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December 1, 1999

U.S. Department of Transportation, Dockets
Docket No. FAA-1999-6411 - 4
400 Seventh Street SW.
Room Plaza 401
Washington DC 20590
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To: FAA Propulsion/Mechanical/Crashworthiness Representatives:

Abstract. The intent of this letter is to assist the FAA and DOT in mitigating any and all possible ignition sources in airplane fuel tanks in response to recently proposed rules (Docket No. FAA-1999, Notice No. 99-1). It includes test data showing JP8-air autoignition, specifically documenting the transition from a cool flame to hot flame autoignition. It also contains recommendations for consideration in the proposed rules.

In response to your notice of proposed rulemaking (NPRM), Docket No. FAA-1999; Notice No. 99-18, "Transport Airplane Fuel Tank System Design Review, Flammability Reduction, and Maintenance and Inspection Requirements [1]," we wish to highlight some technical issues related to autoignition of fuel-air mixtures that may potentially further your effort to eliminate possible ignition sources in aircraft fuel tanks.

The focus of our comments will be on autoignition, cool flames and cool flames that transition to hot flames, i.e., autoignition.

PERSONAL BACKGROUND

For reference, a brief description of who we are and why we are interested in autoignition is provided below.

Dr. Howard Pearlman

I, Dr. Howard Pearlman, received my BS, MS, and PhD from Northwestern University in 1984, 1988, and 1992, respectively. My MS and PhD dissertations focused on acoustic instabilities in premixed and diffusion flames in stagnation and counter-flow geometries, hysteresis in combustion, and rotation effects on droplet combustion.

In 1992, I was awarded a National Research Council Resident Research Associate Position at NASA Lewis Research Center (LeRC) in Cleveland, OH. I studied diffusive-thermal and hydrodynamic instabilities in premixed gas flames at earth and micro-gravity. Experimentally, I obtained the first conclusive experimental evidence to support the high-Lewis number diffusive-thermal pulsating and traveling wave instability which had eluded experimental verification since Sivashinsky's theoretical prediction in 1977.

In 1995, I became a Research Assistant Professor at University of Southern California. At the same time, I proposed a study on autoignition and cool flames to NASA and was funded in September, 1995 to determine the role of natural convection (buoyancy) on low-temperature oxidation reactions and autoignition. We currently have an active cooperative program between NASA and USC, entitled the "Cool Flames Experiment." In February, 1999, I was awarded the Presidential Early Career Award for Scientists and Engineers (PECASE) for our work in autoignition.

Mr. Richard Chapek

Mr. Richard Chapek began his career at NASA in 1984 and received an Associate of Applied Science in Mechanical Engineering Technology in 1985. In 1987, he received a state certified apprenticeship as a research laboratory mechanic. During the past 15 years, he served NASA in a variety of capacities. For four years, he worked as a facility mechanic in the NASA LeRC Rocket Engine Test Facility where he developed skills in the maintenance, installation, and operation of high pressure cryogenic hydrogen and oxygen systems. More recently, he spent four years in the Aircraft Maintenance Office as a flight engineer and aircraft maintenance technician on the DC-9 reduced gravity aircraft. He was responsible for oversight of contract heavy maintenance and development of a computerized maintenance tracking program for the purposes of maintenance planning and reporting. From August 1996 to August 1997, he served as an Aircraft Quality Assurance Representative for the LeRC Aircraft Maintenance Office. From August 1997 to the present, he designed, built, and tested most of the hardware for the Cool Flames microgravity experiment. He is currently the lead test operator for microgravity and ground-based operations for the Cool Flames Experiment.

It is important to emphasize that our motive in writing is not financial or personal. We have no ties to any individual involved in the TWA 800 incident. Our interest is purely scientific. Moreover, the work reported herein is the individual work of the authors and does not represent NASA's or USC's perspective or opinion. If this work is of value to your endeavor, we would be grateful to see our research effort assist in ensuring the safe operation of aircraft.

