubey and co-workers.⁹

Deposition experiments are performed separately using 1.6-m tubes at a fixed flow of 0.25 mL/min. Surface deposits are quantified using conventional surface-carbon burnoff of 5.1-cm sections cut from the tube at the completion of a 72-hr test.

RESULTS AND DISCUSSION

Oxidation behavior at 185°C for three representative fuels is shown in Figure 1. For the JP-7 Fuel 1—a paraffin/cycloparaffin mix—oxidation is very rapid (< 1 min) and cannot be followed accurately with current methods, whereas for Fuel 6 oxidation is quite slow (> 14 min). All of the remaining fuels oxidize at rates between these two limits. The dependence of Fuel 2 is representative of the behavior of a hydrotreated fuel with added hindered phenol as a synthetic antioxidant. The values of t for Fuels 1, 2, and 6 are ~ 0.6, 3.4, and 6.3 min, respectively. The main constituents of fuels are paraffins, cycloparaffins, aromatics, and alkenes. Many constituents of lesser abundance that contain hetero-atoms such as O, S, and N are very important as natural primary anti-

oxidants that serve to terminate free-radical chains or as natural secondary antioxidants that act to reduce self-initiation by destroying hydroperoxides. Hydroperoxides and dissolved metals in trace amounts can act as pro-oxidants by increasing the free-radical pool. The overall distribution of the major constituents, including antioxidants and pro-oxidants, determines the oxidation behavior. Fuels behave differently under conditions of thermal oxidative stress because each has a unique distribution of components.

Assuming that linear combinations of fuel constituents are achieved in the blends, exactly one-half of the antioxidants and pro-oxidants from each neat fuel is present in a 1:1 blend. In a simplistic view with the blend containing an average of the antioxidants and pro-oxidants from each fuel, the oxidation time may be the average of the times for the component fuels. This model can be checked by comparing the measured times and average calculated times, as shown in Figure 2. Only one-half of the blends approach the simple prediction indicated by the dashed line. The other blends oxidize more slowly than predicted and, in fact, usually oxidize more slowly than either component fuel. The origin of this effect that was originally reported⁶ for fuel system (1/6) is not well understood. However, constituents of the slower oxidizing component seem to be more important in determining the oxidation of the blend. This effect occurs in blending two fuels with large differences in oxidation times, one being a severely hydrotreated fuel with reduced aromatic concentration and the other a slower oxidizing fuel of lower thermal stability containing naturally occurring pro-oxidants (dissolved metals) and antioxidants.

The results for many of the blends can be rationalized. For example, the pro-oxidant effect of dissolved metals in Fuel 8 is expected to be reduced by dilution with Fuel 1, and oxidation in that blend will be additionally slowed. An alternative explanation is based on the fact that phenolic antioxidants operate best at an optimum concentration. It can be argued that because lesser quality fuels contain a large excess of phenolic antioxidants, dilution may optimize their antioxidant effect. Both explanations can qualitatively account for the observations, but reliable prediction of the oxidation time for blends cannot be made at this time simply from knowledge of the oxidation behavior of the individual component fuels. The very complicated composition of aviation fuels plays an important role in determining the oxidation time not only for each fuel but also for blends. The presence of naturally occurring antioxidants and dissolved metals as well as the frequent addition to fuels of synthetic antioxidants and metal deactivators preclude simple predictions for blends.

The time dependence of surface fouling was studied in three blends (1/6, 1/7, 1/8) exhibiting unusually slow oxidation. Figure 3 shows the relative difference in surface fouling that resulted from mixing the paraffin Fuel 1 with Fuels 6, 7, and 8. Negative and positive values indicate decrease and increase, respectively, in the extent of surface fouling. Under conditions of 8 - 12 min of stressing, reductions are observed on the order of 0.8 - 1.6 $\mu\text{g}/\text{mL}$, reflecting the observed delays in oxidation. Dilution of Fuels 6, 7, and 8 of lower thermal stability with the severely hydrotreated Fuel 1 creates blends with improved thermal stability.

