Paper # 027IC-0201 **Topic: Spark Ignition**

Fall Technical Meeting of the Western States Section of the Combustion Institute
Hosted by the University of California, Riverside, CA
Oct 17 & 18, 2011.

Statistical Analysis of Spark Ignition of Kerosene-Air Mixtures

Sally P. M. Bane[1], Stephanie A. Coronel[2], Philipp A. Boettcher[2], Joseph E. Shepherd[2]

[1]*School of Aeronautics and Astronautics,*
Purdue University, West Lafayette, Indiana 47907-2045, USA
[2]*Explosion Dynamic Laboratories,*
California Institute of Technology, Pasadena, California 91125-0001, USA

Abstract

Quantifying the risk of accidental ignition of flammable mixtures is extremely important in industry and aviation safety. The concept of minimum ignition energy (MIE), obtained using a capacitive spark discharge ignition source, has traditionally formed the basis for determining the ignition hazard posed by fuels. While extensive tabulations of historical MIE data exist, there has been little work done on ignition of realistic industrial and aviation fuels, such as gasoline or kerosene. In the current work, spark ignition tests are performed in a gaseous kerosene-air mixture with a liquid fuel temperature ranging from 45°C to 65°C, and a fixed spark gap of 3.3 mm. Rather than obtaining a single threshold value of MIE, statistical analysis is performed to obtain a distribution for probability of ignition. The results are compared with previous test results in traditional surrogate mixtures used in safety testing and Jet A (aviation kerosene). In addition, an analytic model is applied to predict the vapor pressure for a range of temperatures, pressures and flash points.

1 Introduction

Assessing the risk of ignition is very important in industry and aviation. The concept of minimum ignition energy (MIE) has traditionally formed the basis for quantifying ignition hazards of fuels. The standard test method used in MIE testing of a given mixture consists of a capacitive spark discharge as the ignition source. Pioneering work to determine MIE values was performed at the Bureau of Mines in the 1940s by Guest, Blanc, Lewis, and von Elbe [1]. However, in aviation, the actual threat is ignition of aviation kerosene (Jet A), which consists of 100-200 hydrocarbons. Nevertheless, it consists of mainly four compounds: paraffins, cycloparaffins, aromatics and olefins [2].

Nestor [3] performed experiments to determine the flammability limits of Jet A in air at atmospheric pressure and pressures corresponding to altitudes of 4572 m and 12192 m. The flammability limits were presented in terms of the temperature range within which there is sufficient vapor pressure of fuel for ignition. Additionally, Nestor [3] investigated ignition of Jet A spray droplets. Ott [4] also studied flammability of aviation kerosene (JP-8) and the effect of fuel slosh on the flammability limits. Following the crash of Trans World Airlines Flight 800 in 1996, a series of studies were performed by Shepherd et al. [5] and Lee and Shepherd [6] on the flammability and ignition energy of Jet A. The minimum ignition energy of Jet A was found to vary between 100 J for a fuel/air temperature of 25°C and 40 mJ for a fuel/air temperatue of 55°C [7]. Despite these previous studies, we still lack a comprehensive database of ignition energy data for use in safety engineering and assessment.

2 Experimental Setup and Results

The experiments are conducted with an experimental setup presented in previous work [7]. The ignition experiments were performed in a closed, cylindrical, stainless steel combustion vessel with a volume of approximately 22 L. Two parallel flanges were used to mount the spark gap electrodes, and the other two flanges held windows for visualization. The gas pressure was measured using a piezoresistive pressure transducer with the output displayed using National Instruments LabVIEW software, and an exhaust line was installed to circulate fresh air through the vessel. A variable-speed fan mixer was used to mix the air and kerosene vapor to ensure homogeneous composition. Kerosene has a very low vapor pressure at room temperature, so to increase the fuel vapor concentration it must be heated. A heating system was designed with the capability to heat the vessel up to a temperature of 150°C. Flexible silicone heaters were mounted on the surfaces of the vessel and the flanges and were divided into four heating zones, each with a separate temperature controller.

Three different methods were used to detect whether or not ignition occurred. First, the pressure rise from the combustion was measured using the pressure transducer. This measurement also allowed us to determine the peak pressure rise in the vessel. Second, the temperature rise was detected using a K-type thermocouple inside the vessel. The third method used to detect ignition was schlieren visualization of the flame propagation recorded using a high-speed camera.

In previous testing with gaseous fuels at room temperature, the vessel was first evacuated and then filled using the method of partial pressures. However, with kerosene or other fuels with low vapor pressures, the experimental method is considerably more complicated. First, the fuel mass loading (mass of liquid fuel divided by the vessel volume) must be chosen to determine the desired volume of fuel. With the vessel at room temperature, the kerosene is then poured into the bottom of the vessel before sealing and heating the vessel. The heating zone at the bottom of the vessel was set to the desired fuel temperature. The other zones were heated to a higher temperature to prevent condensation of the fuel. Once the desired temperature was attained and the fuel vapor and air were sufficiently mixed, a spark with a predetermined stored energy was initiated inside the vessel. If ignition occurred, air was circulated through the vessel and then the lid was removed so that the inside walls and electrodes could be cleaned. After two successful ignitions, the used kerosene was removed and fresh kerosene was introduced to keep the fuel vapor concentration as consistent as possible.