BACKGROUND ON AUTOIGNITION

Foremost, (auto-) ignition manifests itself in fuel-air mixtures when the rate of heat generation due to chemical reaction exceeds the rate of heat loss, where the rate of chemical reaction (for most combustion process) is exponentially sensitive to the reactant temperature, i.e., Arrhenius kinetics, and less sensitive to the mixture composition. In other words, a small increase in temperature results in a large increase in the chemical reaction rate provided there exists the proper mixture of reactants to support the chemical reaction.

As a baseline, consider a perfectly insulated adiabatic system (no heat loss). The slightest temperature increase (due to chemical reaction or heat transfer) will increase the rate of chemical reaction, which **exothermically** generates and releases additional heat. This heat release further raises the temperature of the remaining reactants, which in turn further increases the reaction rate. This process continues until a temperature is reached sufficient to promote a branched-chain reaction (explosion) or until the reactants are sufficiently depleted. The point to emphasize is that "an adiabatic reaction, however slow it may be at the beginning, will become noticeable at some certain moment [2]" since the chemical reaction rate is more sensitive to an increase in temperature than a decrease in reactant concentration. This "moment" is the moment of autoignition. In combustion theory, the duration of time until this occurs generally increases as the temperature of the reactants decreases and is referred to as the chemical induction time.

Adiabatic systems are, however, idealizations and do not physically exist. Heat losses due to conduction, convection and/or radiation heat transfer moderate (lower) the temperature while the heat release from **exothermic** chemical reactions increases the temperature. As noted above, ignition can occur when the balance between the generation and loss rates exceeds unity. It is therefore imperative to understand the factors that influence the generation and loss rates to properly establish the minimum "autoignition temperature" for safe operation.

ASTM Standard Test Method E659-78 (1994) [8] outlines a procedure for determination of autoignition temperatures of liquids and solids. While the test provides a *comparative basis* for the reactivity of fuels, it does not isolate the roles of many parameters on the measured autoignition temperatures. Specifically, fuel structure, surface material, surface temperature, **stoichiometry**, pressure, initial fuel/ air temperature, contact or residence time, surface condition, surface heating rate, surface size, surface orientation [3] and

effective gravitational acceleration [9] affect the measurement and are not well-controlled in the ASTM test methodology. Several of these complexities are recognized in the ASTM Test Method, while others have been recognized in the combustion community, e.g., [4]. For a comprehensive review, refer to [5].

COOL FLAMES

As alluded to above, “if the oxidation occurs at relatively low temperatures, the heat liberated will not necessarily be sufficient to produce a self-accelerating chain reaction [autoignition] which depends upon such factors as temperature, pressure, and concentration of the reactants; this low intensity combustion is the case of cool *flame ignition* or *low temperature oxidation reaction* where luminosity may or may not be observed. Thus combustion may involve rapid or slow oxidation processes, as well as a combination of both types [5].” When both types of combustion are involved, it is referred to as multi-stage ignition; that is, a slow reaction or cool flame which transitions into a hot flame. Note that the ASTM Test Method E659-78 recognizes the possible occurrence of cool flames, denoting the temperature at which they occur as the cool flame autoignition temperature (CFT). In addition, it recognizes that “cool flames generally occur at lower [flask] temperatures than hot flames but may form over an intermediate temperature range, so that the lowest temperature at which any ignition occurs should be recorded. Below these ignition temperatures, nonluminous **pre**flame reactions may occur and are distinguishable by rather weak temperature rises that are barely detectable in some instances [8].” Also, the ASTM test method recognizes the possible occurrence of *pre*flame reactions and further defines the “lowest [flask] temperature at which these reactions are observed [as] is the reaction threshold temperature (RTT).”

In the combustion community, it has long been recognized that most hydrocarbon-air mixtures chemically react at low temperature (below ~1000K) and produce very weak flames called cool *flames*. Cool flames, unlike conventional hot flames, i.e., autoignitions, which produce large amounts of heat, carbon dioxide and water, are weak flames and may produce only a 10°C temperature rise and a negligible amount of carbon dioxide or water. At low temperatures, the fuel and oxygen molecules do not react vigorously and fail to achieve complete combustion. Instead, the molecules pyrolyze (break down and recombine) to produce a wide assortment of different chemical compounds including **aldehydes**, alcohols, acids, peroxides, smaller hydrocarbons and carbon monoxide. In the process of breaking and reforming the chemical bonds, the chemical reactions liberate a small amount of heat. A key feature of cool flames is that they can transition into hot **flames** and lead to explosion.

