

INVESTIGATION OF JET FUEL THERMAL STABILITY USING PHOTON CORRELATION SPECTROSCOPY AND A QUARTZ CRYSTAL MICROBALANCE

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Keywords: Jet Fuels, Particle Size Distribution, Mass Deposition

INTRODUCTION

The thermal stability of aviation fuels is an important concern in designs for enhanced aircraft performance. In addition to its primary use as a propellant, jet fuel serves as a coolant for the environmental control system, engine lubrication, avionics, etc. in present military applications. Thermal loads on the fuel are anticipated to increase concurrently with the demands of advanced aircraft. Unfortunately, elevated temperatures in hydrocarbon-based fuels lead to oxidative degradation, producing insoluble products in the bulk liquid as well as deposits on contacting surfaces.¹ These processes reduce heat exchanger efficiencies and can result in obstructions of critical components, including valves, filters, and injection nozzles.

Efforts to develop highly stable jet fuels and thereby mitigate loss of heat-transfer efficiency and fouling problems in flight systems would certainly benefit from a predictive model that adequately accounts for the global physics and chemistry leading to insoluble particle formation and solids deposition. Recent experiments by Jones and Balster^{2,3} have illustrated the complexity of these processes. In particular, their studies of Jet-A, POSF-2827 fuel³ have demonstrated that observed insolubles are early products of autoxidation chemistry and that the "yield" of these products is directly correlated with O₂ availability. Their results also suggest that surface deposits arise from a precursor material formed in the bulk fuel in one of several independent reaction channels leading to the formation of various degradation products. Additional experimental work incorporating sensitive, real-time diagnostic methods for monitoring incipient particle formation as well as mass deposition on surfaces is clearly needed. To address this need, an experimental assembly designed for simultaneous application of photon correlation spectroscopy (PCS) and a quartz crystal microbalance (QCM) has been assembled and tested. The main aspects of this assembly and preliminary results obtained from integrated PCS and QCM measurements are described in this paper.

EXPERIMENTAL

PCS is a well established and widely used dynamic light scattering technique for quantitative measurement of particle size distributions in liquid samples. Briefly summarized, this technique monitors fluctuations in the intensity of scattered light due to Brownian motion of particles in a laser-illuminated volume. The scattered light is viewed by a photomultiplier, converted into pulse trains by an amplifier/discriminator and processed by a digital correlator, which performs an autocorrelation of the time-dependent intensity signal. For a monodisperse suspension of particles, the autocorrelation exhibits an exponential decay rate $G(\tau) \propto e^{-2\Gamma\tau}$. The decay constant, Γ , is related to the translational diffusion coefficient, D , of the scattering particles and to the geometry of the experiment through the relations

$$\Gamma = q^2 D; \quad q = \frac{4\pi n \sin(\theta/2)}{\lambda}$$

where q represents the magnitude of the scattering wave vector which can be determined from the refractive index of the liquid (n), the scattering angle, (θ), and the wavelength of the incident light (λ). For spherical particles, the particle size can be determined from the Stokes-Einstein equation

$$D = \frac{kT}{3\pi\eta d}$$

where k is the Boltzmann constant, T the absolute temperature, η the fluid viscosity, and d the particle diameter. Detailed discussions of PCS instrumentation and data reduction methods are available elsewhere.^{4,5} Under favorable circumstances, PCS can be used for accurate, noninvasive sizing of particles over a diameter range of a few nm to several microns. Successful application of this technique to real-time, *in situ* measurements of particle formation in heated jet fuels has been reported previously.⁶ Under isothermal conditions, thermally stressed fuels appear to generate simple, monomodal particle size distributions that exhibit a systematic increase in mean particle diameter as a function of time at elevated temperature.

The QCM provides a sensitive, compact system for complementary measurements of surface deposition. This device is a bulk-wave resonator, consisting of a piezoelectric quartz wafer with metal

electrodes on each face, that can be electrically excited into resonance. When the crystal is excited in this manner, it undergoes a shear deformation with displacement maxima at the crystal faces. Mass accumulated on the crystal faces moves synchronously with the oscillating surfaces, resulting in a shift of the resonant frequency. The QCM is typically incorporated in an oscillator circuit, where the oscillation frequency decreases with mass accumulation. The theory that relates measured frequency changes to mass deposition has been presented in detail elsewhere.⁷ Under conditions of constant fluid density and viscosity, the surface mass density (mass/area), ρ_s , is related to the measured decrease in frequency, $\Delta\nu$, as follows:

