Spontaneous Ignition Delay Characteristics of Hydrocarbon Fuel/Air Mixtures

Arthur Lefebvre, W. Freeman, and L. Cowell

Purdue University
West Lafayette, Indiana

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INTRODUCTION

Autoignition is the spontaneous combustion of a fuel and oxidizer mixture in the absence of any external ignition source. This ignition occurs in a finite time after the fuel and oxidizer are combined. In homogeneous mixtures the time necessary for ignition depends on the temperature, pressure, fuel concentration, and oxygen concentration. The effect of pressure on autoignition delay time is the focus of this study.

The characteristics of autoignition have been studied for several different reasons over the past century. Studies have been completed examining the effect of autoignition on diesel engines, the knocking phenomena in spark ignited engines, flame stabilization in gas turbine engines, and presently for the premixed/prevaporized combustor concept in gas turbine engines. The lean, premixing, and prevaporizing (LPP) combustor technology is the motivation for this study.

Concern over the depletion of the ozone layer in the stratosphere due to nitric oxides has prompted NASA to initiate the Stratospheric Cruise Emission Reduction Program
(SCERP). One method of reducing the formation of nitric oxides in gas turbine engines is by mixing the fuel and air prior to combustion, allowing complete evaporation of the fuel drops, and mixing of the fuel vapor with the air. The resultant homogeneous mixture can be burned leaner without the local hot spots associated with combustion of heterogeneous mixtures. Fig. 1.1 illustrates typical reductions found between LPP combustors and conventional combustors [1].

Among the problems associated with this concept are autoignition and flashback in the premixing tube. Autoignition occurs in the premixing tube when the residence time...

![Figure 1.1](image-url)  
**Figure 1.1** NO\textsubscript{x} emissions for conventional and advanced combustor technologies [1].
of the fuel and air mixture is greater than the delay time. Flashback is the propagation of the flame upstream from the combustor to the injector, which occurs when the flame speed is greater than the mixture velocity. Either of these problems can cause structural damage as well as higher pollutant formation. Temperatures and pressures at the exit of compressors in modern gas turbine engines are sufficiently high for autoignition to occur in one tenth of a second or less. Designing a premixing passage requires allowing enough time for complete evaporation while precluding the possibility of autoignition.

The autoignition delay time is composed of two overlapping components: the physical and chemical delay times. The physical delay time dominates the early stages of the autoignition process. This delay time consists of the time for the fuel drops to form, heat up, and evaporate; and the time for the fuel vapor to mix with the air. The chemical delay time dominates after this mixing has occurred and is dependent on the chemical kinetics.

The autoignition delay time is measured with a continuous flow apparatus. In this device the fuel is injected into a flowing air stream at high temperatures, and ignites at some distance downstream depending on the air velocity. This concept is illustrated in Fig. 1.2, where the delay is defined as the length, L, divided by the fluid velocity, U. Several other devices exist to measure
the delay time, such as: constant volume bombs, compression engines, and shock tubes. However, in all these methods control of pressure is impossible. The continuous flow method also most closely simulates flow in a premixing tube.

![Diagram of fuel and air flow](image)

**Figure 1.2.** Basis of ignition delay times measurement technique.
BACKGROUND

The characteristics of autoignition delay time have been subjected to considerable study. A review of previous work is presented here. The major focus is on continuous flow experiments of homogeneous mixtures of hydrocarbon fuels in air. In the majority of these studies the delay time is correlated with temperature, pressure, fuel concentration, and oxygen concentration using global reaction theory. This theory is presented prior to the review. The chapter concludes with a brief review of flashback theory, since flashback has been a considerable problem in premixing tubes and also in this study.

Autoignition Kinetic Theory

The chemical processes governing the ignition of reacting flows are composed of many interwoven reactions between fuel, air, intermediate species, and products. Describing the entire overall reaction in one step is a common simplification of the problem and has been proven as a practical solution [7].

The reaction between fuel and air can be represented by fuel and air going to combustion products.
The forward reaction rate equation is

\[ rr = K \ [\text{oxygen}]^j \ [\text{fuel}]^m P^n \] (2.1)

where \( n = j + m \), is the global reaction order, \( P \) is the pressure in atmospheres, and the fuel and oxygen concentrations are based on volume. The reaction rate constant, \( K \), is expressed from the modified Arrehenius expression as

\[ K = A \ T^{0.5} \exp \left( \frac{-E}{R_u T} \right) \] (2.2)

Here \( E \) is the global activation energy, \( R_u \) is the universal gas constant, and \( A \) is the Arrehenius constant.

