

FINAL TECHNICAL REPORT

FOR NASA GRANT NAG3-2338

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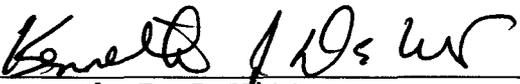
CHEMISTRY OF AVIATION FUELS

Prepared for

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Cleveland, Ohio 44135

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Submitted September, 2004
for the period
4-11-00 to 4-4-04

Chemistry of Aviation Fuels

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Abstract

Minimum ignition energies of various methanol/air mixtures were measured in a temperature controlled constant volume combustion vessel using a spark ignition method with a spark gap distance of 2 mm. The minimum ignition energies decrease rapidly as the mixture composition (equivalence ratio, ϕ) changes from lean to stoichiometric, reach a minimum value, and then increase rather slowly with ϕ . The minimum of the minimum ignition energy (MIE) and the corresponding mixture composition were determined to be 0.137 mJ and $\phi = 1.16$, a slightly rich mixture. The variation of minimum ignition energy with respect to the mixture composition is explained in terms of changes in reaction chemistry.

Introduction

On July 17, 1996, an international passenger flight, Trans World Airlines, Inc. Flight 800 (TWA 800), a Boeing 747-131, from John F. Kennedy International Airport, New York, to Charles DeGaulle International Airport, Paris, crashed into the Atlantic Ocean near East Moriches, New York. The airplane was destroyed and all 230 people on board perished. Investigation by the National Transportation Safety Board (NTSB) indicated that the probable cause of the TWA Flight 800 accident was an explosion of the center wing fuel tank (CWT). [1] Although the source of the ignition energy for the explosion could not be determined with certainty, the most likely cause was a short circuit outside the CWT that allowed excessive voltage across the electrical wiring, causing either heat build-up or spark ignition.

The NTSB investigation of the TWA Flight 800 accident rekindled interest in the measurement of minimum ignition energy (MIE) of aircraft fuels by electrical spark or by other means.[2-4] The MIEs of various gases have been measured by Lewis and von Elbe using a spark ignition method in order to produce crucial information for the prevention of mine explosions.[5-7] Lewis and von Elbe measured MIEs of various fuels (hydrogen, methane, ethane, propane, butane, heptane, hexane and diethyl ether) in a spherical reactor as a function of fuel stoichiometry, pressure, and distance between the spark electrodes.[7] For methane/air mixtures, quenching distances were also measured.[7] Recently, Lee et al.[4] measured MIEs of fuel/air mixtures of propane, dodecane and jet-A fuel over various ranges of pressure and equivalence ratio using laser sparks. At pressures of 1 atmosphere or less, the MIEs of propane/air mixtures from laser sparks were larger than those from electrical sparks measured by Lewis and von Elbe. When dodecane ($C_{12}H_{26}$) was used, a non-isotropic flame propagation phenomenon was observed. For jet-A fuel, the ignition energies showed a similar parabolic trend in terms of equivalence ratio at a given pressure as observed by Lewis and von Elbe in gas phase fuels and in liquid diethyl ether. At elevated pressures, a shift of the ignition energy curve to a higher equivalence ratio was observed. A fuel loading (fuel concentration) effect on the ignition characteristics was also noticed. However, the pressure effect on

MIE became less discernible as the fuel was varied from propane and dodecane to jet-A fuel.

Although considerable advances have been achieved in understanding ignition characteristics through MIE measurement for jet-A fuel, the results are not sufficiently conclusive to be applicable to a practical system: Firstly, jet-A fuel is a mixture of over 200 chemical species, controlled only by defined boiling point ranges.[8,9] I.e., the concentrations of the component species vary with the origin of the jet-A fuel. Thus it is conceivable that one could obtain different MIEs of jet-A fuels depending upon their origin. Secondly, for the application of MIE data of jet-A fuel in the prevention of aircraft fuel tank explosion, one needs to consider the usefulness of the MIE values from electrical spark ignition or laser spark ignition—obviously the MIE value from electrical spark ignition is the more valuable engineering parameter in a practical sense.

In this study, because of the reasons described above, we planned to measure MIEs of a series of fuels in an *ab initio* sense using electrical spark ignition. In other words, instead of using a jet-A fuel of a certain origin, a synthetic jet-A fuel was designed with exactly the same amount of major components. The MIEs of each component were to be measured first and then those of the synthesized jet-A fuel next. In the first set of experiments that are reported here, methanol (CH_3OH) was selected as a test fuel because it is an abundant and simple fuel and is in the same phase of jet-A fuel at the standard state (liquid). We report the experimentally measured MIE values of methanol below.

Experimental Section

A. Apparatus

(a) Combustion Vessel

A spherical combustion vessel was fabricated using SS 304 stainless steel (see Figure 1(a) -(c)). The 2-liter vessel is split into two equal-volume hemispheres. It has two glass (quartz) framed portals and eight penetrations. The portals, located at the apex of each hemisphere, are for viewing the propagation of the spark and the combustion wave via high-speed camera. The purpose of the penetrations are: one for gas input (O_2 , N_2 and purge gas Ar); one for exhaust; one for liquid fuel input or manual exhaust; two for pressure transducers and/or thermocouples; and three for electrodes. The two hemispheres are held together by eight riveted screws. The completely assembled combustion vessel was pressure tested up to 200 psig in compliance with NASA safety requirements.

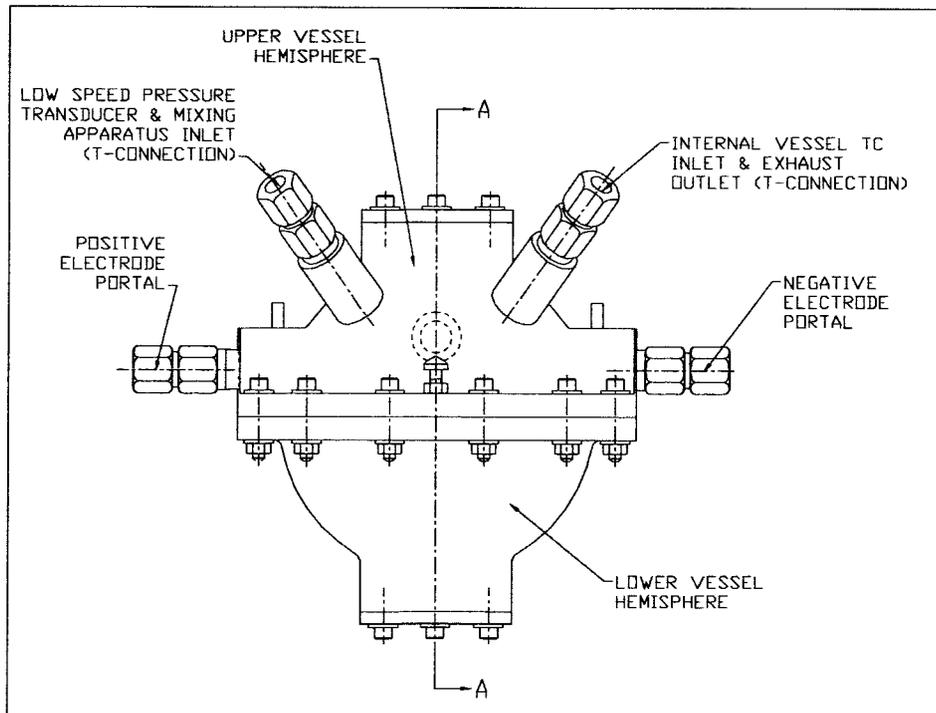


Figure 1(a). Combustion Vessel Schematic (Side View)

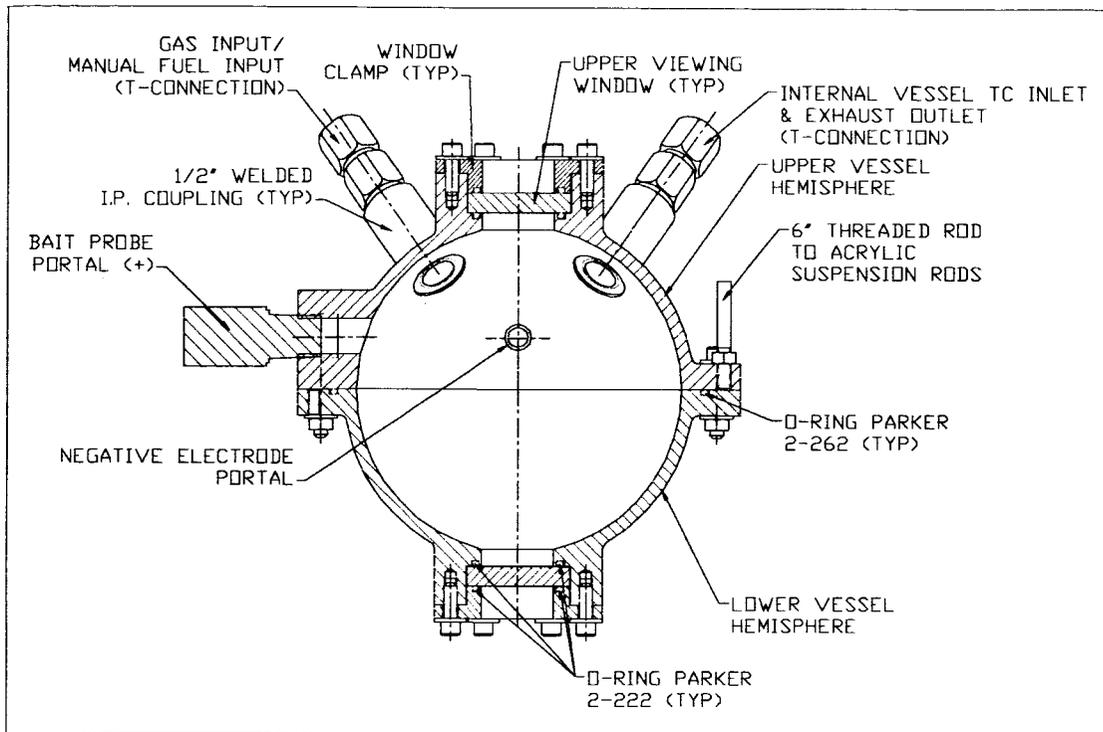


Figure 1(b). Combustion Vessel Schematic (Section A-A)