CONCLUSIONS

The oxidation behavior of 18 blends made from 1:1 mixing of eight component fuels has been studied. Knowledge of the oxidation behavior of the component fuels is not sufficient to permit prediction of the oxidation behavior of blends on the basis of averaging antioxidant and pro-oxidant effects. This is attributed to the complex interaction of fuel constituents including aromatics, naturally occurring antioxidants, and dissolved metals as well as synthetic antioxidants and metal deactivators. Many instances of unusually slow oxidation of blends involving straight-run and severely hydrotreated fuels have been observed. In several of these cases, surface fouling was found to be reduced at shorter stress times in agreement with observed slowing of autoxidation.

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Table 1. Fuels studied.

NO	FUEL	TYPE	TREATMENT	AROMATICS (% vol)	TOTAL SURFACE INSOLUBLES FORMED AT 185°C (µg/mL)	TOTAL SULFUR (ppm)	METALS (ppb)
1	Exxsol D-80	JP-7	hydrotreated	<1	0.5	3	
2	POSF-2976	JPTS	hydrotreated	8	0.1	0	
3	POSF-2747	Jet-A-1	hydrotreated	19	0.1	37	Cu, <5
4	POSF-2980	Jet-A	Mercox-treated	17	1.6	614	Cu, <5; Fe, <5
5	POSF-2934	JP-8	straight-run	18	1.9	755	Cu, 44*
6	POSF-2827	Jet-A	straight-run	19	2.6	790	Cu, <5; Fe, 8
7	POSF-3119	Jet-A	straight-run	~20	4.5	1000	Cu, 7; Fe, 26
8	POSF-3084	Jet-A	straight-run	18	4.8	527	Cu, 35; Fe, <5

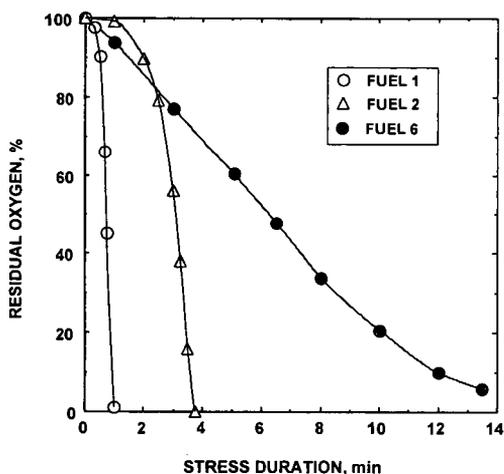


Figure 1. Autoxidation of representative fuels at 185°C.

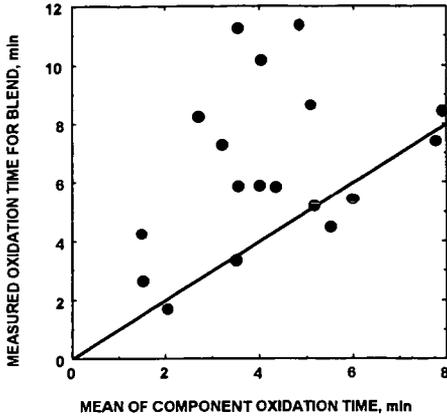


Figure 2. Comparison of measured and calculated oxidation times

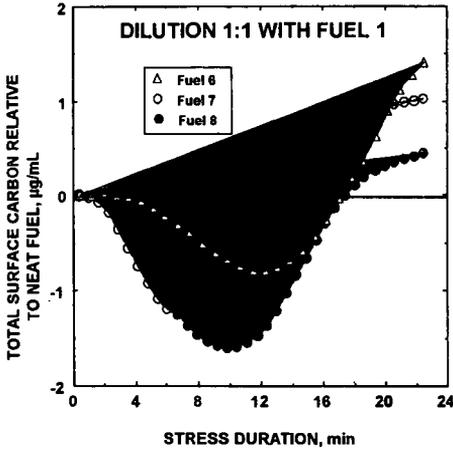


Figure 3. The effect of blending on total surface carbon.