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Jeffrey Bruce Gomach
University of Dayton

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Development of an In-situ Carbon
Deposition Test for the Analysis of
Thermal Stress on Jet Fuel

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

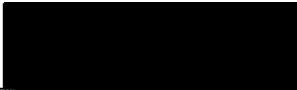
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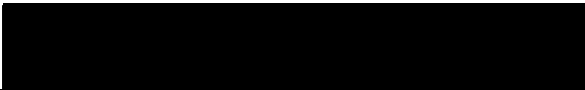
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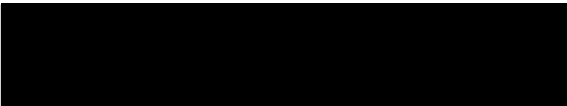
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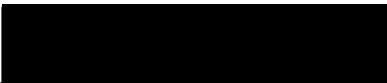
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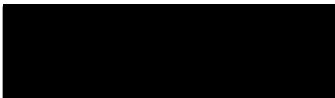
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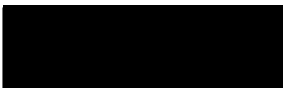

Kevin J. Myers, D.Sc., P.E.
Advisory Committee Chairman
Professor
Chemical and Materials Engineering


Matthew J. DeWitt, Ph.D.
Research Advisor
Senior Research Engineer
University of Dayton Research
Institute
Associate Professor
Chemical and Materials Engineering


Steven S. Zabarnick, Ph.D.
Research Advisor
Distinguished Research Scientist
University of Dayton Research Institute
Professor
Mechanical and Aerospace Engineering


Richard C. Striebich
Research Advisor
Senior Research Engineer
University of Dayton Research
Institute


Tim Edwards, Ph.D.
Committee Member
Senior Scientist
Air Force Research Laboratory


Donald L. Moon, Ph.D.
Associate Dean
Graduate Engineering Programs
& Research, School of Engineering


Joseph E. Saliba, Ph.D., P.E.
Dean, School of Engineering

Abstract

DEVELOPMENT OF AN IN-SITU CARBON DEPOSITION TEST FOR THE ANALYSIS OF THERMAL STRESS ON JET FUEL

Name: Gomach, Jeffrey Bruce

University of Dayton

Research Advisors: Dr. Matthew DeWitt
Dr. Steven Zabarnick
Richard Striebich

Committee Member: Dr. Tim Edwards

Academic Advisor: Dr. Kevin Myers

As thermal demands placed on jet fuel increase, improved knowledge of fuel chemistry is needed for the development of better deposition mitigation techniques. A new tool is needed to examine deposition such as the in-situ carbon deposition test (ICDT) created in this work. Capabilities achieved for the ICDT include: in-situ oxidation and quantitation of deposits, low fuel volumes, and controlled residence time and extent of reaction. Fuels were thermally stressed in a Lindberg Furnace, and in-situ oxidation of deposition to CO₂ was accomplished using the same furnace and a CuO oxidation catalyst. Oxidation of deposition was measured to be complete under a reactor condition of 750°C and a catalyst stage temperature of 400°C. The deposition measurement of this oxidation process was repeatable, and measured in total µg of deposit per mL of stressed fuel. This allowed the in-situ carbon deposition test to accurately distinguish oxidative characteristics of different fuels. A complete thermal oxidative experiment required less than 15 mL of fuel for testing, and total deposition could be quantified as low as 0.5 µg. Deposition trends were consistent for the ICDT

and other systems for different fuels and additives. This verified that data obtained from the ICDT was applicable to deposition studies and especially useful for preliminary evaluation of fuel oxidation characteristics. The low volume and excellent reproducibility makes the test ideal for explorative studies or use with novel fuels or additives. Deposition characteristics were also compared for different temperature ranges over the range of complete oxidation. A trend of increasing deposition with temperature was found over the 250°C to 400°C temperature range with a leveling of deposition over the range of 400°C to 500°C.

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Chapter I

Introduction

1.1 Jet Fuel and Increasing Thermal Demands

Aviation fuel has changed significantly since the advent of flight in 1903. Modern day jet aircraft burn billions of gallons of fuel to provide power to engines and electronic systems.¹ The modern fighter aircraft, however, derives more than just energy from the onboard jet fuel. Many systems aboard the aircraft, such as electrical, engine, and hydraulic, have cooling requirements that are provided by the onboard fuel.² Similar to how a car uses a water/glycol mixture in a radiator, thermal management of propulsion systems is accomplished through heat exchangers which use jet fuel as the cooling medium. Carrying a separate coolant onboard an aircraft would impose an additional weight penalty, which would directly affect payload and performance. Although this has been an effective strategy for legacy systems, thermal demands placed on the fuel will grow rapidly as modern aircraft utilize more advanced systems and push towards higher speeds. As fuel is exposed to higher temperatures, thermal degradation and deposit formation become serious considerations. The term "thermal stress" is typically used to describe exposure of a fuel to elevated temperature over time.³

Many different approaches have been employed to mitigate the effects of deposition due to thermal stress on aircraft systems. The first mitigation option explored was the use of special thermally stable fuels such as JP-7 and JP-TS. JP-7 is a highly refined fuel for extremely high thermal stability. JP-TS is a thermally stable refined fuel with an additive package. JP-7 and JP-TS fuels are expensive alternatives to standard fuels. An alternate approach for the mitigation of deposition was the use of thermal stability additives to enhance the performance of the standard Air Force fuel, JP-8. Engineering design changes were also explored to reduce the effects of deposition on fuel heat exchangers, to use catalytic materials for endothermic reactions, and to reduce the concentration of key species in the deposition process.⁴ The altering of key species concentrations is done through fuel additives.

The increasing thermal demands that future aircraft will place on fuel has driven the development of enhanced thermal stability via additives. This approach has been shown to be a viable, cost effective alternative to more complex deposition mitigation techniques.⁵ Rather employing only specialty fuels, additives can allow conventional fuel systems to operate safely.

1.2 Thermal Deposits

The formation of thermal oxidative deposits is an important concern in jet fuel application. The thermal stability of a fuel is linked to the concentration and composition of trace fuel species. Fuel components such as trace sulfur, nitrogen, oxygen, polar species, metals, and dissolved oxygen have been linked to deposit formation due to reactions between these species and bulk fuel

hydrocarbons.⁶ Oxidative and pyrolytic forms of deposition occur in fuels at different temperatures. Oxidative deposition occurs at moderate temperatures over the temperature range of 150°C to 300°C. These deposits occur from the reaction of dissolved oxygen with fuel species. Pyrolytic deposition occurs at temperatures above 500°C when bulk fuel species thermally decompose. The operating conditions of current aircraft limit the scope of deposition to the oxidative form. Deposit formation itself is not entirely understood; however, the chemical composition of oxidative deposits shows a higher concentration of the trace heteroatomic species compared to that of the fuel. The deposit composition is typically estimated at 70% carbon, with hydrogen, nitrogen, oxygen, and sulfur comprising the remainder.⁷ The chemical structure of oxidative deposits is similar to that of coal, an amalgam of cross-linked species creating a varied pattern similar to that of an organic polymer.⁸ A high concentration of aromatic species with linked sulfur and oxygen chains creates a dense and complex structure.

Solid deposits can block fuel passageways and can be very difficult to remove. Often, replacement of hardware is chosen over attempting to clean the obstructions. Not only do surface deposits disrupt flow through close-tolerance passages, but also in combination with bulk-insoluble solids, they can foul filters, valves, and nozzles.⁵ Blockage in filters and valves can reduce the effectiveness of fuel control systems, while fuel nozzle fouling can affect combustion efficiency. The latter may result in inadequate fuel flow to the engine and distortion of the fuel spray pattern and atomization. These can produce high temperatures on turbine blades and combustor liners, which may not be capable of handling the

stress with resulting material fatigue. This type of damage places aircraft at risk and increases maintenance costs. The solution to these problems lies in understanding how to mitigate deposition at the high temperatures fuel is exposed to in aircraft.

As modern aircraft begin to push the bounds of thermal stress, there is a need for improved knowledge of deposition chemistry. The formation of oxidative deposits from jet fuel is a complex chemical process that is not completely understood. From the simplest perspective, fuel and dissolved molecular oxygen in the presence of heat combine to form carbonaceous deposits. Long residence times at temperatures above 150°C begin to show significant levels of oxidative deposition.⁹ These can either be insoluble bulk or surface deposits. The deposits can range from a thick gum to a dense solid; the rate of deposit formation increases with increasing temperature.

While less is understood about the formation of deposits, the autooxidative process in the fuel is well studied. Autooxidation is the cyclic reaction process whereby fuel and dissolved oxygen react as shown in Figure 1. The reaction is a free radical chain process, which eventually produces deposit precursors. The process is initiated via a free radical reaction that is not yet fully understood. Peroxide and non-stable radical formation may occur during fuel storage and enter aircraft systems during refueling. Upon initiation, radicals within the fuel react with dissolved oxygen to form peroxy radicals. The peroxy radicals react with fuel species to produce a new fuel radical and a hydroperoxide, reinitiating the chain. This process can auto-accelerate as fuel undergoes hydroperoxide

decomposition that results in a net increase in chain carriers. The mechanism can be catalyzed by metallic surfaces, which can provide lower activation energies for peroxide decomposition. Other hydrocarbon species may begin to react with the chain as well. Naturally occurring antioxidants, such as phenols and thiols, have weakly bonded hydrogen and a more stable radical form. The reaction of antioxidants with peroxide radicals reduces the overall propagation rate by preventing the reaction with fuel species, but may have the adverse effect of producing deposit precursors. While the mechanism is not known, there is a correlation between oxygen consumption and deposition.¹⁰

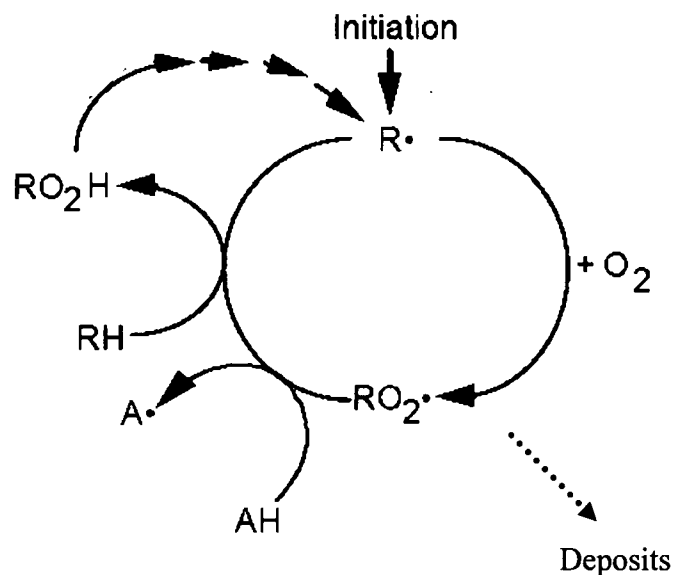


Figure 1. Simplified autoxidation mechanism for hydrocarbon fuels⁵

1.3 Fuel Additives

Some fuel characteristics are governed by bulk fuel composition, but other characteristics are influenced by very minor concentrations of key species.¹¹ Fuel additives are chemicals added to jet fuels, typically at low concentration, to achieve specific goals. There are many different forms of fuel additives serving

many different purposes. Additive fuel chemistry has addressed many challenges for fuel systems, including thermal stability. Conventional additive types include: thermal stability improvers, antioxidants, metal deactivators (MDA), corrosion inhibitors/lubricity enhancers, fuel system icing inhibitor, electrical conductivity enhancers, leak detectors, and dyes.¹² Of specific interest to fuel oxidation chemistry are the antioxidant, metal deactivator, and thermal stability improver.

Antioxidants act to inhibit oxidation in long-term storage and during moderate thermal stress. The use of antioxidants helps delay the onset of autoxidation by slowing the oxidation process and the formation of gums and peroxides during storage, as shown in Figure 1 (see AH).¹³ Antioxidants approved for jet fuel are typically types of hindered phenols, such as 2,6-di-tert-butyl-4-methylphenol (BHT).¹³ Since antioxidants are consumed during reaction, long-term exposure to elevated temperature will consume them and return fuel to its normal oxidation rates. Overall, antioxidants delay the onset of oxidation but do not permanently prevent the process. The rate of consumption of antioxidants is dependent on the temperature and time of exposure. Additionally, this chemical process may yield deposit precursors, which can increase deposition for a fuel under complete oxygen consumption.¹⁴ This makes antioxidant chemistry very useful for low percentages of oxygen consumption, but potentially detrimental in the regime of complete oxygen consumption.

Thermal stability improver additives are used to directly reduce the formation of oxidative deposits and solubilize potential deposit precursors. The Thermally Stable Jet Fuel (JP-TS) requires an additive, which was approved

March 1970 for high temperature applications. The additive, JFA-5, is composed of polymers, organic amines, and amides dissolved in kerosene.¹² JFA-5 is a proprietary additive developed by DuPont, which also has dispersant effects. The dispersant operates to prevent agglomeration of degradation products by means of a polar "head" and fuel soluble "tail." As coking precursors form in the fuel, the dispersant surrounds and solubilizes them; this prevents the particles from growing large enough to form deposits and creates an affinity for the deposits to remain in solution. The package is presumed to have synergistic effects as well.¹² Metal deactivators help prevent deposits from adhering to the walls of fuel systems as well as reducing the catalytic effects of the metal.¹² Overall this assists in preventing the decomposition of hydroperoxides.

Another fuel oxidative stability additive, the "JP-8+100" package, is used in current USAF aircraft.⁵ The name is derived from a 100°F increase in thermal stability over typical JP-8. The thermal stability limit for neat JP-8 is approximately 325°F (163°C). The goal of the additive package was to produce enhanced JP-8 performance near that of JP-TS.¹⁵ This could provide a cheaper, more readily available fuel with similar thermal stability performance. The "JP-8+100" package is comprised of a proprietary dispersant (~70 mg/L), BHT (25 mg/L), and MDA (10 mg/L). The cost goal is approximately \$0.005/gal of jet fuel. The additive has been shown to be very effective under the regime of partial consumption of the dissolved oxygen in fuel.⁵ The typical fuel temperature limits for "JP-8+100" are around 425°F (218°C). Current aircraft are typically designed to operate in this regime of partial oxygen consumption. An important note is that

the package has shown synergistic effects, allowing lower consumption rates of individual inhibitors, and thereby permitting each component in the additive package to function better during stress. Deposition reactions are lower than accounting for the individual effect of each component.

