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Fundamental studies of the oxidation and deposition of jet fuels

Mark Steven Mick

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FUNDAMENTAL STUDIES OF THE OXIDATION
AND DEPOSITION OF JET FUELS

Thesis
Submitted to
The School of Engineering of the
UNIVERSITY OF DAYTON

In Partial Fulfillment of the Requirements for
The Degree
Master of Science in Chemical Engineering

by
Mark Steven Mick

UNIVERSITY OF DAYTON
Dayton, Ohio
August 1998
FUNDAMENTAL STUDIES OF THE OXIDATION AND DEPOSITION OF JET FUELS

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FUNDAMENTAL STUDIES OF THE OXIDATION AND DEPOSITION OF JET FUELS

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A Parr bomb reactor, fitted with a quartz crystal microbalance (QCM), an oxygen sensor, and a pressure transducer is used in this study to evaluate the deposition and oxidation characteristics of jet fuel. This system is a batch reactor operated at 140°C which allows for very sensitive, in-situ measurements of deposition and oxidation. The goal of this effort is the development of additives at acceptable cost which will improve the thermal stability of the current U.S. Air Force fuel, JP-8, where the bulk maximum temperature of the fuel increases by 100°F (55°C). Although nearing the completion of this so-called “JP-8+100 program”, there are still numerous additives that require analysis in tests like the QCM, and fundamental jet fuel chemistry investigations to be performed.

In this work, the pretreatment method of solid phase extraction (SPE) is studied, and the effects on the deposition and oxidation of a fuel are evaluated. It was determined that SPE is an effective method of reducing thermal-oxidative deposition and increasing
the oxidation rate by the removal of heteroatomic species, like phenols, which are frequently found in jet fuels.

Next, we explore two different additive types to slow the oxidation cycle. The first, peroxy radical inhibitors, intercept alkyl peroxy radicals and thus slow the autoxidation chain. The second, hydroperoxide decomposers, bimolecularly decompose hydroperoxide species into non-radical products. The suppression of autoxidation is important because of the close correlation between deposition and oxidation. We show a dramatic synergistic effect when the two additives are introduced to a fuel together to produce an oxidative delay significantly greater than the sum of the two individual effects. A chemical kinetic model is also employed and validates the experimental results.

Finally, to learn more about the thermal stability of jet fuels and to explore new avenues for fuel additives, silylation is used to chemically transform naturally occurring heteroatomic species which have been implicated in deposit forming and oxidation inhibition processes. Silylation is widely used in chromatographic analysis to improve analytical quantitation. We show that adding the silylation agent hexamethyldisilazane (HMDS) to jet fuel significantly reduces deposition and significantly increases the oxidation rate. Furthermore, silylation and SPE are shown to reduce deposition and increase oxidation in similar ways.
ACKNOWLEDGEMENTS

Upon my arrival at Wright-Patterson Air Force Base, I knew little about military aircraft, and even less about jet fuel. Upon my departure, I feel I have become rather proficient in an interesting and exciting field. I am, therefore, extremely thankful and indebted to my research advisor, Dr. Steven Zabarnick. Our numerous and lengthy discussions about the fundamental chemistry and applications of jet fuel have allowed me to better develop my experimentation, analytical, and writing skills.

My thanks also goes to my office-mates: Rich Striebich, for the early morning technical discussions, endless help with the GC-MS, and especially for serving on my thesis committee; and Becky Grinstead, for guidance in the laboratory and for helping with the direction of my work. I would like to thank Dr. Dilip Ballal for offering me a research assistantship, financial support, and the opportunity to work in an environment committed to science and learning. I would also like to acknowledge other University of Dayton Research Institute co-workers Dr. Shawn Heneghan and Dr. Jamie Ervin for their support and encouragement, and Mr. Steve Anderson of the U.S. Air Force.

To my professors at the University of Dayton, umm, thanks for the homework? It was rarely boring, frequently frustrating, but always enlightening. Specifically, I would like to acknowledge Dr. Tony Saliba and Dr. Kevin Myers for their friendship, guidance, open-door policies, and for serving on my thesis committee. Thanks also to Janet Pastor for keeping many of my “official” academic on-goings in check.

Most importantly, I would like to thank my wife, Cassia. Her love, support, and motivational talks have made this all possible. I could not have made it, and would not
want to have made it, without her. I'd like to finally thank my parents for their guidance and advice in just about everything I have done.

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>amu</td>
<td>atomic mass unit</td>
</tr>
<tr>
<td>A•</td>
<td>antioxidant radical</td>
</tr>
<tr>
<td>AH</td>
<td>antioxidant molecule</td>
</tr>
<tr>
<td>AOO•</td>
<td>peroxy radical of antioxidant species</td>
</tr>
<tr>
<td>AOOH</td>
<td>hydroperoxide of antioxidant species</td>
</tr>
<tr>
<td>BHT</td>
<td>butylated-hydroxy-toluene; 2,6 di-tert-butyl-4-methyl-phenol</td>
</tr>
<tr>
<td>f₀</td>
<td>initial crystal frequency of vibration (MHz)</td>
</tr>
<tr>
<td>F-x</td>
<td>fuel inventory code</td>
</tr>
<tr>
<td>GC-MS</td>
<td>gas chromatography with mass spectrometry detection</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazane - a silylation agent</td>
</tr>
<tr>
<td>JPTS</td>
<td>Jet Propellant Thermally Stable</td>
</tr>
<tr>
<td>K²</td>
<td>quartz electromechanical coupling coefficient</td>
</tr>
<tr>
<td>M</td>
<td>moles/liter</td>
</tr>
<tr>
<td>MDA</td>
<td>Metal Deactivator Additive</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>n</td>
<td>number of crystal faces contacting liquid</td>
</tr>
<tr>
<td>N</td>
<td>harmonic number</td>
</tr>
<tr>
<td>O₂</td>
<td>oxygen molecule</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>PID</td>
<td>feedback control system with proportional, integral, and derivative action</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz Crystal Microbalance</td>
</tr>
<tr>
<td>rf</td>
<td>radio frequency</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>R•</td>
<td>fuel hydrocarbon radical</td>
</tr>
<tr>
<td>RH</td>
<td>fuel hydrocarbon molecule</td>
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<tr>
<td>ROO•</td>
<td>peroxy radical</td>
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<tr>
<td>ROOH</td>
<td>hydroperoxide molecule</td>
</tr>
<tr>
<td>SH</td>
<td>bimolecular hydroperoxide decomposing molecule</td>
</tr>
<tr>
<td>SPE</td>
<td>solid phase extraction</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature (K)</td>
</tr>
<tr>
<td>UDRI</td>
<td>University of Dayton Research Institute</td>
</tr>
<tr>
<td>USAF</td>
<td>United States Air Force</td>
</tr>
<tr>
<td>η</td>
<td>liquid absolute viscosity (g/cm \cdot s)</td>
</tr>
<tr>
<td>μₚ</td>
<td>quartz shear stiffness (dimensionless)</td>
</tr>
<tr>
<td>ρ</td>
<td>liquid density (g/cm³)</td>
</tr>
<tr>
<td>ρₚ</td>
<td>quartz mass density (g/cm³)</td>
</tr>
<tr>
<td>ρₛ</td>
<td>areal mass density of surface deposit (µg/cm²)</td>
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CHAPTER I

INTRODUCTION

Background

In modern military aircraft, jet fuel not only serves as the propellant, but also as the primary heat sink to cool the aircraft's engine components and various other parts. Many of the subsystems of the aircraft (power generation, hydraulics, environmental control, etc.) generate significant heat during normal operation which must be removed to insure adequate life and reliability of the components. Fuel is circulated throughout the airframe to match heat loads with available heat sink capacity and required engine cooling and burn rate.

In an age dominated by rapid technological advancement, highly maneuverable military aircraft with high performance engines and advanced subsystems are being developed. With such advances, management of thermal requirements is becoming significantly more complex. Typically, the fuel and ram air are used as the primary heat sinks for the aircraft. However, the use of ram air for cooling restricts the flight envelope and can actually heat the aircraft at supersonic speeds. This can reduce the performance and reliability of specific components because air has relatively poor heat transfer characteristics and cannot dissipate the required heat (Edwards et al., 1993). Therefore, the designers of aircraft are focusing primarily on using the fuel to provide the necessary system cooling.
Using the fuel as a heat sink can cause numerous problems because, when it is
exposed to high temperatures, it can decompose oxidatively or pyrolytically and lead to
damaging deposition. Malfunctions associated with these deposits and gums can include
the fouling and clogging of heat exchangers and valves. Additionally, the collection of
deposits on fuel nozzles can disrupt combustor spray patterns and eventually lead to
damage of engine components. Also, improved engines will inevitably increase the
operating temperatures of the aircraft, and problems with the thermal stability of the fuel
could become much more frequent. Of course, the most severe of any of the instances of
component fouling by fuel degradation is that of complete, and perhaps catastrophic,
system failure.

Problems of this nature were first recognized by Pratt & Whitney in the 1950's
when fuel was exposed to elevated temperatures in various engines. Upon lengthy
exposure to such temperatures, insoluble deposits that formed resulted in erratic heat
transfer and ultimately engine damage. The damage was traced to fuel nozzles partially
plugged with carbon and varnish deposits (CRC, 1979). Some of the most serious
incidents of deposit formation in widely used commercial jet engines occurred in the mid-
1960's. A task, therefore, was initiated by the United States Air Force (USAF) to research
the minimization of such deposition and surface fouling to ultimately increase the
capabilities of aircraft and to minimize maintenance costs.

Jet Fuel Thermal Stability

When jet fuel is heated to elevated temperatures it decomposes into soluble and
insoluble products via two distinct mechanisms: thermal oxidative and pyrolytic. In the
pyrolytic regime (temperature range of >400°C) deposition occurs from the free-radical
mechanism involving the supercritical-phase, high-temperature, and high-pressure
cracking of carbon-carbon bonds (Song et al., 1994). Typically, a straight chain alkane
might decompose into alkenes, lower molecular weight alkanes, and insoluble particulates, gums, and deposits. In contrast, thermal oxidative deposition occurs in the approximate temperature range of 100-300°C as a result of free-radical reactions with oxygen.

In general, a jet fuel's thermal stability refers to its ability to withstand temperature without thermally degrading into these insoluble gums and deposits. Thus, the higher a fuel's thermal stability, the less likely it is to thermally degrade. As aircraft become more technologically advanced and produce significantly higher temperatures, the requirements on the fuel will increase to improve its cooling potential. Under certain flight conditions (related either to the fuel or the type of aircraft), the temperature of the components with which the circulating fuel is in contact can exceed the "heat sink" ability of the fuel. This is the point at which deposition becomes a major concern.

Since the problems associated with jet fuel deposition were first recognized, much work has been performed to try to understand the chemistry involved in fuel oxidation and degradation. Perhaps the most challenging facet of evaluating the thermal stability of jet fuels is their varied and complex composition. Because of the variety of sources of crude oil and the differences in the refining processes, there are hundreds of naturally occurring species and, consequently, an unlimited number of possible combinations of species in fuels. Because a fuel's deposition and oxidation behavior are strongly dependent on its composition, the result of the different combinations of species is the production of a number of inherently different fuels.

The challenge to understand thermal stability, and to attempt to develop a solution that is effective not only for one fuel but for the whole range of fuels available, is to focus not on their differences, but rather on their similarities. A unifying factor common in all fuel systems, which will prove to be crucial to this work, is the availability of oxygen. There is ample evidence describing the close relationship between oxidation and deposition. Therefore, it may be possible to manage the deposition (thermal stability) of a
fuel by controlling its oxidation. Also, by making simplifying assumptions, chemical kinetic modeling can be employed to help better understand the fundamental chemistry of the system.

**Thermal Stability Evaluation Methods**

The characteristics of a fuel can change significantly during storage in surface and aircraft wing tanks, and during the recirculation through the aircraft to provide cooling. For example, a fuel might partially or completely degrade before ever reaching the plane, thus potentially altering its use as a propellant and/or as a coolant. In surface storage tanks, the fuel temperature remains relatively stagnant around 20°C. Once in the plane, the fuel is repeatedly heated and cooled during recirculation. As a result, many different test environments are necessary for the overall evaluation of the thermal stability of the fuel.