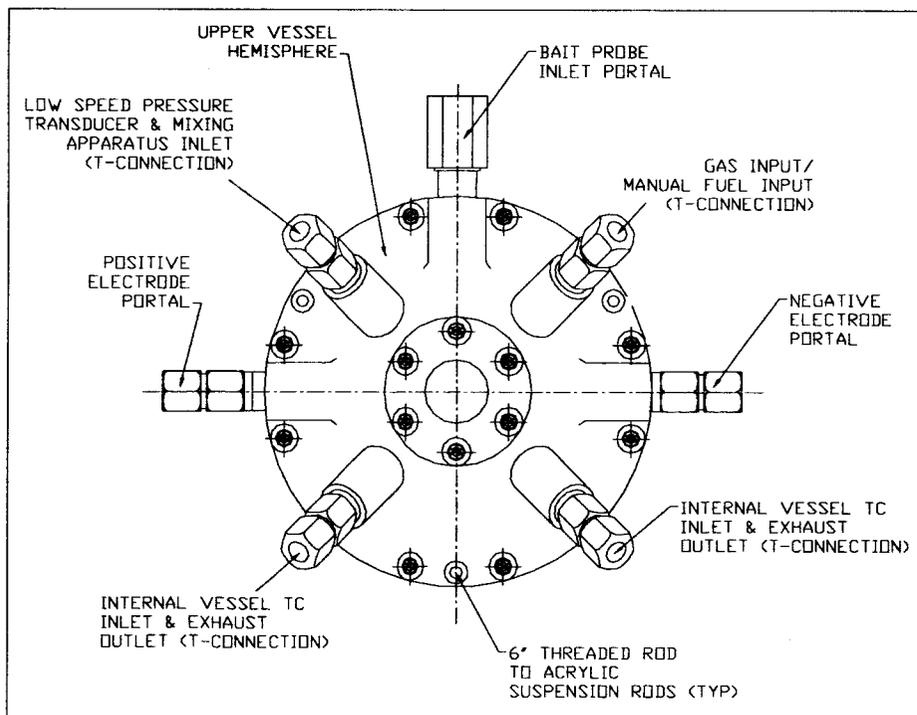


Figure 1(c). Combustion Vessel Schematic (Top View)

(b) Ignition circuit

The ignition circuit diagram is shown in Figure 2. The three electrodes (anode, cathode and bait electrode) are arranged such that each electrode tip is located at the apex of the isosceles (Figure 3). Before the initiation of the major electrical spark (dc-arc) between the cathode and anode, an ionization voltage (breakdown voltage) was applied to the bait electrode to create the electric charge cloud (plasma) which facilitates the smooth later propagation of the dc-arc from the cathode to the anode. The voltage to the ignition electrodes was supplied by a Thorn EMI PM28B high voltage power supply. The main components of the ignition circuit are a capacitor (C2) and a resistor (R4). During the experiments, the ignition energies (dc-arc discharge energy with a fixed breakdown energy) were supplied by the systematic variation of the current, resistance, and supply voltage.