Oxidative deposition studies have begun to examine additive effects within the regime of complete oxygen consumption. The goal of a "JP-8+225" additive is to replace the necessity for specialty JP-7 fuels.¹⁶ Innovative ideas for fuel additives are beginning to be examined, but the goal creates unique challenges. As previously discussed, the "+100" additive functions in the realm of partial oxygen consumption.¹⁷ Fuel stress at this temperature regime is not sufficient to fully consume the dissolved oxygen during the course of a typical nozzle residence time. For "+225" temperatures, additives must be developed to confront much more rapid oxidation reactions. Complete consumption of dissolved oxygen during the nozzle residence or in upstream fuel systems will be readily attained as engine systems operate at higher temperatures.¹⁷ Future additives will most likely have to function in different ways to address this regime of oxidative deposition. Hexamethyldisilazane (HMDS) is an example of a silylation reaction, which shows potential to reduce fuel deposition.¹⁸ Silylation reactions can be used to intercept degradation reaction products. A greater understanding of fuel chemistry and better deposition analysis techniques is needed to address future deposition problems and develop viable mitigation strategies.

1.4 Deposition Analysis Methods

Improving the understanding of deposition chemistry has led to the development of numerous deposition tests. Characterization of deposition can be extremely subjective in nature because fuel experiences many different environments onboard an aircraft. It is difficult to investigate all of these environments simultaneously, so the use of various reactor types allows a broad range of simulation. This has led to the development of many different deposition analysis techniques.

The only approved fuel thermal stability test for specification evaluation is the Jet Fuel Thermal Oxidation Tester (JFTOT). In the JFTOT, fuel flows around a resistively heated tube with a constant heat flux. After fuel stress, the tube is inspected visually to rate the level of deposition. Ratings are used to either pass or fail a fuel for use. While this is useful for determining the application of a specific fuel, it provides little quantitative information for research. The test has been used as the standard for fuel qualification since 1973, but many more fuel deposition tests have been developed and used since that time.

One of the most useful batch operation tests developed is the Quartz Crystal Microbalance (QCM) / Parr bomb system.¹⁹ The QCM can measure extremely low levels of deposition in real-time. The system uses 60 mL of fuel in a 100 mL stainless steel vessel, which is heated through a band heater. A stir bar ensures adequate mixing during operation. Online oxygen measurements of the headspace are made with a pressure transducer and oxygen sensor. A thermocouple measures the fuel temperature, and the resonant frequency of a

quartz crystal exposed to the fuel is recorded. Once the system is at temperature, headspace oxygen is recorded in time with deposition measured at the quartz crystal. As oxidative deposition occurs, the frequency of the crystal changes with the total mass of deposits. This real-time monitoring is very useful for oxidative deposition studies.¹⁹ The QCM is limited to relatively long residence times and low temperatures. Long residence times result in long test time, usually several hours. Temperature is limited by long test runs and the interference of reactions which can occur prior to reaching an isothermal test temperature.

The ECAT Flow Reactor System is a single tube flow reactor used for fuel studies. The ECAT uses a Lindberg Furnace to heat fuel as it flows through a 36-inch tube. Tube diameters are typically 0.125 inches with a flow rate of 10-15 mL/min. Testing is typically conducted for 6 hours to obtain quantifiable deposition from about 4 L of fuel. The ECAT does not offer an isothermal temperature profile, but temperatures are measured via thermocouples to correlate with deposition levels. One of the strengths of the system is that it provides a profile of deposition as fuel is exposed to temperature stress over time. Upon completion of a test, the tube is cut into 2-inch sections, and deposition is estimated via offline oxidation of carbon to carbon dioxide (CO₂) using a LECO carbon analyzer. The process is destructive of the tubing. Deposition measurement sensitivity is approximately 15 µg per tube segment; typical deposition levels are several tens to hundreds of micrograms during testing. Data from the ECAT provides information about deposition, and is

especially useful in additive studies due to the nature of its profile measurements of deposition.¹⁷ The complexity of the long test time and off-line analysis is one of the major disadvantages to the ECAT.

The Near Isothermal Flowing Test Rig (NIFTR) is another single pass flowing test. The NIFTR is a smaller scale system using about 1 L of fuel, but instead of utilizing a radiative heating scheme, the tubing is packed inside a copper block to maximize conductive heat transfer. At low flow rates, this provides very high isothermality for upwards of 80% of the reactor length. The NIFTR provides online oxygen measurements at the exit of the reactor. Similar to the ECAT, the tubing must be cut and destroyed to quantify carbon deposition levels. The NIFTR is very similar to a plug flow reactor and is primarily used for studying oxygen consumption as a function of residence time. Long test times and residence times are necessary to produce quantifiable deposits.

In principle, reactors are divided into two types: flowing and batch. Each system type provides intrinsic advantages and limitations during testing. Flowing systems simulate high concentrations of reactants and limit oxygen supply. Examples of these types of systems at the Air Force Research Laboratory at Wright Patterson Air Force Base (WPAFB) include the ECAT, NIFTR, and JFTOT.⁵ The flowing reactor more closely simulates the short residence time and high temperature environment of many real aircraft systems. They are also able to emulate the high-pressure environment that aircraft fuel systems experience. A benefit is that realistic temperature profiles and flow rates can provide a better understanding of when aircraft systems may expect deposition and how fuel

reacts as it is heated. The drawback of flowing systems is a combination of detection limitations and volume requirements. Flowing reactors can produce deposits over the entire length of the reactor, and large volumes of fuel may be necessary to achieve quantitative deposition. Another consequence of many flowing reactors is that they provide a non-isothermal reaction temperature at moderate flow rates. Non-isothermal operation makes it more difficult to determine kinetic parameters from experimentation.

Batch systems, such as the Quart Crystal Microbalance (QCM), may offer greater advantages for fundamental kinetic deposition studies.¹⁹ After an initial heating, a stirred tank type reactor offers isothermal temperature exposure and concentrations throughout the reactor. The major consequence of batch systems is the residence time limitations; batch reactors have long heat-up and cool-down periods, which makes the start-up reaction period less isothermal. Due to a significant preheat stage and long reaction times, the batch system often operates at lower temperatures than flowing reactors. This results in longer residence time than a higher temperature flowing system being necessary. The preheating period allows other reactions to occur prior to reaching the designated stress temperature. Lower concentrations in batch systems (due to reactants being consumed during the preheat stage) also provide different kinetic representations of fuel stress reactions. Different reactions may be favored or "back mixing" may allow products to continue reacting to secondary and tertiary products. These derivative reactions may not actually occur during application. A batch container is not easily replaced with different materials, while tube type

reactors can easily be changed for different reactor walls. This makes it difficult to test material influences on surface deposition. Despite limitations, each system offers unique qualities that are beneficial to the understanding of the fuel deposition process. With an understanding of their limitations, a great deal of knowledge can be attained from using each of these systems.

1.5 Experiment and Design Goals

Ongoing fuel thermal stability studies will continue to examine deposition chemistry and characteristics for higher temperatures and explore different deposition mitigation techniques, such as novel fuels and additives. Improved knowledge of the fuel deposition chemistry will assist in the development of better additives aimed at preventing oxidative products from becoming deposits. It may no longer be reasonable to attempt to delay the onset of deposition due to complete oxygen consumption in the extremely short reaction times for the autoxidation process. The current "JP-8+100" package has been shown to decrease deposition at these higher temperatures, but the goals of the "JP-8+225" are still a long way from being achieved.

Higher temperature and explorative additive studies have created demand for a low volume, flowing deposition test: a short time scale experiment capable of screening new additives without the need for large quantities of fuel or additive. For rapid, small-scale analysis, the deposit quantitation would also have to be done in-situ within the fuel stress reactor. Many tests use destructive techniques to section the reactor tube and measure each independently. This destructive technique requires many hours of labor and analysis. It also creates a

higher detection limit for deposition. The development of an in-situ deposition system could offer improved sensitivity along with a more rapid analysis.

Previous work on the System for Thermal Diagnostic Studies (STDS) has demonstrated excellent versatility while conducting low volume fuel experiments.²⁰ The reactor system was scaled down from other flowing test designs to fit within a standard gas chromatography (GC) oven and linked with online mass spectrometry (MS) analysis. Previous work has shown that this variable setup allows many unique tests to be designed on the framework of the initial STDS design. The major system components included two HP 5890 Gas Chromatography Ovens, a Lindbergh furnace, and a HP 5970 Mass Selective Detector. Previous work on the STDS utilized a Condensed Phase Test Cell to conduct experiments on flowing liquids at high temperature and pressure. The system has proven successful for testing reaction chemistry under both subcritical and supercritical conditions. Utilizing this groundwork for thermal diagnostic studies, the thermal stress reactor was enhanced into one that could analyze deposition.

The objective of this work was to generate an in-situ deposition analysis tool for thermal degradation studies. As many fuel deposition-testing systems are large scale or time consuming, a rapid analysis tool capable of readily handling many different fuel types and operating conditions while maintaining analytical accuracy is needed. Goals for this project include in-situ deposition detection, low fuel consumption, accuracy, and repeatability of analysis. In addition, a basic principle behind the design was rapid test and analysis. Many systems are

currently capable of performing in-depth analysis of fuel deposition, but testing times are long due to required test duration and separate analysis tasks. To create a low volume in-situ carbon deposition test, a flowing system with extremely low volume and high surface to volume ratio was chosen. Deposition is estimated from the in-situ oxidation of carbon and quantitation of CO_2 . The design is similar to that of other flowing systems like the ECAT discussed previously, but scaled down to utilize a mass spectrometer as a mass quantification tool. It creates an excellent system for fundamental deposition kinetic studies. This also mimics the real world deposition that occurs in jet aircraft components, such as the fuel nozzle. In-situ analysis allows for reactor tubes to be reused after being cleaned by oxidation of deposits. This decreases the time required for consecutive analyses and allows for studies on the effects of an oxidized tube wall and use of regenerated tubing. Collection and analysis of stressed fuel can be combined with deposit information to examine reaction chemistry and kinetics.

Chapter II

Experimental Procedure

2.1 Design and Setup

The basic design of the In-situ Carbon Deposition Test (ICDT) is shown in Figure 2. Fuel is prepared and reacted, followed by oxidation of deposits to CO_2 and analysis by GC-MS. Subsequent discussion will examine each of these phases, explaining how each operates to both create and analyze carbon deposits.

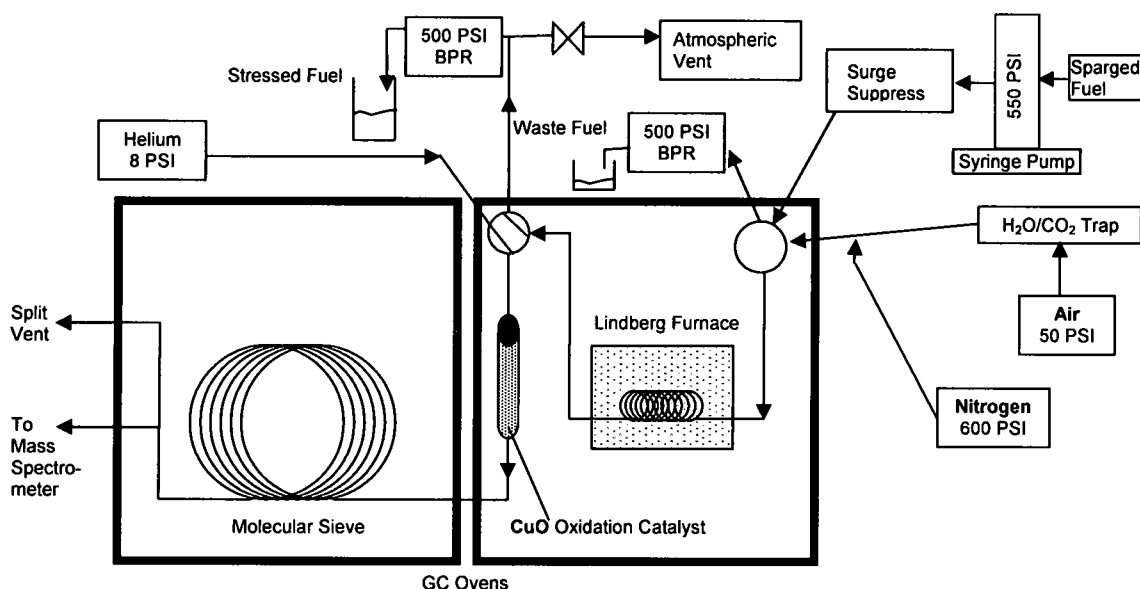


Figure 2. In-situ carbon deposition test process flow diagram

Fuel preparation is initiated with an offline sparging with air or helium and then storage of the fuel inside the syringe pump. Here, it is pressurized and

pumped to the reactor oven. The oven preheats the fuel via convection prior to introduction to an internal Lindberg furnace, which provides temperatures for reaction. Only the fuel within the Lindberg furnace will be exposed to reaction temperatures sufficient for deposit formation. The fuel flow is then passed through a 500 psi backpressure regulator to fuel waste. After fuel stress and deposit formation, the entire flow path is purged and dried with nitrogen, air is introduced, and deposits are oxidized to CO_2 and carbon monoxide (CO). Only the portion of tubing contained within the Lindberg furnace will experience sufficient temperatures to oxidize deposits. The product gases flow through an oxidation catalyst to the analytical oven. This copper-oxide (CuO) catalyst drives the oxidation of CO to completion. Within the analytical oven, the CO_2 is trapped and subsequently quantified via selective ion monitoring (SIM) by the mass spectrometer. SIM mode allows the mass spectrometer to accurately quantify ions at very low concentrations. The quantification of CO_2 is used as a direct indicator of the total mass of carbon deposits.