With respect to safety, autoignition, cool flames, and low temperature oxidation reactions deserve special attention since a spark, hot-wire or hot surface is unnecessary to begin the chemical processes. They spontaneously occur and manifest themselves when the heat generation rate exceeds the heat loss rate.

*The important points to emphasize are: (1) nonluminous **pre**flame reactions “may occur and are distinguishable by rather weak temperature rises that are barely detectable in some instances” [8], (2) cool flames often occur at temperatures lower than the autoignition temperature (AIT), and (3) cool **flames** can develop into hot flames (autoignitions) under appropriate conditions [6,9]. (1)-(3) have been recognized for at least 70 years, predating the early work on engine knock (“ping”) and autoignition in automotive engines.*

In reference to the Proposed Rules, I strongly suggest that ample consideration be given to low temperature oxidation reactions, cool flames and specifically multi-stage ignitions (i.e., a transition from a cool flame to a hot flame), in addition to hot flame autoignition, when determining the “lowest expected autoignition temperature of the fuel in the fuel tanks [1].” Perhaps, the lowest value of the RTT, CFT, and AIT (with a factor of safety) should be chosen as the minimum temperature below which all parts in the tank must be maintained. As mentioned in the ASTM test method, careful attention should be given to ensure that the conditions under which these values (RTT, CFT, and ATT) are obtained are representative of the conditions relevant to the configuration, i.e., airplane fuel tanks.

Below is an excerpt from the Proposed Rules [1], which suggests that a safety factor of 50°F be used. This is questionable unless special care is taken to properly define the *lowest expected autoignition temperature*.

*Fuel Tank Ignition **Source** Proposal [1]*

*The title **of** Sec. 25.981 would be changed from “Fuel tank temperature” to “Fuel tank ignition prevention.” The FAA proposes to retain the substance **of** existing paragraph (a), which requires the applicant to determine the highest temperature that allows a safe margin below the lowest expected auto ignition temperature **of** the fuel; and the existing paragraph (b), which requires precluding the temperature in the **fuel** tank from exceeding the temperature determined under paragraph (a). These requirements are redesignated as (a) (1) and (2) respectively.*

*Compliance with these paragraphs requires the determination **of** the **fuel** flammability characteristics **of** the fuels approved **for** use. Fuels approved **for** use on transport category airplanes have differing flammability characteristics. The fuel with the lowest autoignition temperature is JET A (kerosene), which has an autoignition temperature **of** approximately 450 deg.F at sea level. The autoignition temperature **of** JP-4 is approximately 470 deg.F at sea level. Under the same atmospheric conditions the autoignition temperature **of** gasoline is approximately 800 deg.F. The*

*autoignition temperature **of** these fuels increases at increasing altitudes (lower pressures). For the purposes of this rule the lowest temperature at which autoignition can occur **for** the most critical fuel approved **for** use should be determined. The FAA intends that a temperature providing a safe margin is at least 50 deg.F below the lowest expected autoignition temperature **of** the fuel throughout the altitude and temperature envelopes approved **for** the airplane type **for** which approval is requested.*

One additional point that is important to note is that cool flames generally occur in fuel-rich mixtures, outside of the normal “flammability limits.” It is therefore not prudent to assume that if the composition of the **premixture** is outside of the flammability limits (e.g., richer than the standard definition of the rich flammability limit), a cool flame could not develop under appropriate conditions (e.g., heating) and possibly transition to a hot flame (autoignition).

NEW TEST RESULTS

To illustrate the possible occurrence of cool flames and multi-stage ignitions in jet fuels at elevated temperature and atmospheric or subatmospheric pressures, a preliminary experiment was conducted at NASA GRC. The experimental apparatus consisted of an oven which housed a fused-silica, spherical vessel of given diameter (i.d.=10cm), and a gas delivery system. The oven employed resistive heating elements in the rear and top panels, a mixing fan to circulate the hot air, 7.5cm diameter quartz windows on both the top and side walls for viewing and a gas feedthrough built into the door. Random spatial thermocouple measurements suggested that the temperature uniformity within the oven is $\pm 10^{\circ}\text{C}$ throughout its operating range (20-600°C).

