

AUTOXIDATION OF DILUTED AVIATION FUELS

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INTRODUCTION

In addition to its role in combustion, aviation fuel serves as the primary heat sink for cooling component systems in military aircraft.¹ The efficiency of heat exchangers and the operation of many other critical fuel-line components can be compromised by fouling of surfaces caused by the accumulation of intractable gums. Products from autoxidation are the major source of surface fouling at temperatures below 400°C.² Although pure paraffins and hydrotreated fuels have high thermal stability, i.e., a low propensity for fouling surfaces, they can oxidize very rapidly in the absence of antioxidant protection. Species containing heteroatoms (present in low concentrations in most fuels) tend to inhibit or retard oxidation by acting as antioxidants. However, on the basis of the high relative abundance of O, S, and N in insoluble products, these same types of species have been implicated in surface fouling.

The thermal stability of lesser quality aviation fuels can be improved through hydro-treatment processes at the refinery which reduce the concentration of many heteroatomic species as well as dissolved metals and alkenes.³ More severe hydro-treatment can also lower the concentration of aromatics. Thermal stability can be improved at a lower cost by the introduction of additives or additive packages.⁴

Our laboratory has been investigating the effect of fuel blending upon autoxidation.^{5,6} Adding a small amount of a straight-run fuel that contains naturally occurring antioxidants to a hydrotreated fuel whose natural antioxidants have been removed during refining is equivalent to adding a small amount of antioxidant.⁵⁻⁷ Conversely, the addition of a severely hydrotreated fuel to a straight-run fuel can be viewed as a means of diluting the concentration of many deleterious fuel components including antioxidants as well as aromatics. Such dilution causes compositional changes analogous to those achieved during hydrotreatment. In the present study this concept was explored by investigating the autoxidation of neat and diluted fuels and the changes in autoxidation arising from the introduction of some simple additives.

EXPERIMENTAL

Blends (1:10) are prepared by stirring together 10% aviation fuel and 90% Exxsol D-110, the latter being a mixture of paraffins and cycloparaffins containing no antioxidants and less than 1% aromatics. The methodology has been described in detail previously.⁵ Liquid-phase oxidation occurs as air-saturated fuel passes through a single-pass heat exchanger operated isothermally at 185°C. A system pressure of 2.3 MPa ensures a single reaction phase with no headspace. It is assumed that the amount of dissolved O₂ is approximately the same for each fuel and blend.⁸ Fuel reaction time (residence time) in the 0.81-m tube (i.d. 0.216 cm) is varied by changing the flowrate. Dissolved O₂ in the stressed fuel is measured by the GC method developed by Rubey and co-workers.⁹ For the oxidation experiments, tubing treated with the Silcosteel process¹⁰ was used to minimize catalysis that occurs on the surfaces of stainless-steel tubing. Additives employed in this study include the DuPont metal deactivator N,N'-disalicylidene-1,2-propanediamine [designated MDA (2 mg/L)], the hindered phenol antioxidant BHT (25 mg/L), and the Betz proprietary dispersant 8Q405 (100 mg/L).

RESULTS AND DISCUSSION

Oxidation of neat and diluted fuel: effect of additives on POSF-3084. POSF-3084 is a Jet-A fuel of low thermal stability containing 35 ppb of Cu. The oxidation behavior of neat and diluted fuel at 185°C is shown in Figure 1. In each case oxidation is autocatalytic as a result of formation and subsequent thermal and Cu-catalyzed¹¹ dissociation of hydroperoxides, which increases the source of free radicals. The impact of autocatalysis is reduced somewhat in the neat fuel because of the abundance of naturally occurring antioxidants which act either as primary antioxidants in a radical chain-breaking mechanism or as secondary antioxidants by destroying hydroperoxides. Diluted fuel contains fewer secondary antioxidants, resulting in higher hydroperoxide concentrations and more rapid oxidation at high conversion.