$$\rho_s = \left(-2.21 \times 10^5 \frac{g}{cm^2 s} \right) \frac{\Delta\nu}{\nu_0^2}$$

where ν_0 is the unperturbed resonant frequency of the device (~ 5 MHz). The QCM permits quantitative measurements at very low deposition rates; a typical system can easily achieve a resolution of ~ 0.1 – $0.2 \mu\text{g}\cdot\text{cm}^{-2}$. The utility of QCM instrumentation in jet fuel thermal stability studies was demonstrated by Klavetter et al.⁸ Most of these initial tests were performed under conditions of abundant oxygen availability. Recently, Zabarnick and co-workers have used QCM systems to investigate the thermal stability of various jet fuels at relatively low oxygen availability,⁹ and to evaluate the effect of several jet fuel additives.¹⁰

A schematic diagram of the jet fuel test system designed for integrated PCS and QCM measurements is shown in Figure 1. The stainless steel pressure vessel (300 ml. capacity, Parr Instruments) provided optical access for the PCS source laser (typically a HeNe laser, 35 mW peak power) as well as a viewing port for the PCS collection optics at a 90° angle to the incident light. The lid of the vessel was modified to accommodate a mounting clamp for the QCM sensor and a hermetic, rf feedthrough assembly, as described previously.⁸ The QCM was mounted vertically in the fuel in order to mitigate gravitational effects on deposition. Gas inlet and outlet ports were also located on the fixture lid, permitting fuel exposure to an oxidative or inert atmosphere at variable pressure, as desired. In order to reduce the time required to attain the target temperature and to optimize temperature uniformity in the cell, heating was supplied by band heaters attached to the window "arms" in combination with the heating mantle provided with the vessel. Temperatures were monitored by thermocouples positioned in the fuel sample and at several points on the outside of the vessel. The desired stress temperature was maintained by using one of the thermocouples as a feedback device for a programmable temperature controller (Eurotherm Model 818).

In all tests described in this paper, samples were prepared by filtering the fuel through a $0.2\text{-}\mu\text{m}$ PTFE filter, sealing the vessel, and then sparging with the desired gas (oxygen or nitrogen) for ~ 45 minutes. Typically, the vessel was filled to within $0.75''$ of the lid. For some tests, a 50 psig atmosphere of O_2 or N_2 was imposed prior to heating. In other experiments, the fuel was heated under ambient pressure conditions. Data acquisition included the frequency and dc voltage output of the QCM oscillator circuit as well as the output of the digital correlator (Langley-Ford, Model 1096). Intensities of transmitted and scattered laser light were monitored by a laser power meter (located at the output port of the test vessel) and a frequency counter (coupled to the amplifier/discriminator), respectively. In reducing the PCS data, several available algorithms were utilized, including a discrete exponential fitting program and two Laplace inversion routines.¹¹

RESULTS AND DISCUSSION

Previous investigations^{6,8} of jet fuel thermal stability have shown that the rates of both particle growth and mass deposition are sensitive to the temperature of the sample. Hence, reasonable uniformity of the temperature field in the test vessel is required for facile, quantitative interpretation of PCS and QCM data. Evaluation and optimization of temperature conditions in the assembly described above has been achieved by conducting heating tests employing an array of thermocouples. The results of one test are given in Figure 2. In this case, five thermocouples were placed in the fluid. Measurements were obtained near the bottom (TC1), center (TC4), and top (TC5) of the fluid volume, as well as along the side of the vessel (TC3) and within one of the three arms containing window ports (TC2). Another device (TC6) was used to monitor the outside wall temperature. The target temperature for this test was 150 C. Both fairly rapid heating and acceptable temperature uniformity in the fuel were achieved. At the target point, temperatures throughout the main body of the cell were uniform to within 0.8 C. The temperature in the extension arms was slightly hotter (~ 2 C). Similar results have been obtained in tests with other target temperatures.

Thus far, integrated PCS and QCM tests have been performed on Jet A 91-POSF-2827, a non-hydro-treated fuel that is known to resist oxidation but produce surface deposits in appreciable quantities at elevated temperatures, and Jet A-1 POSF-2747, a hydro-treated fuel that is highly stable with regard to surface deposition even though it consumes O_2 rapidly.⁹ Results on the first substance are more developed and will be described here. Jet A 91-POSF-2827 contains a relatively high level (up to 0.1 mass percent) of sulfur compounds; these components are thought to play a significant role in both inhibition of oxidation and deposit formation.³ A summary of mass

deposition results from QCM measurements in this fuel is provided in Table 1. Figures 3 and 4 illustrate selected QCM data in graphical form; relevant particle growth curves (as determined by PCS) and transmitted/scattered light intensity plots are shown in Figures 5 and 6, respectively.