Ignition of kerosene-air mixtures at atmospheric pressure and various fuel temperatures was examined. The tests were performed using 1-K kerosene at fuel temperatures of 45°C, 50°C, 55°C, 60°C and 62°C and at a fuel mass loading of approximately 50 kg/m^3. A fixed spark gap of 3.3 mm was used and the spark energy was varied by changing the discharge circuit capacitance. The capacitance was varied from approximately 11 pF to 68 pF with breakdown voltages between 6.4 kV and 11.4 kV, which yielded possible spark energies from approximately 300 μJ to 2.3 mJ. The results are shown in Figure 1 along with the measured flash point and the gray shaded region which represents the temperature at which ignition was not obtained with the capacitor set at its maximum. By varying the kerosene liquid temperature, the most sensitive mixture was found to be around 55°C. In addition, since sufficient data points were gathered for the 60°C kerosene-air tests, statistical methods [8] were used to derive a probability distribution, as shown in Figure 2. The probability of ignition is shown against the spark energy density, which was obtained by dividing the spark energy by the spark gap length of 3.3 mm.

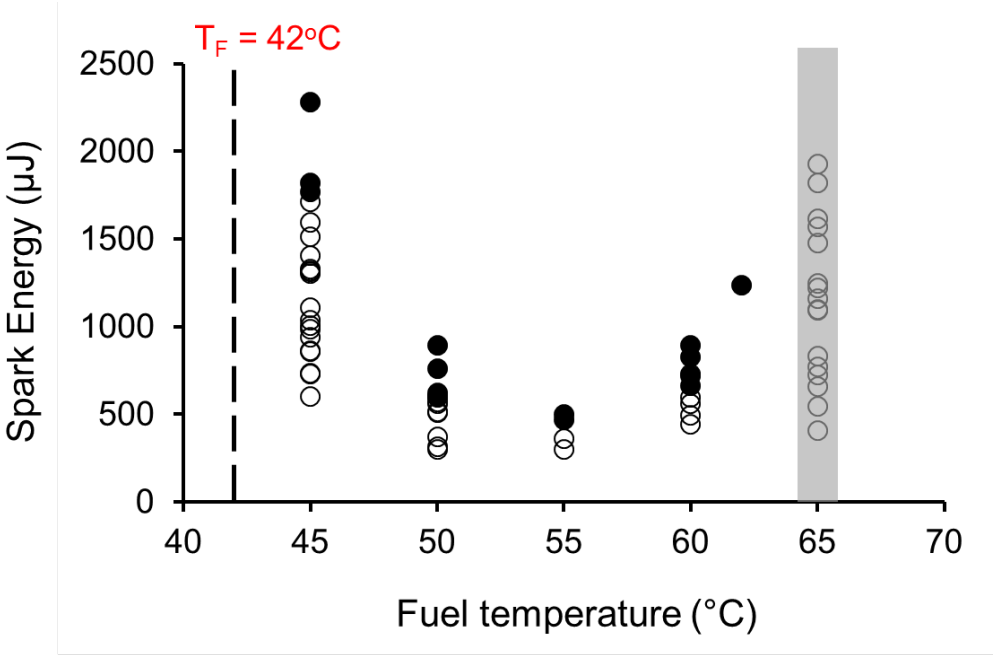

Figure 1: Spark ignition energy for 1-K kerosene-air mixtures at 45°C, 50°C, 55°C, 60°C, and 62°C (approximate location of flammability limits are shaded gray)

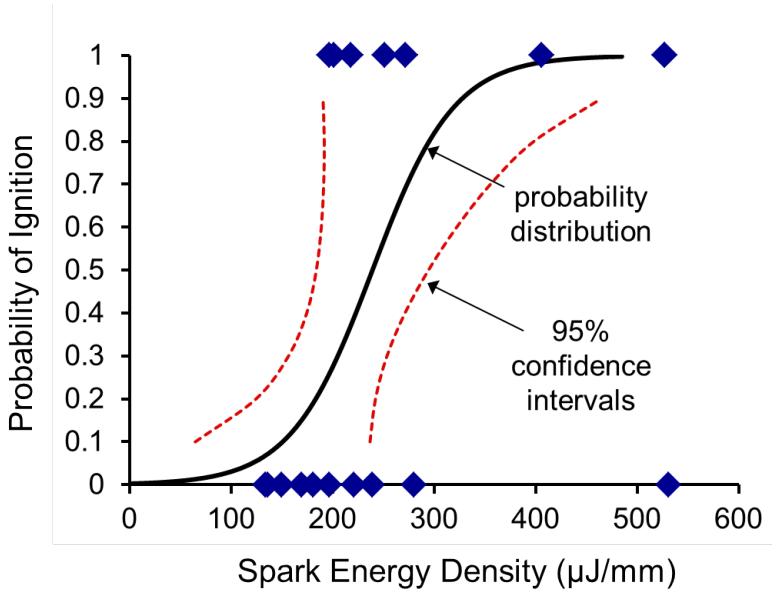

Figure 2: Probability distribution for ignition versus spark energy density for the 60°C kerosene-air mixture