2.2 Fuel Preparation

Fuel is prepared prior to testing to maintain constant initial conditions. Figure 3 shows the fuel preparation flow path for samples prior to being introduced to the reactor. Fuel to be studied is loaded into an HPLC reservoir and sparged with air or helium. Air sparging ensures air saturation in the fuel, while helium sparging ensures low dissolved oxygen levels for oxygen-free or pyrolytic fuel studies. The liquid is drawn into the syringe pump directly after sparging. An ISCO 500D syringe pump is used with an ISCO Series D pump controller to

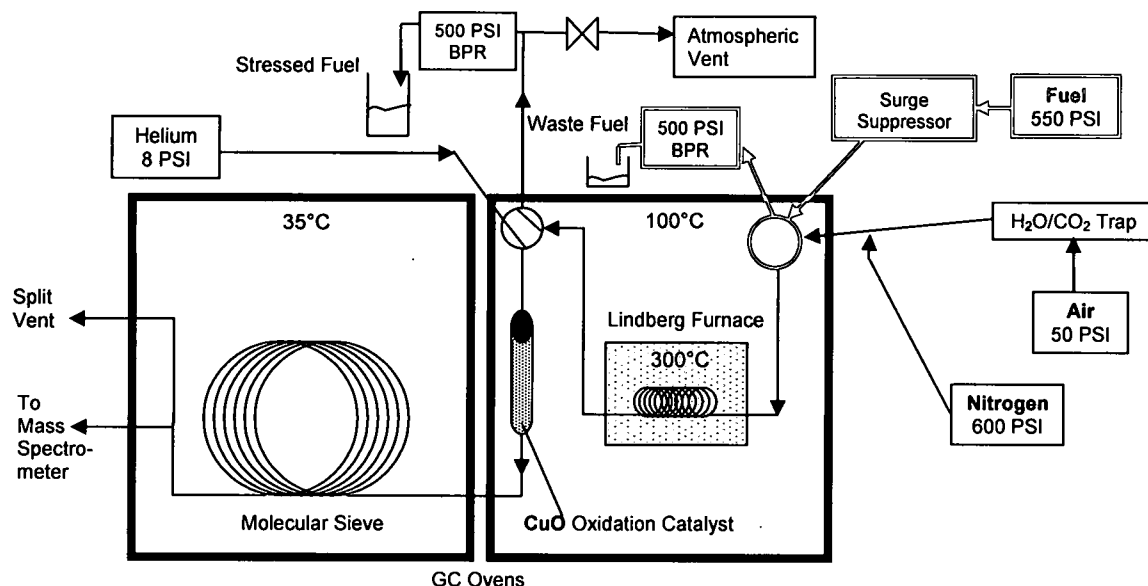


Figure 3. Pressurization flow path for test startup

deliver a constant volumetric flow rate to the reactor system. Type 316 Stainless Steel tubing is used to carry the fuel from the pump and throughout the entire system.

Fuel is maintained at high pressure during reaction to sustain a condensed phase. A surge suppressor prevents pressure spikes from the pump, and a check valve (not shown) prevents backflow from the reactor system. Pressure is measured via an analog gauge at the surge suppressor where a pressure relief valve prevents the system from over pressurizing. By flowing fuel through an auxiliary line to a 500 psi back pressure regulator (BPR), pressure is established prior to testing. This flow path is highlighted in Figure 3. Nitrogen flows through the reactor until fuel flow is initiated. When sufficient pressure has developed to establish flow, the six-way stainless steel switching valve prior to the furnace is used to initiate flow to the reactor.

2.3 Fuel Stress and Deposition Test

Fuel is reacted by stressing it in the reactor oven of the in-situ carbon deposition system. The reactor section is composed of the GC oven (right) and internal Lindberg furnace shown in Figure 4. The outer oven is a low temperature

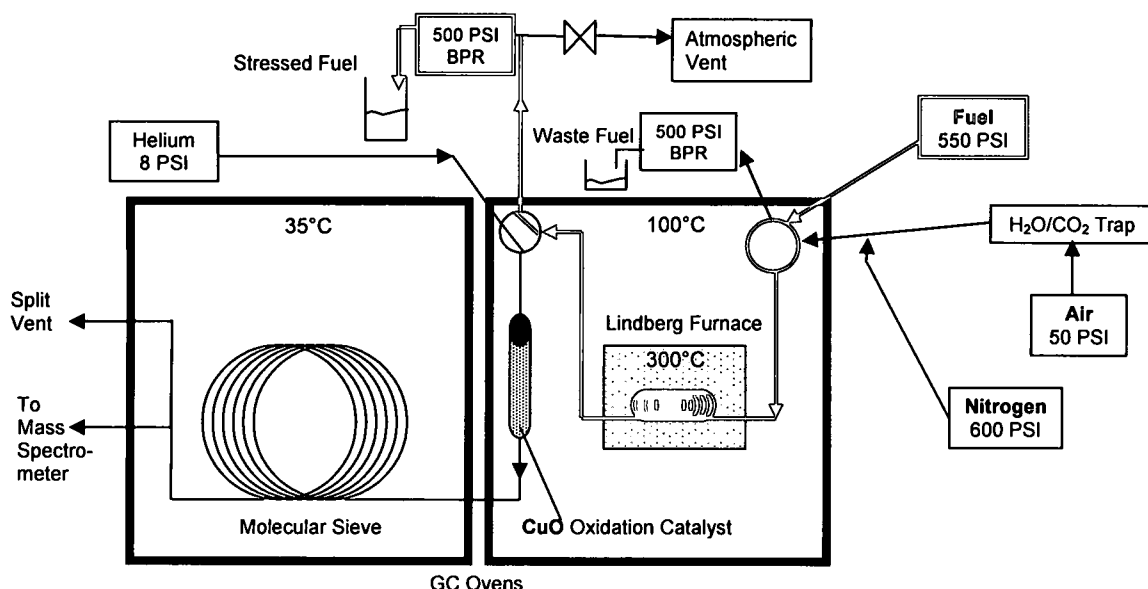


Figure 4. Fuel flow path through heated reactor during deposition testing

(typically 100°C), stirred air environment used to preheat and cool down the fuel as it enters and leaves the high temperature reactor. The inner Lindberg furnace provides a high temperature region where reaction and deposition chemistry occur due to high fuel oxidation reaction rates. The temperature difference between these two sections is a minimum of 100°C to assure reaction rates are faster inside the Lindberg Furnace. Operating ranges for the GC oven and Lindberg furnace are 25-300°C and 25-800°C, respectively. The preheat phase helps the reactor approach isothermality without contributing enough heat to begin significant reactions. For oxidative studies, this fuel preheat stage in the

outer GC oven does not exceed 100°C. Beyond this temperature, the fuel will undergo reactions with dissolved oxygen prior to entering the reactor and can produce precursors to deposition and deposits in significant quantities. Any deposit formation prior to the reactor will not be readily oxidized during analysis and can alter results or cause the reactor tube to plug. This would yield incorrect results for deposition tests. It is therefore important that all reaction be kept within the Lindberg Furnace portion of the tubing shown in Figure 5. The fuel travels approximately 19.7 inches through the preheat zone before reaching the entrance of the reactor.

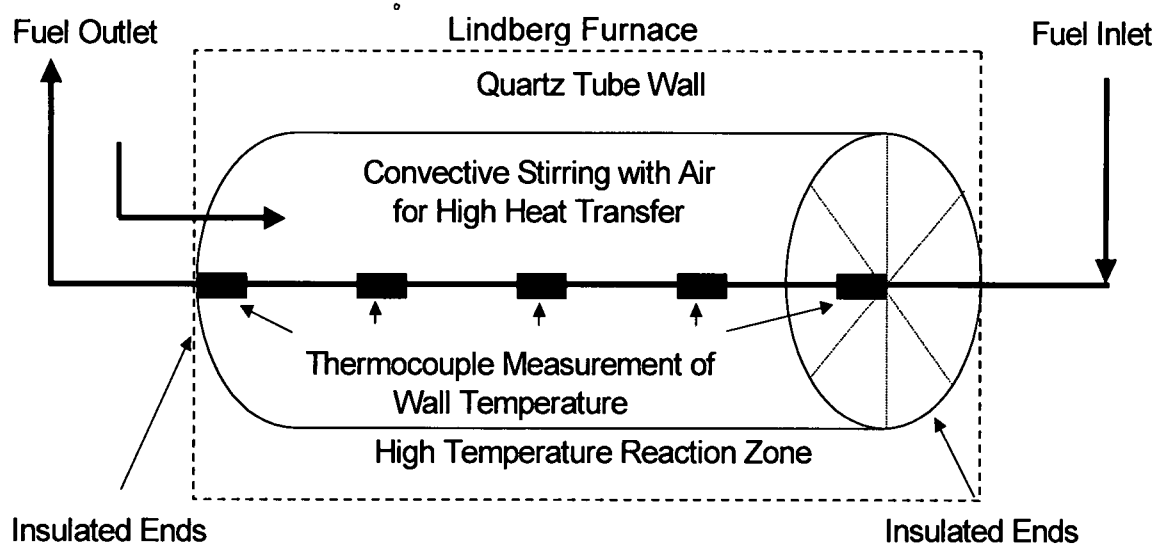


Figure 5. In-situ carbon deposition reactor diagram inside Lindberg furnace

The internal Lindberg furnace provides the temperatures for fuel stress and deposit oxidation. The reactor cell is composed of a 23.6-inch section of stainless steel tubing coiled inside a small quartz tube within the Lindberg furnace. The reactor is a continuous segment of type 316 stainless steel tubing

with 0.0625 inches OD and 0.020 inches ID. This section of the tubing is insulated with a quartz tube and glass wool from the rest of the GC oven. Insulation helps maintain uniformity after temperature has been achieved and prevents the convective air in the GC oven from mixing with the air inside the Lindberg Furnace. Compressed air is fed into the insulated reactor section to assist in establishing high convection to the tube walls and provides mixing for temperature uniformity. The temperature is monitored by thermocouples strap-welded on the reactor tubing outer surface. The 23.6-inch length reactor section is monitored with thermocouples welded at the beginning and every subsequent 5.9 inches. The starting and ending thermocouples are embedded within the insulation at 0 inches and 23.6 inches. The fuel temperature profile is capable of achieving moderately uniform temperatures for reaction temperatures of 200 to 400°C, the range of interest for oxidative deposition. Higher temperatures can be used for pyrolytic deposition studies or other applications.

While within the reactor, convection, radiation, and conduction through the insulation all heat the coiled reactor tubing. As fuel enters the reaction zone, it is rapidly heated. Initial calculations using a constant wall temperature heat exchanger model indicate that within the first 4.7 inches to 7.1 inches (20-30%) of the reactor, the fuel has achieved at least 90% of the target temperature. This provides a relatively isothermal reactor section for 70% of the reactor. Temperatures generally continue to increase by 5°C to target temperature from 7.1 inches (30%) to the end of the reactor within an oven setting range of 100 to 400°C. Higher overall temperatures yield higher temperature differentials across

the reactor, but for the range of 100 to 400°C, the reactor is fairly isothermal compared to other flowing tests. Detailed temperature profiles are presented later.

As fuel is heated, it expands, moving more quickly through the reaction zone due to a decrease in density. Without knowing the time of exposure, it is impossible to estimate the rate of deposition, conduct kinetic studies, or compare temperature effects. When temperature is varied between experiments, the rate of expansion has to be taken into account to determine proper residence times. Phase changes between liquid and supercritical phase can also occur which can greatly change the overall density of the fuel in the reactor. It is important to estimate these values to maintain residence time between tests.

Fuel density can vary from sample to sample due to differences in composition. Measurements of fuel density would have to be taken for each fuel to be tested across a broad temperature range to account for differences in each fuel. However, a surrogate approximation can predict fuel densities within reasonable limits. Dodecane is used to approximate most jet fuel, but some exotic fuels may require more temperature dependent property data. The density difference between dodecane and JP-8 is less significant, but the trend in density change during heating should be similar considering JP-8 is mainly composed of normal, branched, and cyclic alkanes. For higher density fuels with high concentrations of cycloparaffins, the properties of decalin are used to approximate the system residence time. Approximating fuel properties must be

done with care. Critical temperature and density changes can have a dramatic influence on the overall residence time.

An approximation of residence time was used to permit the analysis of temperature effects independent of time. To conduct a numerical approximation for residence time, dodecane properties were taken from Supertrapp, and decalin properties were extrapolated from the literature.²¹ Supertrapp utilizes the Peng-Robinson Equation of State to calculate hydrocarbon properties from a database of critical properties from the National Institute of Standards and Technology. Figure 6 shows the calculated variance in density for decalin and dodecane as temperature increases. Using this information, residence time in the reactor can be held constant by simply varying the flow rate. The pump flow rate is decreased for higher operating temperatures because fuel expands as it is heated in the reactor. Accounting for temperature effects on density allows residence time to be maintained independent of temperature.

Figure 6 shows that a cycloalkane structure's density is more influenced by temperature than a straight chain. The density varies over a broader range as the temperature increases, and this consequently causes the flow rates to shift more rapidly within the reactor, decreasing residence time. As the temperatures continue to rise, the species are in a high temperature supercritical phase, which is largely governed by gas laws. This causes both species to reach similar densities at high temperature.

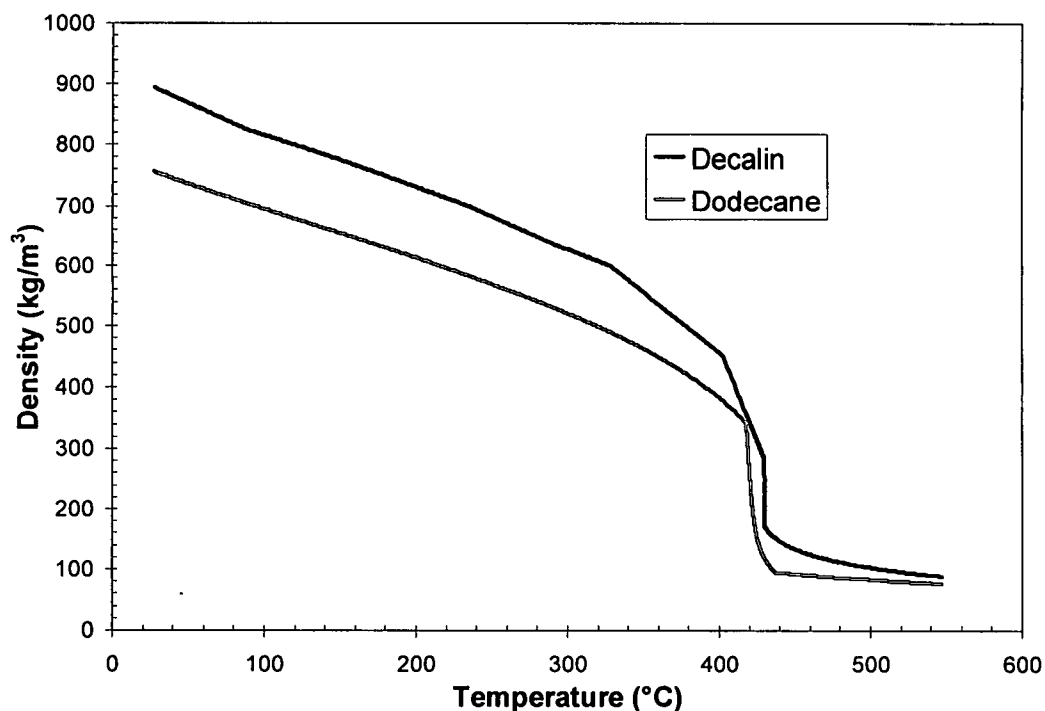


Figure 6. Density variance with temperature for dodecane and decalin from literature and Supertrapp

Stressed fuel is another important source of information on oxidation reactions. Figure 4 shows stressed fuel flow emptying from the back pressure regulator into a waste fuel reservoir; the samples can be collected for offline analysis of the stressed fuel products. The relative isothermality and residence time approximations may make the ICDT useful for simple kinetic studies on deposition. This is a unique capability for a flowing test with a short residence time.