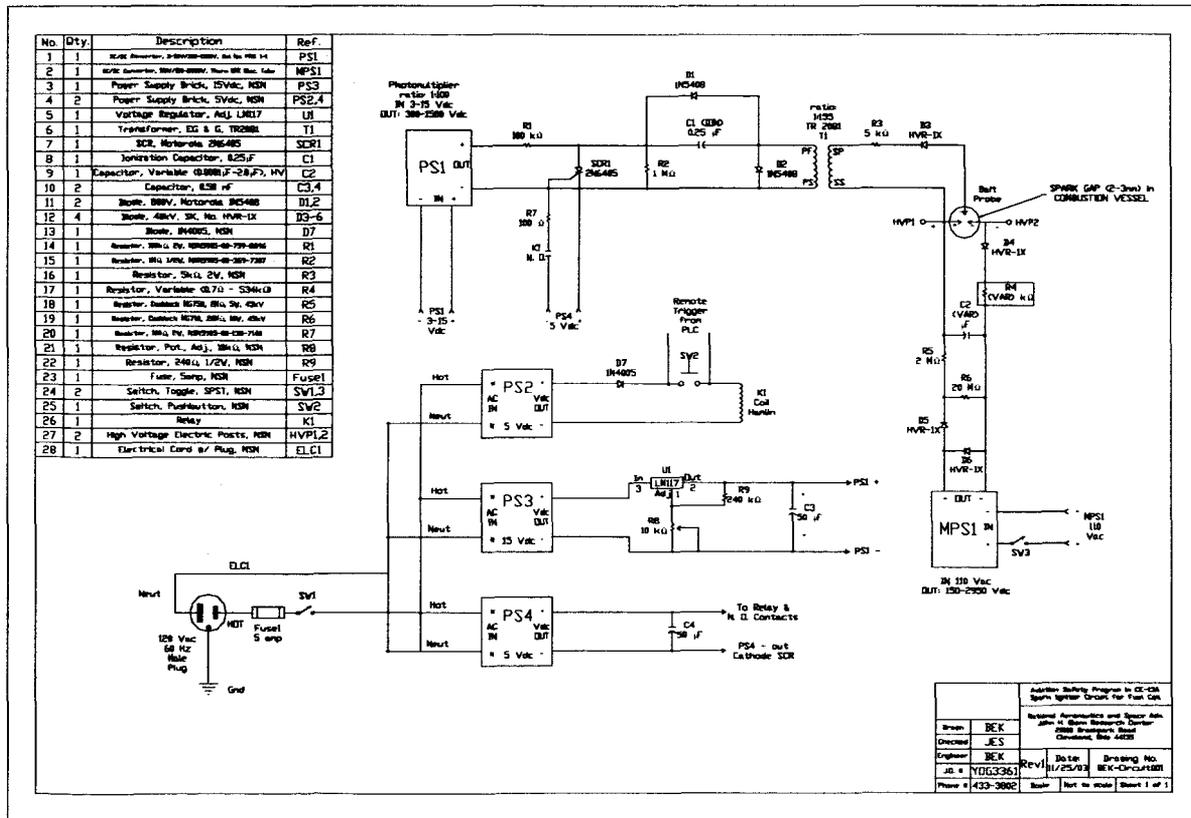


Figure 2. Ignition Circuit

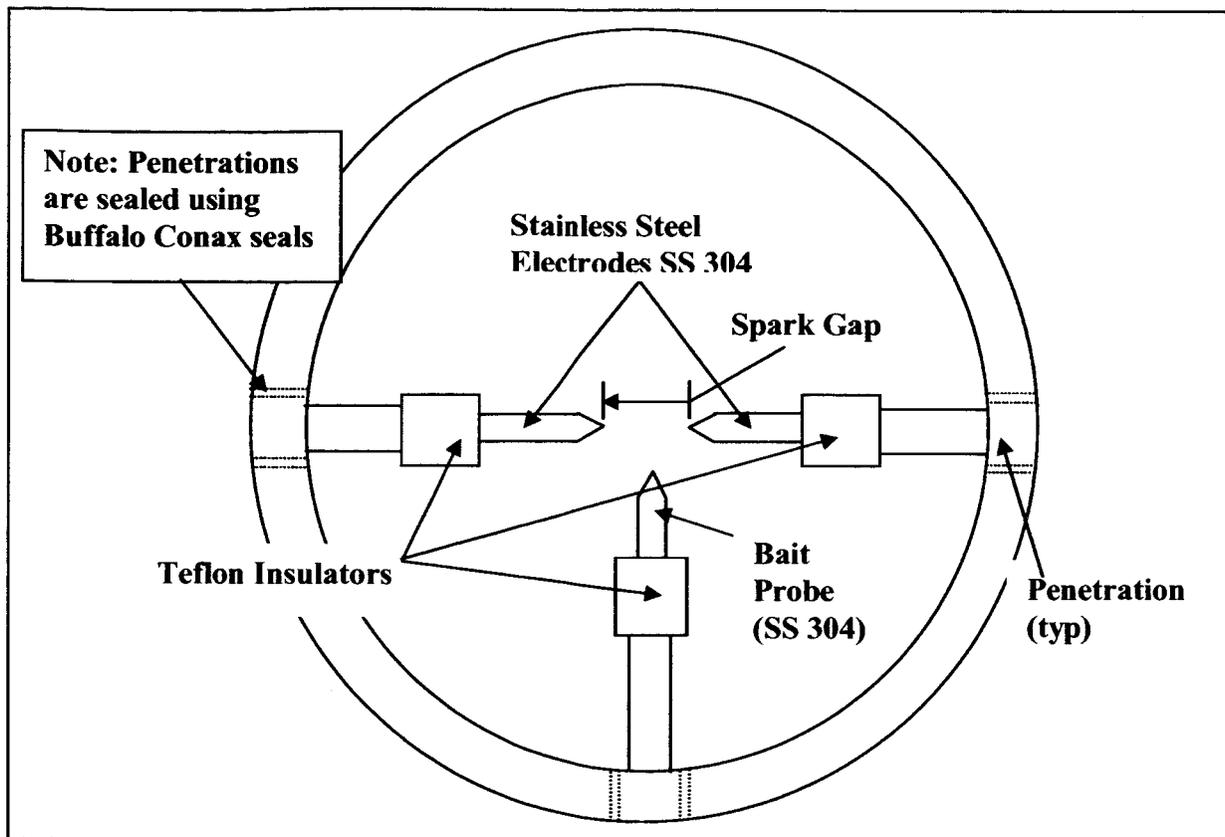


Figure 3. Electrode Configuration (Top View)

(c) Electrode material

For the spark electrode material, copper (Cu), nickel (Ni), tungsten (W), and stainless steel (SS) were considered. Previously Lewis and von Elbe [7] and Calcote et al. [10] used stainless steel while Ko et al. [11] used nickel as the electrode material. Since the cathode becomes very hot during dc-arc discharge, the candidate material must possess a high melting and boiling point, and low electrical resistivity.[12] Based upon the electrical, physical, and material properties (see Table 1) and the previous usage by other investigators, tungsten and stainless steel were selected for consideration—stainless steel has properties similar to nickel.

Table 1. Electrode Material Properties ^a

Material	Melting Point (°C)	Boiling Point (°C)	Specific Heat (cal/g °C)	<i>k</i> at 20°C (cal/cm sec °C)	ρ at 20°C ($\mu\Omega$-cm)	Hardness HV or HB
Cu	1084	2560	0.092	0.940	1.694	35(V)
Ni	1455	2910	0.104	0.210	6.9	45(V) 85(B)
W	3410	5555	0.032	0.400	5.4	262(B) as wire
SS 304 ^b	1399	2500	0.200	0.186	7.2	201(V)

^a Buch, A. "Pure Metals Properties: A Scientific-Technical Handbook," ASM International; Materials Park, Ohio, 1999.

^b Composition of SS 304 (71% Fe, 18% Cr, 10.5% Ni, 2% Mn); www.MatWeb.com, 2004.

Wires of various diameters were cut and mounted as electrodes, and the tips were shaped to be pointed or rounded. Spark tests were then performed for reliability. After several spark tests, the electrodes were examined visually for any damage. A "Phantom" high-speed camera system was employed to locate exactly where the spark occurred. It was found that pointed tip electrodes gave the best results for generating "point to point" sparks. Tungsten electrodes showed that, while sparking occurred in a consistent manner, the electrode itself was hard to maintain. After high energy sparks, metal pieces were chipped off of the electrodes causing the spark to deviate from the "point to point" arc. Overall, stainless steel was found to be the best material for repeatability and low maintenance. Thus, stainless steel electrodes with pointed tips were selected and used in this work. Three 50 mil diameter electrodes were secured by cylindrical teflon insulators inside the vessel.

(d) Temperature control system

A key component of the experimental apparatus is the temperature control system of the combustion vessel since the equivalence ratio of the methanol/air mixtures was determined using the vapor pressure of methanol at a given temperature (*vide infra*). The temperature control unit used is a Julabo FP-50-HP, which has a programmable range of -50~200°C with a temperature stability of 0.01°C. For maintaining the combustion vessel at a prescribed temperature, an in-house thermostatic bath was built and was insulated with polyurethane foam. Four heat exchanger units connected to the Julabo FP-50-HP were placed inside the thermostatic bath. For the heat conducting media, air was used instead of ethylene glycol in order to avoid rather long heating/cooling times and spillage. Air was circulated inside the bath by four electrical fans installed behind each of the heat exchange units. The temperature inside the combustion vessel was measured with a type-J thermocouple having an accuracy of 0.1°C.

(e) Data acquisition system

Two 4-channel Tektronix TDS-3014B oscilloscopes were used for data acquisition. Channel 1 of the first oscilloscope (TDS 1) monitors the current profile (I), while Channel 2 follows the voltage supplied (V) across the spark gap. The power signal ($V \cdot I$) was displayed on Channel 3. A MATH function was utilized to compute the spark energy supplied to the ignition electrodes (*vide infra*). The second oscilloscope (TDS 2) displayed the pressure change after ignition. Either the breakdown voltage or the current signal from the ionization circuit was used as a trigger source for both oscilloscopes.

A current probe (Tektronix A-6303), followed by a current probe amplifier (Tektronix AM-503B), was utilized for current measurements. Actually, the current was converted to voltage and displayed on Channel 1 of TDS 1. Current-to-voltage conversion was achieved by passing the current through a selected resistor having a known resistance. A (1/1000)X voltage probe (Tektronix P6015A) was used in the voltage measurement.

In a composite spark system such as used in this study, the electrical energy supplied across the spark electrodes is

$$E = 1/2[C_b \cdot V_b^2] + \int_0^\tau P(t) dt = 1/2[C_b \cdot V_b^2] + \int_0^\tau (V_g(t) \cdot I_g(t)) dt$$

where C_b is the capacitance between the electrodes, V_b is the breakdown voltage, τ is the dc-arc discharge duration time, and $V_g(t)$ and $I_g(t)$ are the dc-arc discharge voltage and current across the electrode gap, respectively. The breakdown energy ($1/2[C_b \cdot V_b^2]$) provided by our ionization circuit through the bait, cathode, and anode electrodes was 0.07 mJ. The dc-arc discharge energy ($\int_0^\tau (V_g(t) \cdot I_g(t)) dt$) was calculated using the MATH function supported by Tektronix (*vide ante*).

Pressure was measured using a pressure probe (PCB 123) located at one of the penetrations in the top hemisphere of the reaction vessel. The pressure signal from this probe, displayed on TDS 2, was used for routine confirmation of the ignition event. The current, voltage, power, and pressure traces were transferred to a laboratory computer and also stored on disks for further analysis.

(f) Control system for experimental measurement and gas handling

Figure 4 shows a schematic of the gas handling system for feeding Test Air to the combustion vessel, exhausting reaction products after an experiment, and refreshing the combustion vessel for a new set of experiments by purging with N_2 or Ar. The pneumatic valves, gas flow meters, exhaust valves, and ignition circuit were all controlled by a laboratory PC using a Programmable Logic Control (PLC). The PLC allows for operation by touch screen monitors. The “Wonderware” software employed by the PLC uses Logic Blocks to instigate a “chain of command” system. In short, when a gas feed valve is opened on the touch screen, a logic block is opened for commands following it to occur. A signal is then sent to the valve to open. The control of the feed gas flow requires another logic block and a separate touch screen command. There are several available “Modes” in the “Wonderware” software—“Safe Mode,” “Test Mode,”

and “Emergency Stop,” which enable the safe operation of the test equipment. For example, it is not possible to energize the ignition circuit without obtaining an approval from an appropriate monitor on the touch screen. The pressure, status of the ignition circuit, and all gas flows are monitored by the PLC and are displayed instantaneously on the touch screen monitors.