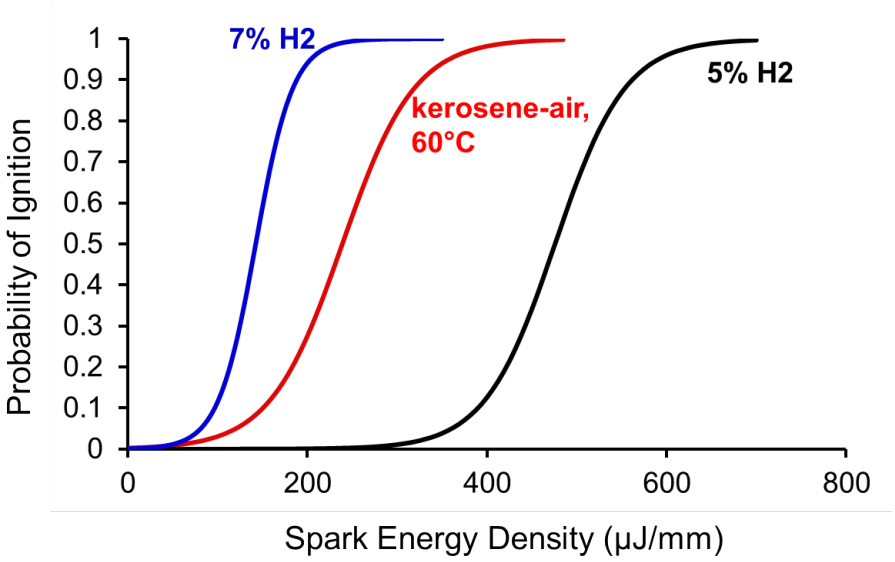

Figure 3: Ignition probability distributions for the 5% H_2 mixture recommended by the SAE for aviation safety testing and a mixture with 7% H_2 [7] compared with the 60°C kerosene-air mixture

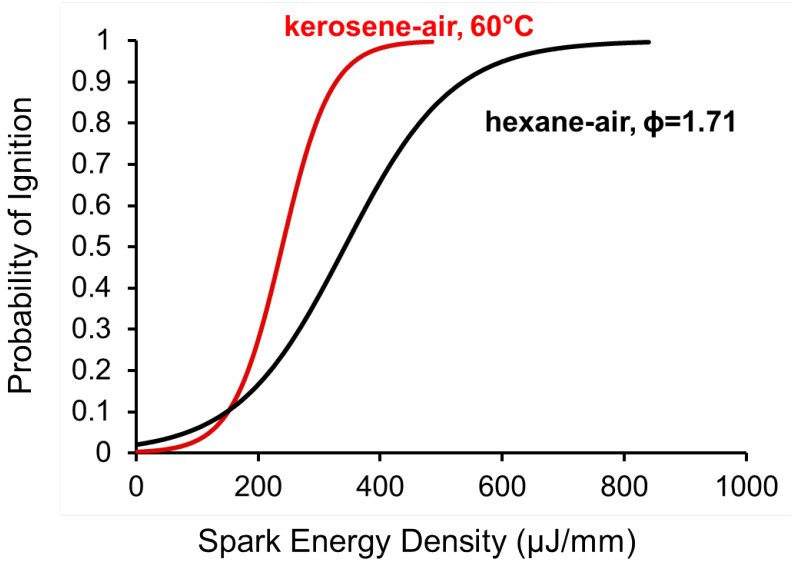

Figure 4: Ignition probability distributions for the hexane-air mixture [7] compared with the 60°C kerosene-air mixture

The current work was then compared with the probability distributions of previous ignition tests in hydrogen and hexane done by Bane et al [7]. A lean hydrogen test mixture recommended by the SAE for use in aviation safety testing [9] (5% H_2, 12% O_2, 83% Ar), as well a mixture with 7% H_2 and the most sensitive hexane mixture with an equivalence ratio of 1.7, were used in the comparison. The probability distributions for the hydrogen test mixtures, compared with the 60°C kerosene-air mixture, are shown in Figure 3, and the hexane mixture compared with the 60°C kerosene-air mixture is shown in Figure 4.

The comparison shows that the kerosene ignition energies of the fuel used in this study are even more sensitive than the 5% H_2 test mixture in terms of the spark energy density required for ignition. Therefore a different test mixture or surrogate fuel must be used for aviation safety testing.

Further testing should be done in this field as there are limited data available on the minimum ignition energies for kerosene-based fuels. It is also necessary to examine how a given set of conditions affects the fuel vapor composition, which we did by implementing an analytic model for pressure prediction, as explained below.

3 Analytic Model for Vapor Pressure Prediction

Aviation kerosene fuels are complex mixtures containing hundreds of hydrocarbons in varying amounts that depend on the refinement process, the crude oil, the time of year and storage conditions [5]. In addition, the vapor composition is different from that of the liquid composition, and is highly sensitive to changes in temperature, pressure and fuel mass loading. There are several methods for characterizing aviation kerosene fuels such as liquid chromatography, distillation curves, and gas chromatography. Although gas chomatography of each batch of 1-K kerosene fuel used in this study is ideal for finding its vapor composition, it is too expensive and laborious; therefore an alternative is needed to obtain the vapor composition. The fuel vapor composition can be found through the liquid fuel composition obtained through the methods mentioned above. Knowing that a kerosene-based fuel consists of hundreds of hydrocarbons, the next step is to model its liquid composition. Two different approaches were found, one by Woodrow [10] who obtained the liquid composition of twelve different kerosene based fuels with varying flash points using a gas chomatograph and another by Thomas [11] who obtained distillation curves for Jet A, Jet B, JP-5 and TS-1. Woodrow's analysis was done by injecting the liquid into a gas chromatograph and using a flame ionization detector to determine the retention times for compounds grouped by the number of carbon atoms [5]. The composition of each fuel was modeled by using sixteen alkane reference standards (C_nH_{2n+2} where *n = 5,6,...20*). In Thomas's analysis, the alkane boiling points were used as a guide to cut the fuel into a number of "buckets" and all species of the same carbon number were placed in the same bucket. Therefore, Thomas's analysis simplified the approach to focus on nineteen buckets rather that several hundred buckets. The ASTM D2887 distillation curve is used to determine the weight of each bucket. Two adjustments were introduced by Thomas to account for the fact that the compounds in any one bucket are not all alkanes. The first was to decrease the hydrogen content as the carbon number is increased, such that C_nH_{2n+c} where

$$c = 2 - 0.25(n-1) \text{ for } n = 1, 2, ..., 19. \quad (1)$$

The second adjustement was made to the "cut temperature" (i.e., the boiling temperature separating each bucket in the distillation curve) to better match the predicted vapor pressure to the actual vapor