To minimize radical/ wall interactions, the internal reaction vessel walls were initially chemically treated with SylonTM, a silicon-based deactivating agent. Once treated, exposure to the environment was minimized by holding it under vacuum or filling it to atmospheric pressure with dry N₂ or He. The tests were conducted by initially evacuating the vessel, preheating it to 250°C (482°F)*, and subsequently injecting (through a vacuum tight rubber septum) a measured volume (1.0cc or 2.5cc) of JP-8 (a fuel essentially equivalent to Jet A) using a calibrated Hamilton syringe. Room air was then introduced into the vessel until the total pressure of the vaporized fuel and air equaled 7.4psia (1/2atm). Note, that this value is near the pressure at which the TWA 800 incident occurred, i.e., the ambient pressure at 14kft is approximately 8.6 psia [7].

Two intensified array cameras (Xyberion model no. IMC-201) operated at maximum gain then recorded the integrated ultraviolet and visible light emission. Note that cool flames

*It is recognized that the 250°C (482°F) vessel temperature is greater than reported values of the AIT for Jet A (~400-450°F). Recognize that the vessel in this illustration is 10.2cm i.d, orders of magnitude smaller than aircraft fuel tanks. Larger vessels (tanks) will have smaller conduction heat loss and the RTT, CFT, AIT values are expected to decrease. See comment (3) in the section CONCLUSIONS AND RECOMMENDATIONS.

can not be seen with standard video cameras. One camera was positioned at the top and the other at the side. A Setra 0-25 psia pressure transducer (accuracy ± 0.25 psia) recorded the vessel pressure at 100Hz. Figure 1 shows a schematic of the apparatus.

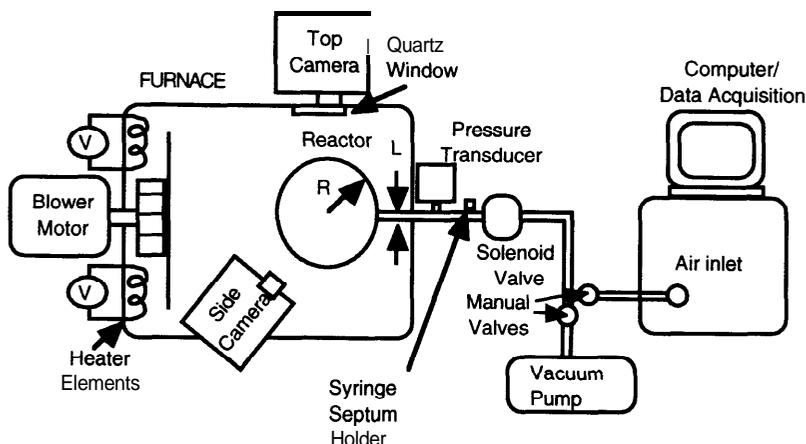


Fig. 1: Schematic of the Static Reactor Apparatus

Injecting a 2.50cc JP8 fuel sample into the hot ($T_{\text{vessel}}=250^{\circ}\text{C}$), pre-evacuated flask, and then adding room air until the pressure equaled 7.4psia resulted in the occurrence of a two-stage ignition. The pressure trace is shown in Figs.2a and 2b, where Fig.2b is an expanded view of Fig.2a during the course of reaction. Note that it took approximately 30s to establish the initial pressure. The gas mixture then was heated by the hot vessel walls and equilibrated for approximately 45s, at which time the camera recorded that a cool flame appeared at the top of the vessel (see Fig.4). The cool flame then proceeded to propagate downward into the vessel. Approximately 1/2s later, the cameras showed that a hot flame developed, also at the top of the vessel. This can be clearly seen with the side camera view shown in Fig. 4.

A second test was then conducted using 1.0cc JP8, all other parameters the same. As before, it produced a two-stage ignition. The pressure trace for this test is shown in Fig.3.