The delay time is proportional to the inverse of the reaction rate and can be expressed as

\[ \tau \propto \frac{1}{A} \exp \left( \frac{E}{R_u T} \right) \ [\text{oxygen}]^{-j} \ [\text{fuel}]^{-m} P^{-n} T^{-0.5} \] (2.3)

This correlation indicates that plotting the log of delay time against the inverse of temperature should result in a straight line if the other variables are held constant and \( T^{-0.5} \) is ignored. This is the most common method of correlating autoignition data.

**Previous Work**

The results of earlier workers have been studied and compiled by the physical variables which influence ignition
delay time in homogeneous mixtures. For a review of the physical variables influencing the delay time in heterogeneous mixtures, literature surveys have been completed by Chiappetta and McVey [3] and Freeman [4].

Pressure

Pressure influences the autoignition delay time through the reactants concentration. Pressure is inversely related to delay time as

\[ \tau \propto P^{-n} \]  \hspace{1cm} (2.4)

To include the pressure term the fuel and oxygen concentrations must be based on volume. The exponent \( n \) varies from 0.5 to 2.5 in the literature. The log of delay time versus the log of pressure of previous workers' results for homogeneous mixtures is shown in Fig. 2.1. The slopes of the lines, shown in parentheses, represent the pressure exponent, \( (n) \). Only Burwell and Olson [5], using vaporized iso-octane, took measurements at pressures greater than one atmosphere. Mullins [6] found the value of the pressure exponent to be fuel-type dependent at pressures below atmospheric for a vitiated air supply.

Fig. 2.2 illustrates the delay time versus pressure relationship for heterogeneous mixtures, as compiled by Chiappetta and McVey [3]. For these aircraft fuels the pressure exponent varies from 0.8 to 2.0. In heterogeneous
Figure 2.1. Summary of results showing the effect of pressure on ignition delay times for homogeneous mixtures.
Figure 2.2. Summary of results showing the effect of pressure on ignition delay times for heterogeneous mixtures. Compiled by Chiapetta and McVey [3].
mixtures pressure also influences the evaporation rate of the fuel drops. Anderson [8] found this dependence to be small, while Chin and Lefebvre [9] found the effect of pressure on evaporation rate to increase with increasing temperature. The lack of understanding of the effect of pressure on evaporation rate may explain some of the variations in the results of workers using the same fuel. For example both Spadaccini [23] and Taback [32] used JP-4 fuel, but Spadaccini found $n=1.8$ while Taback found $n=0.9$. Still the results in Fig. 2.2 are similar enough to suggest that the effect of pressure is more dominant in the chemical delay time than in the physical delay time.

Temperature

According to the global reaction theory temperature affects the delay time through the Arrehenius expression.

$$\tau \propto T^{-0.5} \exp \left( \frac{E}{RT} \right)$$

(2.5)

The term $T^{-0.5}$ comes from molecular collision theory, and has generally been neglected by most previous researchers. Both Miller [15] and Mullins [6] correlated their data with the collision term, and found a negligible effect over a 200°C temperature range. They concluded that its effect could only be realized over a very large temperature range.

Ignoring the collision term, the log of delay time versus the reciprocal of temperature should yield a
straight line. Fig. 2.3 shows previous workers' results as compiled by Chiappetta and McVey [3] and updated by Freeman [4] as the log of pressure times the delay time versus the reciprocal of temperature. Chiappetta chose a pressure exponent of 1.0 as being the most representative for all the studies available. The majority of work with heterogeneous mixtures was performed at pressures greater than atmospheric. The slopes of the lines represent the global activation energy, but since the pressure exponent was set for comparison the activation energies determined from this graph may be misleading. Only Freeman [4], Lezberg [12], and Mullins [6] found the activation energy in the range of 40.0 - 50.0 kcal/kg-mol, which is the commonly accepted range for gas turbine fuels. These researchers performed their studies at atmospheric pressure only, which could explain their good correlations.