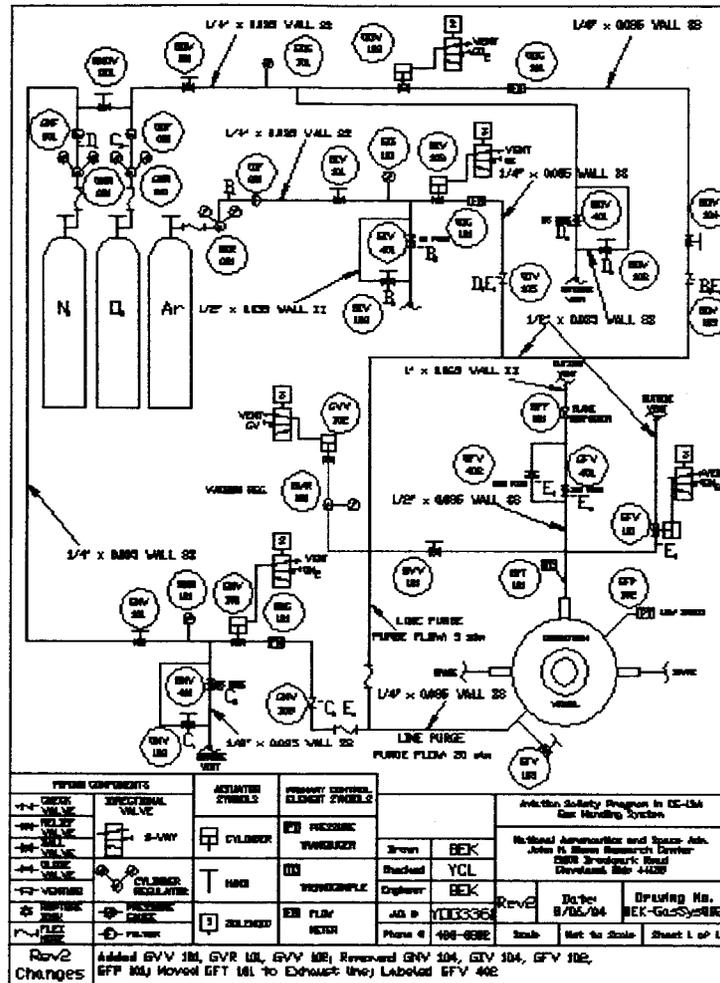


Figure 4. Gas Handling System

B. Preparation of fuel/air mixtures

Methanol (CH₃OH) was used in this study for MIE measurement. Since methanol is a liquid fuel, the equivalence ratio of the methanol/air mixture was determined using the vapor pressure of methanol in the reaction vessel at a given temperature. In the

calculation of the vapor pressure of methanol, the Clausius-Clapeyron equation could be used,

$$P = P^* \exp\left[\frac{-\Delta H_{\text{vap,m}}}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)\right]$$

where T^* is the boiling point of methanol (337.8 K), P^* is the vapor pressure of methanol at the boiling point (760 mmHg), $\Delta H_{\text{vap,m}}$ is the molar enthalpy of vaporization of methanol (35.278 kJ mol⁻¹), and R is the universal gas constant (8.314 J mol⁻¹ K⁻¹). However, because several assumptions made in the derivation of the Clausius-Clapeyron equation cause the equation to fail in accurately predicting vapor pressure at high pressures and/or near the critical point, the Antoine equation with 3 Antoine coefficients was used from the compilation of Ohe [13]:

$$\log_{10} P = A - \frac{B}{T+C}$$

where $A = 8.07717$, $B = 1578.433$, and $C = 239.247$. The unit of P is mmHg and T is °C. The vapor pressure of methanol at a given temperature can be obtained from the web search machine "Google" using the key word "vapor pressure of methanol."

Preparation of the methanol/air mixture followed certain steps. The combustion vessel containing about 20 mL of methanol is placed in the thermostatic bath at a given temperature setting, and the methanol vaporized at the given temperature. After a sufficient time is allowed for the methanol vapor to equilibrate with the air, the combustion vessel is then isolated and the mixing fan inside the reaction vessel is run for complete mixing. Since the MIE of a fuel is strongly dependent on the equivalent ratio (ϕ), we describe here how to calculate ϕ values of methanol/air mixtures at a given temperature. The definition of ϕ is

$$\phi = \frac{[\text{fuel}/\text{O}_2]_{\text{actual}}}{[\text{fuel}/\text{O}_2]_{\text{stoichiometric}}}$$

For methanol, $[\text{fuel}/\text{O}_2]_{\text{stoichiometric}} = 2/3$ because $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$. For calculation of $[\text{fuel}/\text{O}_2]_{\text{actual}}$, partial pressures of methanol and O_2 are used, i.e., $[\text{fuel}/\text{O}_2]_{\text{actual}} = [p(\text{CH}_3\text{OH})/p(\text{O}_2)]_{\text{actual}}$. The $p(\text{CH}_3\text{OH})$ (mmHg) at a given temperature is calculated as described above. Then $p(\text{O}_2)$ is $p(\text{O}_2) = p(\text{air}) \times X(\text{O}_2) = [(p_{\text{total}} - p(\text{CH}_3\text{OH})) \times 0.21 = (760 - p(\text{CH}_3\text{OH})) \times 0.21$ mmHg, where $X(\text{O}_2)$ is the mole fraction of O_2 in air. Thus the equivalence ratios of the methanol/air mixtures at the combustion vessel temperatures of 12.5, 14.5, 17.5, 20.0, 22.5, 25.0, 27.5 and 32.5 °C employed in this work are, respectively, 0.66, 0.75, 0.90, 1.05, 1.23, 1.43, 1.68, and 2.31 (See Table 3).

C. Test procedure.

The detailed test procedure is given in the Appendix.

Results

(a) Characterization of the electric circuit-electrode-combustion vessel

For the measurement of the MIEs of the fuel/air mixtures, it is necessary first to examine the behavior of the electric circuit-electrode-combustion vessel as a whole system. In this work, the breakdown energy from our ionization circuit is fixed at 0.07 mJ. Theoretically, the dc-arc energy could be stored in an RC circuit with various combinations of the supply voltage, resistance, and capacitance. I.e., the dc-arc discharge energy is a function of V (voltage), I (current) and the arc duration time (τ). Therefore, in the measurement of MIE, it would be very informative to determine the minimum energy for spark generation in air that a combination of breakdown energy and dc-arc discharge (V_0 , R4 and C2) could provide. One would expect that the MIE of a fuel/air mixture at a given condition would be close to the minimum energy of the spark generation in air.

A series of exhaustive tests was performed to find the minimum energies of spark generation in air as a function of dc-arc discharge duration time (τ)— τ is approximately proportional to the RC time constant although there are always sudden drops of V_g and I_g

to their zero level, preceded by the normal characteristic decay of V_g and I_g . As mentioned before, our electrodes were mounted on the top hemisphere of the combustion vessel. A series of measurements have been done with the electrode spark gap of 2 mm without attaching the bottom hemisphere. In the experiments, the capacitance of the C2 capacitor was varied from 0.54 μF to 0.0001 μF and the resistance of the R4 resistor from 103.7 $\text{k}\Omega$ to 41 $\text{k}\Omega$. With the selected R4 and C2 (selected τ), the supply voltage was varied systematically from high to low for the sparking event. Once a successful sparking was achieved, the dc-arc discharge energy, τ value, the peak voltage, and current were recorded. The minimum energy for spark generation was obtained by adding the breakdown energy of 0.07 mJ to the dc-arc discharge energy. In Figure 5, the minimum energies for spark generation in air are plotted as a function of τ . Detailed information for V_0 , R4 and C2 combination are also tabulated in Table 2.

Table 2. Minimum Energy for Spark Generation at 2 mm Spark Gap in Open Air.

Series #	R ($\text{k}\Omega$)	C (μF)	Supply (Actual) Voltage (V)	Arc Discharge Duration (μs)	Minimum Energy (mJ)
1 Δ	103.7	0.1200	2700 (2489)	25667	235
2 \circ	103.7	0.0110	2700 (1867)	1410	7.36
3 $+$	103.7	0.0010	1100 (1037)	73.3	0.14
4 \diamond	103.7	0.0001	1500 (519)	67.2	0.04
5 \square	84.0	0.54	2400 (2352)	72267	953
6 Δ	84.0	0.12	2500 (2184)	19267	193
7 \circ	84.0	0.011	2400 (1512)	1225	5.90
8 $+$	84.0	0.001	1000 (1176)	69.0	0.11
9 \square	41.0	0.54	1700 (1353)	35200	335
10 Δ	41.0	0.12	1700 (1230)	7867	65.8
11 \circ	41.0	0.011	1900 (1394)	661	4.10
12 $+$	41.0	0.001	800 (533)	65.8	0.06
13 \diamond	41.0	0.0001	1200 (328)	37.6	0.03

(b) Measurement of the ignition energies of methanol/air mixtures

After the characteristics of the electric circuit-electrode-combustion vessel system were determined for the energy of spark generation in air, we performed a series of measurements for the ignition energies of the various equivalence ratios (ϕ) of methanol/air mixtures. Utilizing the information obtained in the above section (a), a combination of R4 and C2 (τ value) was chosen and then the supply voltage was varied to obtain successful ignition and flame propagation. Typical signals of current, voltage and power are displayed in Figures 6(a) - (c). As in the equation shown above, the MIE was determined by adding the breakdown energy to the dc-discharge energy.