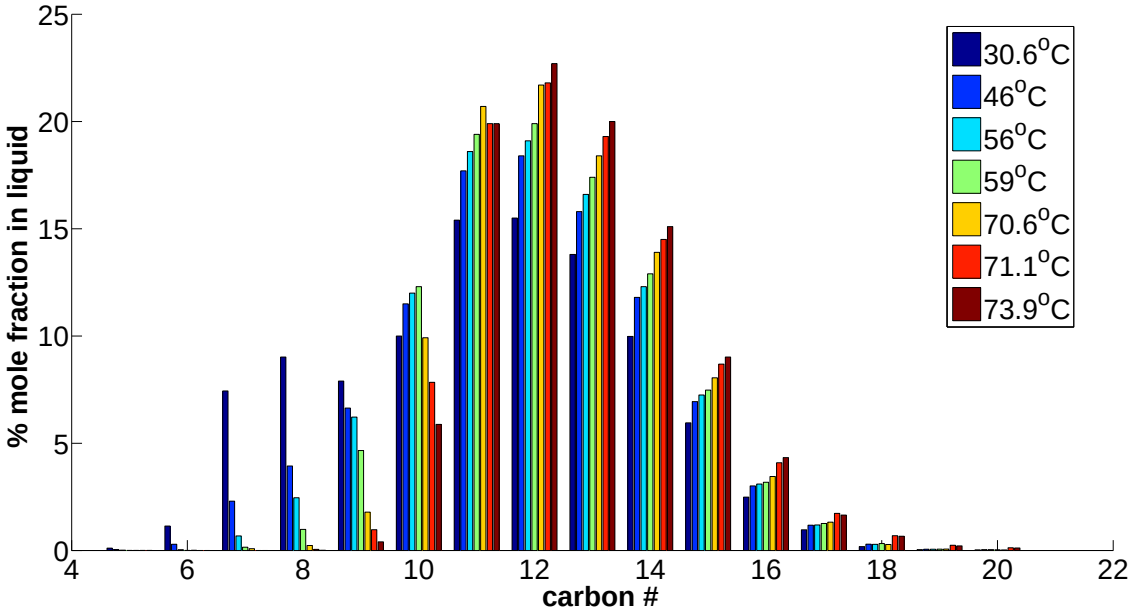

Figure 5: Percent mole fraction of liquid fuel samples [10]

pressure of the fuels analyzed in Thomas's study [11]. Once the liquid composition is known, Woodrow's method for modeling the fuel vapor composition can be applied. In this study, data from Woodrow are used and applied to the ignition energy results. Woodrow provides the liquid composition, shown in Figure 5, for different Jet A fuels formulated to have a range of flash points, shown in Table 1. The flash point is the minium temperature that gives sufficient fuel vapor to form a flammable vapor-air mixture [2]. We can observe that as the flash point is increased, the % mole fraction of the lighter hydrocarbons is decreased. Therefore higher temperatures are required to vaporize the heavier hydrocarbons and cause the mixture to be flammable.

Table 1: Flash point for jet fuel samples [10]

Sample	*Flash Point (°C)*
2.5 wt% OH	30.6
Base Jet A	45.6
97.5 wt% Btm	55.6
95 wt% Btm	59.4
92.5 wt% Btm	64.4
90 wt% Btm	70.6
87.5 wt% Btm	71.1
85 wt% Btm	73.9

Linear interpolation of Woodrow's data is done, allowing us to input any flash point (corresponding to a kerosene based fuel) between 30.6°C and 73.9°C and obtain its liquid composition. We chose to focus on a flash point temperature of 42°C since preliminary investigations indicate that this is

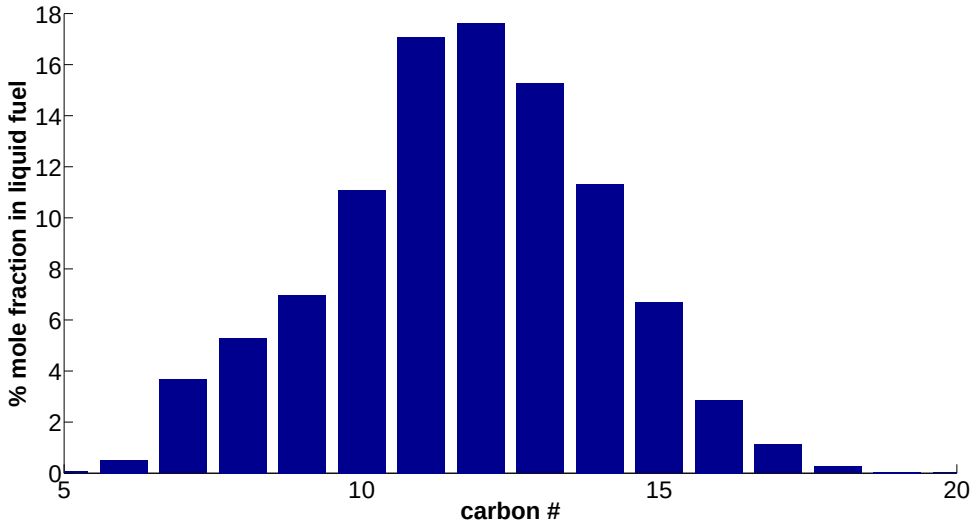

Figure 6: Prediction of percent mole fraction of 1-K kerosene corresponding to a flash point of 42°C