The data obtained in this work are generally consistent with results of previous jet fuel thermal stability tests performed under similar conditions. The critical role of dissolved oxygen has been emphasized in earlier studies^{3,8,9} and is again demonstrated by the tests conducted near 150 C using O₂ and N₂, respectively, as the sparge and confining gas (cf. Table 1). With abundant oxygen, the QCM system registered a mass deposition rate of 0.88 $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$. A substantially lower rate was obtained when oxygen was effectively purged from the system. In fuel sparged with nitrogen and heated to 148 C under 50 psig N₂ confinement, the observed rate was only 0.13 $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$. This low value compares favorably with previous QCM results acquired under oxygen-depleted conditions.^{8,9} Similarly, particle formation in the fluid was very heavy with abundant oxygen but largely suppressed when the fuel was stressed with severely limited oxygen availability. In the latter case, the PCS technique was unable to provide meaningful correlations at any time during testing at elevated temperature; however, some hints of particle generation were seen in the raw data and, after the fuel cooled to room temperature, a small concentration of particles with mean diameter near 200 nm was observed. Processes leading to the generation of bulk and surface insolubles in the absence of O₂ are evidently minor but not negligible.

The remaining tests have also addressed the role of oxygen availability. For example, Figure 3 shows QCM results for a Jet A 91-POSF-2827 sample sparged with O₂ and heated to 139 C under ambient pressure. A plot of temperature measured by a thermocouple positioned in the fuel is also included in this figure for comparison. After the sample attained a constant temperature, mass accumulation closely corresponding to a linear deposition rate of 0.23 $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$ was registered. The rate determined in this test compares favorably to the results of Zabarnick⁹ which indicate similar deposition behavior (accumulation of 3.6 $\mu\text{g}\cdot\text{cm}^{-2}$ at a nearly linear rate in 15 hours) for Jet A POSF-2827 sparged with air and heated to 140 C under ambient pressure. The most significant difference in experimental conditions for these two tests was the choice of oxygen vs. air for the sparging gas. The similarity in recorded mass accumulation rates suggests that the additional oxygen availability has a negligible effect on surface deposition at this temperature. In this case, added oxygen in the confining atmosphere should also play a minor role. The slightly higher deposition rate of 0.27 $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$ seen in Jet A 91-POSF-2827 heated to 138 C under 50 psig O₂ (cf. Table 1) supports this expectation. Similarly, Klavetter et al.⁸ reported nearly identical rates for the same fuel sparged with O₂ and heated to 160 C under 50 psig O₂ and N₂ overpressures (1.18 vs. 1.23 $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$, respectively). These results all appear to be linked to this fuel's tendency to consume oxygen relatively slowly.

An additional comparison can be made with deposition rates determined by Klavetter et al.⁸ for Jet A 91-POSF-2827 (confining pressure of 50 psig O₂) over a temperature range of 160-200 C. The QCM results acquired in the present work expand this range down to 133 C. Figure 4 shows an Arrhenius plot with data from three relevant tests (1, 3, and 4; cf. Table 1) added to the earlier results obtained at higher temperature. The Arrhenius "line" derived from a linear least-squares fit to the data implies an activation energy of 20 kcal/mol for the global deposition process. This value is somewhat lower than the 26 kcal/mol activation energy calculated for this fuel in Ref. 8; however, it is consistent with the behavior of other fuels examined in that study.

The simultaneous PCS and light intensity measurements provide added insight. In all tests where some oxygen was supplied in the sparge gas and confining pressure, large concentrations of particles formed in the fluid within several hours. Consistent with previous PCS measurements,⁶ particles were detected earlier and the mean particle diameter increased more rapidly with increasing stress temperature. The influence of added oxygen at a given temperature is illustrated by the PCS results in Figure 5. At 133 C, significant particle formation was observed earlier in the presence of abundant oxygen; however, the initial rate of increase in particle size was approximately the same in the both cases. Dissimilar behavior was observed at later times. At ambient pressure, the mean particle size inferred from the PCS data increased steadily throughout the test whereas, under 50 psig O₂ confinement, the particle size appeared to level off near 300 nm. This phenomenon is probably an artifact arising from multiple scattering effects that can occur when particles are present in high concentration. The scattered light intensity data are consistent with this interpretation. Figure 6 demonstrates the complex behavior of the scattered light intensity vs. time for the test performed under 50 psig O₂. The intensity increased rapidly during the first two hours of this test, reaching a maximum value at approximately 150 minutes. This time period corresponds to the initial phase of particle formation and growth (cf. Figure 5). Thereafter, the intensity fell to roughly half the peak value at about 300 minutes and then recovered slightly. This period coincides with the observed "saturation" in particle diameter. The fuel exhibited a very "cloudy" appearance at these times, a further indication that particle formation had occurred to such an extent that the laser intensity reaching the PCS measurement volume (i.e., center of the cell) was