The level of oxygen consumption is also essential to properly interpret deposition data. Conducting all tests at complete oxygen consumption allows deposit formation to be examined at the same extent of reaction since different fuels have different oxidation rates. This also prevents deposition products from forming downstream of the high temperature furnace; these deposits would not

be detected during subsequent analysis and could eventually plug the system. Previous studies have correlated increased deposition with increased consumption of dissolved oxygen.²² Controlling oxygen as a limiting reactant helps set a baseline for comparison with other systems and between fuels.

It is essential to rapidly quench reactions occurring at the end of a test. To accomplish this, fuel is rapidly removed from the reactor with pressurized nitrogen after the desired test volume has passed through the reactor. Flowing nitrogen rapidly removes reactants while the furnace slowly cools. The gas is left flowing for 20 minutes while the outer oven temperature is increased to 200°C and pressure is released via an atmospheric vent, as shown in Figure 7. This temperature and flow is sufficient to remove residual fuel vapors from the reactor tubing. This phase of the experiment is required to ensure that all hydrocarbons except the surface deposits are driven from the tubing and valves. Any remaining fuel would be quantified as carbon deposit mass during subsequent analysis.

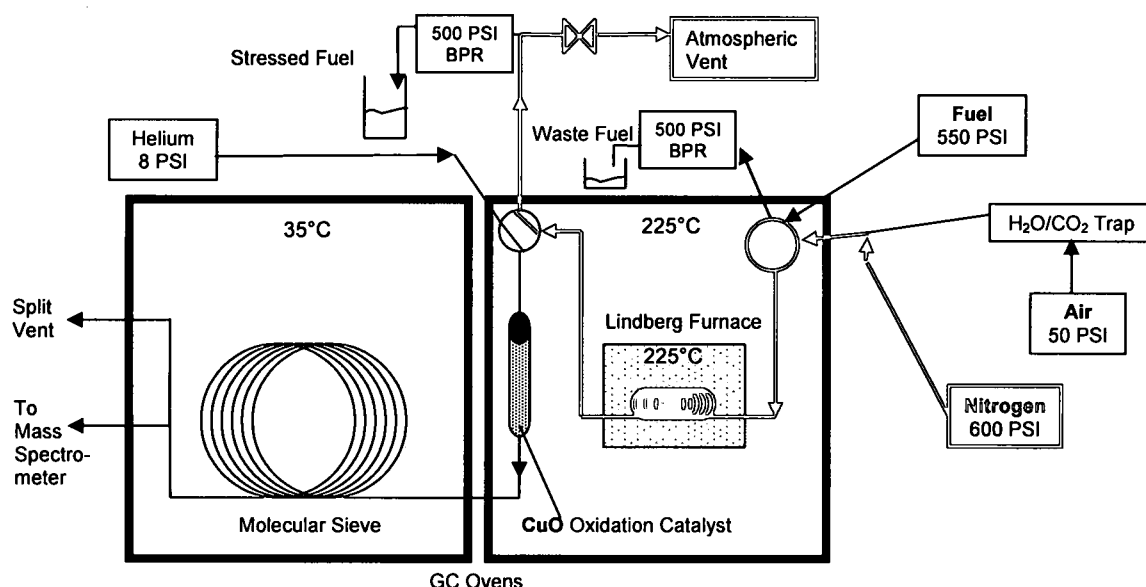


Figure 7. Drying of the reactor after completion of an oxidative deposit test

2.4 Deposit Analysis

The actual deposition cannot be measured directly, so an indicator is used to approximate total deposition. Oxidative fuel deposits are primarily composed of carbon; therefore total carbon is representative of the relative amount of deposition. Specifically, deposits are oxidized in air and analyzed by detection of CO_2 via mass spectrometry. Nitrogen flow is stopped once the reactor is dried, and a 4-port valve directs airflow to a heated catalyst as shown in Figure 8. Air was selected in place of pure oxygen due to safety constraints, but was found to be sufficient to completely oxidize the surface deposits. The compressed air is pre-filtered through 5Å molecular sieve and Dry-rite desiccant (CaSO_4 and CoCl_2) to remove water and gas impurities, including carbon dioxide. This is required since any carbon dioxide which enters with the air would be detected and quantified as deposit.

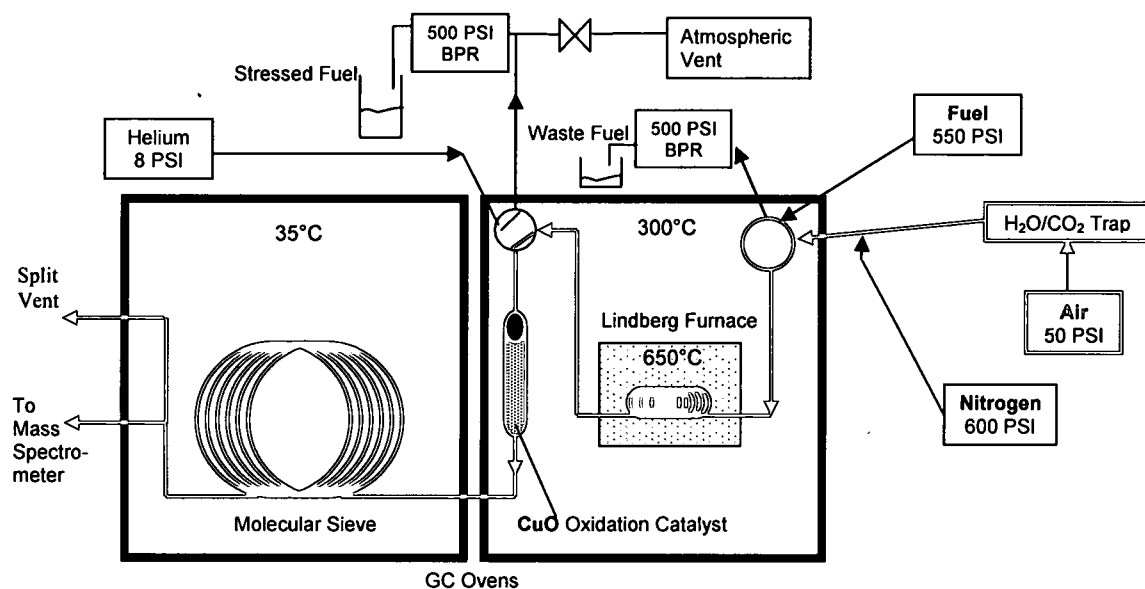


Figure 8. Air flow path for deposit oxidation and CO_2 trapping prior to detection

The Lindberg furnace and flowing air are used to oxidize deposits in the reactor. Prior to oxidation, the Lindberg furnace temperature is increased to 650°C. Oxygen in the air reacts with the carbon deposits to produce CO₂ and CO. The reactor must be maintained at high temperature for sufficient time to assure all deposits are oxidized. The reaction is slow due to the temperature and the concentration of oxygen. Previous work on fuel coke removal by Huang and Spadaccini shows reaction temperatures of 650°C for 12 minutes were sufficient for much larger scale coke removal.²³ The deposits in their coke analysis were pyrolytic which were shown to be oxidized more slowly than the oxidative deposits formed in this study. While higher temperatures will cause the deposits to react more quickly with oxygen, temperature is limited because the carbon in the steel tubing can begin to leach out in significant quantities above 750°C.²⁴ The leaching carbon causes interference in the baseline signal and increases measurement error. This signal is apparent when the reactor is first run under high temperature conditions in oxygen. Even at 650°C, carbon begins to leach from the type-316 stainless steel. Therefore, it is necessary to precondition new reactors, and the carbon signal must be monitored until it decays to baseline prior to actual testing with a new reactor. Preconditioning is accomplished through repeated 15-minute oxidation runs on a clean, dry reactor. Acceptable background levels are less than 0.5 µg of total carbon during a 15-minute deposit oxidation run. New reactors may require several hours of tempering prior to first use due to this carbon leaching.

Detection of CO₂ by mass spectrometry is used to determine the total mass of carbon deposits for the in-situ carbon deposition test. Some of the oxidized deposits are only partially oxidized and produce CO. CO is not detected because it is not retained on the molecular sieve column discussed later; therefore, all carbon must be completely oxidized to CO₂ to be analyzed. The mass spectrometer operates in SIM mode, which is only set to detect the 44 ion for CO₂ and the 57 ion for hydrocarbons. The catalyst stage is a packed bed of CuO rare earth metal, which is maintained at 400°C with Thermolyne heating tape. The bed is made of stainless steel tubing with an inner diameter (ID) of 0.1875 inches and a length of 4 inches. The tube is packed with 2.71 grams of CuO. The converted CO₂ flows out of the catalyst stage to the analytical oven.

The low concentration of CO₂ from deposit oxidation cannot be detected well in flowing air, so a CO₂ trap is used to assist the quantification of carbon deposits. In addition, air is not a good carrier gas for the mass spectrometer. Thus, gaseous CO₂ from the reactor needs to be collected over time for analysis because trapping and separating the CO₂ provides lower detection limits for total deposition. A CO₂ trap is used to provide a better signal to noise ratio; a low signal over time allows more interference in the detection baseline. Trapping CO₂ results in a large peak that stands out well from the baseline signal on the mass spectrometer and eliminates this problem. It also allows the carrier gas to be changed to Helium during the detection procedure.

A molecular sieve column is used as a trap to retain CO₂ at ambient temperature during the period of deposit oxidation. At low temperature, CO₂

accumulates on the column as air flows from the reactor. Then, after oxidation of deposits is complete, the temperature of the column is raised to desorb the CO₂, which flows to the mass spectrometer for quantification. The connection between the column and the mass spectrometer includes a flow split because the total flow rate on the column is much larger than can be provided to the mass spectrometer. The mass spectrometer monitors both the 44 ion and the 57 ion to both detect CO₂ (44) and to ensure no fuel vapors from the reactor are contaminating the analysis process (57).

6

Chapter III

Results & Discussion

3.1 Evaluation of Temperature Profile

Knowledge of the temperature profile of the reactor during deposition testing is necessary to interpret reaction rates from observed deposits. The temperature the fuel is exposed to during testing is also crucial to understanding the deposition data. The nature of the deposition obtained after the fuel undergoes oxidative reactions is a strong function of the temperature. Reaction rates increase exponentially with increasing temperature; therefore, control of wall and bulk temperatures in the reactor is very important. Residence time is also affected by the temperature profile, so accurate temperature measurements are required for those calculations. Accordingly, initial calculations were conducted using a simple heat exchanger model, and an approximation for residence time was determined from a profile of density as a function of temperature. The Appendix includes a list of the calculation algorithm.

The model approximates a constant wall temperature for the heat exchanger. To verify this as an acceptable approximation, measured wall temperatures were compared with those from the heat exchanger model. For operation in oxidative deposition regimes (~100 to 300°C), the thermocouple temperatures matched the approximated wall temperature fairly well. Figure 9

shows the measured and calculated temperature profile for a 300°C set point for the Lindberg Furnace and a fuel flow rate of 0.266 mL/min. These conditions are the same as those used later during deposition tests. Higher temperatures and flow rates result in the profiles exhibiting less isothermality, while lower temperatures and flow rates increase reactor isothermality. The experimental temperature profile confirms the constant wall temperature as an adequate approximation. The measured wall temperatures are within 2% of the set point temperature, which was used to approximate the wall temperature of the reactor. The reactor wall achieved 90% of temperature within the first 7.8 inches (~30%) of the heated zone. Fuel converges to the wall temperature as the wall temperature approaches the furnace temperature in the latter 70% of the reactor.

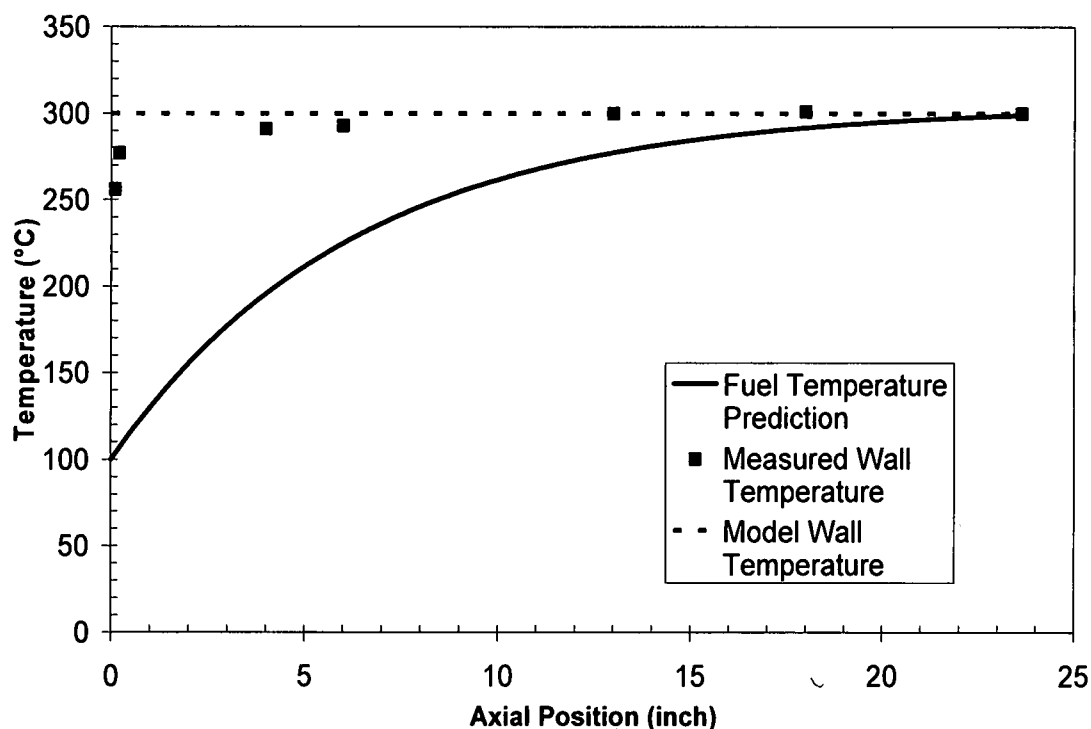


Figure 9. Predicted fuel temperature using a reactor temperature model for reactor at 300°C and 0.266 mL/min flow (10 second residence time) with experimental wall temperature measurements

3.2 Oxygen Consumption Curves

It was essential to know the extent of reaction for comparison of results with other experiments and to compare fuels with various oxidation rates. To determine temperature effects on deposit formation at the same level of oxygen consumption, all reactions were conducted at complete oxygen consumption. This allowed deposit formation to be examined at the same extent of reaction because the rate of deposition is a function of the consumption of oxygen. A fuel characterized by other systems as a slow oxidizer, POSF-2827, was used as an extreme case of low reactivity with oxygen.¹³ Other fuels or additives tested would likely oxidize at faster rates, so identical reaction conditions for complete oxygen consumption of POSF-2827 should be applicable for complete oxygen consumption of other fuels.