the flash point of the 1-K kerosene used in this study. A prediction of the liquid composition for the 1-K kerosene is shown in Figure 6. The liquid fuel composition of the 1-K kerosene is nearly symmetric across C_{12}, however, there are still more light components than heavy ones.

With the predicted liquid composition of the 1-K kerosene known, the saturation vapor pressures for each subsection hydrocarbon at each temperature used in the ignition tests (45°C, 50°C, 55°C, 60°C, and 62°C) are calculated using the following equations [12],

$$ln(P_{vp}/P_c) = (1-x)^{-1}[Ax + Bx^{1.5} + Cx^3 + Dx^6] \tag{2}$$

$$x = 1 - T/T_c \tag{3}$$

$$ln(P_{vp}) = A - B/T + ClnT + DP_{vp}/T^2 \tag{4}$$

$$ln(P_{vp}) = A - B/[T + C] \tag{5}$$

where *A, B, C* and *D* are taken from Appendix A of Reid et al. [12]. The saturation pressures of the n-alkanes with a carbon number of 5, 6, 7, 8, 9 and 10 are calculated using equations 2 and 3, those with carbon numbers of 11, 12, 14, 15 and 16 are calculated using equation 4 and those with carbon numbers of 13, 17, 18, 19 and 20 are calculated using equation 5. Using Raolt's Law:

$$P_i = X_i P_{vp,i} \text{ for } i = 5, 6, ..., 20 \tag{6}$$

where X_i is the subsection mole fraction of the liquid, the subsection partial pressure of the vapor, P_i, is obtained. The number of moles, n_i, in each subsection of the fuel vapor is then found by applying the ideal gas law:

$$P_i = \frac{n_i R\, T}{V_v} \tag{7}$$

where V_v is the volume of the fuel vapor. The volume of the fuel vapor can be rewritten as the difference between the volume of the vessel, *V*, and the volume of the liquid, V_l, as shown in the next equation.

$$V_v = V - V_l = V - \frac{\sum W_i N_i - \sum W_i n_i}{\rho} \tag{8}$$

In equation 8, W_i is the molecular weight of each hydrocarbon in the fuel, N_i is the number of moles of each hydrocarbon and ρ is the liquid fuel density. Raolt's law does not take into consideration the mass loading when calculating the partial pressure of each subsection, therefore, the expression know as the "headspace equation," shown in equation 9 from Ioeffe and Vitenberg [13], is applied.

$$C_G = \frac{C_L^o}{K + V_v/V_l}. \tag{9}$$

C_G is the concentration in the vapor, $C_L\circ$ is the initial concentration in the liquid, and *K* is the hydrocarbon liquid-vapor distribution coefficient. Equation 9 shows that for a given value of *K*, as V_v/V_l is increased, C_G decreases since the number of moles of each hydrocarbon in the liquid fuel that can be vaporized is decreased. By rearranging the equation, *K* is found to be:

$$K = \frac{C_L^o}{C_G} - V_v/V_l \tag{10}$$

In equation 10, the value of V_v/V_l is 1.2, which corresponds to 45% of a tank filled with liquid fuel. This value is chosen to find *K* since the partial pressures predicted using Raolt's law correspond to the partial pressures of the vapor headspace of the tank volume filled to 45% found by Woodrow using gas chromatography. A fuel mass loading of 50 kg/m^3 was used in the present study, which corresponds to V_v/V_l=13.9. By applying equation 9, the concentration in the fuel vapor can be found. Knowing the concentration in the vapor, the fuel to air ratio and equivalence ratio can be found. Taking the ignition energy data of this study, plots can be made of ignition energy versus equivalence ratio, ϕ, and the fuel-to-air ratio, *f:a*, as shown in Figures 7 and 8. The figures are predictions of what ϕ and *f:a* will be; however, in the future a more thorough analysis should be performed that uses the liquid mole fractions of the 1-K kerosene obtained through gas chromatography or a distillation curve rather than an estimate obtained through linear interpolation. The most sensitive mixtures occur at an equivalence ratio of 1.96 which corresponds to a fuel-to-air ratio of 0.08.