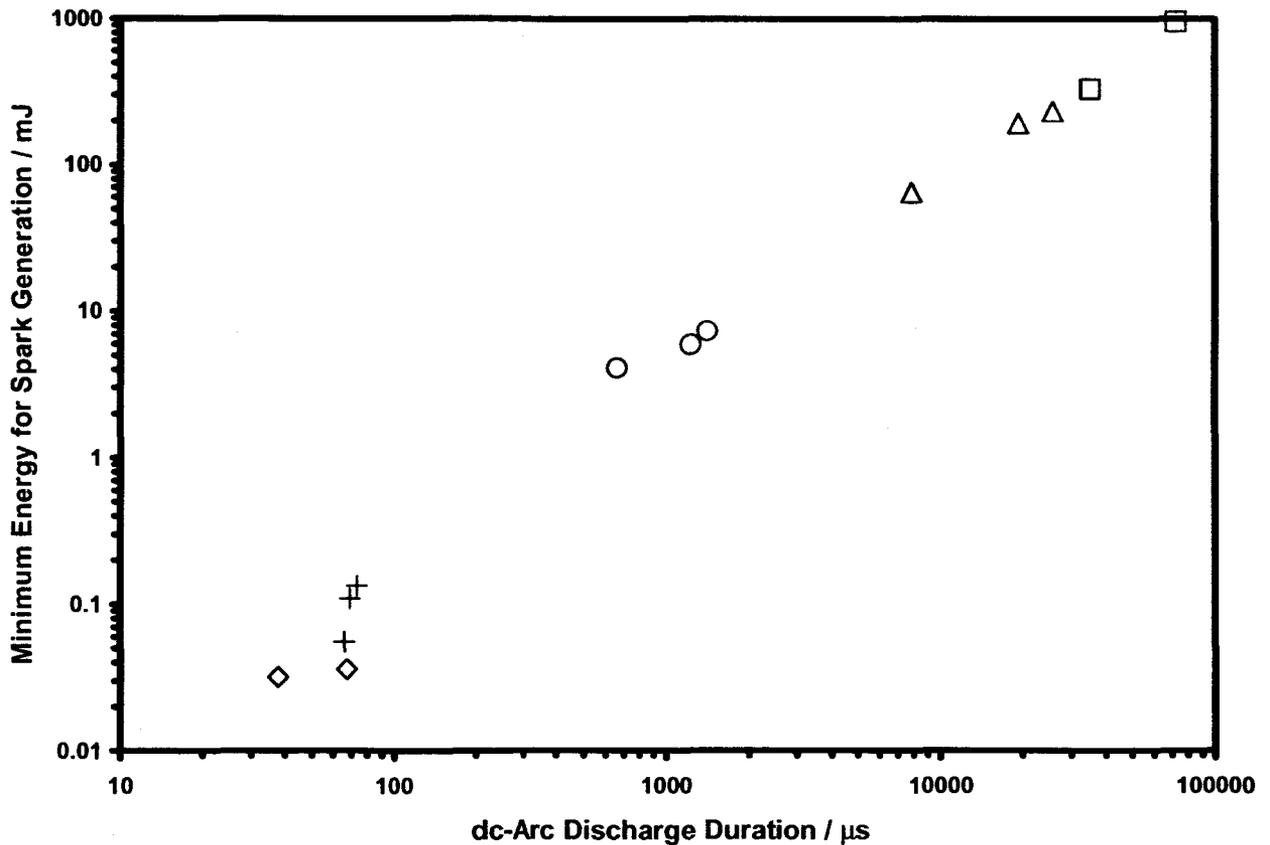


Figure 5. Minimum Energy for Spark Generation at 2 mm Spark Gap in Open Air at Room Temperature.

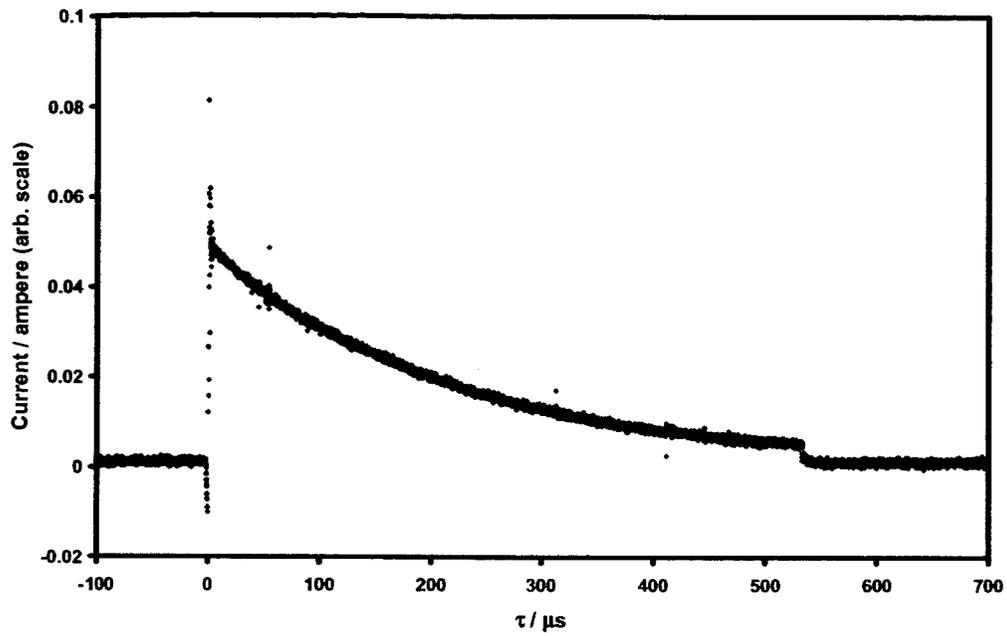


Figure 6(a). A Typical Current Profile.

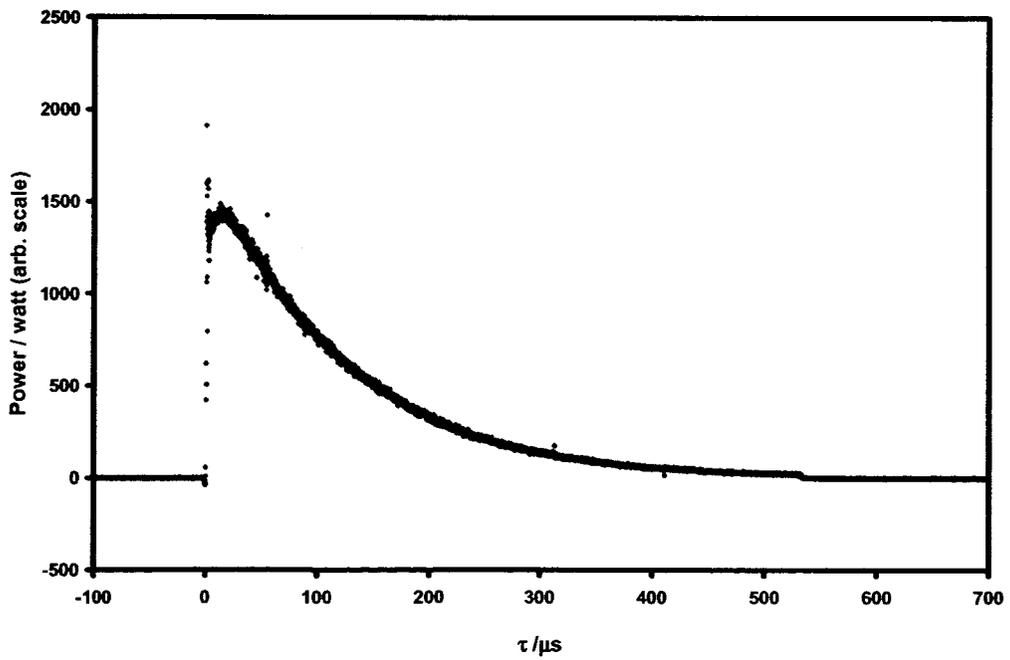


Figure 6(b). A Typical Voltage Profile.

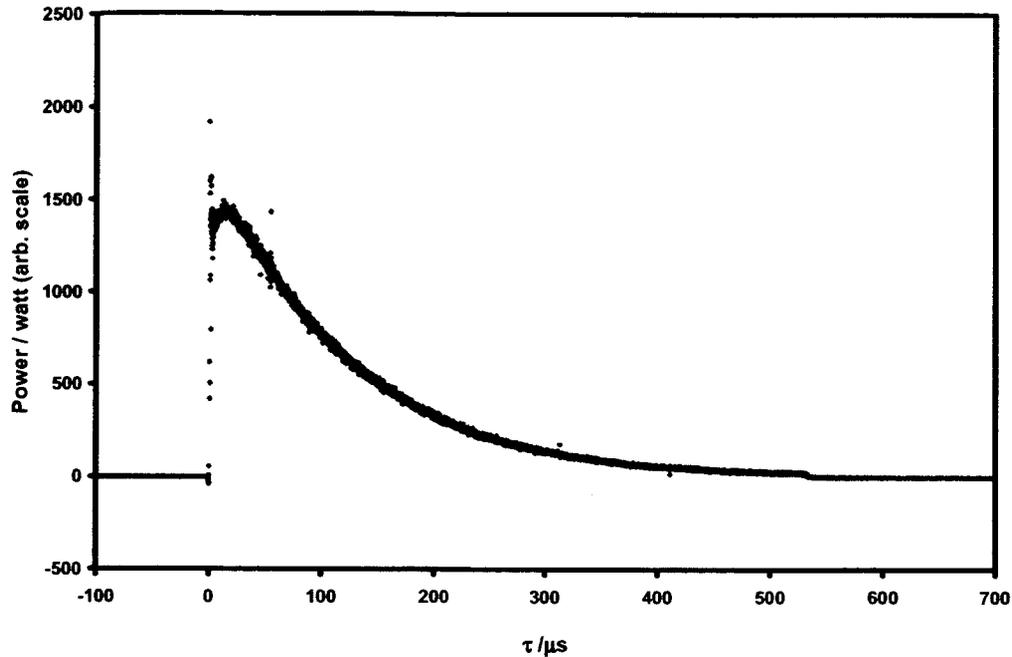


Figure 6(c). A Typical Power Profile.

