

## LIQUID-PHASE OXIDATION KINETICS OF AVIATION FUELS

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### INTRODUCTION

Liquid-phase oxidation occurs when fuel that contains dissolved  $O_2$  is used as the primary heat sink for cooling aircraft subsystems.<sup>1</sup> Insoluble products of oxidation reactions can foul heated surfaces, resulting in expensive downtime for cleaning and replacement of heat exchangers, fuel-control valves, and injectors. Computational fluid dynamics (CFD) models<sup>2</sup> have been successful in calculating the extent of surface fouling in selected fuel systems. The general application of such models depends on calibration using experimental fouling data and is limited by simple representations of very complicated oxidation chemistry. Furthermore, the fact that each fuel is unique in its distribution and abundance of components adds to the complexity of the oxidation processes. More detailed knowledge of oxidation kinetics of several representative aviation fuels is needed to assist in improving CFD calculations and the understanding of the fundamentals of fuel autoxidation.

Over the past several years, our laboratory has been measuring the depletion of dissolved  $O_2$  under elevated-temperature (150-225 °C), elevated-pressure, and isothermal conditions to simulate the thermal oxidative stress conditions existing in aircraft fuel lines. An important factor in these studies has been the reduction of surface catalysis. Stainless-steel surfaces were found to catalyze autoxidation; however, the use of passivated tubing (Silcosteel process)<sup>3</sup> enabled the study of autoxidation with minimal effects from surface catalysis.<sup>4</sup>

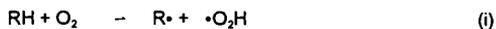
This paper summarizes recent kinetic studies of the oxidation of several representative aviation fuels. Results are reviewed for a Jet-A fuel, POSF-2827, that has been studied both as a neat fuel<sup>5</sup> and as a mixture catalyzed by  $Fe_2O_3$ .<sup>5</sup> New data are presented which extend the range of studied fuels to include both a rapidly oxidizing paraffin blend, Exxsol D-80, which is analogous to a JP-7 fuel, and a hydrotreated Jet-A fuel, POSF-3428.

## EXPERIMENTAL

The methodology used in NIFTR (Near-Isothermal-Flowing-Test-Rig) studies of oxidation and deposition has been described in detail previously<sup>7</sup>. 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 head space. Fuel reaction time (residence time) in the 0.81-m tube (i.d. 0.216 cm) was changed by varying the flowrate. Dissolved O<sub>2</sub> in the stressed fuel was measured by the GC method developed by Rubey and co-workers.<sup>8</sup> In experiments where the initial O<sub>2</sub> concentration was varied, fuel was sparged with different gas blends of O<sub>2</sub> and N<sub>2</sub> using a Porter CM 4 interface module and F200 thermal mass flow controllers.

## RESULTS AND DISCUSSION

**POSF-2827.** POSF-2827 is a Jet-A fuel with a thermal stability ranging from average to below average. Reduced thermal stability coupled with very slow oxidation, as shown at 458 K in Figure 1, has been attributed to a large excess of natural antioxidants.<sup>5</sup> The overall effect of these antioxidants is a low steady-state concentration of hydroperoxide, ROOH, and the absence of autocatalysis at higher O<sub>2</sub> conversion. Such a system with an approximately constant rate of initiation provided an excellent test for application of the NIFTR technique in collecting data for evaluating Arrhenius kinetic parameters. Since the reaction is 0.5 order in O<sub>2</sub>, it is explained according to the following simplified autoxidation mechanism:



where  $R\cdot$  is a radical,  $RO_2\cdot$  is a peroxy radical, and  $RO_2H$  is the hydroperoxide. Reactions (i) and (i') represent initiation, (ii) and (iii) are propagation, and (iv) termination. Reaction (i') is the major initiation reaction in hydrotreated fuels; it is of minor importance in fuels containing large concentrations of heteraromatic species and natural antioxidants. Data analysis over the temperature range 438–478 K yielded  $\log(k_{ap}/M^{-1/2}s^{-1}) = (12.9 \pm 0.4) - (36.9 \pm 0.8)/\theta$ , where  $k_{ap}$  is the apparent rate coefficient and  $\theta$  is  $2.303 RT$  kcal mol<sup>-1</sup> ( $R$  is the ideal gas law constant and  $T$  is absolute temperature). At lower temperature, the self-initiation of the autoxidation is negligible.