The thermal stability evaluation methods can be grouped into two distinct categories: flowing and static tests. Flowing tests usually use large volumes of fuel and are often quite large and complex. The benefit of such tests is that they most closely simulate the actual flowing aircraft fuel system. The fuel is generally pretreated to establish a known dissolved oxygen concentration. Once it enters the system, no oxygen is available for reaction other than that which is initially dissolved. Fuel degradation in flowing systems is usually measured by the amount of deposits formed in the inside of the tube through which the fuel flows. Oxidation can also be measured on flowing systems.

Three examples of flowing tests are the Phoenix Rig (Heneghan et al., 1993), the Nearly Isothermal Flowing Test Rig (NIFTR) (Jones et al., 1996), and the jet fuel thermal oxidative tester (JFTOT), (see ASTM D3241). The Phoenix Rig and the NIFTR use stainless steel tubes which, at the conclusion of the test, are measured for deposition by
carbon burn-off. Gas chromatography is commonly employed to measure the oxygen concentration at the tube outlet. Deposition of the JFTOT tube is measured visually with a standard color rating. These large-scale flowing tests can provide realistic simulation of parameters like temperature (although usually accelerated), flow conditions, oxygen levels, and recirculation. However, their limitations are found in the complexity, large volumes of fuel, and the lengthy test times.

Conversely, static tests are usually rather simple in nature and use small quantities of fuel. For example, while a flowing system might use several hundred liters of fuel, a static test may use only 0.1 liter of fuel. Since deposits are typically on the order of milligrams in static tests, they must either use excess oxygen or have extremely high sensitivity to measure very small amounts of deposits. Static tests that are constantly open to air are difficult to correlate to closed tests because of the unlimited availability of oxygen. They are, on the other hand, the easiest tests to prepare. The isothermal corrosion oxidation test (ICOT) (Grinstead, 1997) is an example of an open, static test. In the ICOT, the fuel is heated with constant bubbling of air. The stressed fuel is filtered and the deposits are weighed.

The Quartz Crystal Microbalance (QCM)/Parr bomb system is an example of a closed static test (Klavetter et al., 1993). This system is sealed before the test begins, resulting in a limited amount of available oxygen during the experiment. Recent work has demonstrated that the QCM/Parr bomb system, the test used in this work, is capable of effectively evaluating both jet fuels and jet fuel additives because of the high sensitivity it has for deposition (Zabarnick and Grinstead, 1994). The distinguishing characteristic of this system is the real-time, in-situ monitoring of both oxidation and deposition. An oxygen sensor and pressure transducer allow the operator to monitor the headspace oxygen concentration throughout the duration of each experiment.
Oxidation and Deposition

The reactions of jet fuel with oxygen occur as a result of three categories of reactions involving free radicals: initiation, propagation, and termination. This cycle of reactions is termed autoxidation (Hazlett, 1991). The autoxidation methodology of a simplified mechanism has been described in detail previously (Zabarnick, 1993). As jet fuel is comprised largely of alkanes, the fuel is represented as a single straight-chain alkane, RH. This simplification, which does not compromise the test results, is important because it is impractical to identify and account for each component in the wide variety of fuels.

![Diagram of the autoxidation cycle](image_url)

**Figure 1: The autoxidation cycle consisting of the reaction of oxygen with a free radical, ultimately producing another free radical.**

The production of a "fuel radical", R*, initiates the cycle seen in Figure 1, which then reacts with oxygen to form a peroxyl radical, RO₂*. The peroxyl radical then reacts with the fuel according to the following reaction to form a hydroperoxide and a new fuel radical, thus propagating the cycle:

\[
RO_2^* + RH \rightarrow ROOH + R^* \quad (1)
\]
The multi-arrow line in Figure 1 indicates that the hydroperoxide generates two $R\cdot$ radicals via a series of reactions involving its unimolecular, thermal decomposition, as is seen below:

$$ROOH \rightarrow RO\cdot + OH\cdot$$ (2a)

$$RH + RO\cdot \rightarrow ROH + R\cdot$$ (2b)

$$RH + OH\cdot \rightarrow H_2O + R\cdot$$ (2c)

The hydroperoxide is first decomposed into an $RO\cdot$ radical and an $OH\cdot$ radical. Reaction of either of these species with the fuel, $RH$, produces the propagating $R\cdot$ radical. The alkyl peroxy radical, $RO_2\cdot$, and the hydroperoxide, $ROOH$, produce significant quantities of $R\cdot$ radicals, thereby promoting oxidation.

Although jet fuels can produce deposits in the absence of oxygen, deposition is much more severe when the fuel is saturated with air. Therefore, it is clear that deposits result from thermal stressing of jet fuel can be correlated to the oxygen consumption of the air saturated fuel, see Figure 2 (Zabarnick and Whitacre, 1998).

![Figure 2: Plots of mass accumulation and headspace oxygen in the QCM/Parr bomb system at 140°C for F-3145 with 5.8 mg/L MDA (Zabarnick and Whitacre, 1998).](image-url)
The figure demonstrates that in the early hours of this experiment there is little oxygen consumption, corresponding to the low mass accumulation. However, at approximately seven hours there is a rapid increase in oxygen consumption, and a corresponding increase in deposition. When all of the oxygen has been consumed at approximately 11 hours, no additional mass accumulation is observed. It is important to note that the correlation between oxidation and deposition see in Figure 2, although very frequent, is not always evident. For example, a hydrotreated fuel might oxidize very quickly and deposit very little. However, for the most part the deposition and oxidation of jet fuels are closely related, and is an area in need of further study.

The goal of improving jet fuel thermal stability is sometimes dominated by attempting to control the deposition of the fuel. We have chosen to also approach the problem by controlling a fuel's oxidation. The purpose of this approach is two-fold. First, it is easier to control the oxidation, as opposed to controlling the less understood deposition, because of the complex nature of the formation and composition of jet fuel gums and deposits. Second, providing insight into the autoxidation mechanisms will allow us to better understand the mechanisms by which fuels oxidize.

Jet Fuels - Past, Present, and Future

For nearly 45 years between 1951 and 1995, the military had used one primary jet fuel, JP-4 (JP = Jet Propellant). As compared to the high volatility aviation gasolines, this gasoline/kerosene blend was restricted to a relatively low vapor pressure (on the order of 0.2 atmospheres) to reduce vapor lock and relight problems at high altitudes, and to minimize boil-off losses. JP-8, which has an even lower vapor pressure, was developed to improve fuel handling and crash safety, and to serve as the single battlefield fuel. This is because JP-8 can be used in ground diesel equipment as well as in aircraft. This fuel is classified as Jet A-1 (a kerosene based fuel used in international commercial airlines)
with an icing inhibitor, a corrosion inhibitor/lubricity enhancer, and a static dissipating additive (Martel, 1987).

The Air Force began the transition from JP-4 to JP-8 in 1979. JP-4 was not totally phased out until the early 1990's. This was clearly not a trivial task. The size of the U.S. Air Force made implementation of a new fuel difficult, time consuming, and quite costly. The current initiative for improving the thermal stability of JP-8 is a similarly arduous, but important, task. There are a number of techniques available that can improve the thermal stability of jet fuels. For example, the removal of dissolved oxygen, the treatment of metal surfaces, hydrotreatment, and clay filtration all have proven to be effective means of reducing deposition due to thermal stressing. The USAF has selected, however, the use of additives as the primary means to improve the thermal stability based on practicality, cost, and efficacy.

The use of additives will provide a low cost option to increase jet fuel thermal stability. The Air Force also partially relies on hydrotreatment and refinement in its aircraft-specific specialty fuels. Refinement, however, can be expensive. Two specialty fuels used by the Air Force are JP-7 and JP-TS (Jet Propellant - Thermally Stable). JP-7 is a highly refined kerosene consisting mostly of paraffins. Used in the SR-71, JP-7 was especially formulated for high altitude, and high speed (faster than Mach 3) operation. JP-TS is a highly refined kerosene with a low freeze point (-53°C) that is used specifically in the U-2. Figure 3 (Zabarnick and Whitacre, 1998) depicts the advantages of refinement. Mass accumulation and headspace oxygen concentration are plotted for F-2827, a straight run fuel, and F-2747, a hydrotreated fuel. (NOTE: F-x is a USAF inventory classification, and will be used throughout this thesis.) The mass accumulation and oxygen consumption differences are clear. Hydrotreatment significantly reduces the deposition. However, oxygen consumption is also much more rapid as F-2747 completely oxidizes in approximately 5 hours, while F-2827 does not approach complete oxidation at the end of the 15 hour experiment. Experience has shown that the “ideal” fuel would be a
combination of these two fuels: a low depositor and a slow oxidizer. Such is the goal of the JP-8+100 program.

**Figure 3:** Plots of mass accumulation and headspace oxygen concentration from the QCM for a hydrotreated jet fuel, F-2747, and a normally processed fuel, F-2827 (Zabarnick and Whitacre, 1998).

**JP-8+100 Program**

The discussions of the improvement of thermal stability are extremely important to the underlying goal of this work: the U.S. Air Force's JP-8+100 Program. The USAF predominantly uses the fuel JP-8. The thermal stability of this fuel restricts the maximum bulk temperature to 325°F at the inlet to the main burner nozzle, and to a wetted-wall temperature of 400°F inside the nozzle passages. These limits were established based on operational history of aircraft, and in efforts to minimize deposition. In preparation for the increasing heat loads of future aircraft, the USAF has set a goal of increasing the thermal stability limit of JP-8 by 100°F (56°C) through the use of additives, without compromising its performance requirements. This more thermally stable fuel is,
appropriately, referred to as JP-8+100 (Anderson et al., 1994). The discussion of the lengthy transition from JP-4 to JP-8 mentioned previously adds a great deal of perspective to this newest JP-8+100 initiative.

The JP-8+100 program has set practical limits. Increasing the upper temperature limit at which the fuel is thermally stable by 100°F will increase the heat sink capacity by almost 50 percent. Included in this program are strict financial limits that must be met to make the project, both in research and implementation, economically beneficial. The program has called for additives to be developed, with which the fuel can be blended, at a cost equal to or less than $1 per 1000 gallons of fuel. The monetary considerations have made the project all the more challenging. The need to develop an improved fuel at such a low cost will alleviate the need to use more expensive specialty fuels, like JP-7 and JP-TS mentioned earlier, in future aircraft.

The QCM is one of several tests that the Air Force and UDRI uses to evaluate an additive's impact on a fuel. Hundreds of additives have been evaluated. To date, the JP-8+100 program has achieved great success. The additive package in current use, named Betz-Dearborn SPEC*AID 8Q462, has been examined in a variety of fuels. One such application is shown in Figure 4 with the high-depositing fuel F-3119. This figure shows that through the use of an additive, the mass accumulation of F-3119 is reduced from 18.6 to 0.6 μg/cm². Also, the oxygen consumption rate was greatly reduced. Unlike the neat fuel which oxidizes completely in 14 hours, the presence of the additive slows the oxidation such that it does not come close to complete oxidation at the end of the 15 hour experiment. Recall that the "ideal" fuel (Figure 3) is one with low deposition (like the refined F-2747) and slow oxidation (like F-2827). It can be seen that 8Q462 does an excellent job of achieving ideality, and greatly improving the thermal stability of the fuel.

Additive addition must not have a detrimental effect on fuel quality. The additive package formulation process, especially one that will be used in a wide variety of fuels, certainly involves verification that the additives improve the thermal stability of the
depositing fuels. Additionally, one must insure that the additives do not make the fuel worse by, for example, increasing deposition. In this, and all other tests run to date, no such increase in deposition has occurred as a result of the addition of the 8Q462 additive package.

Figure 4: Plots of mass accumulation and headspace oxygen of neat F-3119 and F-3119 with 256 mg/L 8Q462 (the JP-8+100 additive).

The success of this single additive package raises the question: why continue the work? The reason is two fold - economic and scientific. From an economic standpoint, developing additional additive packages will encourage competition among the additive manufacturers. Therefore, additional research for this program serves as a cost saving strategy to promote manufacturer competition which will potentially drive additive prices lower. From a scientific standpoint, further research will continue to provide fundamental insight and understanding of the oxidation and deposition of fuels.