The initial mixture temperature was used to correlate the data. However, in a reacting flowing mixture the temperature will not remain constant. Variations in temperature along the flow path have been reported from a 200°C drop by Mestre and Ducourneau [13] to a 200°C rise by Burwell and Olson [5]. Burwell and Olson used a nearly-adiabatic flow channel, and their temperature rise reflects that of reacting mixtures. Mestre and Ducourneau [13] used a variably heated channel and found only a minor difference between adiabatic conditions and flow with heat loss.
Figure 2.3. Summary of results showing the effect of temperature on ignition delay times. Compiled by Chiapetta and McVey [3].
Chang et al. [14] also operated an essentially adiabatic flow scheme using propane, and found a 25°C increase between his results and Freeman's [4], who employed propane with a 50°C drop along the test section length.

Oxygen Concentration

The oxygen concentration influences the delay time by changing the probability of reaction. Oxygen concentration is related to the delay time via

\[ \tau \propto [\text{oxygen}]^{-j}. \] (2.6)

The oxygen concentration exponent, \( j \), has been found to vary from 0.25 by Brokaw and Jackson [7] to 2.0 by Mullins [6] for a vitiated air supply. Freeman [4], Chang et al. [14], and Miller [15] found better agreement with values of 0.59, 0.74, and 1.0 burning propane, propane, and calor gas respectively at atmospheric pressure. Most recent work has not investigated the effect of oxygen concentration on delay time in premixing tubes because there the oxygen concentration does not vary strongly in the inlet air.

Fuel Concentration

Fuel concentration affects the delay time in an identical manner to oxygen concentration. Its influence on the reaction is given by
However, only Burwell and Olson [5] (m=1.0) burning vaporized iso-octane, and Brokaw and Jackson [7] (m=.74) burning propane, have found a strong influence. Freeman [4], Mullins [6], Spadaccini [10], Miller [15], and Stringer et al. [16] found little influence for lean mixtures. Mestre and Ducourneau [13] found a strong effect for rich mixtures. Tacina [17] noticed no effect using a simplex nozzle in heterogeneous mixtures, but found an increasing effect as the number of fuel injection points in an airblast atomizer was increased. Improving the atomization shortens the mixing time and provides a more uniform fuel-air mixture. This trend illustrates the difficulty of determining fuel concentration in heterogeneous mixtures, since large variations in fuel concentration occur locally around fuel drops.

Fuel Type

The volatility and structure of a fuel have been found to influence the delay time. In global reaction theory this is reflected through changes in pressure, fuel, and oxygen exponents. Stringer et al. [16] observed a decrease in ignition delay time with an increase in cetane number, a decrease in octane number, and in changing fuel type from aromatics to branching paraffins to napthenes to straight paraffins. They also found a slight reduction in delay
time with increasing number of carbon atoms. In liquid fuel sprays the effect of fuel type on evaporation rate has also been noted. Yoshizawa [18] performed shock tube studies with n-butane, n-hexane, and n-octane and noticed no difference in delay time between these fuels. He concluded that, with the exception of lighter hydrocarbon fuels, such as methane and ethane, fuel chemistry has no influence on delay time.

A number of investigators have suggested mechanisms for the autoignition process which follow the findings of Stringer et al. [16]. Edelmen [19] and Henein and Bolt [20] propose that the heavier hydrocarbon fuels decompose to paraffins such as methane and ethane, which then react to autoignition. Hauptman et al. [21] suggests a four-step mechanism whereby the heavier hydrocarbons are reduced to intermediate olefinic species, such as ethene and propene, which then react to form carbon monoxide and hydrogen. The carbon monoxide and hydrogen then react with oxygen to the point of ignition producing carbon dioxide and water. Hauptman has demonstrated good correlation between his theory and the data he obtained in a shock tube study.

Turbulence

Turbulence influences delay time in several contradictory ways. First, air turbulence enhances mixing which decreases delay time. Secondly, Lefebvre and Ballal [22]
suggest that turbulence hinders ignition by more efficiently dissipating the thermal energy. Ballal and Lefebvre are referring to external sources of ignition, but their theory applies here because in reacting flows the temperature profile is flattened by turbulence.

The influence of turbulence on delay time has not received much attention. Chang et al. [14] placed 4, 10, and 20 mesh screens upstream of the fuel injector to vary turbulence intensity and found no effect. Likewise, Stringer et al. [16] used screens to vary the turbulence intensity from 3 to 17 percent, and found no effect. Mullins [6] put baffles downstream of the injector to increase the turbulence scale, and found a slight increase in delay time for liquid fuels.