Oxygen levels were monitored by a Mettler Toledo Oxygen Sensor with Type T membrane during several sample runs with fuel POSF-2827. This information was used to estimate necessary residence times for complete oxygen consumption. During the test, a flow rate for fuel was selected, and temperature was slowly decreased until the percent saturation of oxygen was greater than 1%. Temperature was incremented in 5°C steps and the system was given 10 minutes to reach steady-state.

A comparison of the final wall temperature required for complete oxygen consumption as a function of flow rate is shown in Figure 10. These data represent the minimum temperature required for complete oxygen consumption at a specific flow rate for fuel 2827. Any testing conducted for oxidative

deposition should use this template to specify temperatures and flow rates (which correspond to residence times) to obtain complete oxygen consumption. Faster oxidizing fuels would have lower temperature requirements for complete oxidation at any given flow rate. Any temperature and flow rate corresponding to a point above the curve should be sufficient to completely consume dissolved oxygen. As temperature was decreased in 5°C intervals, the actual temperature of 99% oxygen consumption may be within 5°C below the curve in Figure 10.

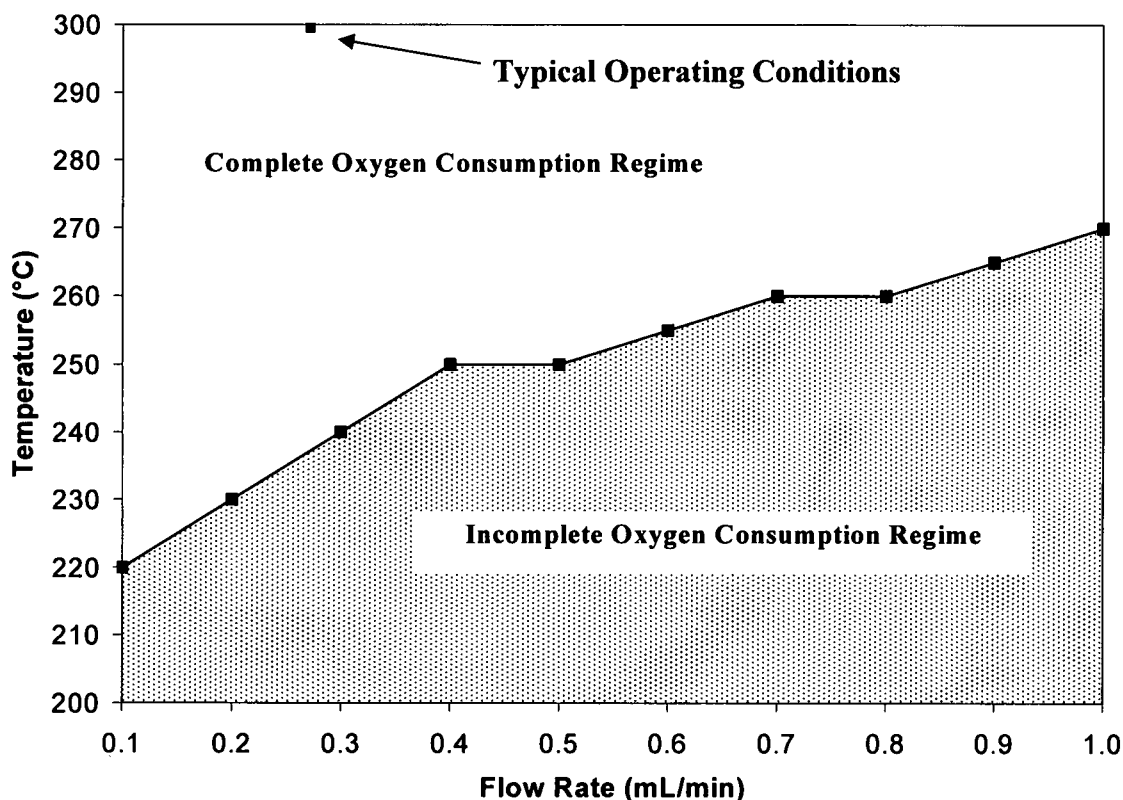


Figure 10. Oxygen consumption regimes for temperature and flow rate for fuel POSF-2827 at 500 psi

A margin of safety was left to ensure complete oxygen consumption when operating with additives that significantly slow oxidation or for an even slower oxidizing fuel. Operating at least 15°C above the curve should be sufficient to oxidize a fuel that has half the oxidation rate as that measured in this experiment.

This information provided guidance for temperatures that would be needed at particular flow rates to assure complete oxygen consumption for all testing.

3.3 Column Trapping of Carbon Dioxide from Deposits

Due to the low release rate and extremely low concentration of CO₂ emitted during deposit oxidation, CO₂ was collected over time to be concentrated and introduced to the mass spectrometer. A chromatographic column was employed as a trap. The in-situ carbon deposition analysis system placed two demands on this trap: high retention efficiency and rapid release. The deposit oxidation process typically required at least 15 minutes, so trapping efficiency had to be sufficient for this requirement. In addition, the release of CO₂ needed to be rapid and uniform. Two high residence time columns for CO₂ were selected for evaluation: a molecular sieve PLOT column and a carbosphere packed column. The carbosphere packed column was 6 feet long and 0.085 inches ID. The packing was 80/100 mesh, which readily retains water and air in the passing gas. The HP-PLOT molecular sieve column dimensions were 98.4 feet long with a 0.021-inch (0.53 mm) I.D. and a film thickness of 50 μm. Each column was installed in-line with a thermal conductivity detector (TCD) on a separate GC oven and subjected to repeated injections of CO₂ gas equivalent to 2.5 μg of carbon. Three injections were made at ambient temperature to be equivalent to an average deposition run. After 15 minutes, the temperature of the column was elevated to desorb the CO₂ from the column packing. Each column was tested using a temperature ramp from 35°C to 300°C at 25°C/min.

Columns were evaluated based on their ability to efficiently retain and rapidly release CO₂. The carbosphere column was capable of retaining passing CO₂ at room temperature with 99% efficiency. Subsequent injections were retained and the total CO₂ detected was relative to the quantity injected. This indicated that the volume of CO₂ did not saturate the packing. However, the release was a broad irregular peak once the column was heated to 140°C. Heat transfer to the packed column is much slower than the PLOT column. Inadequate heat transfer caused a slower release and created a very broad peak, which produced a variance of more than 20% in the carbon detection.

The HP-PLOT molecular sieve column was able to trap carbon and water at room temperature with 99% efficiency, but did not release the CO₂ gas until it reached approximately 225°C. Even with the higher release temperature, the CO₂ peak resulting from the PLOT column was much narrower than that of the carbosphere column. The narrower peak was less subject to error in the mass spectrometer baseline and therefore well suited as the trap column. Another important function for this application was that the retention time for CO₂ on the column was long. During another test, the CO₂ was introduced several hours prior to elevating column temperature and detection, yet the detector signal remained consistent with total injection mass. A CO₂ injection of 9.5 µg of carbon was accurately retained for one hour with a reproducibility of +/- 0.1 µg. During deposition testing, this allowed a longer deposit oxidation time without a significant loss of carbon dioxide.

An evaluation of the total column retention capacity was conducted after selecting the molecular sieve column. The selected PLOT column was 98.4 feet long, though shorter lengths could likely be used depending on the total amount of the carbon deposit. Over the course of numerous injections, the column was able to retain 550,000 μg of carbon from CO_2 . At this point, detector overloading became more of an issue than column retention. A larger split would have to be introduced for detection at such high levels, but these levels of carbon production were not likely to occur during testing.

The HP-PLOT molecular sieve column was installed and calibrated on the ICDT. As CO_2 and air enters the analysis GC, it was passed through the column. Flow through the column was 1 mL/min of gas as the carbon oxidation proceeds. The flow rate was selected for efficient operation of the catalyst, yet was a relatively low flow rate across the column to allow ample time for trapping. After complete oxidation of deposits, the carrier gas was switched to helium flow for quantitation. Total helium gas flow rate was 3 mL/min through the column. The exit of the column was connected via a split to the mass spectrometer. The split flow rate was measured by a glass bubble flow meter. Helium pressure was adjusted to ensure that while the system was at temperature, the helium split flow rate was 2.3 mL/min. The mass spectrometer then drew the remainder of the total flow by vacuum, 0.7 mL/min. This maintained the total flow across the column at 3.0 mL/min. All flow rates were measured at 253°C, which was the measured release temperature of CO_2 during a temperature ramp from 35°C to 300°C at 25°C/min. At this flow rate and temperature, the column inlet pressure

was calculated to be approximately 5 psig, with a column velocity of 0.3 m/s, and a total column holdup of 1.5 minutes. Using the column holdup, the approximate temperature for the carbon dioxide release was estimated to be 216°C. This was consistent with previous data obtained while testing column performance on the TCD. In this test, a CO₂ standard was injected on the column, and temperature was stepped over 10°C intervals from 100°C to 230°C while held for 5 minutes at each temperature. This process showed carbon release on the GC-TCD to occur at 220°C.

3.4 Calibration of the Mass Spectrometer for CO₂ Quantification

The mass spectrometer response was calibrated for CO₂ measurement using a gas standard. The standard used was a 9.1% CO₂ gas sample in a nitrogen balance. The trapping column was held at ambient temperature and various volumes from 0.01 mL to 0.50 mL of sample gas were introduced via syringe into the helium carrier gas at the system inlet. Total carbon mass during injections was between 0.50 and 25 µg. The temperature in the analytical oven was increased, and these samples were then detected by the mass spectrometer. The peak area in each injection was correlated with total carbon mass.

Figure 11 shows the calibration curve that was used to quantify carbon mass deposits. It is important to monitor the split flow at the detector interface during operation because small changes in split flow can cause large alterations in the calibration curve. Split flow is checked between runs by elevating oven temperature to 253°C for 5 minutes and measuring the flow. The calibrations and

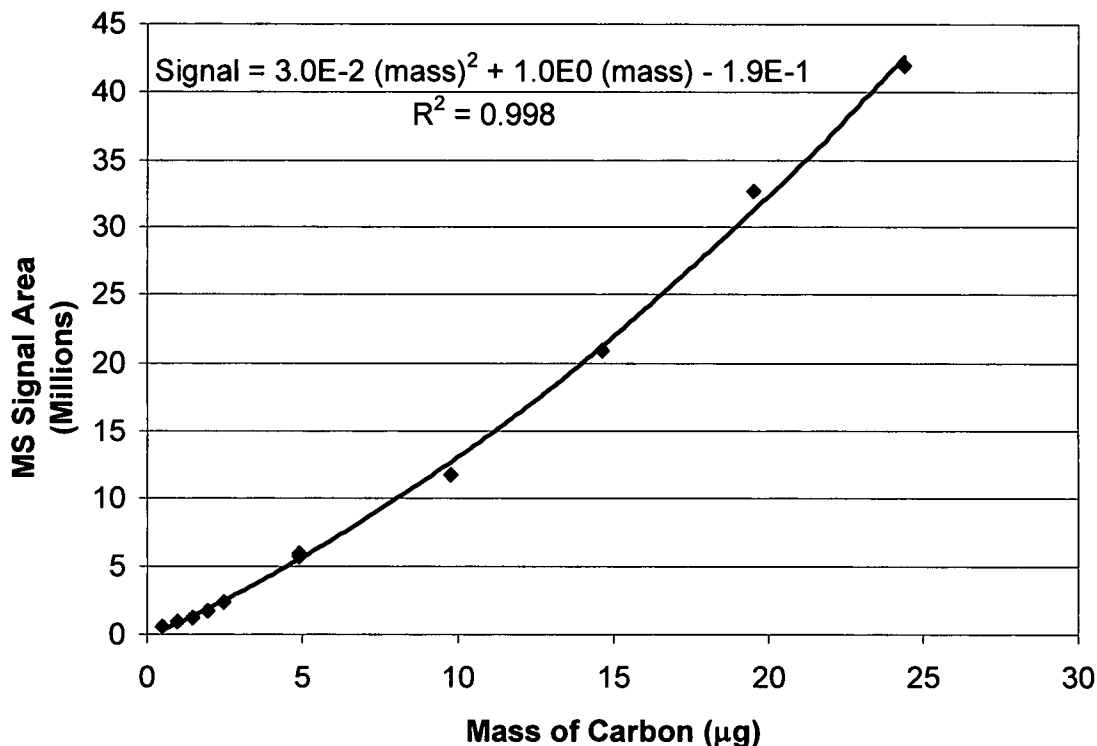


Figure 11. Carbon from CO₂ calibration curve for mass spectrometer

all testing were conducted at a 2.3 mL/min split flow. The curve is a quadratic fit of the calibration data. Larger masses of carbon yield stronger signal per unit mass. This curve is characteristic of irreversible adsorption behavior because the relative amount of signal lost decreases with increasing mass.