Finally, the effect of mass loading on subsection partial pressure can be predicted in Figure 9. We can see that mass loading only has an effect on pressure for low mass loadings. However, a steady value for pressure is reached as mass loading is increased. As the mass loading increases,the vapor pressure of the lighter hydrocarbons is increased significantly, as shown in Figure 10, and as temperature increases, the vapor pressure of each hydrocarbon is noticeably increased, as shown in Figure 11. For low mass loadings, the lighter hydrocarbons are scarce in the liquid fuel. As the mass loading increases, more lighter hydrocarbons are added to the liquid fuel that can be evaporated which is why the vapor pressure for the lighter hydrocarbons has a significant incrase. For example, for heptane we can see an increase in the vapor pressure of 1.25 mbar from 3 kg/m^3 to 50 kg/m^3 and only a 0.05 mbar increase from 50 kg/m^3 to 100 kg/m^3. As temperature increases, more of the hydrocarbons will evaporate since the saturation vapor pressure increases, thereby increasing th partial pressure of the fuel. We can also observe that the fuel vapor blend peaks

at C_7, corresponding to heptane. Finally, Figure 12 shows the effect of flash point on the fuel vapor composition for a fixed fuel temperature and mass loading. As the flash point increases, the lighter hydrocarbons are fewer and the heavier hydrocarbons are dominant in the fuel vapor. This is attributed to the fact that the initial liquid composition contained fewer lighter hydrocarbons for the higher flash point.

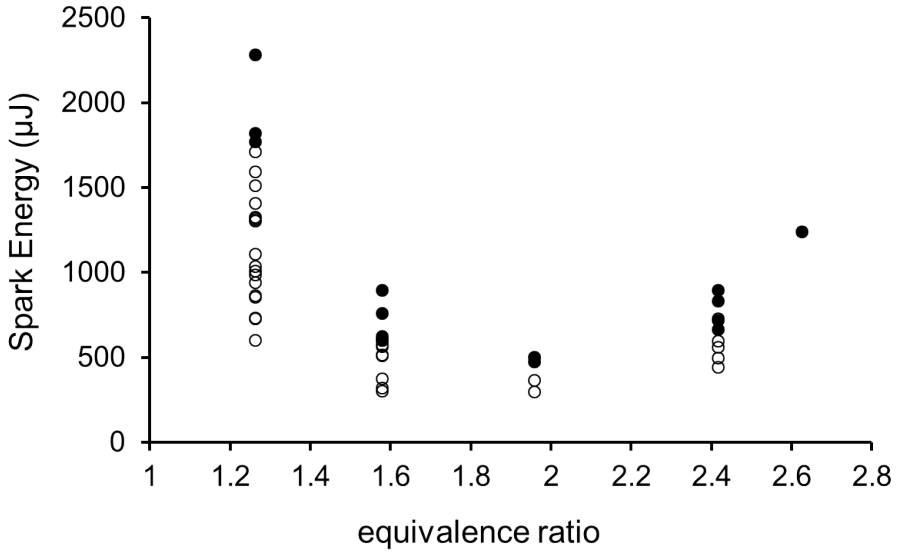

Figure 7: Spark ignition energy for 1-K kerosene-air mixtures versus predicted equivalence ratio

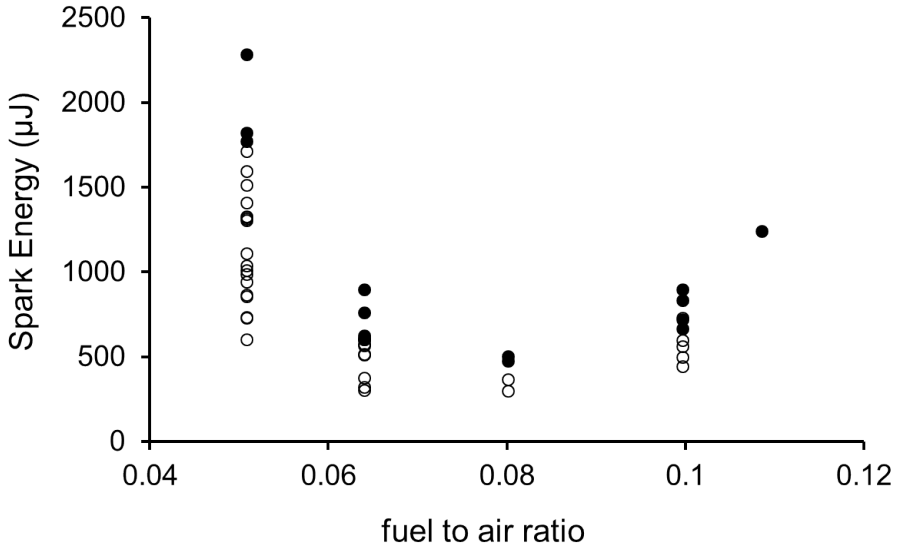

Figure 8: Spark ignition energy for 1-K kerosene-air mixtures versus predicted fuel to air ratio