Fuel Temperature

In all previous work surveyed the inlet fuel temperature was always less than the inlet air temperature. In heterogeneous mixtures fuel temperature determines the evaporation rate of fuel sprays, and thereby influences the delay time [6,10]. However, in homogeneous mixtures fuel temperature only alters the mixture temperature locally, downstream of the fuel injector, until the fuel and air are completely mixed. If mixing is completed quickly compared to the delay time no effect should be noticed [4].
Test Section

Brokaw and Jackson [7] varied the test section surface material between vycor, stainless steel, and potassium chloride, and observed no effect on delay time at atmospheric pressure. They concluded that three-body reactions have no effect on delay time. Freeman [4] found varying the test section length had no effect, while Spadaccini [10] observed a noticeable increase in delay time with length, especially at low equivalence ratios. Spadaccini used a test section with water-cooled walls, whereas Freeman's test section was heavily insulated.

Remarks

All the results presented in this section were correlated using global reaction theory, which models only the chemical delay time. The variations of results obtained in studies using heterogeneous mixtures indicates the influence of the physical delay on the overall delay time. Since the results of previous workers are of the same magnitude, the autoignition delay time must be dominated by the chemical delay component.

Flashback Theory

Aside from autoignition another problem encountered in premixing fuel-air passages is flashback of the flame from the combustor to the injector. Flashback occurs when the
flame speed is greater than the fluid velocity.

The first studies of flashback were made in connection with burner tubes. Lewis and Von Elbe [24] proposed the classical theory of flashback in laminar flows. They defined that for flashback to occur in the boundary layer the velocity gradient must be less than the flame speed divided by the quenching distance as shown below

\[
\left. \frac{\partial U}{\partial r} \right|_{r=R} < \frac{S_L}{q_D}
\]

where \( U \) is the fluid velocity, \( S_L \) is the laminar flame speed, and \( q_D \) is the quenching distance. This concept is illustrated in Fig. 2.4 where the velocity profile is approximated as a straight line. The velocity profile that intersects the flame speed profile at only one point is the flashback limit, and represents the smallest fluid velocity for a given flame speed profile at which flashback will occur. Putnam and Jensen [25] used the Peclet number to relate the flame speed and fluid velocity in the Lewis and Von Elbe model.

\[
\text{Pe}_L^2 = k \text{Pe}_U
\]

The Peclet number is a dimensionless independent heat transfer number equal to the Reynolds number times the Prandtl number. The subscript \( S_L \) or \( U \) indicate the velocity used in the Peclet number. Khitrin et al. [26] found
Figure 2.4. Flashback theory of Lewis and von Elbe [24].
in turbulent tube flows that flashback still occurs primarily in the laminar boundary layer and applied a similar Peclet number criteria.

Forsythe and Garfield [28] examined the factors which influence the size of the dead space between the burner rim and flame base. They found that dead space decreases with increase in pressure, temperature, and equivalence ratio to stoichiometric conditions. Forsythe also found a decrease in dead space with a decrease in wall conductivity.

Plee and Mellor [28] conducted a literature survey of flashback and concluded that flashback from the combustor was rarely the cause of combustion in the premixing tubes. Rather a flow disturbance in the passage creates a recirculation zone where autoignition occurs. They used a loading factor as defined by Lefebvre [29] to set the limits of flashback with equivalence ratio. The loading factor is based on turbulent burning velocity theory and indicates that the tendency to flashback increases with increase in tube diameter, equivalence ratio, pressure, temperature, or decrease in flow rate.

Marek and Baker [30] examined flashback in a heterogeneous flow system over different shaped plates. They were able to photograph the flame as it propagated up the plate's boundary layer from the trailing edge. They related flashback to the bulk fluid velocity and found that
inlet temperature and pressure have no influence over "flashback velocity".

These studies suggest that to eliminate flashback the velocity gradient at the wall should be increased, the flame speed should be decreased, or the quenching distance increased. The velocity gradient can be increased by increasing the bulk fluid velocity. Flame speed can be decreased by decreasing the fluid temperature or fuel concentration. The quenching distance can be increased by increasing the temperature gradient at the wall, which occurs with an increase in wall conductivity and with lower pressure.
EXPERIMENTAL

To measure the autoignition delay time at high pressures a continuous flow apparatus was designed and built. A description of this apparatus and the procedure for its operation follow.

Experimental Apparatus

The system for establishing autoignition and controlling mixture temperature, pressure, and fuel concentration has three main components. This section describes each of these components: the high pressure air supply, the fuel delivery system, and the instrumented test section.