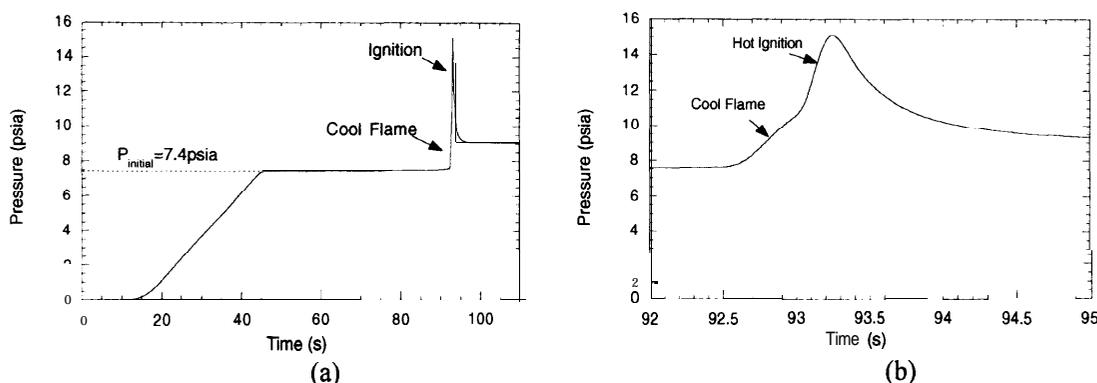


Fig.2: Pressure Trace as a Function of Time, 2.5cc JP8, $T_{\text{vessel}}=250^{\circ}\text{C}$, 10cm fused-silica i.d. vessel
(a) Entire test time, (b) Expanded view during the reaction

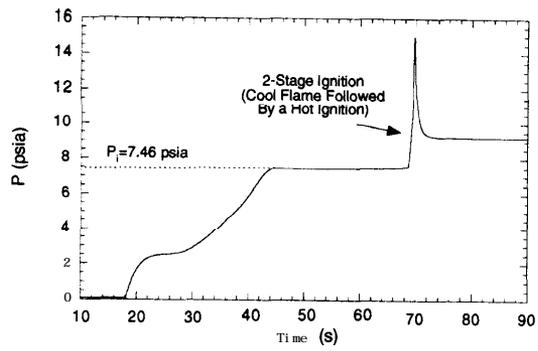


Fig.3: Pressure Trace as a Function of Time, 1.0cc JP8, $T_{\text{vessel}}=250^{\circ}\text{C}$, 10cm fused-silica i.d. vessel