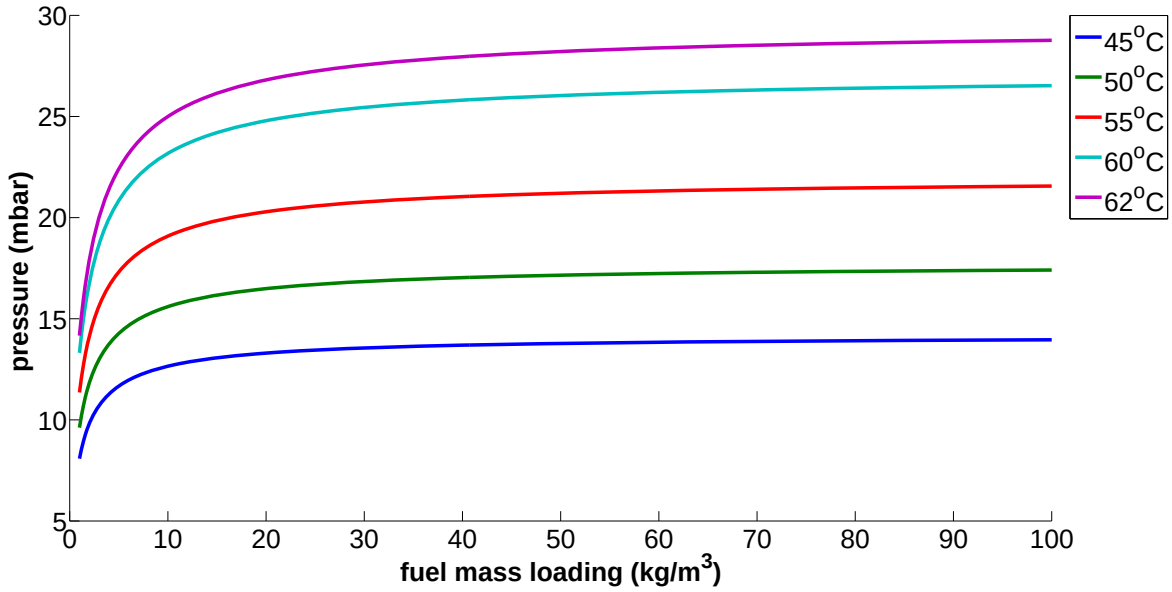

Figure 9: Effect of mass loading on pressure for 1-K kerosene corresponding to a flash point of 42°C for various fuel temperatures

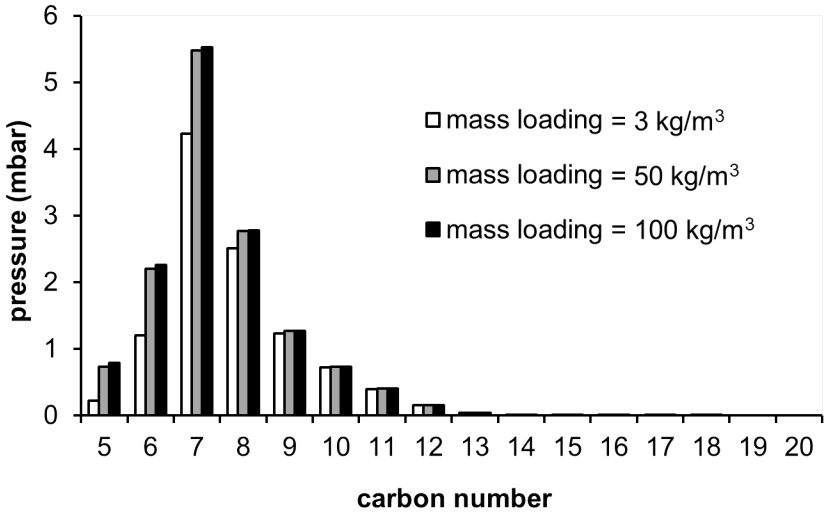

Figure 10: Effect of mass loading on vapor pressure of each n-alkane for a flash point of 42°C at a fuel temperature of 45°C

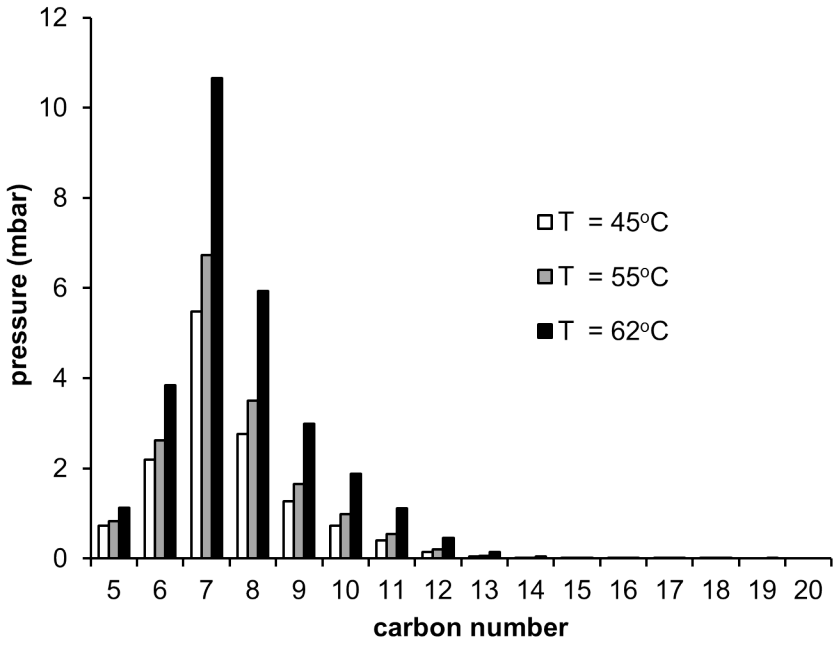

Figure 11: Effect of temperature on vapor pressure of each n-alkane for a flash point of 42°C at a mass loading of 50 kg/m^3