Background levels of approximately 0.5 µg were monitored during testing, and subtracted from the total mass during analysis. A signal to noise ratio of 2:1 resulted in a minimum total signal of 1.0 µg of carbon. The background signal was likely caused by carbon leaching from the reactor walls or small amounts of residual fuel vapor.

3.5 Catalyst Performance for Oxidation of Carbon Monoxide

Carbon deposits from the reactor section undergo reaction with oxygen in the air at high temperature, but the carbon may not be completely oxidized to CO_2 . The 650°C temperature held in the reactor favors high equilibrium concentrations ($>50\%$) of carbon monoxide (CO) during the reactor burn-off.²⁵ This, combined with incomplete oxidation can yield significant quantities of CO during the deposit oxidation process. Since CO is not trapped on the PLOT column, it is important to convert it to CO_2 for trapping and quantitation.

A copper oxide (CuO) catalyst bed was placed in the flow line prior to the molecular sieve trap. Two thermocouples monitored the temperature of the bed at the outer surface, and one was connected to the heater controller. The second thermocouple monitored temperatures near the beginning of the bed. Overall, the diameter of the catalyst pellets was estimated to be approximately 0.05 inches and the pellets were approximately spherical. The void fraction was about 0.5, which was estimated from average diameter and assuming spherical catalyst particles.²⁵ During deposit oxidation, the gas flow was adjusted to 1.0 mL/min providing a residence time in the catalyst bed of about 0.90 minutes.

Typical light-off temperatures for CO on CuO are around 200 to 300°C ; this is the temperature where reaction rates within the catalyst bed begin to accelerate very rapidly with increasing temperature. A temperature of 400°C and nearly 1 minute of residence time should be sufficient to provide complete CO oxidation. This was verified experimentally by dosing the air stream with CO at various catalyst temperatures and monitoring the CO to CO_2 conversion. Figure

12 shows that increasing the temperature beyond 350°C did not increase levels of CO₂ detection. This suggests that despite faster oxidation rates, the reactor was sufficiently oxidizing CO at 350°C. To further confirm sufficient oxidation, CO₂ standard injections of known concentration and volume were compared with CO standard injections. The CO₂ standard concentration was 9.1% by volume in N₂. The CO standard concentration was 0.49% by volume in N₂. The CO injections actually showed a slightly higher response. The total carbon detected was consistently within 10% for known CO₂ concentrations and detected CO converted to CO₂. Both CO and CO₂ injections are shown for various total carbon masses in Table 1.

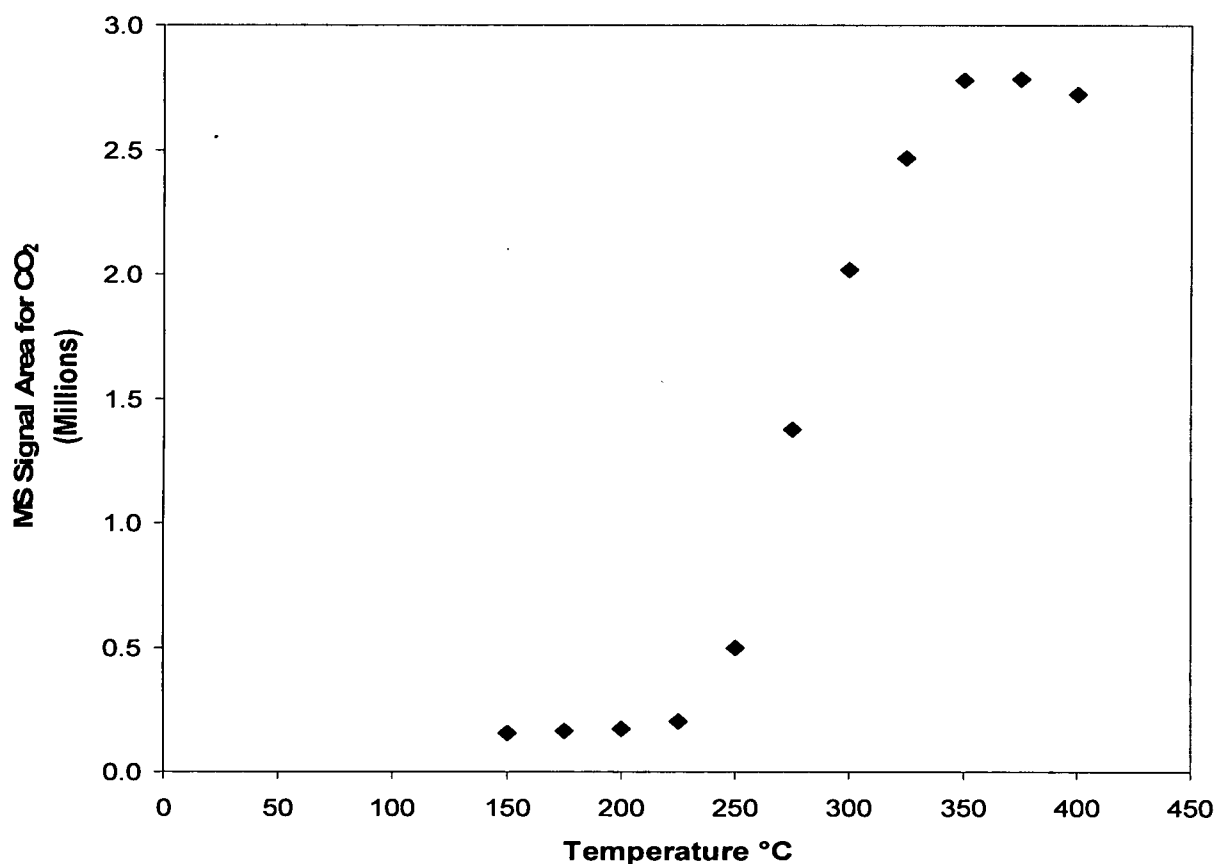


Figure 12. Oxidation of CO at increasing CuO catalyst temperature

Table 1. Evaluation of catalyst conversion efficiency for CO at 400°C

Carbon Mass of injection (μg)	Measured Carbon Mass (μg)		% Conversion
	CO converted to CO_2	Pure CO_2	
2.63	2.70	2.74	99%
2.36	2.50	2.55	98%
2.10	2.30	2.35	98%
1.84	1.90	1.94	98%
1.58	1.60	1.65	97%
1.31	1.30	1.43	91%
1.05	1.20	1.36	88%
0.79	0.80	0.89	90%
0.53	0.60	0.74	81%
0.26	0.30	0.32	94%

Each line in the Table 1 represents a constant carbon mass based on injection size and concentration of sample. The volume of injection was changed so that a large CO injection of low concentration and a small CO_2 injection of higher concentration had equal amounts of total carbon. The CO was converted to CO_2 on the catalyst bed, trapped by the molecular sieve column, and measured as CO_2 by the detector. For comparison, CO_2 injections passed through the same catalyst bed into the trap and detector. The error in the CO_2 signal represents some of the background noise discussed above. Since the same total mass was injected, the signal for CO was compared with the CO_2 signal. This value was taken as the actual catalyst conversion. The results are all within 10% in most cases, but the total carbon mass is slightly larger than calculated.

This test demonstrates the benefits of the use of a catalytic bed to completely oxidize CO from the reactor into trappable CO_2 . The catalyst also shows preferential conversion of carbon monoxide instead of fuel vapors. CuO is an ineffective catalyst for hydrocarbon oxidation at this temperature. If the reactor was not completely dried (i.e. contained residual amounts of fuel), the catalyst

allowed fuel vapor to reach the GC column and mass spectrometer. This is important for observing if a test failed due to incomplete evacuation of fuel vapors from the reactor. Fuel vapors, even in small quantity, would be less likely to oxidize to CO_2 . Since fuel vapors can make it through the catalyst bed, the 57 ion, which is indicative of alkanes, can be detected by the mass spectrometer if the tubing and valves did not completely dry. Monitoring 57 ensures the reactor is sufficiently dried after each run.

3.6 Oxidative Deposition Data for Different Fuel Types

An important stage to establishing any new analytical system is to insure reproducibility of data. Since jet fuel is not a single synthesized reactant, reproducibility can be difficult to achieve. Jet fuels meet a specification standard, but individual samples may vary in composition. This alone suggests that an acceptable range of reproducibility will have to be established. In addition, it is important to characterize the system performance to better understand and analyze the test results.

Previous studies have shown that the magnitude of carbon detected during deposition analysis can be wide-ranging for the same fuel on different tests.⁵ When comparing two fuels, different deposition tests can have conflicting conclusions on the thermal stability; a given fuel may deposit more on one system than another. The general characteristics of the systems can add variance to results, but the trend of high to low deposition over a range of fuels should be consistent between multiple systems. To begin analyzing the performance of the in-situ carbon deposition analysis, fuel has to be varied to

demonstrate that the system distinguishes thermal stability between high and low depositing characteristics.

To compare deposition trends of the in-situ carbon deposition test, several fuels were selected with different thermal stability ratings based on other thermal stability tests. These fuels represent a broad spectrum of thermal stability characteristics. Test conditions were held constant for each run. The fuel flow rate was 0.266 mL/min at 500 psi. It was preheated to 100°C in the GC oven and reacted at 300°C for a 10 second residence time. Total run length was 25 minutes providing a total volume of 6.65 mL of fuel. Overall, four fuels were tested for carbon deposition for oxidative thermal stress, and the results are shown in Table 2.

Table 2. Normalized deposition data for 4 fuels under 300°C stress for 10 seconds

POSF	4177	2976	3219	3166
	JP-8	JP-TS	Jet-A	Jet-A
ICDT μg/mL	1.27	0.05	0.62	3.1
	1.32	0.07	0.68	3.5
	1.21	0.10	0.77	3.3
	1.25	0.06	0.85	2.5
Avg.	1.26	0.07	0.73	3.1
Stdev	0.05	0.02	0.10	0.43
CI	0.04	0.02	0.08	0.36
CI%	3%	25%	11%	11%

The confidence interval (CI) and confidence interval percentage (CI%) are based on a 90% probability interval. This means the true mean is 90% likely to lie within this range. The large size of the confidence interval percentage for the JP-TS fuel is a result of the extremely low average deposition. The system maintains a confidence interval approximately 10% of the mean in a majority of cases. This is an average reproducibility, but acceptable for a system with a reactant such as jet fuel. It is, however, important to remember system limitations during testing.

The strong variability in extremely low deposition results is likely due to the background noise in detection and quantitation. Total deposition in the range of 0.5 to 30 μg is ideal, and larger amounts of fuel may be necessary to run accurate testing of deposition below 0.1 $\mu\text{g/mL}$. The statistical reproducibility establishes grounds for differentiating deposition levels during these tests. A graph of the average deposition levels is shown in Figure 13.

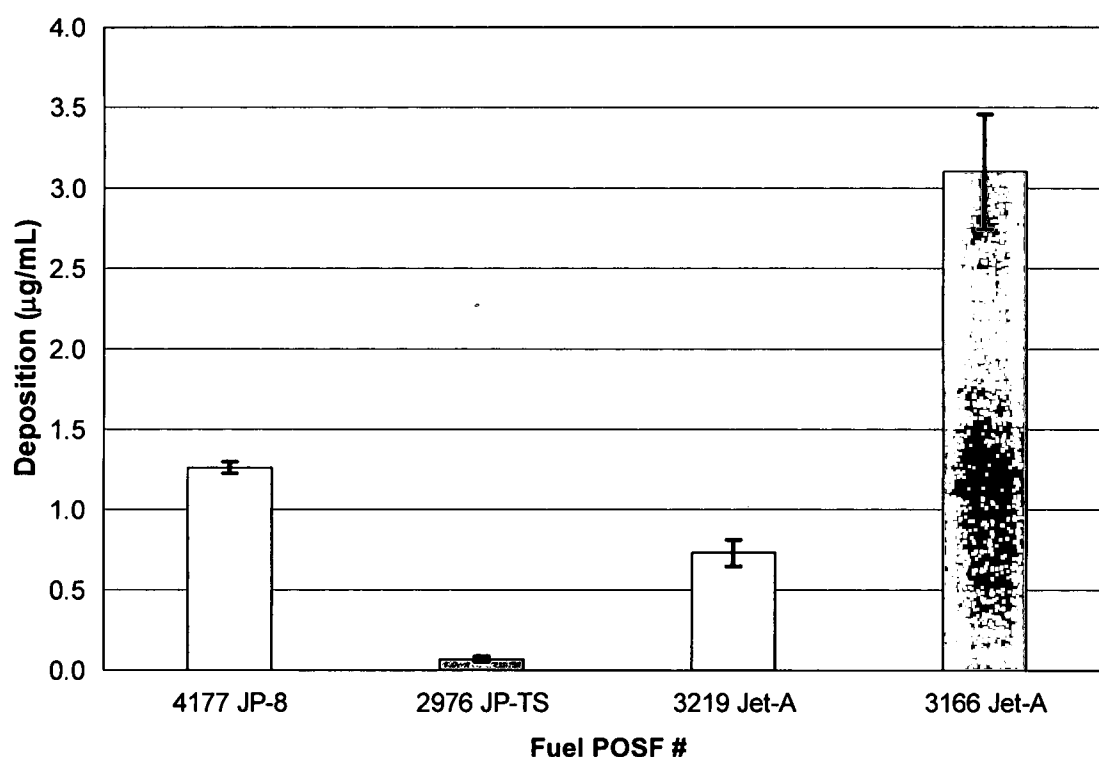


Figure 13. Average oxidative deposition for 4 fuels under 300°C stress for 10 seconds

The system does, however, supply great confidence that deposit values between these different fuel types are distinct. This makes it feasible to differentiate low, medium, and high deposit tendency fuels. In this study, the in-situ carbon deposition test was able to statistically isolate each of the fuels based on deposition levels. POSF-2976 was a JP-TS fuel designed for high thermal

stability, and, as expected, produced the least oxidative deposits. Deposition tests have rated POSF-4177 and POSF-3219 as moderate depositing fuels, and the test confirms those ratings. POSF-3166 was expected to have the highest deposition of the fuels selected. The in-situ carbon deposition test was able to determine the deposition levels of each fuel relative to their deposition rating on other systems. The deposition trends for these fuels were determined and will later be compared with deposition results from other systems.