The objective of our research is the formulation of cost-effective additives which can be added to JP-8 fuel to increase its thermal stability at elevated temperatures. We first study the fairly well understood pretreatment method of solid phase extraction
(SPE), and the effects of the removal of heteroatomic species from fuels, like phenols. What was elucidated by studying SPE, will then be applied to the study of potential jet fuel additives. We explore two different types of additives which affect the oxidation rate, peroxy radical inhibitors and hydroperoxide decomposers. The mechanisms by which these additives and species in the fuel react are studied to better understand their individual and combined impacts on the slowing of the oxidation rate. Finally, to examine new avenues for fuel additives, we study the effects of silylation on fuels and the effects of chemically transforming naturally occurring heteroatomic species, which have been implicated in deposit forming and oxidation inhibition processes.
CHAPTER II

EXPERIMENTAL

The Quartz Crystal Microbalance System

This work was performed using a quartz crystal microbalance (QCM)/Parr Bomb system which allows in-situ, real time measurements of the mass deposited on the surface of a quartz crystal. A diagram of the apparatus is shown in Figure 5. This device is especially significant because it operates at temperatures that closely approximate current flowing fuel systems (Klavetter et al., 1993). The data acquisition is performed by a personal computer (PC), allowing for lengthy, data-intensive runs without continual human supervision. The QCM system is a static test in which 60 mL of the fuel is added to the 100 mL stainless steel Parr Bomb reactor. The lid, which has been modified to allow an rf feedthrough, is attached to the body of the reactor with a gasket and clamps. This allows the pressurization of the reactor to prevent boil-off losses, and closes the system to provide a limited oxygen regime. The fuel is heated with a clamp-on band heater. A magnetic stir bar and stirrer are used to minimize the spatial temperature and concentration gradients.

The system is fitted with an oxygen sensor (Ingold Model 4300) which measures the headspace oxygen concentration, and a pressure transducer (Sensotec Model TJE/713) which measures the absolute headspace pressure. Both of these devices are used to make real-time measurements of oxygen consumption, which will prove to be extremely useful for this work.
Because only 60 mL of fuel is used in a 100 mL reactor, there is approximately 40 mL of headspace volume. It is from this volume that the oxygen measurements are made. The concentration of the oxygen in the fuel is proportional to the partial pressure of the oxygen in the headspace. As oxygen is consumed in the liquid fuel, it diffuses into the fuel from the headspace. This causes a corresponding decrease in pressure in the reactor, and thus is an indirect way to measure oxidation. The oxygen sensor is a more direct, and
consequently more accurate, method of oxidation monitoring. The sensor provides more accurate and more quantitative measurements of oxidation because, unlike the pressure transducer, it is generally not affected by the vapor pressure of the fuel's volatile components or additives. In general, the pressure transducer is used to verify the measurements of the oxygen sensor. Therefore, each of the oxidation plots presented throughout this paper represent the percent of oxygen in the headspace of the reactor.

The reactor is also fitted with a gas inlet line below the level of the liquid through which gases can flow for sparging. A vent above the liquid level allows for the sparging gases to escape. Both the inlet line and the vent are sealed before commencing the test to limit the oxygen availability to that present in the air-saturated fuel and in the small headspace. This more closely approximates the oxygen availability of flowing tests and real fuel system conditions.

The QCM provides extremely sensitive measurements of surface deposition on quartz crystals. The thin crystals used are of AT-cut quartz with electrodes on both sides, and are shown in Figure 6. The sensitivity of the QCM is on the order of 0.2 μg/cm². An oscillator circuit that was developed at Sandia National Laboratories allows it to oscillate at its characteristic frequency of 5 MHz (Klavetter et al., 1993). Deposition is measured by monitoring the changes that surface accumulation has on this frequency.

Figure 6: Figure of a quartz crystal, with a grounded electrode and, on the other side, an electrode at rf potential.

The quartz crystals used in these experiments, provided by Maxtek, Inc., are 2.54 cm in diameter, 0.33 mm thick wafers with two gold electrodes. A crystal is suspended vertically in an assembly which is connected to the quartz crystal resonator via the rf
feedthrough. The crystal is positioned vertically to minimize gravitational settling of the bulk insolubles in the fuel on the crystal's surface.

![Block diagram of the data acquisition system](image)

**Figure 7:** A block diagram of the data acquisition system which is centered around the QCM apparatus and the personal computer.

In addition to the hardware fitted directly on the QCM/Parr Bomb system, there are a number of setting/output devices which control the experiments. A block diagram of the system set-up is shown in Figure 7. A frequency counter (HP Model 5384A) is used to read the oscillator frequency output, and a digital multimeter (HP Model 3478A) is
used to read the amplitude output. A PID temperature controller (Parr Model 4842) connected to the clamp-on band heater controls the temperature at which the experiment is to be run via measurements from the thermocouple immersed in the fuel. The temperature of the system is normally maintained at 140°C, with fluctuations of approximately ±0.2°C. (NOTE: From this point on, unless otherwise specified, implicit upon referral to “the QCM” is the whole QCM system described previously including the deposition measuring microbalance, the oxygen sensor, pressure transducer, thermocouple, etc.)

QCM Theory

The QCM is a powerful technique because of its ability to make highly sensitive measurements of mass deposition. The piezoelectric properties and crystalline behavior of the quartz results in a shear deformation of the crystal (Figure 8) upon the application of a voltage between the electrodes.

![Quartz Crystal Shear Deformation](image)

**Figure 8:** Diagram of the shear deformation of a quartz crystal which occurs when the crystal is excited to its resonant frequency.

The (converse) piezoelectric effect was verified by Jacques and Pierre Curie, describing how the application of a voltage across the quartz crystals afforded a corresponding mechanical strain. This strain field initiates a vibrational motion in the crystal resulting in standing waves. The characteristics of the particular quartz define the specific resonant frequency at which the crystal will preferentially vibrate (Ward and Buttry, 1990).
The quartz crystals are nearly ideal oscillators because of their ease of fabrication, ruggedness, and their low cost. Especially of significance from a jet fuel experimental standpoint is their chemical inertness. The crystals consist of gold electrodes patterned on both sides of the quartz disk. A grounded electrode is on one side, and an electrode at rf potential is on the other. These allow the crystal to be electrically excited into resonance. The piezoelectric strain and corresponding vibration are confined to the area between the two electrodes. The shear deformation of the crystal that results is very similar to the waves traveling in a string. When the string of a guitar, for example, is plucked, it is driven by impulses at a frequency matching its fundamental frequency. Upon application of an electric field, the quartz crystal vibrates in an analogous fashion at its fundamental frequency - in our experiments, approximately 5 MHz.

The crystals are electrically excited by an oscillator circuit. Mass accumulation on the crystal surface, because of the jet fuel thermal degradation discussed earlier, results in a decrease in the oscillation frequency (Martin et al., 1991). Also, a thick layer of liquid can be entrained by the surface resulting in a decrease in the resonant frequency. Reconsider the discussion of the guitar string. An increase in the length or thickness of the string results in a decrease of the frequency. The case of the fundamental frequency of a quartz crystal, as used in these experiments, is extremely similar. The fundamental frequency is proportional to:

\[ f_0(\text{Quartz}) \propto \frac{1}{2t_q \times \rho^{1/2}} \]  

where \( \rho \) is the mass density of the quartz and \( t_q \) is the crystal thickness. When fuel deposits collect on the crystal faces or liquid is entrained on the crystal surface, it increases the thickness. This, in an analogous fashion to the musical strings, results in a lowering of the fundamental frequency.
The decrease in frequency for the AT-cut quartz crystal resulting from the deposition processes and liquid contact discussed is given by:

\[
\Delta f_0 = \frac{2f_0^2N}{N(\mu q \rho q)^{1/2}} \left[ \rho_s + \left( \frac{\rho \eta}{4 \pi f_0} \right)^{1/2} \right]
\]  

(4)

In this equation, \(f_0\) is the initial resonant frequency, \(N\) is the harmonic number (\(N=1, 3, 5\ldots\)), and \(\mu_q\) is the quartz shear stiffness, which is equal to \(2.947 \times 10^{11}\) dyne cm\(^{-2}\). The other terms in Equation 4 are \(\rho_q\), the quartz mass density which equals \(2.648\) g cm\(^{-3}\); \(\rho_s\), the surface mass density; \(\rho\), the liquid density; \(\eta\), the liquid viscosity; and \(n\), the number of sides of the crystal in contact with the liquid or coated by a mass layer. Equation 4 is complicated by the fact that little is known about the changes in liquid density and viscosity during the course of the experiment. The test is based on measuring the fundamental frequency, not the liquid properties. However, this problem is alleviated by making one simplifying, and physically logical, assumption: in the constant temperature regime, the liquid properties are assumed not to change appreciably. Only the values of frequency taken under isothermal conditions are used in thermal stability (deposition) evaluation. This will allow the direct measurement of mass accumulation on the surface of the crystal by simply monitoring the frequency changes. Following mathematical manipulation and simplification of Equation 4 and substitution of the appropriate liquid property values, \(N=1\) (for resonators operating in the fundamental resonance), and \(n=2\) (for the two sides of the crystal), the surface mass density of accumulated fuel decomposition products on the crystal can be reduced to (Klavetter et al., 1993):

\[
\rho_s = -\left(2.21 \times 10^5 \frac{g}{cm^2s}\right) \frac{\Delta f}{f_0^2}
\]

(5)
As can be seen from Equation 5, measurements of surface mass density can now be made by simply noting the initial oscillating frequency of the crystal, and monitoring its changes.

The resonant frequency of the crystal can be changed both by mass deposition and liquid loading. As seen in Equation 4, the measurement of frequency alone cannot distinguish between the two. It is important that the fluid properties, and therefore the liquid loading, do not fluctuate too much because this can lead to erroneous deposition data. One way to monitor this is through the motional resistance, $R$. This is a measure of the crystal damping, which arises because of viscous coupling to the adjacent liquid - in our case, jet fuel. The motional resistance is related to the liquid properties as:

$$R = \frac{N\pi n}{8K^2C_o} \left( \frac{\rho \eta}{\pi f_s \mu \rho q} \right)^{1/2} \quad (6)$$

In Equation 6, $K^2 = 7.74 \times 10^{-3}$ is the quartz electromechanical coupling coefficient, and $C_o = 4.25 \text{ pF}$ is the static capacitance of the device (Klavetter et al., 1993).

This motional resistance can be monitored on the output device of the experimental equipment. Any changes in the damping voltage help to distinguish the oscillation frequency changes that are due to the liquid loading, as opposed to the mass deposition. It has been shown previously, and was corroborated in these experiments, that except for a few cases in which the jet fuels were additized, the damping voltage exhibited little change. This confirms our assumption of constant liquid properties, and validates the use of Equation 5.

**Test Procedure**

In general, each experiment is initiated in the same manner, and centered around the QCM and the personal computer. The set-up begins by selecting the particular fuel or
fuel/additive mixture to be tested, and adding 60 mL of it to the 100 mL reactor. The crystal is prepared by adding two small pieces of indium metal, cut from a 0.5 mm diameter wire, to the electrodes to provide better electrical contact between the oscillator circuit (via the clamp attached to the reactor lid) and the crystal.

The crystal is clamped in place and the lid is set on the reactor, lowering the crystal into the fuel. The lid is fastened to the reactor bomb by six bolts which are tightened securely with a wrench. The power to the oscillator circuit is turned on to insure that the crystal is oscillating properly. Should the frequency counter not measure 5 MHz it would be clear that there was a problem with the assembly.

The oxygen sensor, pressure transducer fitting, and thermocouple are all attached to their respective devices on the lid of the reactor. The gas inlet and vent hoses are firmly attached and tightened with a wrench. Air is sparged through the fuel for approximately one hour to insure air saturated conditions. If necessary, the oxygen sensor, measuring in percentage of O_2, is then calibrated to read 20.9 percent O_2 in air. Once the preliminary set-up is complete, the heater is turned on, set to the typical temperature set-point of 140°C, and the data acquisition program is started. The system takes about 45 minutes to reach 140°C. The computer acquires measurements of temperature, frequency, pressure, damping voltage, and headspace oxygen at one minute intervals for the duration of the entire, typically 15 hour, experiment. The heater is controlled by a timer, and is set to automatically shut off after the 15 hours is complete.