Dilution also reduces the concentration of dissolved Cu to ~ 4 ppb. Thus, Cu-catalyzed initiation is expected to be less important in diluted fuel than in neat fuel. By chelating the dissolved Cu with MDA, most of the effects of metal-catalyzed initiation can be eliminated. The results of introducing 2 mg/L of MDA into neat and diluted fuel are

shown in Figures 2a and 2b, respectively. With regard to slowing oxidation, MDA has a significant effect on the neat fuel and a minimal effect on the diluted fuel. This observation illustrates that ten-fold dilution of POSF-3084 almost totally removes any contribution from dissolved metals.

Hydrotreated fuels usually require the addition of a hindered-phenol antioxidant, such as BHT, for improved storage stability to offset the removal of natural antioxidants. Such fuels are sensitive to the introduction of additional BHT. For example, concentrations of BHT up to 70 mg/L have been shown to have an approximately linear effect in extending the delay in autoxidation of the severely hydrotreated JPTS fuel POSF-2976.¹² Figures 3a and 3b show the effect of introducing BHT into neat and diluted fuel, respectively. Both fuels exhibit delays in autoxidation, but the response to BHT is greater in the diluted fuel.

Dispersants are not expected to alter autoxidation. However, in some metal-containing fuels (POSF-3084, -3119) autoxidation has been reported to be slowed by the introduction of 8Q405.⁴ It has been suggested that this behavior is due to metal deactivation rather than a radical chain-breaking mechanism.^{4,13} Response to the addition of dispersant 8Q405 is shown in Figures 4a and 4b. The reduced sensitivity following dilution is not consistent with 8Q405 acting as a primary antioxidant; rather it supports another role, possibly related to metal deactivation.

Finally, is the oxidation behavior of diluted POSF-3084 similar to that of hydrotreated fuels? Figure 5 shows the similarity between diluted POSF-3084 and three severely hydrotreated fuels.

Oxidation of a series of diluted fuels. The oxidation behavior of twelve diluted aviation fuels is shown in Figure 6. This series includes fuels covering a broad range of thermal stability. Three points can be made. First, the fuel discussed in detail above is a representative example of this series. Second, with one significant exception (namely, POSF-2985), the curves are very similar in shape but rapid reaction is delayed in the same manner as we observed previously at this temperature with the addition of a primary antioxidant such as BHT to JPTS.¹² Since dilution has removed most of the impact of species such as metals and secondary antioxidants which require interaction with hydroperoxides, the observed delays may provide an indirect measure of the efficiency of naturally occurring primary antioxidants in slowing oxidation of the diluent.

CONCLUSIONS

Results presented here show that fuels diluted ten-fold with paraffins exhibit behavior more characteristic of hydrotreated fuels than of the original undiluted fuel with regard to autoxidation and response to additives. This is attributed to a reduction in the impact of dissolved metals and heteroatomic species that is analogous to compositional changes achieved during hydrotreatment.

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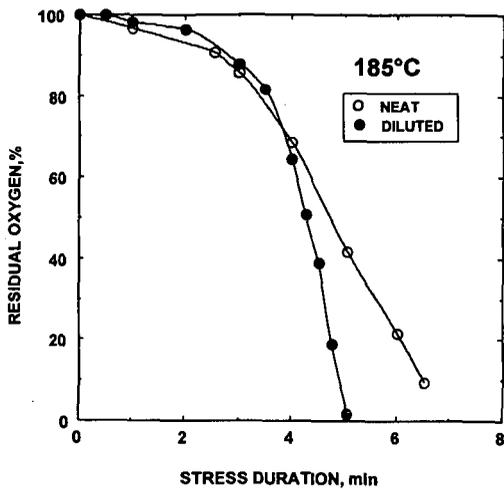


Figure 1. Autoxidation of neat and diluted POSF-3084.

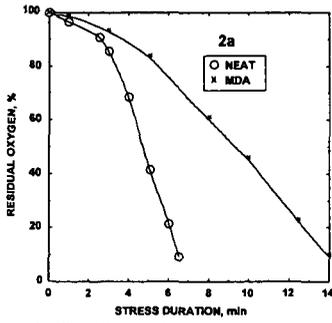


Figure 2a. Effect of MDA (2 mg/L) on neat fuel.