3.7 Oxidative Deposition Data for Different Fuel Additives

Additive effects on deposition were examined under complete oxygen consumption conditions. Specifically, fuel POSF-3166 was selected for a range of additive testing to examine system performance at differentiating deposition levels with several additives. This fuel was selected because it shows characteristics of being a moderate-to-high depositing fuel during temperature stress.²⁶ Selecting a moderate depositing fuel allowed testing to distinguish between both an increased or decreased deposition effect.

Testing was conducted in the same manner as the oxidative deposition data in the previous section. The thermal stress was 300°C with a 10 second residence time. Test conditions included neat fuel, the JP-8+100 additive at 256 mg/L, 2,6-di-tert-butyl-4-methylphenol (BHT) at 25 mg/L, and deoxygenated fuel. Previous work with these additives provided a background and hypotheses for what was likely to occur during testing.¹⁴ The JP-8+100 additive was designed to reduce deposition, and though not specifically designed for complete oxygen consumption conditions, the dispersant quality of the additive should still greatly

affect overall surface deposition.¹⁶ BHT acts as an antioxidant in this system; while this will delay the onset of autoxidation, the species produced during this have been suggested as deposition precursors in other work.¹³ Therefore, the total deposition should increase as antioxidant reactions produce precursors to deposits.¹⁴ Deposition may occur at an axial distance further along the reactor, but this system does not differentiate location. Finally, the deoxygenated fuel should have extremely low deposition since autoxidation cannot occur without a supply of dissolved oxygen and temperatures are too low for pyrolytic deposition reactions.¹⁷ Table 3 includes a list of normalized deposition measurements for POSF-3166 under four different additive and dissolved oxygen conditions, and Figure 14 shows a graphical representation of the deposition per milliliter for each test run.

Table 3. Normalized deposition from POSF-3166 with different additives at 300°C with 10 second residence time

POSF-3166	Jet-A			
Additive	Neat fuel	JP-8+100	BHT	He Sparged
Concentration		256 mg/mL	25 mg/L	<5 ppm O ₂
ICDT μg/mL	3.1	0.78	4.1	0.20
	3.5	0.80	4.6	0.15
	3.3	0.75	4.3	0.17
	2.5		4.5	0.22
Avg.	3.1	0.78	4.4	0.19
Stdev	0.43	0.03	0.22	0.03
CI	0.36	0.02	0.18	0.03
CI%	11%	3%	4%	14%

The data is consistent with the expected behavior from the fuel and additive mixtures. The JP-8+100 package reduced oxidative deposition by 75%. BHT increased deposition despite using a significantly lower dosage than previous experiments on the ECAT.¹⁷ Similar concentrations of BHT were used

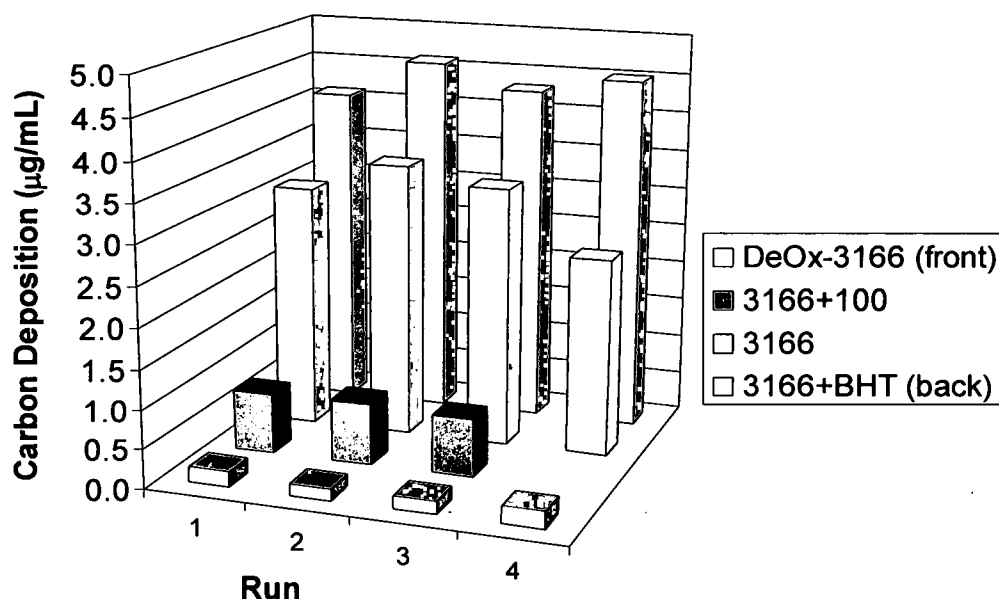


Figure 14. Results of deposition testing for POSF-3166 with additives and deoxygenation during QCM testing and yielded similar changes in total deposition.¹³ Both the ICDT and QCM had approximately a 33% increase in final deposition. Deoxygenating the fuel proved the most effective deterrent to oxidative deposition. The standard deviations remained a relatively low percentage of the total deposition with the highest deviation occurring with low deposition systems where uncertainty in the blank contributes the most experimental error. This confirms previous deposition results obtained on the QCM and ECAT under similar conditions.¹⁷ Consistent data from multiple sources provides verification of these deposition trends and of the accuracy of the ICDT.

3.8 Effects of Temperature on Total Deposition

Temperature influences deposition by increasing reaction rates and favoring different reactions. As reaction rates increase, more oxygen is

consumed during the same interval of time, which causes complete oxygen consumption to occur earlier during the residence time. The test examined the temperature effect on carbon deposition at complete oxygen consumption for POSF-3166. Results from the test are shown in Table 4. Average deposition levels were calculated from 4 repeated runs at each temperature from 250°C to 500°C. A 10 second residence time was found sufficient for complete oxygen consumption for temperatures over 250°C as discussed in Section 3.2. This allows a deposition study to examine the nature of deposit formation at various temperatures, independent of the level of dissolved oxygen consumption. The ability to adapt the in-situ carbon deposit analysis system to various temperatures with a constant residence time allows an in-depth analysis of fuel deposition. Knowing the system is operating at complete oxygen consumption validates a comparison between different temperatures.

Table 4. Temperature effects on fuel deposition for POSF-3166

Temperature °C	250	300	350	400	450	500
Run 1	3.2	3.1	3.2	4.8	4.1	3.9
Run 2	3.0	3.5	3.1	3.5	4.2	3.8
Run 3	2.7	3.3	3.8	4.1	4.5	4.0
Run 4	2.8	2.5	3.9	4.4	3.9	4.1
Average Deposition (µg/mL)	2.9	3.1	3.5	4.2	4.2	4.0
STDEV	0.22	0.43	0.41	0.55	0.25	0.13
CI	0.18	0.36	0.34	0.45	0.21	0.11
CI%	6.2%	11%	10%	11%	4.9%	2.7%

The confidence interval for this test was similar to most other operations on this instrument, 10% of the average deposition. The quantity of deposition increased with temperature. An analysis of variance of these deposit values shows little probability that these data are arranged so randomly. Figure 15 shows a plot of the deposition trend with temperature. The trend shows

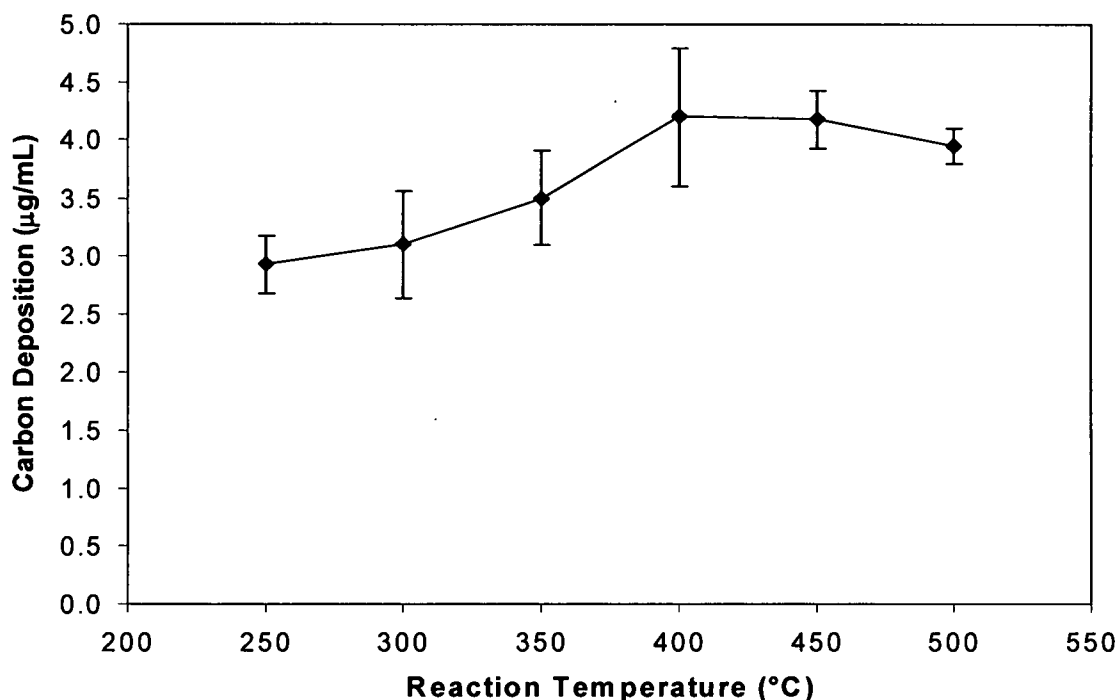


Figure 15. Temperature effects on total deposition of POSF-3166 (all runs at 10 s residence time, complete oxygen consumption)

increasing deposition from 250°C to 400°C, and no significant change after temperatures go higher. It is important to note that the values from 400°C to 500°C do not show statistically significant differences from each other.

The data shows a 33% increase in deposition from 250°C to 400°C temperature stress despite the same level of total oxygen consumption. This test demonstrated that higher temperature stress on fuel may cause increased deposition even when only examining the realm of total oxygen consumption. This revealed that the rate of deposition may not only depend on oxygen consumption, but also on temperature.

Previous work with the ECAT has shown similar results to these temperature effects. As bulk outlet temperature increased from 300°C to 354°C, deposition occurred more quickly and in greater amount. Total deposition on the

ECAT increased by 70% from 1.2 mg at 300°C to 2.0 mg at 354°C. This shows a similar occurrence of increasing total deposition with higher temperatures. While both tests do not show the same magnitude of deposition change, the trend still demonstrates increasing deposition with temperature.²⁷ Several tests have shown differing results for lower temperature ranges.

3.9 Residence Time Effects

Total residence time was maintained during previous tests, but the impact of changes in residence was also studied. The effect of residence time was examined using fuel POSF-3219. Reducing the pump flow rate increased the time of isothermal temperature exposure. Other test conditions were the same as those from previous oxidative deposition tests. Approximate residence times of 10 and 20 seconds were examined at 300°C. Table 5 shows the results of this test.

Table 5. Residence time effects on oxidative stability of POSF-3219 at 300°C and 500 psi

POSF	3219	3219
	Jet-A	Jet-A
Residence time (s)	10	20
ICDT	0.62	0.73
μg/mL	0.68	0.78
	0.77	
	0.85	
Avg.	0.73	0.76
Stdev	0.10	0.04
CI	0.08	0.04
CI%	11%	5%

The data showed that increasing residence time had little or no effect on the overall quantity of deposition. The 10-second residence time at 300°C was

earlier shown to be a sufficient to completely consume the dissolved oxygen in the fuel. An increase in residence time showed no increase in total deposition. This data supports that the limiting reagent in the oxidative regime is dissolved oxygen. The importance of dissolved oxygen to oxidative deposition was shown earlier during deoxygenated fuel tests. The removal of oxygen dramatically reduced the deposition levels from fuel stress. Here, it is reaffirmed that after complete consumption of oxygen, the fuel is relatively non-reactive under these reaction conditions.

3.10 Comparison of Deposition Measurement for Several Fuels across Deposit Monitoring Systems

Potential use of the ICDT for preliminary deposition analysis or additive studies is dependent on the applicability of the data generated. Consistency between various deposition tests is used to confirm the accuracy and consistency of subsequent measurements. For this work, a flowing and batch system were chosen for comparison. NIFTR and QCM data for deposition were compared with results for similar trends. While deposition quantification is performed using many different techniques, no single standard for fuel deposition is used for comparison between systems. Therefore, a comparison of the deposition level relative to a single fuel was best suited for understanding system performance. Figure 16 shows system performance for three fuels normalized to neat POSF-3166. Each of these three systems is compared under this normalization, and deposition trends are consistent between tests. Therefore, the same distinction for overall thermal stability can be made between fuels. A low

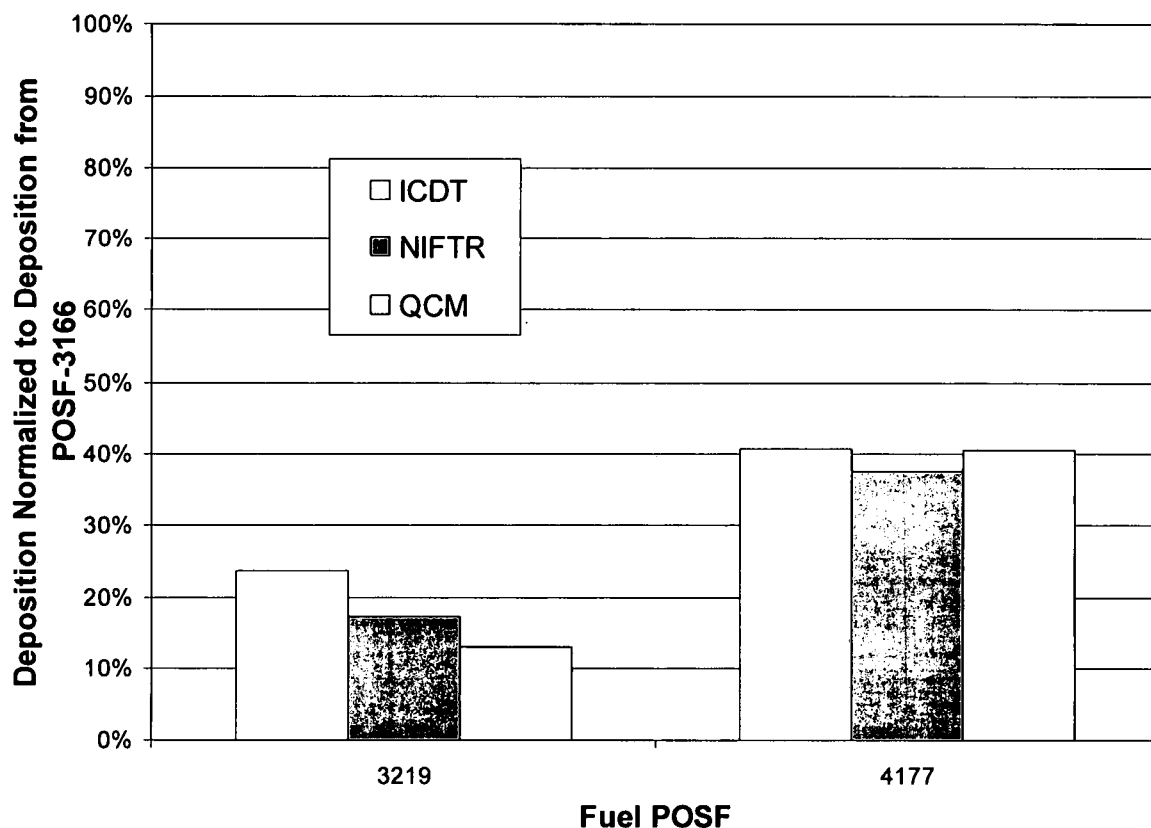


Figure 16. Deposition for two fuels normalized to POSF-3166 on the ICDT, NIFTR, and QCM

depositing fuel on one test will yield a relatively low deposit on another test. The relative amount of deposit also appears to be consistent between systems. This suggests that fuels deposit at similar levels relative to each other no matter which system is used for the analysis.