Once the experiment is complete, the data is retrieved to be analyzed graphically. As mentioned previously, because of the assumption of constant liquid properties, only the data taken under isothermal conditions is used for analysis. In other words, because it is assumed that little deposition, if any, occurs during the 45 minute heat-up time, this data is ignored. The mass deposition is calculated at each time interval, according to Equation 5. The total data is typically reported in the form of two figures. The first shows the mass deposition and headspace pressure versus time, and the second illustrates the
headspace oxygen concentration versus time. Both plots prove to be extremely useful in evaluating the thermal stability characteristics of a particular fuel.

Upon completion of the experiment, the QCM is allowed to cool - which can take approximately two hours. All fittings are disassembled, and the crystal is removed from the clamp. The fuel is either discharged to a scrap tank or saved for analysis at a later date, for example, to examine hydroperoxide concentration. The QCM is cleaned rigorously with a toluene, acetone, and methanol (TAM) solution, mixed in equal proportions. Static-free wipes, pipe cleaners, and Q-tip applicators are used to clean all accumulated deposits from the surfaces. The system is then allowed to dry in a hood before being used again.

**Experimental Discussion**

Generally, the deposition measurement reproducibility of the QCM is limited to ±20%. This number was determined through several different runs of the same fuel, and then performed for various fuels. The difference in deposition can be largely attributed to the nature of the fuel. Because of the varied composition and complexity of the fuels, it is very likely that there will be scatter in the data due to the number of deposit-forming species present. We have experienced such reproducibility differences in the same fuel run on two consecutive days. The limits of reproducibility, especially evident in the low depositing fuels, are also due to the high sensitivity of the experiment.

The system temperature, controlled by a PID temperature controller, is set at 140°C. The fluctuations in the temperature of the system, once a constant value has been reached, are approximately ±0.2°C. These fluctuations result in minimal frequency changes which are not significant to the overall mass deposition measurements, and are therefore ignored.
Finally, an explanation of the oxidation plots is warranted. The reader will notice that although the oxygen sensor is calibrated to 20.9% oxygen in air and the system is closed, the headspace oxygen values can reach as high as 35% (Figure 9).

![Graph showing plot of headspace oxygen](image)

**Figure 9: Plot of headspace oxygen, demonstrating the liberation of oxygen from the fuel during initial heat-up time of approximately 45 minutes.**

This occurs because oxygen is liberated from the fuel into the headspace during the heat-up period, causing the measured headspace oxygen concentration to rise. The concentration of the oxygen in the fuel is proportional to the partial pressure of the oxygen in the headspace. As the system pressurizes, the partial pressure of the oxygen rises, as do the oxidation plots like in Figure 9. When the target temperature is reached and the system is completely pressurized, no more oxygen is liberated from the fuel and the partial pressure no longer increases. The autoxidation of the fuel causes the subsequent decline in headspace oxygen concentration.
Jet fuel deposition occurs in two distinct, yet rather poorly understood regimes: thermal-oxidative and pyrolytic. We seek to better understand the thermal-oxidative deposition because it is more prevalent in current jet fuel systems, and is more conducive to thermal stability improvement via additive addition. But the improvement of jet fuel thermal stability can also occur by fuel pretreatment. Two common pretreatment techniques are clay filtration and hydrotreatment refining. Both are extremely effective because they remove species which promote deposition. While ultimately we experiment with additive addition, we first examine previous experimental results, and continue the research of a fairly well understood pretreatment technique to provide initial insight into the chemistry of oxidation and deposition.

**Solid Phase Extraction**

Solid phase extraction (SPE) is a preparative technique which is typically used to concentrate or fractionate a particular sample. The term solid phase is used because the SPE column is comprised of a solid support material through which the material to be concentrated is passed. This technique is extended to jet fuel studies because it has proven to be useful in determining which components might be detrimental to fuel thermal stability. In addition to the straight and branched alkanes of fuels, there are hundreds of naturally occurring polar and non-polar heteroatomic species. These species
are important in jet fuel studies because they are the first to react due to their relatively weak bonds (for example the O-H bond of a phenolic compound) and therefore can propagate or inhibit the oxidation. These species can also often promote the production of deposits. It is the presence or absence of these species which is thought to account for the different oxidation and deposition characteristics of different jet fuels.

The SPE technique of these experiments uses a plastic cartridge with a solid packing bed, silica gel, contained between two 20μm porous Teflon frits. We use silica gel because it strongly retains polar compounds. The mechanism by which the polar species are retained on the column involves groups that contain a hydrogen atom bonded to an electronegative atom like nitrogen or oxygen and another group having an electronegative atom. The actual structure of the silica gel is quite complex, but the general structure includes the Si-OH functional group. The majority of the compounds binding to a polar sorbent like silica gel occur by hydrogen bonding, as seen in Figure 10.

![Figure 10: Diagram of the SPE mechanism for the retention of polar compounds by hydrogen bonding (dashed lines) between the Si-OH groups of the silica gel and a phenol.](image)

The sorbent bed is first activated by passing a normal alkane, like heptane, through the column. This wets and swells the column packing to make the column a "gel", which increases the surface area for extraction. This wetting of the silica gel can also act as a cleaning solvent to remove contaminants. The sample is then passed through the column. Factors such as the compound's polarity relative to the solvent bed, and the
presence of positively or negatively charged functional groups, determine how strongly
the compound will be retained by the silica gel.

Elution, or disruption of polar interactions, is achieved by polar solvents like
methanol which can compete more effectively with the heteroatomic compounds for the
sorbent. We wish to explore to what extent the oxidation inhibiting and deposit
promoting species are removed and the effects that this removal has.

**Thermal Stability Improvement**

Previously, experiments have been performed in the QCM using jet fuels and
solid phase extraction. The most significant of these results are shown in Figure 11
(Zabarnick, 1994).

![Graph showing mass accumulation](image)

**Figure 11:** Plots of mass accumulation in the QCM, demonstrating
the impact of the removal of species by SPE from a high depositing
fuel and adding them to a low depositing fuel (Zabarnick, 1994).

Using solid phase extraction, Zabarnick removed species from a high depositing jet fuel,
F-2827, and added them to a low depositing fuel, F-2747. The solid phase extracted
sample of F-2827 demonstrated a reduction in deposition from 3.0 to 0.5 µg/cm².
Subsequently adding those species that were removed from F-2827 to F-2747, raised its deposition from 0.7 to 3.0 μg/cm². This is an extremely important result because it strongly implicates these species as those which most contribute to the deposition in jet fuels. Also note that when the F-2827 extract is added to the F-2747 fuel, the deposition occurs during the first 5-6 hours of the experiment. Thus, this fuel still appears to consume oxygen readily, but produces significantly more deposits. Identifying the species that are removed by solid phase extraction and determining more specifically their effect on jet fuel oxidation, as well as deposition, is very important.

At the time of the previous experiments, direct measurements of the oxidation of the fuels were not performed (pressure measurements, however, were used quite effectively). Since then, the QCM has been fitted with an oxygen sensor which measures the headspace oxygen in the reactor. Figure 12 presents the headspace oxygen plots of three fuels with clearly different oxidation rates.

![Figure 12: Plots of headspace oxygen concentration in the QCM at 140°C for two normally processed fuels and Exxsol D-110, demonstrating the variety of oxidation characteristics in different fuels.](image-url)
F-2827 and F-3084 are normally processed Jet-A fuels. Exxsol D-110 is a highly refined, dearomatized solvent which has an extremely low sulfur content. Since it is highly refined, it contains very few naturally occurring antioxidants. The differences seen in Figure 12 raise questions concerning the way in which a fuel oxidizes. Exxsol D-110 oxidizes extremely quickly, F-2827 oxidizes very slowly, and F-3084 oxidizes only moderately quickly.

Figure 13 shows the result of solid phase extraction in a high-depositing jet fuel, F-3084 on deposition and oxidation. This figure demonstrates, as in Figure 11, that SPE causes a substantial reduction in thermal oxidative deposition. The deposits are reduced from 14 µg/cm² to 2 µg/cm². Also, an increase in the rate of oxygen consumption is observed since the neat fuel headspace oxygen was only 65% consumed after 15 hours, whereas the SPE fuel was completely oxidized after only 9 hours. Why does solid phase extraction cause these changes?

![Figure 13: Plots of mass accumulation and headspace oxygen for F-3084 in the QCM at 140°C, demonstrating the impact of solid phase extraction (SPE).](image)

We propose that the naturally occurring heteroatomic species determine how a particular fuel oxidizes. For example, the oxidation of a fuel can be slowed if phenolic
species intercept alkyl peroxy radicals, thus preventing them from reacting with the fuel to form additional R• radicals (Ingold, 1961). This process might also be the major contributor to the reduction of the deposition. Because of the affinity of silica gel for polar compounds, it appears that it may be these species that solid phase extraction removes, producing the changes seen above.

**SPE and Gas Chromatography**

We have employed gas chromatography with mass spectrometric detection (GC-MS) to examine the changes in the chemistry of the fuel. We want to see that if the changes in the oxidation and deposition characteristics of the fuel with SPE treatment are a result of the removal of the polar, heteroatomic species, like phenols. We performed SPE on 10 mL of F-3084, the fuel used in the SPE study above, using a one gram silica gel cartridge. We collected the fuel at the outlet of the cartridge and set it aside. Heptane is used to wash the column of any fuel, leaving only the polar species on the column. We then use methanol to elute the column of the polar species for analysis by GC-MS. The fuel that originally passed through the first SPE column is then passed through a new silica gel column. Following the same procedure as before, and eluting the cartridge with methanol will demonstrate whether the polar, phenolic species are removed, and if so, with what efficiency.

The results of the examination of the two samples by GC-MS are shown in Figure 14. Each chromatogram is the ion chromatogram of the 135 amu peak, which is a characteristic ion of C3 and larger alkyl phenols. Thus, the peaks show the relative amounts of these species in each sample. The chromatograms of Figure 14 show that solid phase extraction is extremely effective at removing phenols from jet fuels. Understanding such a simple, yet fundamental, difference in the chemical nature of a fuel is important because it suggests that the SPE oxidation plots of Figure 13 are analogous
to the plots of the neat fuels in Figure 12. They both show that the different oxidative behaviors result from varying amounts of heteroatomic species present. We have exploited the ability of silica gel SPE to remove polar heteroatomic species, while the remainder of the fuel passes through. Lacking the deposit promoting and oxidation inhibiting species, the solid phase extracted fuels demonstrate reduced deposition and increased rates of oxidation.

![Figure 14: GC-MS ion chromatograms (135 amu) showing the removal of phenols by SPE. Top: Before SPE, Bottom: After SPE.](image)

While the differences in the neat fuels occur because of the variety of the naturally occurring antioxidant species and the differences in the refining processes, the SPE sample of F-3084 differs from its parent neat fuel because of the pretreatment separation.

**Autoxidation and Solid Phase Extraction**

Solid phase extraction is a research tool that can be used to better understand the autoxidation chemistry of jet fuels. Because of its affinity for polar compounds, SPE can
remove these species from the fuels. This is useful not only to see the impact on the fuel, but also to further analyze the species themselves, as in GC-MS. Dependent largely on the source petroleum and the degree of refinement of the fuel, the presence or absence of heteroatomic species, like phenols, can vary widely. This helps to explain the different oxidation behaviors seen in Figure 12.

The thermal-oxidative regime (100-300°C) of deposition forms particulates, gums, and deposits from free-radical reactions with oxygen, which emphasizes the connection between deposition and oxidation. But the mechanisms of the formation of deposits in jet fuels are not clearly understood. The free-radical mechanism of oxidation is fairly well understood, however, and serves as a more suitable area to study to improve the thermal stability of jet fuels. We have shown that solid phase extraction increases the rate of oxidation and effectively removes phenols. We believe that these two results of SPE are closely related. Typically, a phenol will react with an alkyl peroxy radical, thus preventing the formation of a new R• radical. This slows the oxidation cycle since reaction 1 will not occur as frequently. The removal of such phenols by solid phase extraction results in an increased oxidation rate because the phenols are no longer present, and the R• radical production is uninterrupted.