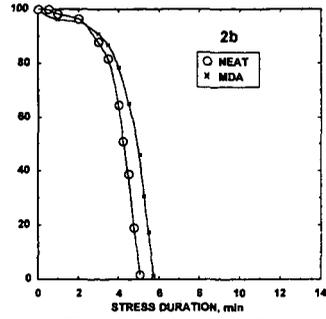


Figure 2b. Effect of MDA (2 mg/L) on diluted fuel.

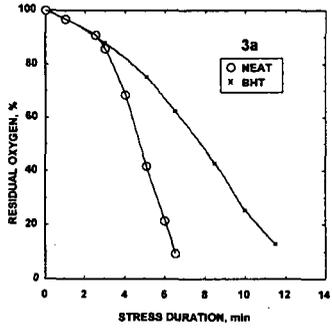


Figure 3a. Effect of BHT (26 mg/L) on neat fuel.

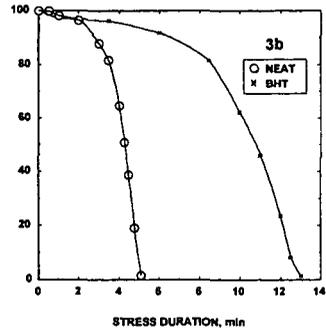


Figure 3b. Effect of BHT (26 mg/L) on diluted fuel.

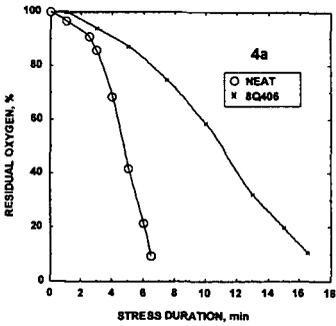


Figure 4a. Effect of BQ408 (100 mg/L) on neat fuel.

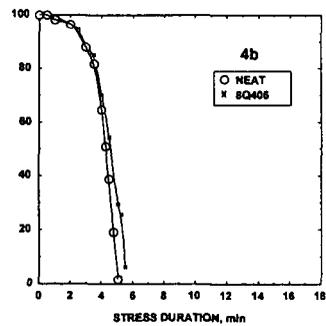


Figure 4b. Effect of BQ408 (100 mg/L) on diluted fuel.

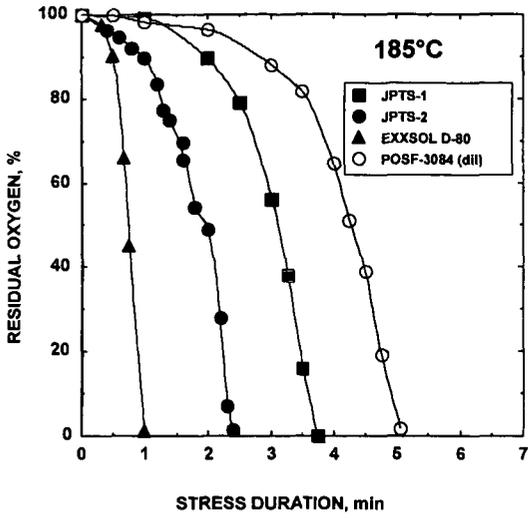


Figure 5. Comparison of diluted POSF-3084 with severely hydrotreated fuels.

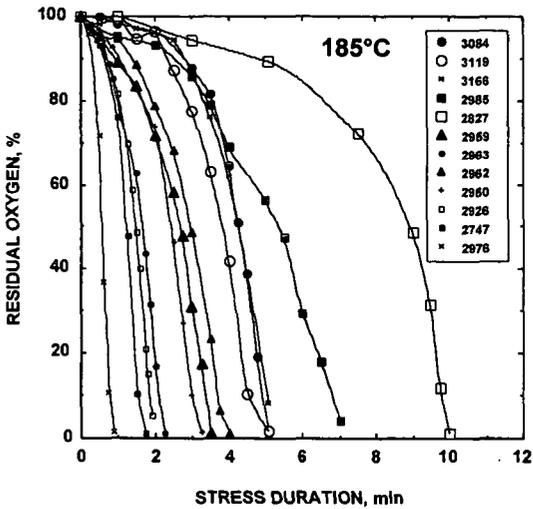


Figure 6. Oxidation of a series of diluted fuels.