The addition of an external initiator (2,2'-azobis[2-methylpropionitrile], AIBN) over the temperature range 393–414 K resulted in  $\log(k_d/(2k_t)^{1/2}/M^{-1/2}s^{-1/2}) = (7.08 \pm 0.3) - (18.6 \pm 0.5)/\theta$ .<sup>5</sup>

**POSF-2827 (4 ppm Fe<sub>2</sub>O<sub>3</sub>).** Figure 1 shows changes arising from the introduction of 4 ppm of Fe<sub>2</sub>O<sub>3</sub> into POSF-2827. Fe<sub>2</sub>O<sub>3</sub> acts as a heterogeneous catalyst in accelerating autoxidation. The kinetic data for oxidation in the presence of Fe<sub>2</sub>O<sub>3</sub> are consistent with reaction acceleration from dissociation of an Fe<sub>2</sub>O<sub>3</sub>-ROOH adduct formed by the adsorption of ROOH on the Fe<sub>2</sub>O<sub>3</sub> surface; and subsequent H-atom abstraction by surface adsorbed radicals. Data analysis yielded  $\log(k_{ap}/M^{-1/2}s^{-1}) = (11.7 \pm 0.5) - (27.7 \pm 0.9)/\theta$  for the catalytic oxidation. The average value of  $E_{ii} - E_{iv}/2 = 18.6$  kcal mol<sup>-1</sup> determined from AIBN initiation coupled with  $E_{ap} = 27.7$  kcal mol<sup>-1</sup> implies  $E_i = 18$  kcal mol<sup>-1</sup> for initiation by Fe<sub>2</sub>O<sub>3</sub>.<sup>6</sup>

**Paraffin/cycloparaffin blend (Exxsol D-80).** This blend is representative of the highly thermally stable JP-7 fuel (in the absence of a lubricity additive) as used in high performance military aircraft such as the SR-71. With very low concentrations of aromatics (< 1%) and no natural or synthetic antioxidants, Exxsol D-80 oxidizes rapidly. Depletion of O<sub>2</sub> over the low-temperature range 408–438 K is given in Figure 2. Unlike POSF-2827 oxidation, this system is dominated by thermal dissociation of ROOH, as evidenced by acceleration at higher conversion. The kinetic data are described by  $\log(k_{ap}/M^{-1/2}s^{-1}) = (9.5 \pm 0.2) - (26.3 \pm 0.4)/\theta$ ; the solid lines illustrate fits from these parameters. Oxidation has been studied at 413 K for different initial concentrations varying from 10 to 100% O<sub>2</sub>-saturation at room temperature. The results, shown in Figure 3, are also fitted with the same kinetic parameters. Initial rates are independent of O<sub>2</sub> concentration, consistent with initiation by trace quantities of ROOH. Analysis of the ROOH data led to  $\log(k_d/(2k_t)^{1/2}/M^{-1/2}s^{-1/2}) = (3.3 \pm 1.3) - (12.5 \pm 2.6)/\theta$ .

**POSF-3428.** The fuels discussed above represent two extremes both in thermal stability and oxidation behavior. POSF-3428 is more representative of a broad spectrum of aviation fuels having intermediate stability and reaction rates controlled by hydroperoxides. The oxidation behavior shown in Figure 4 is autocatalytic and the solid lines were calculated using the same mechanism as that for Exxsol D-80, with thermal decomposition of ROOH as the dominant source of initiation. The kinetic data are summarized by  $\log(k_{app}/M^{-1/2}s^{-1/2}) = (12.3 \pm 0.9) - (34.7 \pm 1.8)/\theta$

## CONCLUSIONS

The apparent rate coefficients describing liquid-phase oxidation have been measured in four fuel systems using the NIFTR apparatus. The fuel reactivities may be ranked inversely according to the magnitudes of the apparent activation energies for autoxidation. Apparent activation energies follow the trend: POSF-2827 > POSF-3428 > POSF-2827 (4 ppm Fe<sub>2</sub>O<sub>3</sub>) > Exxsol D-80. The most unreactive fuel with respect to autoxidation is POSF-2827; the reason being that the fuel the fuel contains heteroaromatic species (sulfur compounds) that scavenge ROOH. The most reactive fuel is Exxsol-D80 which contains less than 1% aromatics and is devoid of natural ROOH scavengers. The extremes in reactivity are also reflected by the rates of initiation. Since appreciable ROOH does not accumulate in neat POSF-2827, initiation is controlled by reaction (i). This results in  $E_i = 37 \text{ kcal mol}^{-1}$  for the spontaneous initiation of POSF-2827. For Exxsol D-80, initiation is dominated by ROOH dissociation with  $\log(k_i/s^{-1}) = 16 - 33/\theta$ .