Figure 7 shows the results at the spark gap distance of 2 mm and the combustion vessel temperature of 12.5, 14.5, 17.5, 20.0, 22.5, 25.0, 27.5 and 32.5 °C. In the experiment, the resistance of R4 and the supply voltage were varied, respectively, from 228 k Ω to 1 Ω , and from 2950 V to 400 V. The capacitance of C2 was also varied accordingly (ranging from 0.72 to 0.0001 μ F) to give τ values from 170 ms to less than 6 μ s. Perusal of Figure 7 reveals that, for all mixtures tested, the ignition energy decreases with τ , reaches a minimum value, and then increases with τ . The MIE at a given equivalence ratio should be located at the minimum of the ignition energies. Due to the scatter of the data points we fitted the measured ignition energies as a function of τ using a third order cubic function. The MIE values at given temperatures (equivalence ratios) were then obtained from the fitted curves.

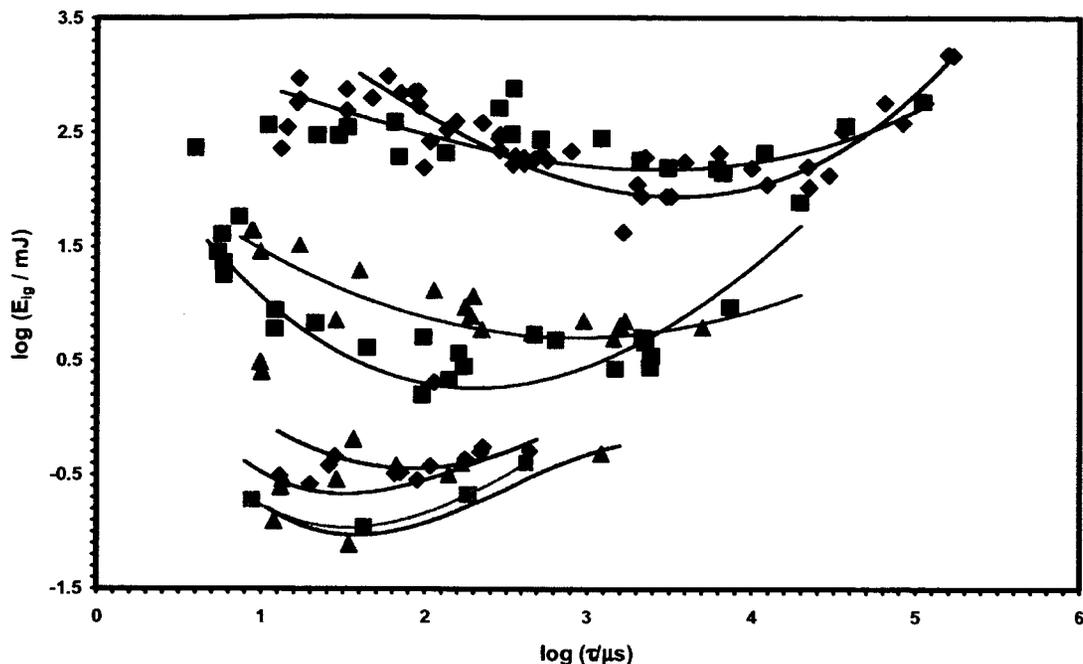


Figure 7. The dc-arc Discharge Time Dependence of the Ignition Energies of Methanol/Air Mixtures at Various Temperatures Using a 2 mm Spark Gap. Symbols and Lines are:

■ —12.5 °C; ▲ —14.5 °C; ◆ —17.5 °C; ■ —20.0 °C;
 ▲ —22.5 °C; ◆ —25.0 °C; ■ —27.5 °C; ◆ —32.5 °C

The minimum ignition energies obtained in this manner for a spark gap distance of 2 mm are plotted as a function of equivalence ratio in Figure 8 and are tabulated in Table 3. In the equivalence ratio span of 0.5 ~ 2.5, the MIE value decreases as the methanol/air mixture composition changes from lean to rich (as ϕ increases), reaches a minimum at $1.0 < \phi < 1.25$, and then increases with further increase of ϕ . The decrease of MIE values from lean to stoichiometric mixtures is much faster than the increase from stoichiometric to rich mixtures. I.e., the MIE curve as a function of ϕ is not symmetrical. A higher order polynomial or an exponential function could be used for the curve fit. However, we used a second order quadratic function because it would make little difference in evaluating the minimum of the minimum ignition energy from a higher order polynomial and also would show the departure from symmetry at high ϕ values. Two important results deduced from this figure are: i) the lowest minimum ignition energy measured for

methanol for a spark gap distance of 2 mm is 0.137 mJ (breakdown energy, 0.07 mJ + dc-arc energy, 0.067 mJ), and ii) a slightly rich mixture ($\phi = 1.16$) gives the lowest minimum ignition energy.

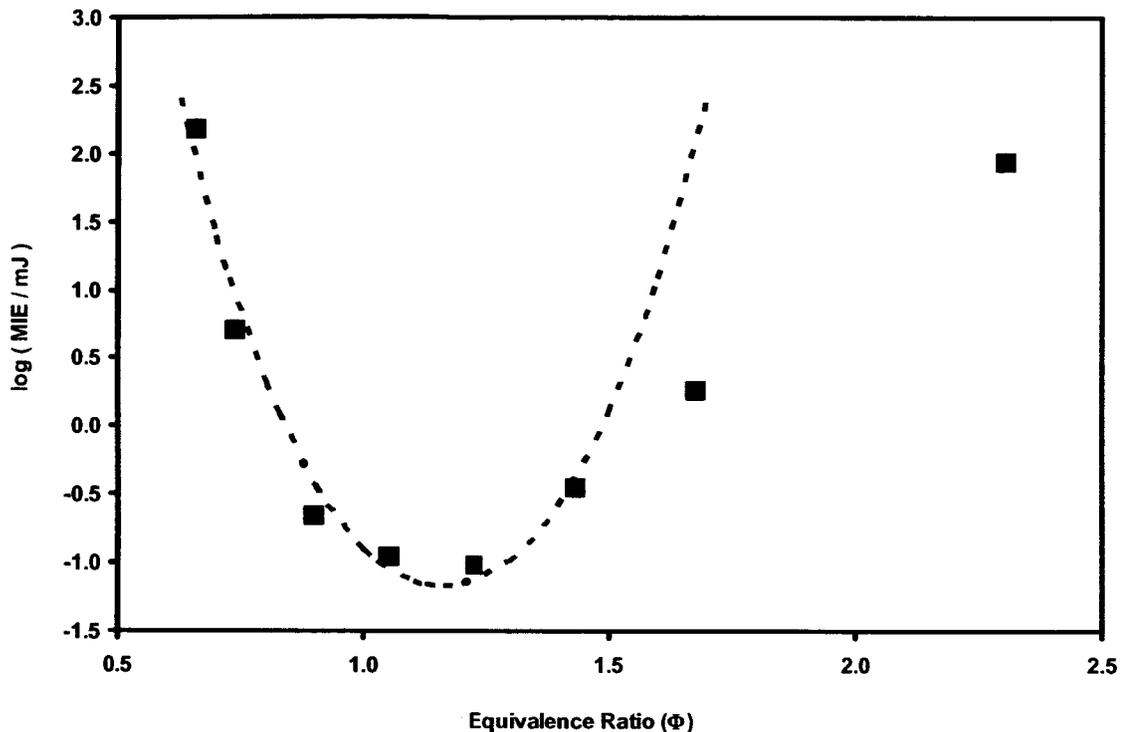


Figure 8. Minimum Ignition Energy of Methanol at 2 mm Spark Gap.

Table 3. MIE of Methanol/Air Mixtures at 2 mm Spark Gap.

Temperature °C	Equivalence Ratio (ϕ)	Minimum Ignition Energy (mJ)
12.5	0.66	150
14.5	0.75	5.08
17.5	0.90	0.22
20.0	1.05	0.11
22.5	1.23	0.10
25.0	1.43	0.36
27.5	1.68	1.82
32.5	2.31	87.1

Discussion

The MIE is the smallest quantity of energy that must be added to a system to initiate successful flame propagation. In spark ignition its value is dependent on the electrode configuration, electrode gap distance, electrical breakdown and discharge characteristics, mixture strength, and the system temperature and pressure. It is also dependent on the spark duration. The optimum spark duration is again dependent on the mixture strength and the flame quenching effects of the electrodes (electrode configuration and gap distance).