The distinction between fuels is consistent. The normalized fuel obviously all have the same response, but POSF-3219 and 4177 show no more than 10% variance between all test systems. This type of information makes it very simple to rate fuels qualitatively as high, medium, or low deposit tendency. It is important that multiple systems give similar results for deposit rates for a fuel or, rather, similar deposition trends for fuels of various thermal stabilities. Multiple sources

of corresponding data help confirm conclusions on fuel thermal stability with supporting evidence. This also demonstrates that the ICDT is consistent with other systems and makes it viable for basic research and other studies. The capacity to rapidly analyze deposition with an in-situ test offers benefits over systems like the QCM and ECAT. This will be especially useful when the test results are needed quickly or there are limitations to fuel or additive quantities. While it is not known which system gives the best correspondence to real world scenarios, more evidence can only help affirm hypotheses about a specific fuel's characteristics.

Kinetic studies require more precise measurements, and the temperature profile of this in-situ carbon deposition test may provide an opportunity for such analysis in a flowing reactor. The temperature profile reaches final reaction temperature quickly, and this is unique for such a versatile flow system. This can be attributed to the low fuel cross-section and high heat transfer. The ratio of inner to outer diameter is 0.32. This generates a cross section, which is mostly metal inside the reactor. The cross sectional area of metal is 9.7 times larger than the cross sectional area of the flowing fuel. This creates a large thermal mass, which helps maintain temperature during reaction. Overall, the mass flow per surface area for heat transfer is extremely low in this system, which allows superior control of reactor temperatures. Other systems, such as the NIFTR, attempt to balance larger mass flow to surface area by increasing heat transfer to the tube wall. Copper heating blocks are used for heat transfer, but this is still limited by the capacity of the metal tube walls to carry energy to the flowing fuel.

By reducing total mass flow rate and dramatically increasing the ratio of surface area, the compact reactor design of the in-situ carbon deposit analysis system maintains far more isothermal temperature profiles at short residence times.

The NIFTR must be run for extended periods of time to achieve sufficient deposit for detection. The total fuel reacted still has to be high despite reducing flow rates for more isothermal temperature profiles. Every decrease in flow rate corresponds to a linear increase in run time. The detection limits for the process are still limited by the offline destructive analysis on the LECO carbon analyzer. The detection limit for a 2-inch reactor section is about 15 μg . The low detection limit of the in-situ carbon deposit analysis system, 0.5 μg , prevents this from being necessary. The reactor destruction and analysis phase of NIFTR experiments is a large amount of total test time. This factor, coupled with the high surface-to-volume ratio of the reactor provides for rapid, uniform analysis of fuel deposition.

The QCM applies very different conditions to fuel compared to flowing systems. Being a stirred batch process, there is no temperature profile for reaction. It is extremely isothermal after the initial startup, but fuel stress lasts 8 or more hours. Combined with an environment that includes a headspace, the deposition process is potentially very different from that of flowing systems. The batch reactor also consumes reactants during the preheat stage. The QCM reports deposition in $\mu\text{g}/\text{cm}^2$, which is different from the $\mu\text{g}/\text{mL}$ reported in many flowing systems. The reaction vessel does have the benefit of examining both oxygen consumption and deposition profiles simultaneously, however. Where the

in-situ carbon deposition analysis system only gives a final deposition value, the QCM is able to quantify deposition and correlate deposition rates with oxygen consumption. Many flowing systems use several gallons of fuel, but the QCM uses only 60 mL. The in-situ carbon deposition analysis system allows a flowing test with minimal fuel consumption that rivals this performance. Low volume tests provide a unique opportunity to explore rare or expensive fuels and additives. The in-situ carbon deposition analysis system provides a flowing test with this capability.

Chapter IV

Conclusions

4.1 In-Situ Carbon Deposition Test (ICDT)

Thermal demands on future aircraft have created need for improved methods to mitigate deposition. The thermal stress placed on fuel will continue to increase in advanced applications, and this creates a need for better deposition mitigation techniques than have currently been developed. An improved understanding of deposition chemistry is needed to advance this technology. This requires the development of advanced analysis and modeling tools for deposition studies.

The increasing thermal stress placed upon jet fuel has created demand for a new testing apparatus that can rapidly conduct analysis of low fuel volumes. A new tool useful for evaluation of thermal stability characteristics of novel fuel studies, additive studies, and kinetic studies was necessary to expand knowledge for deposition mitigation techniques. The System for Thermal Diagnostic Studies (STDS) was an ideal framework to enhance into a rapid, low volume analysis tool for deposition studies. Previous work on a condensed phase test cell was further developed into an oxidative deposition test. The mass spectrometer on the STDS was an ideal tool for on-line detection of low quantities of deposit. By utilizing the thermal stress reactor, it was possible to

create and oxidize deposits on the same apparatus. This was a unique development for a quantitative flowing test system. Only a small quantity of fuel is necessary for deposition tests because of the mass spectrometer's capability to detect trace species at low concentration. The low fuel volume had the added effect of reducing the total test time.

The detection limits of the in-situ carbon deposition test are unique to a flowing system. The repeatability of analysis was demonstrated through multiple tests discussed previously, and a 90% confidence interval shows a reproducibility of $\pm 11\%$ relative to deposition levels. The repeatability was demonstrated relative to other flowing tests such as the ECAT and NIFTR. The total quantity of carbon that can be accurately quantified is between 0.5 and 30 micrograms, though a broader calibration curve could increase the upper limit. This means the amount of required fuel varies depending upon the thermal stability and test temperature, but typical JP-8 fuels require only 2 mL for accurate testing at 300°C. Low deposition additives and fuels require larger volumes for testing so that the total deposition must be greater than 0.5 μg . Deposition testing systems such as the ECAT require much larger volumes to accurately quantify total deposition above 270 μg . Lower temperature testing would require more total fuel because of the lower deposition amounts demonstrated in the results, but volumes will still be much lower than those required for other flowing deposition tests.

One of the strengths demonstrated throughout testing was the rapid analysis procedure for in-situ deposition quantification. The complete test time,

from fuel preparation to completion of analysis was less than two hours. This is a very short test time compared to the time required for other flowing deposition analysis systems. The utility of an accurate and rapid deposition test makes the system ideal for explorative additive testing. Instead of a multiple day test system, it can offer quicker testing and more data on deposition kinetics.

An important development was the in-situ analysis of the nature of deposits. Testing can be repeated on the same reactor under repeatable conditions. The ICDT is a nondestructive deposition test that combines the use of a flowing system, which can provide new knowledge on equipment such as material properties. Future studies can examine the influence of an oxidized tube wall and different types of steel tubing. The ICDT is ideal for this type of study because the same reactor can be reused for several experiments.

The trends in total deposition quantities on the ICDT were comparable to those of other deposition tests. The consistency of deposition trends is important for deposition studies to determine the thermal stability of fuels. Measurement of deposition was compared with QCM, ECAT, and NIFTR. The trends across systems show similarity, and relative deposition levels were comparable for several fuels. Demonstrating actual accuracy is a relative term, but the in-situ deposition test has shown usefulness in producing practical data.

The in-situ carbon deposition test has shown a number of advantages over other existing deposition testing systems. The system provides accurate quantification of deposits for low quantities of deposition. This also makes it ideal for testing low quantities of fuel or additives. The short residence time, combined

with the low detection limit of the ICDT, provides a suitable platform for explorative studies with rare additives or expensive fuels. The deposition data is repeatable due to the isothermal reactor profile and controlled residence times. This will also allow kinetic information to be taken from deposition tests on the reactor, which is a unique benefit to a flowing deposition test.

4.2 Deposition Testing

During testing, deposition observations included: the effect of oxygen consumption, the effect of temperature, and the effect of residence time. The residence time and oxygen consumption were related elements in terms of oxidative deposition. Earlier results demonstrated a correlation between total residence time and oxygen consumption. Further testing showed the correlation of oxygen consumption with deposit formation. This information correlates with previous deposition studies and validates the results from in-situ carbon deposition testing. The results showed negligible deposition changes for increased time of exposure after the threshold of complete oxygen consumption. This was an important observation because it confirms previous testing that demonstrated oxygen was the limiting reagent for temperatures at or below 300°C. This hypothesis was further confirmed by the deoxygenated fuel testing, as this showed very low depositing characteristics. The temperature effects were further explored by examining how deposition changes in the realm of complete oxygen consumption at different temperatures. Complete consumption of oxygen was achieved at several different isothermal temperatures, and the results showed a 33% increase in deposition as temperature is increased from 250 to

400°C. After 400°C, there was no significant increase in deposition up to 500°C. This information is important when comparing different deposition tests which may analyze at different temperatures or to compare similar fuels run on this system.

Chapter V

Recommendations

A new deposition test, the in-situ carbon deposition test (ICDT), was developed providing many capabilities, which open new avenues of testing. The ICDT analyzes deposits in-situ, providing rapid testing analysis, and is small-scale. However, recommendations for improvement and future development of the system could offer improved testing performance. These improvements include design changes, operational changes, and techniques for future research. Among these, several could be easily implemented during future studies and are strongly recommended.

Several design changes to the in-situ carbon deposition test are straightforward alterations to reduce contamination and fuel consumption. Changes in instrument layout could decrease the flow path length during testing. The pressure gauge and cracking valve located at the surge suppressor could be removed to reduce the volume of the flow path. This would reduce dead volume in the fuel inlet. The collection process for reacted fuel could also use a shorter flow path and a variable volume container (i.e., a sample bag) to capture fluid and volatile gas products. These adaptations would reduce the total quantity of

fuel required for testing and increase the recovery of reaction products for off-line analysis.

Larger scale design changes to the setup could improve the oxidation of deposits and detection sensitivity. A more active catalyst such as a platinum based oxidative catalyst could be used to improve the rate of conversion of CO to CO₂. This would allow for higher flow rates of air during the oxidation phase and decrease the total time required to oxidize deposits. The only drawback would be that vapors would likely be less noticeable in the detection process due to enhanced oxidation of hydrocarbons. Currently, the 57 ion can be detected during analysis if the reactor was insufficiently dried. Using a stronger catalyst will likely oxidize the fuel and cause a higher quantity of deposits to be detected on an insufficiently dried reactor, rather than allowing fuel to reach the molecular sieve column. As a result, the oven could be kept at a higher temperature during evacuation to ensure no fuel vapors remain for testing. This would allow a greater margin of error for safely drying the test reactor. It is also recommended that the length of the trapping column be reduced. The molecular sieve material adsorbs a large amount of CO₂ gas before becoming saturated, and a column length of several feet may be able to sufficiently trap CO₂ while improving resolution of peaks and shortening the length of time necessary to complete the analysis process. This could be an order of magnitude smaller than the column used in this study. A shorter column will reduce mixing with the carrier gas and improve the ratio of signal to noise. Determination of the optimal column length requires additional testing. Additional deposit species could also be analyzed via

the incorporation of other trap systems. Installing other forms of traps on the ICDT could allow the investigation of other deposit components such as hydrogen, sulfur, or nitrogen.

Online monitoring of reaction products could be conducted to provide information about the stressed fuel. The GC-MS used for trapping could be used in conjunction with a sample loop to analyze reaction effluent during fuel stress. A sample loop inserted after the back pressure regulator would allow sampling and quantification of reaction products. A separate column could be installed in the trapping oven to analyze the fuel components via mass spectrometry. This would allow for online analysis of oxidation products as well, making the deposition analysis test more efficient with simultaneous analysis of stressed fuel and deposits. If this is done, it is important to ensure that both the molecular sieve and the new column have an operating temperature range of 35 to 300°C. A new sampling valve would be required, but this could provide comprehensive information for rapid analysis.

Future studies on the ICDT should investigate the effects of some of the unique attributes due to the in-situ oxidation of deposits. The in-situ analysis and conditioning creates an oxidized metal reactor wall that may influence the process of deposit formation. The effect of reactor size should also be investigated in this study. The high surface to volume ratio may affect the rate and total quantity of deposition. The rapid analysis procedure and low fuel requirements of the ICDT make it ideal for analysis of multiple reactor conditions such as these.

Appendix: Calculation routine for wall temperature heat exchanger model

1. Step size for heat exchanger length 0.1 inches
2. Calculate average convection coefficient for heat exchanger
(Mass flow * Average heat capacity * (Exit temperature – Inlet temperature))/(Pi * Diameter * Length * LMTD)
3. Look up heat capacity based upon step temperature
4. Determine step temperature
(Avg. Conv. Coef. * Pi * Diameter * step length)/(Mass flow * Cp) = dT/LMTD
5. Look up density
6. Determine residence time
Step length / (Mass flow/(density* Pi / 4 * Diameter ^ 2))
7. Step through reactor length
8. Calculate residence time sum
9. Step flowrate (increase for long residence/decrease for short residence)
10. Return to step 2 and iterate

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