severely attenuated by particle absorption and scattering. In contrast, the scattered light intensity was observed to be still slowly increasing after five hours of heating Jet A 91-POSF-2827 at 133 C under ambient pressure and the fuel appeared to be only slightly "cloudy" at this point.

Figure 6 also provides results of laser power measurements taken at the exit optical port of the test vessel during the test under 50 psig O₂ confinement. The maximum in scattered light intensity accompanied a steep decline in the transmitted laser power, illustrating the important role of particle scattering and absorption at this point in the experiment. The late-time recovery of both signals shown in Figure 6 may be due in part to particle settling as the mean size increased. Also, Mie theory predicts a complex dependence of scattering cross section vs. particle diameter at sizes > 400 nm. Estimates of the relative mass involved in particle formation under an O₂ overpressure vs. ambient pressure were calculated from Mie intensity parameters in combination with the light intensities. A Beer's Law-type relationship was used to infer the laser power reaching the center of the cell from power measurements incident on and transmitted by the sample. Attenuation of the scattered light intensity by particles in the sample was accounted for in a similar fashion. These calculations suggest that the mass associated with particle formation in the fuel heated under 50 psig O₂ is 3-5 times higher (for a given time during the test) than in fuel heated at ambient pressure. For Jet A 91-POSF-2827 under these conditions, excess oxygen clearly affects the generation of bulk insolubles more substantially than it accelerates surface deposition.

CLOSURE

An experimental setup for simultaneous, real-time investigation of particle formation and surface deposition in heated jet fuels has been assembled and tested. The design permits integrated PCS and QCM measurements in a nearly isothermal environment. Data obtained from integrated measurements on Jet A 91-POSF-2827 are generally consistent with earlier results from tests performed with the individual techniques. With this fuel, oxygen availability is a factor in both particle formation and mass accumulation on surfaces. In particular, excess oxygen (at a given temperature) leads to substantially larger concentrations of particles in the bulk liquid. Integrated PCS and QCM measurements should find application in thermal stability tests of a wide range of fuel types and should permit detailed evaluation of various additives, including antioxidants, dispersants, etc. Under some conditions leading to extensive generation of bulk insolubles, quantitative particle sizing using PCS may be limited by multiple scattering effects.

ACKNOWLEDGMENTS

This work was jointly supported by the U. S. Air Force, Aero Propulsion and Power Directorate of Wright Laboratory, Wright-Patterson AFB, and the U. S. Department of Energy, Pittsburgh Energy Technology Center (PETC) through Sandia National Laboratories under contract DE-AC04-94AL85000. The support of W. E. Harrison III and Dr. W. M. Roquemore of Wright Laboratory as well as S. Rogers of the U. S. DOE PETC is gratefully acknowledged. The excellent technical assistance of Jaime Castañeda is greatly appreciated.

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Table 1: QCM Results in Jet A 91-POSF-2827

Test #	Spurge Gas	Confining Pressure	Temp. (C)	Deposition Rate ($\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$)
1	O ₂	50 psig O ₂	151	0.88
2	N ₂	50 psig N ₂	148	0.13
3	O ₂	50 psig O ₂	138	0.27
4	O ₂	50 psig O ₂	133	0.39
5	O ₂	Ambient	133	0.63 (early) 0.15 (late)
6	O ₂	Ambient	139	0.23