The three fuels shown in Figure 12 all have similar bulk compositions and properties. They each consist nearly entirely of straight, branched, and cycloalkanes, along with aromatic compounds (although Exxsol D-110 is dearomatized). The actual autoxidation reactions each fuel has with oxygen are largely the same. The differences are found in the rates at which these reactions occur. From the chromatogram of Figure 14, we can conclude that the oxidation reaction rates are a function of the heteroatomic species present. There are other oxidation controlling factors like the metal concentration, and amounts of other naturally occurring species. Nevertheless, if we can begin to understand the roles of the heteroatomic species, like phenols, and the respective impacts
of their removal or addition, we can begin to understand the deposition and oxidation of jet fuel.
CHAPTER IV

THE SUPPRESSION OF AUTOXIDATION

The suppression of the autoxidation cycle is a topic that has been studied for a number of years. In addition to jet fuel, antioxidants are used widely in items such as food products, rubber and plastics. As has been discussed, the minor species in fuel, such as polar species, sulfur compounds, and metals can greatly affect the rate of oxidation. Autoxidation can be inhibited by the addition of such compounds which lengthen the initial induction period or reduce the production of $R^\cdot$ radicals. Solid phase extraction is certainly an effective means of reducing deposition. However, the removal of the polar, deposition promoting species, also increases the oxidation rate. This can be detrimental, especially in situations like long term storage because the fuel can oxidize and degrade. Thus, it is important not only to reduce the deposition, but also slow the rate of oxidation.

We want to study potential additives which inhibit reaction 1 and compete with reaction 2a, such as those species which are removed by SPE. One of the key components of the JP-8+100 additive package, 2,6-di-tert-butyl-4-methylphenol (BHT), is a hindered phenol antioxidant which intercepts alkyl peroxy radicals. Figure 15 demonstrates the mechanism by which an alkyl peroxy radical reacts with a hydrogen atom of BHT, instead of a fuel molecule, RH. The peroxy radicals are converted to a hydroperoxide and an antioxidant radical; thus, preventing the production of additional $R^\cdot$ radicals, and the propagation of the autoxidation cycle.
We also studied a second, less utilized method of autoxidation suppression: the bimolecular decomposition of hydroperoxides. Hexyl sulfide was the hydroperoxide decomposing compound used, as seen in the mechanism of Figure 16.

Figure 16: The reaction of hexyl sulfide, "SH", with an alkyl hydroperoxide to form a sulfoxide and an alcohol, preventing the formation of a new free radical.

Figure 17, shows the addition of the two antioxidant reactions to the autoxidation cycle described previously in Figure 1. The species AH and SH are the peroxy radical inhibiting and the bimolecular hydroperoxide decomposing species, respectively.

Because of the varieties in the source petroleum and the refining processes, as mentioned in the discussions of solid phase extraction, jet fuels can naturally contain various antioxidant species. Therefore, to better study the fundamental nature of autoxidation, we initially use the solvent Exxsol D-110 in our experiments. Because it is highly refined, it contains very few naturally occurring antioxidants and will therefore minimize complications from unknown reactions. The isothermal, static nature of the Parr bomb reactor will also help to minimize complications.
Figure 17: The autoxidation cycle showing the suppression mechanisms of the peroxy radical inhibition species, AH, and the hydroperoxide decomposing species, SH.

**Peroxy Radical Inhibition**

In rapidly oxidizing fuels stressed in the QCM system at 140°C the addition of antioxidant additives can greatly decrease the oxidation rate (Zabarnick and Grinstead, 1994). We added BHT in varying concentrations from 4.2 to 50 mg/L. The results are shown in Figure 18. As can be seen from Figure 18, an increase in BHT provided a corresponding increase in the delay of the fuel oxidation. Each fuel mixture eventually oxidizes very quickly until there is no oxygen left in the headspace. Figure 18 demonstrates a strong concentration dependence on the length of the oxidation delay, this is thought to occur because of the eventual consumption of the antioxidant as the autoxidation cycle continues. Pederson has proposed that the loss of antioxidant behavior seen in Figure 18 can be due (in addition to the reactions of antioxidant and active free
radicals) to reactions of the antioxidant species with peroxides and/or oxygen to form non-antioxidant products (Pedersen, 1949).

![Figure 18: Plots of headspace oxygen curves of Exxsol D-110 with varying concentrations of a peroxy radical inhibiting antioxidant, BHT.](image)

A study that measured the concentrations of peroxy radical inhibiting species as a function of time was performed, and demonstrated a strong correlation to the plot of the headspace oxygen concentration (Zabarnick and Whitacre, 1998). This strongly supports that the rapid increase in the rate of oxidation occurs upon consumption of the antioxidant. Referring to the autoxidation cycle of Figure 17, the antioxidant species, AH, intercepts the peroxy radicals, RO$_2^*$, formed as a result of the reaction the fuel radical, R$, and oxygen. The mechanisms by which the AH species operates are not trivial, and are only presented in a simplified manner, as in Figure 15. But the significance of the peroxy radical inhibiting species is that they prevent the formation of a free R$^*$ radical, as seen in reaction 1.

The JP-8+100 additive package currently contains a dispersant, a metal deactivator, and a hindered phenol antioxidant, BHT. While a wide variety of additives
have been studied, the use of hydroperoxide decomposers to inhibit oxidation has received little attention.

**Hydroperoxide Decomposition**

The reactions by which hydroperoxide decomposing species slow and/or delay oxidation have been studied previously, specifically by Denison and Condit (Denison and Condit, 1945). They showed that when sulfides are added to white lubricating oil, substantial oxidation delays resulted. They concluded that the sulfides react with the hydroperoxides to form sulfoxides and alcohols, preventing additional free radical formation via a series of reactions following the unimolecular hydroperoxide decomposition (see Figure 16).

![Figure 19: Plots of headspace oxygen demonstrating that with significant increases of hexyl sulfide concentration, there is no corresponding delay in oxidation.](image)

In order to verify these results, we added an organic sulfur compound, hexyl sulfide, in varying concentrations to Exxsol D-110. The results for the neat fuel with four
concentrations of hexyl sulfide are shown in Figure 19. As can be seen, with increasing amounts of hexyl sulfide there is no corresponding slowing of the oxidation.

Hydroperoxides promote oxidation via the mechanisms of Equations 2a-2c. They are normally unimolecularly decomposed, and following a series of reactions, form R radicals which propagate the oxidation cycle by reacting with the oxygen. Reaction with hexyl sulfide, presumed to be a decomposer of hydroperoxides, would follow the reaction of Figure 16. However, the observations of Figure 19 appear to indicate that hexyl sulfide is not an effective hydroperoxide decomposer, and conflict with the results of Condit and Denison. To test the theory that the hexyl sulfide is, in fact, not decomposing the hydroperoxides, we measured the hydroperoxide concentrations of the post-test samples using cyclic voltammetry (Kauffman, 1994).

Table 1: Measured hydroperoxide concentration in Exxsol D-110, neat and with varying concentrations of hexyl sulfide.

<table>
<thead>
<tr>
<th>Exxsol D-110 with Hydroperoxide Decomposer (all stressed samples performed in the Parr reactor)</th>
<th>Peroxide Concentration (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exxsol D-110 stressed</td>
<td>0.49 ± 0.10</td>
</tr>
<tr>
<td>Exxsol D-110 with hexyl sulfide 1662 mg/L stressed</td>
<td>0.05 ± 0.10</td>
</tr>
<tr>
<td>Exxsol D-110 with hexyl sulfide 3290 mg/L stressed</td>
<td>0.04 ± 0.10</td>
</tr>
<tr>
<td>Exxsol D-110 with hexyl sulfide 9966 mg/L stressed</td>
<td>0.06 ± 0.10</td>
</tr>
</tbody>
</table>

Table 1 demonstrates that the addition of hexyl sulfide does decompose the hydroperoxides, despite having little effect on the oxidation rate. The stressed sample of the neat fuel has a hydroperoxide concentration of 0.49 ± 0.10 mmol/L, whereas the samples with hexyl sulfide are all approximately zero. It is interesting to note that even at the lowest peroxide decomposer concentration, the peroxide level is near zero.
Since both peroxy radical inhibitors and peroxide decomposers interrupt the autoxidation chain by preventing the formation of free radicals, we presumed that each individually would have an impact on the oxygen consumption. This is not the case. The addition of the peroxy radical inhibitor slows the oxidation according to its concentration, but the hydroperoxide decomposer, regardless of concentration, has no effect. Having omitted the possibility that hexyl sulfide is not decomposing the peroxides, the question still remains as to why this additive does not delay the oxidation. In theory, the net result of lowering the $R^\cdot$ radical pool with the addition of the peroxy radical inhibitor and the hydroperoxide decomposer should be similar. They both prevent the formation of $R^\cdot$ radicals, which should slow the oxidation cycle. Our results indicate that they are not similar at all, and are also not consistent with the results of Denison and Condit. To explore these discrepancies further, we added hexyl sulfide to the hydrotreated jet fuel, F-2747. The results of this are shown below in Figure 20.

![Figure 20](image)

**Figure 20: Plots of headspace oxygen for F-2747 and F-2747 with hexyl sulfide demonstrating the significant slowing of oxidation by addition of the peroxide decomposer.**

This figure shows that, unlike in Exxsol D-110, the addition of hexyl sulfide has a substantial effect on the rate of oxidation. While the neat fuel completely oxidizes in
about 5 hours, the addition of hexyl sulfide greatly slows the oxidation rate such that at the end of the 15 hour run, there is still about 21% oxygen in the headspace. Also, this plot is much more consistent with the results of Denison and Condit.

There is clearly a fundamental difference between Exxsol D-110 and F-2747 that is causing the oxidation differences seen in response to the addition of hexyl sulfide, as shown in Figures 19 and 20, respectively. Neat Exxsol D-110 oxidizes completely in 2 hours. Requiring 5 hours, more than twice the time of Exxsol D-110, neat F-2747 oxidizes much more slowly than the solvent. We propose that the initial delay in the oxidation rate of F-2747 is the result of naturally occurring and/or added phenol antioxidants. Our previous studies in solid phase extraction (SPE) demonstrate the ability of this technique to remove these phenolic compounds from fuels. Therefore, we performed SPE on a sample of F-2747. The results of the neat fuels, and the plots of SPE F-2747 (with removed phenols) and Exxsol D-110 with added phenol (BHT) are shown in Figure 21.

![Figure 21: Plots of headspace oxygen for Exxsol D-110, F-2747, SPE treated F-2747, and Exxsol D-110 with BHT.](image)
These results offer insight into the oxidation discrepancies we have experienced. The similarities between neat Exxsol D-110 and SPE F-2747 indicate that it is extremely likely that it is the naturally occurring antioxidant species that are causing the initial delay of neat F-2747. The plots of F-2747 and Exxsol D-110 with added BHT reaffirm this conclusion. Having uncovered the likely primary difference between the two fuels, it remains to be seen why there was no effect on the oxidation rate of Exxsol D-110 with only the addition of hexyl sulfide.

Could it be that the presence of peroxy radical inhibiting phenols is required under our conditions for peroxide decomposers to exhibit an effect on the rate of oxidation? It would be consistent, then, if we added hexyl sulfide to the solid phase extracted F-2747 (which would have few, if any, phenolic species), that no oxidation delay would occur. Figure 22 is a plot of this fuel which demonstrates this result.

![Figure 22: Plots of headspace oxygen for neat F-2747, SPE F-2747, and SPE F-2747 with hexyl sulfide, demonstrating the lack of oxidation effect following the removal of phenolic species by SPE.](image)

Following SPE treatment to F-2747, we added approximately 3000 mg/L of hexyl sulfide to this fuel. The result of this experiment is in marked contrast to the effect seen in Figure
20. These results demonstrated in Figures 20 and 22 suggest that both phenols and hydroperoxide decomposers must be present in a fuel to see such an extended delay.