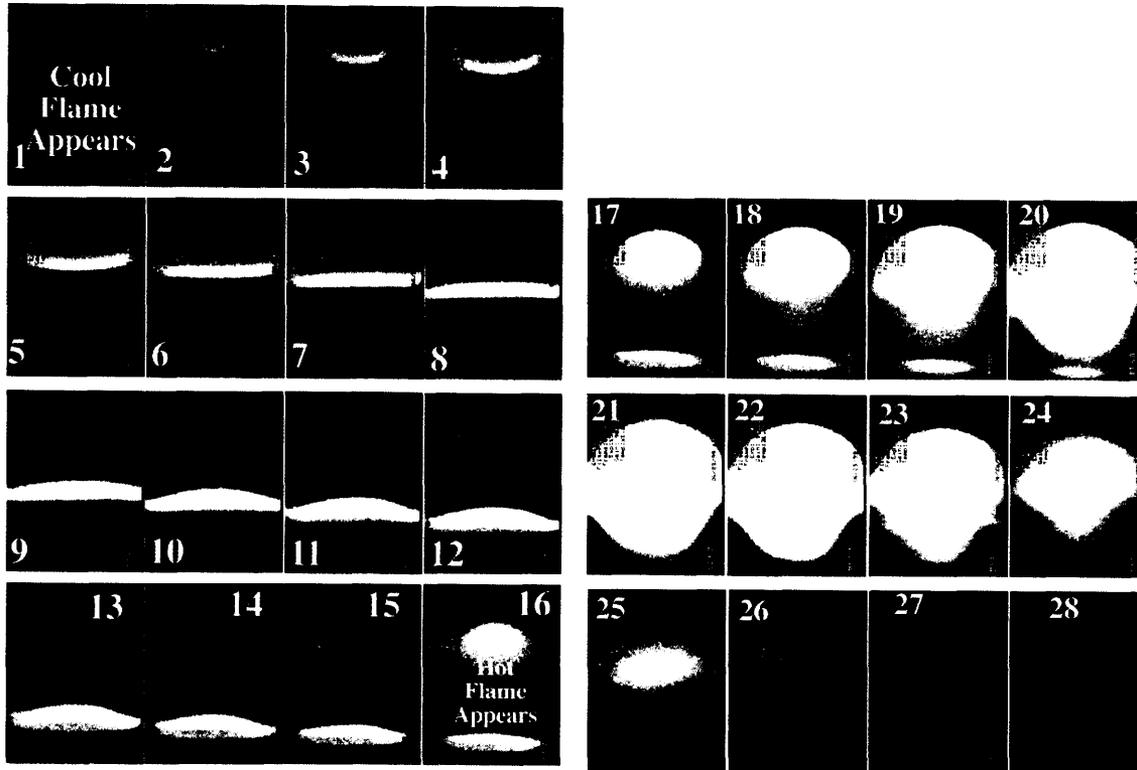


Fig.4: Side Camera View, 30 frames per sec (each frame is 1/30s apart), Multi-Stage Ignition in JP8-Air premixture, 2.5cc JP8-Balance Air, $P_1=7.4$ psia, $T_{\text{vessel}}=250^{\circ}\text{C}$, 10cm fused-silica i.d. vessel, Pressure trace shown in Figs.2a,b

OVERALL CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn:

1. Slow reactions, cool flames and multi-stage ignition may occur at temperatures lower than the classically-defined autoignition temperature. It is important to determine under what conditions (e.g., mixture composition, pressure, and temperature) these different reaction states occur, since slow reactions can transition to cool flames, and cool flames can transition to hot flames (explosions).
2. Slow reactions, cool flames, multi-stage ignitions and autoignitions may occur in mixtures whose compositions are outside of the standard definition of flammability limits. In particular, cool flames and multi-stage ignitions often occur in rich hydrocarbon-air mixtures. In many cases, they occur in mixtures richer than the standard rich flammability limit.
3. It is imperative that the lowest expected autoignition temperature be properly determined. While the ASTM Standard Test Method 659-78 provides general guidance, there are several factors that must be taken into account to ensure that the value of the autoignition temperature is a conservative value. In particular, fuel structure, surface material, surface temperature, stoichiometry, pressure, initial fuel/ air temperature, contact or residence time, surface condition, surface heating rate, surface size, surface orientation [3], and effective gravitational acceleration [9] can affect the measurement and are not well-controlled in the ASTM test methodology.

As stated on page 206 of the ASTM test method [8]:

*“Autoignition, by its very nature, is dependent on the chemical and physical properties **of** the material and the method and test apparatus employed **for** its determination. The autoignition temperature by a given method does not necessarily represent the minimum temperature at which a given material will self ignite in air. The volume **of** the vessel used is particularly important since lower autoignition temperatures will be achieved in larger vessels. ”*

The following recommendations are offered:

4. Obtain data on (1), (2), and (3) for all fuel-air mixtures under ground and possible flight conditions (e.g., large vessels with heat losses representative of ground and flight conditions). Choose the most conservative value of the lowest autoignition temperature (RTT, CFT, or AIT) and then add a factor of safety. If care is not taken in the determination of the lowest possible autoignition temperature, it is impossible to properly determine a safety factor (e.g., 50°F) and decide upon the “highest [tank] temperature that allows a safe margin [1].” For example, if the autoignition temperature is obtained under conditions where the heat losses are much higher than occur in the actual system, the

autoignition temperature will be higher than one obtained in a system with smaller heat loss.

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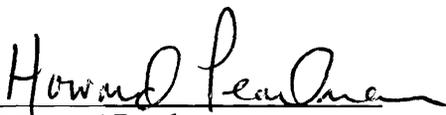
presentation at the Space Technology and Applications Forum-2000, Albuquerque, NM, January 29-February 3, 1999.

We trust that you will take the formentioned suggestions into account in your safety analyses. If you have any questions or comments, please contact us at the following:

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Respectfully yours,


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