The ignition and flame propagation process has been reported in previous studies. First, the breakdown energy released to the flammable gas mixture in the period of a few nanoseconds to a few microseconds produces a small volume of plasma (plasma channel; spark kernel).[14] In the breakdown phase, the transfer of the supplied energy to the plasma is very efficient so that the spark kernel temperature and the pressure jump to extremely high values. Rapid relaxation of pressure in the spark kernel initiates the shock wave expanding outward. As a result the temperature and pressure fall but some of the energy is stored in the form of potential energies of the dissociated molecules. It was found that the shock wave always decays well before the commencement of ignition.[15,16]

In a composite spark, breakdown provides a conductive path for the dc-arc discharge by forming a plasma between the electrodes. During dc-arc discharge, the degree of ionization of the gas kernel is small but dissociation could be high. The gas kernel temperature continuously falls as the arc energy is lost by heat transfer to the electrodes, to the unburned surrounding gas, and by mass diffusion. It was reported that an increase of the breakdown energy does not produce a higher gas kernel temperature, but rather it increases the size of the plasma. Moreover, the dc-arc discharge also does not increase the gas kernel temperature. Instead, it extends the cooling period of the hot gas kernel so that the plasma formed in the breakdown phase can be preserved much longer.[14]

In the layer between the gas kernel and the ambient gas, the temperature rises and induces chemical reaction to produce chemical energy (heat) and hot combustion products—the formation of a combustion wave. In the quiescent environment, this combustion wave propagates outward with approximately spherical symmetry.[7,17,18] Flame propagation is dependent on whether the wave develops to a steady state. I.e., the inflamed volume (flame kernel) must grow to a size that the temperature gradient between the flame kernel and the outer unburned gas has approximately the same value as the temperature gradient in the steady state wave. If the size is too small (if the gradient is too steep), the rate of heat release within the inner spherical zone of the chemical reaction is insufficient to compensate for the rate of heat loss to the outer zone of unburned gas and to the electrodes, resulting in flame extinction. Whether the incipient flame gains its critical size is mainly dependent on the released chemical energy density from a fuel/air mixture.[16]

Based on the concept of electrical spark ignition and flame propagation described above and the previous discovery of the existence of optimum dc-arc discharge duration time on minimum ignition energy [19], our observation for the methanol/air system is analyzed below. The behavior of MIE as a function of τ (Figure 7) can be explained as follows: For a given methanol/air mixture, successful ignition and flame propagation is dependent upon the formation of a combustion wave and the growth of the flame kernel to a critical size. Therefore, if we choose R and C combinations of small τ values, then it is necessary to supply a large amount of energy. For R and C combinations of large τ values, heat loss by conduction and mass diffusion must be compensated through more energy disposal to the spark gap.

It is well known that flame extinction is caused by a combination of heat loss from the flame to the surroundings, flame stretch, flame instability and the extent of chemical reaction.[20] At a given condition, lean methanol mixtures would release less heat by chemical reaction than the stoichiometric mixture. However, the relative heat loss (heat loss/heat production) would be greater. Hence, this usually resulted in low flame temperatures. At low flame temperatures, the reactive chain length becomes small due to

competition between the hydrogen atom chain-branching ($\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$) and the chain-terminating reaction ($\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$)—the extent of chemical reaction is small. To obtain successful ignition and flame propagation in lean methanol mixtures, therefore, disposal of large amounts of energy to the spark gap is necessary. The initial high energy input would yield a high flame kernel temperature, create a high concentration of active chain centers and result in elongation of the active chain length (extent of chemical reaction). As a result, enough heat would be released for sustaining flame propagation. In a fuel rich flame (oxygen deficient flame), chain-terminating reactions by recombination of radical-radical and/or radical-molecule are dominant over chain-branching and chain-propagating reactions. Most importantly, radicals from fuel molecules would compete with the hydrogen atom chain-branching reaction for the hydrogen atoms. Consequently, the extent of chemical reaction gets small and less heat would be released compared to stoichiometric mixture combustion—heat release from recombination reactions is not sufficient enough to sustain the flame propagation. Likewise, for lean methanol mixtures, the high energy disposal to the spark gap is needed for ignition and flame propagation. In our equivalence ratio range, surprisingly it was found that less initial ignition energy is required for rich mixtures than for lean mixtures (Figure 8). The reason is that methanol, an oxygenated fuel, has rather short reaction routes for end-product formation and heat release ($\text{H}_2\text{CO} \rightarrow \text{CO} \rightarrow \text{CO}_2$) than other hydrocarbons, for example, methane.

Two previously reported representative MIEs of methanol are 0.14 mJ compiled by Haase[21], and 0.215 mJ, experimentally measured by Calcote et al.[10] Our value of 0.137 mJ is in excellent agreement with the tabulated value by Haase. A slightly rich methanol/air mixture ($\phi = 1.16$) requires the minimum ignition energy for ignition and flame propagation because of the higher mass diffusion of O_2 in air than for CH_3OH in air—the mass diffusion coefficient (in air) of O_2 ($0.178 \text{ cm}^2/\text{s}$) is greater than that of CH_3OH ($0.137 \text{ cm}^2/\text{s}$).

Conclusions

The minimum ignition energies of various compositions of methanol/air mixtures were measured by electrical spark ignition at a spark gap of 2 mm. The minimum of the minimum ignition energy values (commonly called minimum ignition energy, MIE) of methanol measured in this study is 0.137 mJ. The MIE value of 0.137 mJ is sufficient for ignition and flame propagation of a slightly rich methanol/air mixture ($\phi = 1.16$).

Acknowledgments

The authors wish to thank Dr. Martin J. Rabinowitz at the NASA Glenn Research Center at Lewis Field, the grant monitor, for his invaluable advice and support throughout this study. This study was sponsored by the NASA Glenn Research Center at Lewis Field under grant NASA/NAG3-2338. All of the experiments and computations were performed at the NASA Glenn Research Center at Lewis Field in Cleveland, Ohio. Additional support was provided by the Department of Chemical Engineering at the University of Toledo.

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Appendix : Test Procedure

A: Test Safety Checklist:

(i) OPEN VESSEL (1-5)

Note: Steps 1-5 are included if and only if the combustion vessel is open to the air with the bottom assembly off. If the vessel is already closed, proceed to Step 6.

1. ____ Check the spark gap distance using a magnifying lense and a micrometer. The gap should be either 2 or 3 mm. Also check the ionization bait probe distance.
2. ____ Visually inspect the electrodes for corrosion. If dirty, clean them with a soft cloth. Do NOT use alcohol to clean if possible.
3. ____ Verify that all Pressure Transducers, Thermocouples, and mixing devices, etc., are at the proper distance from the spark gap and are intact.
4. ____ Place the bottom part of the combustion vessel onto the upper assembly. Make sure the Teflon seal is in place between the assemblies and place safety bolts in the holes provided in order to close the vessel. Use hand clamps to hold the vessel together while bolts are tightened.
5. ____ Check for continuities in the whole system. There must not be any leakage and grounding must be present.

Note: Steps 6-11 are included if and only if the combustion rig is not in place under the containment cell marked AVSP Fire Safe Fuels Testing. Upon new test rig design, these steps will become obsolete. If the rig is in the proper position, proceed to Step 12.

(ii) RIG/BATH ASSEMBLY (6-10)

6. ____ Roll the combustion vessel assembly unit into place inside the containment cell. The correct placement of the unit should be dictated by a bracket on the floor, which will prevent the wheels from moving sideways. Lock the wheels.
7. ____ Pump the hydraulic jack so that the thermostatic bath completely covers the combustion vessel. The heating/cooling fans are located inside the bath.
8. ____ Cover any holes with the foam pieces sitting on top of the bath in order to keep the thermal energy inside the bath.

9. ____ Visually inspect the ignition cables leading into the combustion vessel.
Verify that the voltage probes are in the correct position.
10. ____ Verify that the manual exhaust is closed on the combustion vessel.

Normal Operating Procedure:

(iii) SAFETY (11-12)

11. ____ Turn main power switch on via Key-Switch in CE-15.
12. ____ Turn ignition switch to the ON position, which is also located in CE-15.

(iv) HEATING/COOLING (13-14)

13. ____ Power up Heating/Cooling Unit (Julabo FP-50-HP).
 - a. Turn Unit On (FP-50 SW1).
 - b. Turn Programming Unit On (FP-50 SW-2).
 - c. Turn on Heating/Cooling Capability (FP-50 Push).
 - d. Make sure external temperature is displayed on large LED.
 - e. Change Setup 1 to the specified value to reach temperature for test.
14. ____ Turn circulating fans on to heat or cool the vessel by flipping Electric Outlet 4 to the ON position.

(v) GAS HANDLING SYSTEM (15-18)

15. ____ Turn Electric Outlet 1 to ON position. This outlet controls the intercom, flow valves, and touchscreen monitor in CE-13A. The hard drive for the touchscreen can then be turned on. (Located next to Gas Handling Valve Panel)
16. ____ Verify that relief valves for the Oxygen, Argon, and Nitrogen are in the correct position. Input line relief valves should be in the vertical position; Safety valves should be in the horizontal position.
17. ____ Once the relief valves on the gas handling panel are in the correct position, the input lines can be closed. These valves are located at the left-hand side below the panel. The natural position for these two valves is horizontal. Pull the handles to the vertical position. The gases are now able to flow safely into the system.
18. ____ Verify that the safety relief valve connected to the gas cylinders is closed or in the vertical position. Once this is done, open the gas cylinders.