The Synergism

We added both BHT and hexyl sulfide to Exxsol D-110 to attempt to reproduce the extremely long delay seen in Figure 20 with F-2747. The results of this experiment, as well as with the additives added individually, are shown in Figure 23.

Figure 23: Plots of headspace oxygen showing the extended oxidation delay in Exxsol D-110 when both the peroxy radical inhibitor and the hydroperoxide decomposer are present.

Figure 23 is quite important because it begins to make connections between our results in the fuel F-2747 and the solvent. These results confirm that in the presence of both peroxy radical inhibitors and hydroperoxide decomposers, we can achieve an extended delay. This delay is substantially greater than that of the sum of the two individual additives. Synergism between various classes of antioxidants, such as that evident in Figure 23, has been observed in previous experiments (Scott, 1963), and could prove to be extremely
important in the improvement of thermal stability via a new additive package. Therefore, we have chosen to further explore this aspect of jet fuel oxidation.

It is important to attempt to understand the concentration dependence of this synergistic slowing of the oxidation. Will it result for any combination of the two antioxidants? We first fixed the concentration of BHT (a hindered phenol) at 25 mg/L, and experimented with varying amounts of hexyl sulfide. The results are shown in Figure 24.

![Figure 24: Plots of headspace oxygen in the QCM system for Exxsol D-110 with a fixed BHT concentration (~25 mg/L) and increasing hexyl sulfide concentrations.](image)

When 25 mg/L of BHT is added to Exxsol D-110, a delay in oxidation is evident such that the fuel does not completely oxidize until approximately 8 hours. Adding increasing amounts of peroxide decomposer up to 4000 mg/L does not provide any additional delay. However, with concentrations of approximately 10,000 mg/L, a greatly delayed oxidation results. Since hexyl sulfide provides no delay in the absence of BHT, it is apparent that there exists a synergism between these two additives.

We next performed the concentration dependence study with a fixed concentration of hexyl sulfide, and varied the BHT concentration. Since approximately 10,000 mg/L is
required to provide the extended delay in Figure 24, we chose this value as the fixed concentration. The results from this series of experiments are shown in Figure 25. Again, at low concentrations, the only delay that is evident is the delay that results from the peroxo radical inhibiting species. Increasing amounts of BHT from 0 to 15 mg/L provide modest increases in the oxidation delay. However, the relatively small increase from 15 to 20 mg/L clearly results in a substantial delay in the oxidation.

![Figure 25: Plots of headspace oxygen in the QCM system for Exxsol D-110 with a fixed hexyl sulfide concentration (~10,000 mg/L) and increasing BHT concentrations.](image)

The unusual concentration dependencies of Figures 24 and 25 may provide interesting insight into possible oxidation suppression additives. They have also, however, raised significant questions of the fundamental mechanisms of the autoxidation cycle. For example, what is causing the sudden extended oxidation delay effect?

**Chemical Kinetic Modeling**

We have utilized a chemical kinetic model to try to answer some of the questions raised by our experimental data. The importance of developing accurate representative
models for a system under study cannot be understated since they allow for rapid predictions and insight into system behavior. Modeling is employed to simulate the autoxidation of jet fuel, and to specifically address the antioxidant mechanisms of peroxy radical inhibiting and hydroperoxide decomposing species. Zabarnick has developed a pseudo-detailed chemical kinetic model based on the reactions of Table 2, in which the Arrhenius A factors and the activation energies are estimated (Zabarnick, 1993). The mechanism is referred to as “pseudo-detailed” because it has some of the characteristics of a detailed mechanism, such as physically meaningful rate parameters. However, it is less simplified than the simple empirical modeling using one or two reactions that have been used in jet modeling in the past.

Table 2: Reactions comprising the applied jet fuel pseudo-detailed chemical kinetic mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>I --&gt; R*</td>
<td>AO₂* + AH --&gt; AO₂H + A*</td>
</tr>
<tr>
<td>R* + O₂ --&gt; RO₂*</td>
<td>AO₂* + AO₂* --&gt; Products</td>
</tr>
<tr>
<td>RO₂* + RH --&gt; RO₂H + R*</td>
<td>RO₂H --&gt; RO* + OH*</td>
</tr>
<tr>
<td>RO₂* + RO₂* --&gt; Termination</td>
<td>RO* + RH --&gt; ROH + R*</td>
</tr>
<tr>
<td>R* + R* --&gt; R₂</td>
<td>RO* --&gt; Rprime + Carbonyl</td>
</tr>
<tr>
<td>RO₂* + AH --&gt; RO₂H + A*</td>
<td>OH* + RH --&gt; H₂O + R*</td>
</tr>
<tr>
<td>AO₂* + RH --&gt; AO₂H + R*</td>
<td>RO* + RO* --&gt; RO Termination</td>
</tr>
<tr>
<td>A* + O₂ --&gt; AO₂*</td>
<td>Rprime + RH --&gt; Alkane + R*</td>
</tr>
<tr>
<td>RO₂H + SH --&gt; Products</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 shows that this model has lumped jet fuel into a relatively small number of species: I (an initiator), RH (fuel), R* (fuel radical), O₂ (oxygen), RO₂* (peroxy radical), RO₂H (hydroperoxide), AH (peroxy radical inhibitor), and SH (hydroperoxide decomposer). As mentioned previously, because fuels are mixtures of hundreds of species it would be impractical to model the changes in each of the components. Also since fuel
is largely comprised of straight chain alkanes, it is a reasonable simplification to model the bulk fuel as a single component, RH.

This model has been verified previously using experimental data from the QCM as well as different flowing tests. Having been calibrated with previous data of the autoxidation of jet fuel and jet fuel mixtures, the model has demonstrated good agreement with experimental data (Zabarnick, 1998). Wanting to explore the oxidative behavior of fuels when both the peroxy radical inhibiting, AH, and the peroxide decomposing, SH, species are present, and to duplicate the experiments performed, we first modeled the system in which the AH concentration is held constant at a value of 1.0 x 10^{-4} M, and the SH concentration is varied. These results are shown in Figure 26.

![Figure 26: Chemical kinetic model of increasing hydroperoxide decomposing species (SH) and a fixed peroxy radical inhibiting species (AH) concentration of 1.0 x 10^{-4} M.](image)

Comparison of Figure 26 with its experimental analog, Figure 24, shows excellent agreement. In both cases the first curves of the samples with increasing amounts of SH species demonstrate oxidative behaviors that are not significantly different from the sample with 0 M SH concentration. However, when a third incremental amount of SH
species is modeled, the synergistic delay is clearly evident. This is the same behavior we saw in the QCM, which adds confidence to our experimental results.

We next modeled the system in which the SH concentration is held constant at $1.5 \times 10^{-5}$ M, and the AH concentration is varied. As was expected based on the experimental results shown previously, when SH is present and AH is not, there is no delay in oxidation. Two additional curves with increasing AH concentrations show a corresponding increasing delay in oxidation. Finally, with an even higher amount of peroxo radical inhibiting species, the system demonstrates the synergistic behavior that we have seen experimentally. The results of this series of modeling are shown in Figure 27.

![Figure 27: Chemical kinetic model of increasing peroxy radical inhibiting species (AH) for a fixed hydroperoxide decomposing species (SH) concentration of $1.5 \times 10^{-5}$ M.](image)

When comparing Figure 27 with its experimental analog, Figure 25, one can see the similarities between the two. What is it that is causing the synergism when both the peroxo radical inhibiting species, AH, and the hydroperoxide decomposing species, SH, are present? And, when this synergism occurs, for how long does the oxidation delay continue?
In the previous plots of both the experimental data and the chemical kinetic modeling, we extend the results to 15 hour tests. There were initial concerns that the synergistic delay was nothing more than a delay which extended past the ends of our 15 hour experiment. The oxidation might rapidly increase after this point to attain zero oxygen concentration at approximately 17 or 18 hours. To test this possibility, we first employed the chemical kinetic model. Minor modifications to the program extends the run time of the modeling calculations. We modeled the synergistic behavior seen in Figure 27 with an SH concentration of $1.5 \times 10^{-5}$ M and an AH concentration of $2.0 \times 10^{-4}$ M, and extended the time to four times a normal run, 60 hours.

![Chemical kinetic model of increasing AH concentration and a fixed SH concentration of $1.5 \times 10^{-5}$ M, demonstrating synergism well past 15 hours.](image)

The modeled behavior of Figure 28 refutes our initial suppositions that the synergistic effect may not be true. Clearly, the system does not oxidize after 17 or 18 hours, but instead extends to 60 hours. However, experimental evidence is required. We wanted to see if experimental results would support such a long delay seen in the chemical kinetic model. Figure 29 shows that when the experiment of 10,000 mg/L hexyl sulfide and 30 mg/L BHT is allowed to run to 60 hours it, too, does not completely oxidize.
The decrease in headspace oxygen, that is not seen in the model, is probably due to the fact that the model has not yet been "tweaked" to account for each true reaction, or because of side reactions between unknown species or by-product reactions with oxygen.

The Explanation

Remembering Figure 2 (which demonstrated the close correlation to the deposition of a fuel to its oxidation), the synergistic oxidation delay could prove to be extremely important in improving thermal stability. It can only be truly useful, however, if it can be explained. Having demonstrated this synergistic behavior, both experimentally and with the use of a chemical kinetic model, we now propose an explanation as to why this occurs. Figure 17 shows the autooxidation cycle and the two oxidation inhibition mechanisms with the use of the AH and SH species. Consider this cycle as being composed of two loops. The first, "inner loop", is the main oxidation cycle in which the $R\cdot$ radical reacts with oxygen to form $RO_2^\cdot$. Subsequent reaction with the fuel, $RH$,
produces a new $R^\bullet$ and a hydroperoxide, $ROOH$ via reaction 1. The formation of this hydroperoxide begins the second, "outer loop". In this loop, the hydroperoxide is thermally decomposed, eventually producing a new $R^\bullet$ by the reactions of Equations 2a-2c. Thus, we have two loops in the autoxidation cycle which each propagate the oxidation cycle by producing $R^\bullet$ radicals.

We believe that in the absence of alkyl peroxy radical inhibitors the reactions of the inner loop occur significantly faster than the reactions of the outer loop. This explains why addition of only the hydroperoxide decomposing species, and slowing the production of $R^\bullet$ radicals by the outer loop, has no effect on the oxidation rate. Because the inner loop occurs so quickly, decomposing the hydroperoxides does not appreciably reduce the pool of $R^\bullet$ radicals, and consequently does not slow the oxidation. Also, it is consistent that addition of the peroxy radical inhibiting species does have an effect on the oxidation rate. This is because this AH species interrupts the fast mechanism, thereby slowing the overall oxidation.

The synergism, as seen in Figures 24 through 27, occurs after some critical concentrations are achieved. We believe that the role of the AH species is to slow the inner loop so that the hydroperoxide decomposition by the SH species can have an effect. The data demonstrates that the synergistic effect appears to be an "all-or-nothing" effect. In other words, for a yet undetermined reason, there appears to be no intermediate synergistic effect. When the concentrations of the two additives are sufficient such that they produce a long antioxidant effect, we have not seen the system achieve complete oxidation. With experiments extending past 100 hours, the system has only been as low as 15% headspace oxygen.

Having elucidated some of the fundamental aspects of autoxidation suppression, it is clear that the extremely slow consumption of oxygen of F-2747 when hexyl sulfide is added to the fuel, as seen previously in Figure 20, is indicative of a synergism. This is more evident if we combine the results of the F-2747 experiments presented earlier into
one figure (see Figure 30). It is interesting to note the close similarity between these plots and the plots of Exxsol D-110 demonstrating the same behavior, seen in Figure 23.

![Figure 30: Plots of headspace oxygen of F-2747 demonstrating the synergism that results from the presence of both hydroperoxide decomposer and naturally occurring phenols.](image)

With the removal of the phenolic species (the peroxy radical inhibiting antioxidant species) by SPE, the fuel oxidizes much more rapidly. Also, addition of hexyl sulfide to the solid phase extracted fuel has no effect on the oxidation. Addition of hexyl sulfide to the neat fuel, however, has a substantial effect on the oxidation delay.