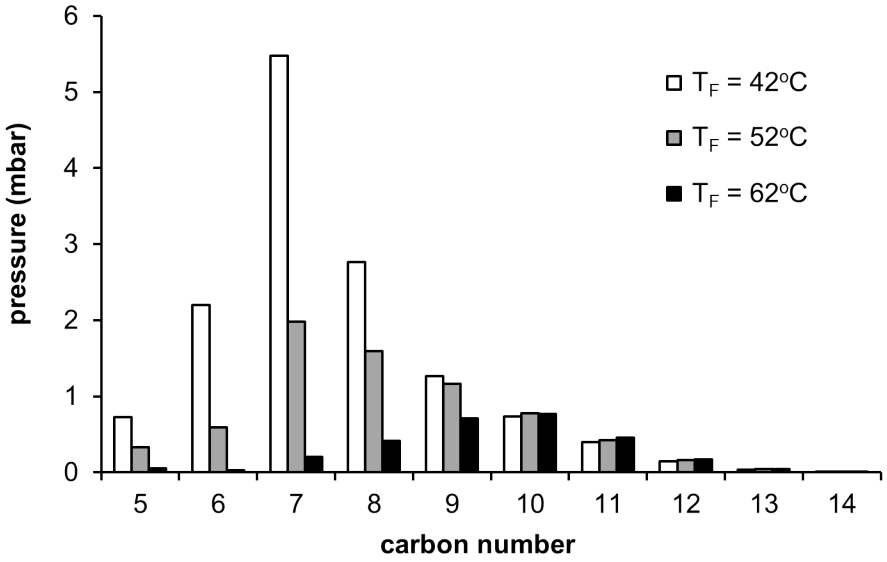

Figure 12: Effect of flash point on vapor pressure of each n-alkane for a fuel temperature of 45°C at a mass loading of 50 kg/m^3

4 Concluding Remarks

Ignition experiments were carried out for a 1-K kerosene-air mixture at different fuel temperatures and it was determined that the most sensitive mixture was a 55◦C kerosene-air mixture. Comparisons were made with previous ignition tests in hydrogen and hexane [7], which showed that the 55◦C kerosene-air mixture is more sensitive than the most sensitive hexane mixture and the current mixture used by the SAE for use in aviation safety testing [9] (5% H_2, 12% O_2, 83% Ar). We also introduced a model to obtain a better understanding of the fuel vapor composition given changes in flash point, temperature, pressure and fuel mass loading. We have determined that it is possible to model a complex hydrocarbon mixture under a given set of conditions through the use of Raolt's law and the "headspace equation" [10]. Knowing the composition of the fuel vapor allows us to better undestand how a kerosene based fuel can be compared with a simple hydrocarbon or a binary mixture. We observed earlier that the fuel blend was dominated by heptane; therefore, in future studies we can determine whether a hydrocarbon such as heptane—which is well studied—can be used as a surrogate in kerosene fuel studies. Also, a continuing goal of this study is to develop a model for minimum ignition energy prediction given a fuel-air composition, temperature and pressure. The fuel-air composition would be obtained from the analytic model for vapor pressure prediction for a given flash point, temperature, pressure and mass loading. Based on a review of the applicable literature, models of MIE prediction are functions of, among other variables,the laminar burning speed and flame temperature, both of which can be obtained through Cantera or Chemkin; therefore it is imperative to use a simple hydrocarbon such as heptane. Finally, further ignition tests are needed to understand the combustion characteristics of a kerosene based fuel, such as the laminar burning speed, and to see how it compares with those of a simple hydrocarbon.

5 Acknowledgements

The experimental work was carried out in the Explosion Dynamics Laboratory of the California Institute of Technology and was supported by the Boeing Company through a Strategic Research and Development Relationship Agreement CT-BA-GTA-1.

References

[1] B. Lewis and G. von Elbe. *Combustion Flames and Explosions of Gases*. Academic Press, NY, 1961.

[2] I. Sochet, J. M. Pascaud, and P. Gillard. *J. Phys. IV Fance*, 12 (2002) 429–435.

[3] L. Nestor. Investigation of turbine fuel flammability within aircraft fuel tanks. Final report ds-67-7, Naval Air Propulsion Test Center, Philadelphia, PA, 1967.

[4] E. Ott. Effects of fuel slosh and vibration on the flammability hazards of hydrocarbon turbine fuels within aircraft fuel tanks. Tech. rep. afapl-tr-70-65, Fire Protection Branch of the Fuels and Lubrication Division, Wright-Patterson Air Force Base, Oh, OH, 1970.

[5] J. E. Shepherd, C. Krok, and J. J. Lee. Spark ignition energy measurements in jet a. Galcit report fm97-9, Graduate Aerospace Laboratories, California Institute of Technology, Pasadena, CA, 1999.

[6] J. J. Lee and J. E. Shepherd. Spark ignition measurements in jet a: part ii. Galcit report fm99-7, Graduate Aerospace Laboratories, California Institute of Technology, Pasadena, CA, 2000.

[7] S. P. M. Bane, J. L. Ziegler, P. A. Boettcher, S. A. Coronel, and J. E. Shepherd. *Journal of Loss Prevention in the Process Industries*, (2011) journal. In press.

[8] S. P. M. Bane, J. E. Shepherd, E. Kwon, and A. C. Day. *International Journal of Hydrogen Energy*, 36 (2010) 2344–2350.

[9] ARP. Aerospace recommended practice aircraft lightning test methods. Arp5416, SAE International, 2005.

[10] J. E. Woodrow. The laboratory characterization of arco jet fuel vapor and liquid. Final report for ntsb, Center for Environmental Sciences and Engineering, University of Nevada, Reno, NV, 2000.

[11] I. Thomas. Fuel air ratio calculator.

[12] J. M. Prausnitz R. C. Reid and B. E. Poling. *The Properties of Gases and Liquids*. McGraw-Hill, New York, 1987.

[13] B. V. Ioffe and A. G. Vitenberg. *Head-Space Analysis and Related methods in Gas Chromatography*. John Wiley & Sons, New York, 1984. Traslated from russian by I. A. Mamantov.