(vi) DATA ACQUISITION (19-21)

19. ___ Turn Oscilloscopes (TDS1-3) on. Make sure that Electric Outlet 2 is in the ON position. Data collection is handled with these scopes—Voltage across the spark gap, current supplied, pressure at ignition inside the combustion vessel, and the energy output (via MATH function on TDS-1).
20. ___ Turn Electric Outlet 5 to the ON position. This controls the Amplifier Probes. Amp Probe 2 is connected to TDS-1. Verify that the switch is turned on at the back of the unit. If a red button is flashing, degauss the probe. To do this, release the probe from the spark ignition cable (white cable; located above the vessel) by flipping the lock switch off and pressing the trigger. While disconnected from the ignition cable, lock the unit and press the degauss switch. Once fully degaussed, the probe can be put back into place on the ignition cable.
21. ___ Zero the amplifier probe. This is done by pressing the SINGLE/SEQ button on TDS-1, then the FORCE TRIG button, followed by the RUN/STOP button. This will give an AUTO trigger which will show the CH1 MEAN in yellow. If this Mean is largely negative, the offset must be adjusted on Amp Probe 2. Adjust the Mean by turning the OUTPUT DC LEVEL knob; clockwise is more positive, counter-clockwise is more negative. If this is not done the ending result of the MATH function can become skewed.

(vii) VISUAL DATA ACQUISITION (22-25)

22. ___ Make sure that the “Phantom” high-speed camera is on by checking to see that the Green LED light (top of unit) is on.
23. ___ Power up the JIMBO laptop. This laptop computer is used to visually inspect the combustion vessel by use of a “Phantom” camera. A Plexiglas viewing window on the top of the vessel allows for the camera to view the spark gap. Once the laptop is on, click on the Version 547 icon to initiate the “Phantom” program software. When the program begins, press ESC, Acquisition, and Setup and Recording buttons, respectively. This will take you to the screen for recording the testing.
 - a. Camera (2630) Defaults:
 - i. Sample Rate: 30000 pps

- ii. Exposure Time: 16 μ s
- iii. Post Trigger: 261630 p (frames)
- iv. Geometry: 256 (width) x 64 (height)
- v. Zoom In: 4 Mode: Auto exposure

b. To adjust white balance: Right Click on visual screen and press Adjust WB button.

- 24. ____ Once the camera and laptop are on, flip on the small Variac unit and verify that the intensity is around 110. This unit is plugged into Electric Outlet 4.
- 25. ____ Adjust the camera mount so that the spark gap is shown in the middle of the viewing area on the JIMBO laptop.

(viii) TOUCHSCREEN/WONDER OPERATION (26-28)

- 26. ____ If the Touchscreen (WONDER 1) is not already on, turn hard drive on (located on shelf left of Gas Handling Panel).
- 27. ____ Once monitor is on, start the MBENET program. This allows the “Wonderware” software to activate the PLC in CE-15.
- 28. ____ Open the InTouch Windowview Icon. Check the box marked Fire Fuels System and Click OK. The main screen for testing should appear.

(ix) FUEL LOADING (29-34)

- 29. ____ Remove fuel to be tested from the yellow flammable storage units.
- 30. ____ Measure out 20-100 mL of the fuel depending on if any fuel is in the vessel already. Use test tubes and a funnel to measure and transfer the fuel safely.
- 31. ____ Pour the fuel into a squeeze bottle for loading into the vessel.
- 32. ____ Open the manual exhaust valve on the top of the combustion vessel. Use this penetration to inject the testing fuel. Once all the fuel is verified inside the vessel, close the manual exhaust.
- 33. ____ Purge the vessel using the pre-assigned values for purging for the given fuel by pressing the PURGE button on the touchscreen. This will ensure that the fuel is mixed inside the vessel with any remaining fuel already present.

(x) CIRCUIT (34-36)

- 34. ____ Verify that Main Power Supply (MPS1) to the circuit is off on the touchscreen and on Electric Outlet 3. Once this is done, the Capacitor and

Resistor can be changed. The circuit is mounted on the inside of the containment cell next to the thermostatic bath.

35. ____ Remove the original Capacitor, found by the label C2. At this point, the Resistor (R4) can also be changed using a small wrench. Once the Resistor is in place, place the new Capacitor in the Capacitor Slots on the Circuit.
36. ____ Turn MPS1 back on via Outlet 3 and the Touchscreen. The fuel is now ready for proper ignition.

B: Test Procedure

1. ____ After successful ignition and purge, add 10-20 mL of the fuel being tested through the manual exhaust. This can be done every other successful run.
2. ____ Change the Capacitor (C2) and/or Resistor (R4) as specified in order to achieve the desired energy output for the experiment. Before handling the circuit, verify that the main power supply and touchscreen both read OFF.
3. ____ Turn the Circuit ON using the touchscreen. Press the START button to enable the sparking mechanism. This will also allow for a live voltage feed to be read on the TDS-1 Oscilloscope. The supplied voltage and current can be checked on the oscilloscope by pushing the SINGLE/SEQ button, then the FORCE TRIG button. This will show the live voltage and current readings in the circuit. The voltage and current can be fine-tuned using the power supply and amperage probe at this point.
4. ____ Adjust the amperage input by changing the Current/Division on Amp Probe 2 up or down depending on the Resistor (R4) being employed. For instance, an $84k\Omega$ resistor would most likely need a 10mA/div input in order to be fully captured on the TDS-1 screen. Zero the live current reading, which is shown as the CH1 Mean. The MATH function must use $VAR2 = (x/10) \cdot (e^1)$, where x = the number of mA/div, for the correct value to be displayed.
5. ____ Turn the Thorn EMI Power Supply (MPS1) ON. Adjust the voltage to the desired output. There will be a voltage drop once the capacitance is discharged. The actual voltage supplied at the spark gap will be shown as the CH2 peak value on TDS-1. Using the same live reading on the oscilloscope, the voltage can be

fine-tuned. The MATH function must use $VAR1 = (y/1000) \cdot 2$, where y is the supplied voltage from MPS1, in order to correct for the on-screen display settings (Voltage has a default setting of 500mV/div on the display).

6. ____ After the current and voltage are set, the test setup is complete. Press the SINGLE/SEQ button on TDS-1 and TDS-2. The oscilloscopes are now primed for the next trigger or spark pulse. Change the scale (both horizontal and vertical) on the oscilloscopes in order to fully capture the voltage, current, power, and pressure waveforms. The pulse duration is determined by the resistor used. Expect the higher resistance to have a longer pulse duration (1000 μ s +) than a small one (100 μ s -). The pressure time/division can be left at the highest setting.
7. ____ Verify that the temperature inside the combustion vessel is within the acceptable range ($\pm 0.10^{\circ}\text{C}$) from the target temperature. The temperature inside the vessel can be found on the LED display on the Julabo unit.
8. ____ Verify that equilibrium has been attained inside the vessel. When the pressure stabilizes, as noted by the pressure reading on the touchscreen, it is recognized that equilibrium has been met. This process takes approximately 45 to 60 minutes after the last successful ignition and subsequent purge.
9. ____ Set up Phantom camera to record at next trigger.
10. ____ Press the SPARK button on the touchscreen.
11. ____ If only an Ionization spark occurs, raise the voltage by 200 V and repeat the specified test.
12. ____ If there is an actual spark, but no ignition, raise the voltage by 100 V and repeat the test. Record the important data: Vessel Temperature, Humidity, Supplied Voltage, Supplied Amperage/div, Actual Voltage across gap, Energy discharged from spark, the Peak Amperage, and Area under the current waveform.
13. ____ If there is an actual spark with ignition of the fuel vapors in the vessel on the first test, purge the vessel (use PURGE button on touchscreen) and redo the test. The typical purge is 1 minute of nitrogen at 5.0 standard liters per minute (slm) and 5 minutes of air at 20.0 slm. On the next test, start with either lower supply voltage from MPS1 or by using a smaller energy combination (C2 & R4). Record

all important data including the Peak Pressure and Time to Peak Pressure. Wait the appropriate amount of time between testing in order to confirm equilibrium.

14. ____ If there is an actual spark and ignition, with at least one successful spark/no ignition run before, the run is considered as an acceptable data point. Purge the vessel. Save the waveforms for voltage, current, power (MATH), and pressure on the internal drives of the oscilloscopes as either .ISF or .CSV files. Record all important data. Save the Phantom file if acceptable.
15. ____ Once a successful ignition occurs, set up for the next range using a different capacitor/resistor combination or at a different temperature.

C: Shutdown Procedure

1. ____ Turn main Power Supply (MPS1) OFF.
2. ____ Turn ability to spark on touchscreen with the OFF button.
3. ____ Turn off Julabo Heating/Cooling unit Electrical Outlets 4 and 5. These outlets control the Amperage Probes, the Circulating Fan, and the light for the “Phantom” Camera.
4. ____ Close the manual valves on the gas cylinders.
5. ____ Evacuate the gas lines at GOV 102, GNV 102, and GIV 102.
6. ____ Close both valves that are connected to the in-house air supply.
7. ____ Manually evacuate the system at the filter, GFF 101.
8. ____ Close out of “Wonderware” and MBENET on the touchscreen. Then shutdown the computer.
9. ____ Close the “Phantom” camera software. Shutdown the laptop (JIMBO).
10. ____ Turn Ignition Key Switch to the OFF position in CE-15.
11. ____ Turn Ignition Circuit Trigger Switch in CE-15 OFF.
12. ____ Turn all remaining Electrical Outlets OFF.