**Synergism with Triphenylphosphine**

The ultimate goal of our work is to achieve effective, yet economical, additive packages which will improve the thermal stability of jet fuels. The relatively high concentrations of hexyl sulfide employed here raise some legitimate concerns of the cost of this additive. Typical values which provide the synergistic oxidation delay are on the orders of 30 mg/L for BHT, and 10,000 mg/L for hexyl sulfide. Additional concerns include the frequent incompatibility problems incurred of sulfur compounds with fuel
system materials, and the fact that they have been shown to increase surface deposition in jet fuels (Kauffman, 1997). Also, there are significant environmental concerns since adding sulfur to a fuel will inevitably lead to increased sulfur emissions. Therefore, it is necessary to explore more appropriate hydroperoxide decomposing compounds that will be more appropriate as jet fuel additives.

Triphenylphosphine (TPP) is a known hydroperoxide decomposer that has been used as a means to quantify the amounts of hydroperoxides in a fuel (Heneghan, 1997). The reaction by which the hydroperoxides are decomposed with TPP is seen in Figure 31.

$$\text{P} \quad + \quad \text{ROOH} \quad \rightarrow \quad \text{P} = \text{O} \quad + \quad \text{ROH}$$

**Figure 31:** Reaction showing the decomposition of a hydroperoxide by triphenylphosphine into triphenylphosphine oxide and an alcohol.

This technique is useful in the measurement of hydroperoxides because triphenylphosphine oxide is easily measured in the Gas Chromatograph-Atomic Emission Detector (GC-AED). By establishing the efficacy of TPP in providing a lengthy, synergistic oxidation delay, it could potentially be used as a less expensive, more material-compatible hydroperoxide decomposer, if used in lower concentrations.

The results of the experiments of Exxsol D-110 with TPP and BHT are shown in Figure 32. To Exxsol D-110, we first add only TPP. Similar to the results with hexyl sulfide, with only TPP there was no delay in the oxidation. BHT was then added with triphenylphosphine. The synergistic delay provided by the BHT/TPP combination is an important one because TPP is not known to cause any deposition increases in jet fuels,
nor is it thought to have problems with compatibility with fuel system materials. But perhaps the most significant aspect of the use of TPP as the hydroperoxide decomposer is the concentration which was used: 100 mg/L.

![Plot of headspace oxygen concentration demonstrating synergism with triphenylphosphine (TPP), a different hydroperoxide decomposer.](image)

**Figure 32:** Plots of headspace oxygen concentration demonstrating synergism with a triphenylphosphine (TPP), a different hydroperoxide decomposer.

The concentration of TPP which provides the synergistic delay is two orders of magnitude less than that used with hexyl sulfide, which makes this an extremely economical additive combination. It is left for future work to evaluate TPP in real jet fuels and to address the effects of this additive on deposition. Also, it will ultimately be important to refine the combination of TPP and BHT to evaluate the economical efficacy. Nonetheless, the synergistic suppression of jet fuel autoxidation should certainly be a major consideration for JP-8+100 and other additive packages of the future.
CHAPTER V

THE EFFECTS OF SILYLATION ON DEPOSITION AND OXIDATION

Heteroatomic species, such as phenols, act as antioxidants because they intercept the peroxy radicals formed during the autoxidation cycle. However, having been implicated in the deposit forming process they can also have a detrimental effect. In the previous chapter of autoxidation suppression, we examined the antioxidant behavior of heteroatomic species. In combination with peroxide decomposing species, phenolic species demonstrate a synergistic slowing of the autoxidation cycle. In this study of a derivatization technique known as silylation, we focus on an examination of the deposit forming tendency of heteroatomic species.

**Derivatization**

Derivatization techniques are common methods for the improvement of chemical analysis by altering the structure of a species, making it less reactive and more detectable. Silylation is one of a number of derivatization techniques in which reactive hydrogen sites on species like acids, alcohols, thiols, amines, and phenols, are converted to larger and less reactive trimethyl silyl groups (see Figure 33). These techniques are applied, for example, in chromatography to improve quantification and detectability, as well as to decrease surface interactions. There are a variety of silylation agents which differ in reactivity, selectivity, side reactions, and character of the reaction by-products, and can therefore be selected to accommodate the user and the nature of the experiment.
Figure 33: Silylation of an alkyl phenol showing the replacement of a hydrogen atom with a trimethyl silyl group.

The higher fuel system temperatures of advanced aircraft will inevitably reduce the ability of typical additives to provide significant benefits in deposition reduction and oxidation inhibition. Therefore, alternative additive techniques need to be explored.

**Effects on Deposition and Oxidation**

We have shown that Exxsol D-110 oxidizes extremely quickly. Real jet fuels like F-2980 and F-3084 oxidize much more slowly because of the presence of heteroatomic species which interrupt the autoxidation, by mechanisms discussed in the previous chapter. These same species, however, can also play a significant role in the formation of surface and bulk deposits. Removal of such species should increase the oxidation rate and decrease deposition. Hydrotreatment, like in the fast oxidizing and low depositing fuel F-2747, and solid phase extraction are examples of this effect. Because these treatment methods can be expensive, silylation may offer a more suitable alternative.

Incremental amounts of the silylation agent hexamethyldisilazane (HMDS) were added to the high-depositing fuel, F-3084, and the samples were stressed in the QCM. The resulting deposition plots are shown in Figure 34.
Figure 34: Plots of mass accumulation of F-3084 in the QCM system with various amounts of silylation agent, HMDS.

This plot shows that HMDS has a substantial effect on the mass accumulation of the fuel. Addition of 0.1 mL HMDS resulted in only a modest reduction in deposits. However, adding 0.3 mL of the silylation agent causes a greater than 90% reduction in deposits.

The corresponding headspace oxygen plots of the experiments shown in Figure 34, are presented in Figure 35. The effect on the rates of oxidation with incremental addition of HMDS, like the deposition plots, show a clear concentration dependence. The neat fuel is a slow oxidizer since at the conclusion of the 15 hour experiment, it still has about 11% headspace oxygen. Addition of 0.3 mL HMDS, however, alters this slow oxidizing fuel into one that is nearly as fast as the hydrocarbon solvent, Exxsol D-110, presented earlier. It was important to verify that this result was not unique to this particular fuel. Experiments performed in four other fuels ranging in amounts of deposits and oxidation characteristics (F-2827, F-2980, F-3119, and F-3166) all show the same result. Incremental addition of HMDS resulted in an incremental reduction of the surface deposits, and an incremental increase in the oxidation rate.
The most substantial change in deposition with HMDS addition was in the fuel F-3119. Addition of 1 mL of HMDS reduced the deposition from 12 μg/cm² to 0.5μg/cm². The most drastic effect in the rate of oxidation was in F-2827. The neat fuel is typically at 26% headspace oxygen at the end of the 15 hour run. Addition of 1 mL of HMDS, however, causes the fuel to completely oxidize after only 5 hours.

Analysis of Silylation with Gas Chromatography

The remarkable decreases in deposition and increases in oxidation rates suggests that the chemical make-up of the species in the fuels are changing. To investigate the chemical changes that occur in the fuel as a result of the addition of silylation agents, we employed GC-MS. Silylation converts reactive hydrogen sites to less reactive trimethyl silyl sites. We first prepared in decane a mixture of 0.6 mg/L 3,5-dimethyl phenol and added 0.05 mL HMDS. This sample was stressed in the QCM, as in a typical jet fuel experiment, to examine the impact of HMDS on the reactive hydrogen of the phenol. We
extracted samples of this stressed mixture at the start of the run, and after four and eight hours during the run. Figure 36 presents the chromatograms of these samples.

Figure 36: Chromatograms, from top to bottom, of 0, 4, and 8 hour stressed samples of 3,5-dimethyl phenol and HMDS in decane.

The peak that develops at 22.25 minutes is the silylated phenol. This peak gradually becomes larger and although difficult to see, the phenol peak gets smaller. Our working assumption, based on the rapid increases in oxidation seen in the previous plots, was that all of the phenols were completely silylated. The results of Figure 36 suggest something completely different since there is still an extremely large phenol peak, at about 20.5 minutes. The fact that all of the phenol is not silylated is not due to the concentration of HMDS. Although not shown in the figure, there was still substantial amounts of HMDS left in the sample at the end of the experiment. Our current theory is that there are catalyzing reactions from species in the fuel, which are not present in the decane solvent, that promote silylation. For example, it has been reported that acid catalysis increases the rate of silylation (Pierce, 1968). Since acids are prevalent in real jet fuels, this is a possible explanation.
It was necessary, however, to verify that the phenols are actually converted in real jet fuels, stressed under the same conditions as our decane mixture. We added 0.5 mL HMDS to F-2980, a fuel that oxidizes slowly because of the known high concentration of phenols. The oxidation curves of the neat and additized fuels are shown in Figure 37.

Figure 37: Plots of headspace oxygen for F-2980 and F-2980 with HMDS addition.

The addition of HMDS results in a substantial increase in the oxidation rate. Based on our model mixture experiments of the phenol in decane, we presumed the change in the rate of oxidation was a result of the conversion of the antioxidizing phenols into relatively unreactive compounds. Again we employed gas chromatography to test this presumption. We prepared three samples for injection in the GC-MS: the neat unstressed fuel, the neat fuel stressed in the QCM for 15 hours, and the neat fuel with HMDS added and stressed for 15 hours. The polar species of each sample were preconcentrated via silica gel solid phase extraction with subsequent methanol elution. In previous SPE experiments we were interested in the fuel which came through the column, void of most of the polar species. In this study, we use SPE instead to analyze the polar compounds that are retained on the cartridge. The chromatograms of the methanol eluants of the three fuels tested are shown...
in Figure 38. Each chromatogram is the ion chromatogram of the 135 amu peak, which is a strong peak in C3 and larger alkyl phenols.

The top chromatogram of Figure 38 is that of the neat, unstressed fuel. As noted, there are a number of phenols in the fuel which contribute to its slow oxidation. The middle chromatogram, of the stressed neat fuel shows no difference between the unstressed and the stressed sample. This is significant because it shows no significant consumption or conversion of any of the phenolic species simply as a result of the sample being heated to 140°C. The bottom sample of the stressed, HMDS additized sample shows a marked decrease in the amounts of phenols, presumably by conversion to their silylated derivatives. These results are in agreement with our assumption that the silylation agent converts the phenols into innocuous species, resulting in an increase in the oxidation rates. This particular neat fuel was initially a low depositor, so it is difficult to see a deposition effect in this fuel. However, combined with previous knowledge of jet fuel
thermal-oxidative deposition, it is likely that the deposition reductions that result from silylation occur because of the conversion of the phenols into species that no longer produce deposits.

The increase in the rate of oxidation with the addition of HMDS raises the issue of compatibility with other additives. In addition to the naturally occurring non-hindered phenols in fuels, there are also synthetic hindered phenols which are added to fuels to prevent fuel oxidation and degradation in storage and in the fuel system. It is known that hindered phenols are more difficult to silylate than non-hindered phenols because the abstraction of the reactive hydrogen is blocked by large groups (Perold, 1984). Silylation of hindered phenols can require elevated temperatures and extended times to achieve complete silylation.

The potential differences in the affinity of a phenol to be silylated leads to the interesting possibility of selectively removing the deposit promoting phenols, but leaving the synthetic and/or hindered antioxidant phenols intact. In previous studies, we added BHT, a hindered phenol, as an antioxidant. BHT is used in this different study to see if it is silylated at 140°C in the QCM. We added BHT and HMDS to Exxsol D-110. HMDS was added in excess to insure that sufficient quantities were present in the sample to allow for partial, or complete conversion. Both the unstressed and stressed HMDS additized samples were analyzed in the GC-MS to see the change in BHT concentration. The chromatograms of these experiments are shown in Figure 39. The BHT peak is evident shortly after 15 minutes. The top chromatogram is of the unstressed sample and the middle is of the stressed sample. The bottom chromatogram, where the unstressed sample is overlaid on the stressed sample, shows that the hindered phenol is not silylated during the course of the experiment. The fact that BHT is not derivatized by HMDS is important because it shows the potential that silylation offers. The next major initiative of the U.S. Air Force is the so-called JP-8+225 program. Like JP-8+100, the JP-8+225 program searches for new ways to improve the thermal stability of jet fuels to even higher
temperatures. Silylation with HMDS may prove to be an ideal additive candidate since it is primarily reactive at elevated temperatures.