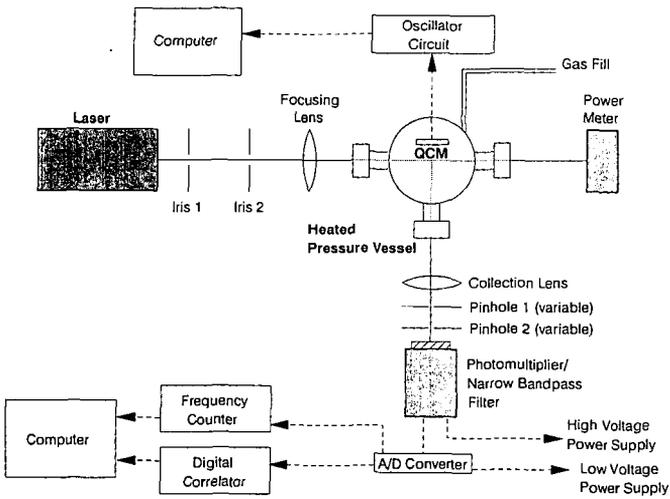


Figure 1. Schematic representation of integrated PCS/QCM system for studies of heated jet fuels.

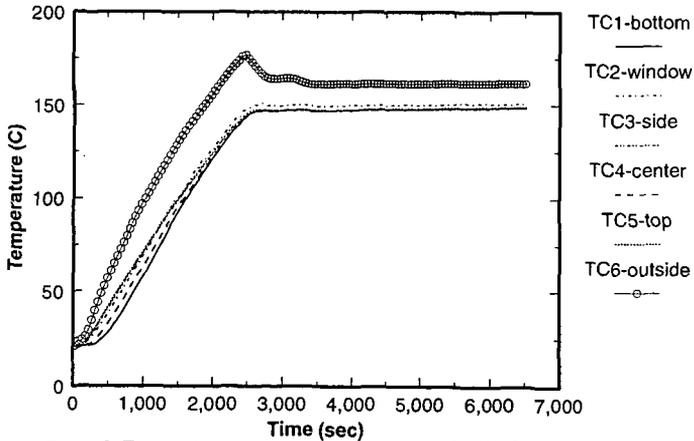


Figure 2. Temperature measurements at various points in the pressure vessel during heating of Jet A fuel. Target temperature was 150 C. Thermocouple locations are noted on legend.

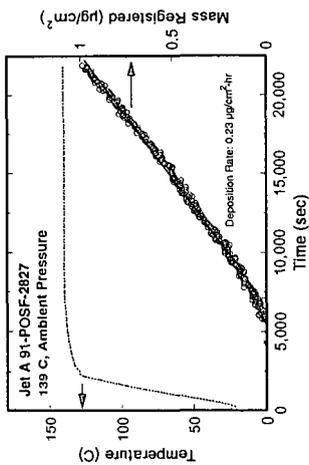


Figure 3. Mass deposition recorded by QCM in Jet A 91-POSF-2827 heated to 139 C. Test performed at ambient pressure. Temperature history in fuel is also shown.

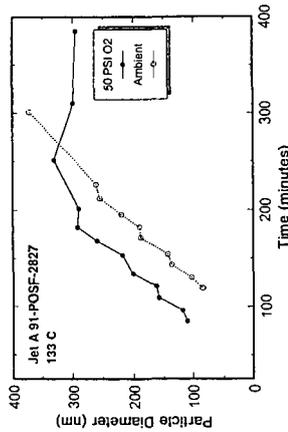


Figure 5. Particle growth measured by PCS for Jet A 91-POSF-2827 heated to 133 C. Tests conducted at two different pressure conditions.

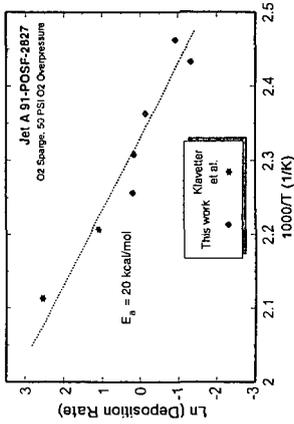


Figure 4. Arrhenius plot for Jet A 91-POSF-2827 tested at temperatures in the range 133-200 C.

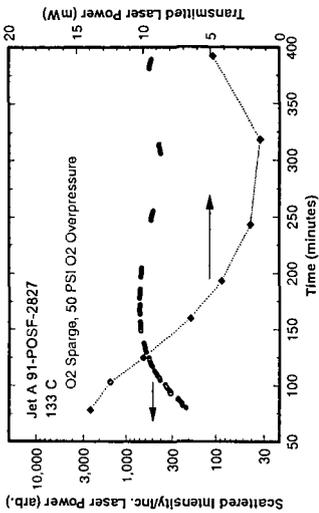


Figure 6. Normalized scattered light intensity (logarithmic scale) and transmitted laser power (linear scale) for Jet A 91-POSF-2827 heated to 133 C.