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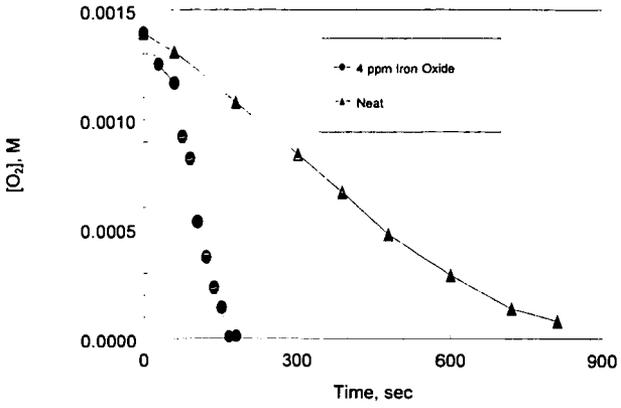


Figure 1. Oxygen depletion vs time for neat and iron-oxide (4 ppm)-treated fuel.

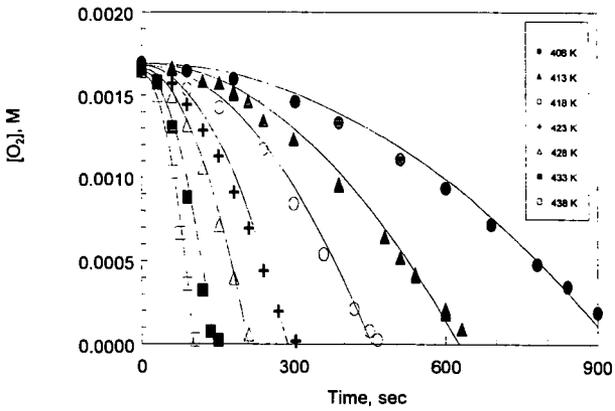


Figure 2. Influence of temperature on oxygen depletion : air-saturated Exxsol D-80 from 408 to 438 K.

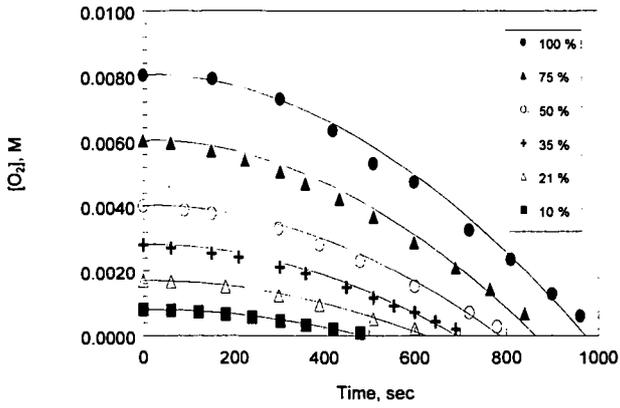


Figure 3. Influence of oxygen concentration on oxygen depletion: air-saturated Exxsol D-80 at 413 K.

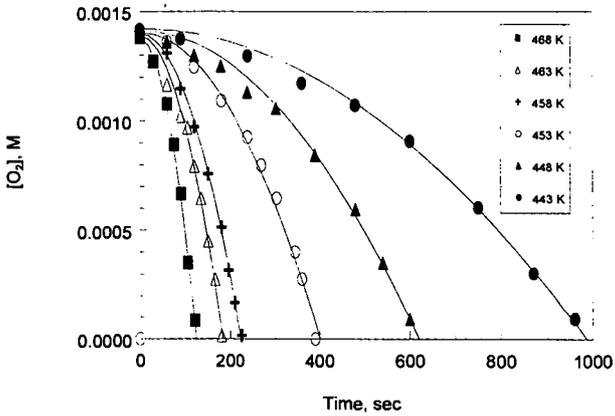


Figure 4. Influence of temperature on oxygen depletion: air-saturated POSF-3428 from 408 to 438 K.