![Chromatograms of Exxsol D-110 with BHT and HMDS](image)

**Figure 39:** Chromatograms of Exxsol D-110 with BHT and HMDS in a solvent, before stressing (top), and after stressing (middle). They are overlaid (bottom) to show that BHT is not silylated by HMDS.

Also, because HMDS does not silylate BHT it offers the advantage of maintaining the positive impact of such hindered phenols in preventing oxidation during long term storage, but also of chemically transforming the deposit producing, naturally occurring phenols into innocuous, non-depositing species.

**Silylation and Solid Phase Extraction**

Previously, we removed the heteroatomic species through solid phase extraction. It is interesting to compare the results of silylation with SPE. Figure 40 shows the effects of silylation and SPE on the mass accumulation of F-3084. This is a high depositing fuel which shows improvements with both silylation and SPE treatment. Individually, we see
that the SPE treatment is substantially better at improving the deposition than 0.1 mL HMDS. However, we have seen in the previous graphs of F-3084 combined with HMDS, that additional silylation agent can reduce the deposition to less than 1.0 μg/cm².

![Figure 40: Plots of mass accumulation of F-3084 with addition of HMDS and treatment with SPE.](image)

Figure 40 also includes the plot of a sample which was first SPE treated and then additized with 0.1 mL of HMDS. Interestingly, the final deposition amount of this fuel is in between that of the samples with only HMDS or only SPE treatment. We performed this same series of experiments in a different fuel, F-3166, and received the identical result with both SPE treatment and HMDS. In these instances, it appears that the absence of phenols after solid phase extraction causes the HMDS to form additional insoluble deposits.

Plots of the oxidation curves for the experiments with F-3084 are seen in Figure 41. This figure shows that SPE treatment results in an oxidation rate which is similar to that produced from the addition of 0.1 mL HMDS. Also, we see that the addition of the silylation agent after SPE treatment results in an oxidation rate that is faster than either the SPE or the HMDS samples alone. This is consistent with the idea that both methods
remove heteroatomic species and consequently increase the rate of oxidation in the same manner. Further evidence that SPE treatment and HMDS addition behave in similar ways is that, as we have shown previously with the combinations of peroxo radical inhibitors and hydroperoxide decomposers, complementary oxidation delaying techniques often show synergism. The lack of a synergistic oxidation delay in the neat fuels, as compared to the individually treated samples also supports our conclusion that these distinct treatments operate in similar ways.

![Figure 41: Plots of headspace oxygen in F-3084 with addition of HMDS and treatment with SPE.](image)

Also, comparison of Figures 14 and 38 show the GC-MS chromatograms of the respective treatment techniques. The similarities in the removal and conversion of solid phase extraction and silylation, respectively, indicate that the physical changes caused by the two are the same.

The benefits of silylation are accompanied by potential disadvantages. The formation of products like silicon dioxide, and incompatibilities with the materials in the combustor or the fuel lines, could cause severe problems. The cost of silylation agents is another concern. Currently, silylation agents are relatively expensive when compared to
the additives currently employed in Air Force jet fuels. A final potential problem is the sensitivity of silylation agents to water. Dissolved water in fuels, or exposure of the fuel to the humid air, is extremely common. Some silylation agents that are reactive at low temperatures could react with water, to produce a silanol, instead of silylating the heteroatomic species. Because HMDS primarily only silylates species at elevated temperatures, however, this problem would be for the most part alleviated.
CHAPTER VI

CONCLUSIONS

Summary

The quartz crystal microbalance (QCM) system is an effective technique for evaluating the thermal stability and fundamental chemistry of jet fuels. The QCM measures extremely small changes in oscillation frequencies of the quartz crystal, and therefore has a unique sensitivity for the determination of surface deposition. Because the system is fitted with an oxygen sensor and a pressure transducer, the headspace oxygen can be measured. Therefore, the in-situ monitoring of both deposition and oxidation throughout the course of an experiment makes the QCM system a valuable tool.

While the ultimate goal of our work is the formulation of additives, analysis of the pretreatment technique of solid phase extraction (SPE) offers insight into the autoxidation cycle and the poorly understood deposition processes. The polar heteroatomic species in fuels, like phenols, have been implicated in the deposit forming processes, and act as antioxidants because they prevent the production of additional $\text{R}^\ast$ radicals by reacting with the peroxo radicals. Silica gel packing in the SPE cartridge retains polar compounds of a fuel. Thus, SPE treatment of a fuel removes the phenols, and therefore reduces the deposition and increases the rate of oxidation.

We have explored the roles of peroxo radial inhibiting (AH) and hydroperoxide decomposing (SH) species in the suppression of the oxidation of jet fuel. We find that the oxidation delay in a hydrocarbon solvent, Exxsol D-110, caused by the peroxo radical
inhibiting species, BHT, is dependent on the concentration. However, addition of only the
hydroperoxide decomposing species, hexyl sulfide or triphenylphosphine, has no effect
on the delay of the oxidation. We find that in combination and in sufficient
concentrations, the AH and SH species demonstrate a synergistic delay in the oxidation.
We employed a pseudo-detailed chemical kinetic model to verify the results as well as to
provide additional insight. The model demonstrated excellent agreement with the
experimental results.

We extended the oxidation suppression studies to true jet fuels. We added the
peroxide decomposing species to F-2747 and observed the synergistic delay in oxidation.
Solid phase extraction of F-2747 followed by the addition of SH did not exhibit any
oxidation delay at all. The results of the experiments with the solvent and the true fuel,
along with the results of the chemical kinetic model, indicate that phenolic species must
be present in order for the SH species to have an effect on the oxidation. The autoxidation
cycle is composed of two loops: the main loop in which the RO$_2^\cdot$ radicals react with the
fuel to produce R$^\cdot$ radicals and ROOH species, and the outer loop in which the ROOH
species are unimolecularly decomposed into additional R$^\cdot$ radicals. We believe that the
main loop is extremely fast relative to the outer loop. It makes sense, then, that addition
of only SH does not appreciably limit the production of R$^\cdot$ radicals, since the main loop is
so fast. Also, addition of only AH does slow the main loop which, because it is the faster
of the two, has a pronounced impact on the oxidation. Finally, addition of both AH and
SH species has a synergistic effect because the AH slows the main loop, which in turn
makes the production of the R$^\cdot$ radicals via the mechanisms of the outer loop much more
significant. The SH species, however, limits this production and dramatically slows the
oxidation.

Understanding the fundamental chemistry has allowed us to begin to distinguish
between the different characteristics of the many types of fuels. For example, reconsider
the fuels F-2747 and F-2827. We know that F-2747 is a fast oxidizing, low sulfur fuel,
and that F-2827 is a slow oxidizing, high sulfur fuel. In our analysis of hydroperoxide decomposing species, we added the sulfur compound (hexyl sulfide) to F-2747, and generated a slow oxidizing fuel. The plots of F-2827, and F-2747 with added sulfur can be seen in Figures 12 and 20, respectively. Previously, it was somewhat unclear why these two neat fuels have such drastically different oxidation behaviors. However, studies of the suppression of the autoxidation cycle have allowed us to better understand fuel oxidation and these differences.

The application of derivatizing agents as jet fuel additives is a relatively new area of study. We have found that silylation is an effective means of reducing thermal-oxidative deposition and increasing the rate of oxidation. The silylation agent, HMDS, converts a reactive hydrogen on heteroatomic species into a much less reactive trimethyl silyl group. Because these species are prevalent in the deposit forming processes and typically act as antioxidants, their removal via silylation accordingly reduces the deposition and increases the oxidation rate. Our studies of silylation with HMDS have shown a strong concentration dependence. At low concentrations, the deposition is reduced and the oxidation rate is increased only moderately. However, with an increase in concentration, the deposition reduction is much more pronounced, as is the increase in the oxidation rate.

We performed experiments to compare the results of jet fuel oxidation and deposition of solid phase extraction and silylation. The two approaches are different since one is an additive, and the other is a pretreatment method. However, they are similar in that they both alter/remove the phenolic species. The results show that the fuel does not seem to discriminate between one approach or another. Both affect the polar, heteroatomic species, and consequently, the oxidation curves are almost identical. However, the mass accumulation plots indicate that the deposition in the SPE sample is significantly less than the sample with the HMDS, for the concentration used. We have shown that addition of more HMDS will reduce the deposition further.
The increases in oxidation rates with silylation interested us in determining whether a hindered phenol which does not increase deposition can be added such that the benefit of the deposition reduction with silylation can still be realized in the high temperature fuels of the JP-8+225 program, while also achieving a delayed oxidation during long term storage. We have found that BHT, a hindered phenol commonly used as an antioxidant, is not silylated. This offers promise that silylation agents might one day be a part of an additive package.

The benefits received from the thermal stability improvements explored do not come without their detritions. Solid phase extraction can be labor intensive and quite costly. The use of sulfur compounds as additives raises concern of promoting additional deposition, as well as the contribution to environmental problems by increased sulfur emissions. Derivatizing agents can react with dissolved water, form additional deposits like silicon dioxide, or have other incompatibilities with materials in the aircraft's fuel system. Both silylation and hydroperoxide decomposing species can be problematic based solely on their cost. Silylation agents are more expensive than additives currently in use, and hexyl sulfide (the hydroperoxide decomposer) is used in such high concentrations that could make it economically unfeasible. Triphenylphosphine is one possible solution to alleviate the cost issue of the hydroperoxide decomposer. Clearly, further research is required.

**Recommendations**

Preliminary experiments with triphenylphosphine (TPP) have demonstrated real potential. We show that it delays the oxidation at a concentration of two orders of magnitude less than the hexyl sulfide. It is also less expensive than hexyl sulfide, and is not known to cause deposition, have any material incompatibilities, or detrimental effects on the environment. For this reason, more work with TPP is warranted.
With the advancement of current aircraft and the higher heat loads to which the fuel will be exposed, much emphasis needs to be placed on the temperature effects of some of the additive packages that are developed. We have begun preliminary oxidation suppression experiments at higher temperatures and have received some extremely positive results. Previously, we noted that some combinations of AH and SH do not show a synergistic delay in oxidation, believed to be because the main loop is not slowed enough by the AH species. We took one such sample and instead of operating at the normal temperature of 140°C, we operated at 155°C. The result of this experiment is seen in Figure 42. This is an unusual result since we would typically believe that with an increase in temperature, the oxidation reactions would be much faster. Instead, at the higher temperature the oxidation is significantly slowed. More research needs to be done in this line of experiments since they could be important for the formulation of additives that are effective at the elevated temperatures of the JP-8+225 fuels.

![Figure 42: Plots of headspace oxygen of Exxsol D-110 with BHT and hexyl sulfide at 140°C and 155°C, demonstrating the unusual effect of temperature on the rate of oxidation.](image)

Future work in the use of silylation agents as jet fuel additives is important because this research is still in its infancy. We have experimented with several types of
derivatizing agents. One such agent N,O-bis(trimethylsilyl)acetamide (BSA), derivatizes products at room temperature. HMDS, however, requires elevated temperatures (>50°C) for reaction. Therefore, we have the potential ability to control the time and/or temperature at which silylation reactions occur. Additionally, the use of HMDS in advanced aircraft might lead to an additive that is not altered or consumed in storage, but reacts and has a positive impact when it is heated to elevated temperatures in the circulating fuel.

We have identified that HMDS does not silylate hindered phenols like BHT. The presence of phenols is desirable in fuel storage because they inhibit the oxidation. Therefore, by proper choice of the silylation agent we may be able to design a fuel in which the deposit producing phenols are preferentially silylated to reduce deposition while leaving the oxidation inhibiting phenols intact.

A final promising use of silylation in jet fuel is for the identification and study of the deposit promoting species. Such deposition reactions are still poorly understood. Silylation of species such as these will allow them to be more detectable in chromatographic analysis and should improve the ability to identify them. Identifying and monitoring the deposit forming species with silylation agents could prove to be extremely useful in studying and preventing the mechanisms of deposition in jet fuels.
BIBLIOGRAPHY