High Pressure Air System

The high pressure air supply at The Thermal Science and Propulsion Center is provided by three Ingersoll Rand Compressors. The system is illustrated in Fig. 3.1.

The air flow rate is measured with a 9.91 mm ASME standard orifice plate located in a 4.44 cm containment pipe. The flow rate is controlled by two valves in parallel. A quarter-inch needle valve provides fine control,
Figure 3.1. The high pressure air system.
while a quarter-inch ball valve extends the range of the flow rate.

A twenty atmosphere heater is used to preheat the air. The heater consists of a three inch stainless steel coiled pipe located inside of a silo lined with fire bricks. In the center of the heater are three natural gas burners each with its own spark-ignited pilot burner. A heater control throttles the fuel flow to the main burners to achieve a set output temperature. A fuel throttling valve can also be set to a constant opening. Due to the low air flow rates required for this study the throttle valve was always set at a constant opening. Typically, the heater is operated at twenty percent of its capacity. At this setting the heater can provide air at 600°C as measured by the heater exit thermocouple. The pipe transporting the hot air to the test cell is heavily insulated. However, because of its length a 100°C temperature drop still occurs.

Fuel Delivery System

The fuel system is capable of handling both liquid and gaseous fuels, as illustrated in Fig. 3.2. Technical grade gases are stored in type 1K cylinders. Commercial propane is stored outdoors in a 800 gallon LP tank. The liquid fuels are stored in a spherical fuel tank in the fuel room. The pressure of the liquid fuels and propane are regulated
Figure 3.2. The fuel delivery system.
with a blanket of nitrogen on top of the fuel. Each of the three supplies are separated with check valves and manual valves.

The flow rate of the fuel is metered with a Gilmount rotameter. For liquid fuels a Gilmount size #2 rotameter, with an eighth-inch stainless steel float, is used. Gaseous fuels are measured with a size #3 rotameter with a quarter-inch stainless steel float. To determine the density and viscosity of the fuel a pressure gauge and thermocouple are located near the flow meter. The fuel temperature is measured just upstream of the flow meter using a thermocouple \* located in the center of the fuel line. The pressure is monitored downstream of the flow meter with a 500 psig pressure gauge. The flow rate is controlled with a quarter-inch needle valve located just downstream of the pressure gauge.

A fuel heater is located just upstream of the fuel injector. The heater serves two purposes. First, heating the fuel lowers the required inlet air temperature for achieving autoignition. Secondly, for liquid fuels the heater serves as a fuel vaporizer to insure that the combustible mixture remains homogeneous.

\* Note: unless indicated otherwise all thermocouples are sixteenth-inch, stainless steel sheathed, and made of chromel/alumel.
Because of the large volume of expanding gas inside the fuel heater, flow surging can be a problem when the path to the fuel injector is opened. Flow surging can cause premature autoignition. To alleviate this problem the fuel vent, see Fig. 3.2, is normally left open. A check valve located upstream of the injector requires an opening pressure great enough to prevent fuel from entering the test section while the fuel vent is opened. The fuel vent valve is an electrically-controlled pneumatic ball valve located downstream of the fuel heater far enough to allow the fuel vapor to cool. To introduce fuel to the test section the fuel vent is closed so that the pressure rises continuously until the resistance pressure of the check valve is overcome.

Another source of premature autoignition is the temperature rise associated with initial fuel flow through the hot fuel injector. Without fuel flow through the injector its temperature is that of the flowing air - typically 600°C. The fuel that first passes through this hot injector is heated to a temperature higher than its steady state value of between 300° and 400°C. This hot fuel mixes with the air yielding a higher mixture temperature, possibly autoigniting with subsequent flashback. To prevent this problem from occurring, a nitrogen purge system was connected between the fuel heater and fuel injector, as illustrated in Fig. 3.2. Before fuel is injected a jet of cold
nitrogen is forced through the injector, cooling the injector below its steady state temperature with fuel flow.

Test Section

The continuous flow apparatus used to achieve autoignition is illustrated in Fig. 3.3. The main feature of the design is the concentric tube arrangement to minimize heat loss.

Air Preparation. Before the air reaches the inlet of the inner tube it is heated by a 15 kW immersion heater and passes through flow-straightening tubes and screens. The heater is used in addition to the twenty-atmosphere heater to provide sensitive temperature control. The heater controls are similar to those used in the fuel heater.

Downstream of the air heater are flow-straightening tubes and screens. The resultant velocity profile produced at the test section inlet is shown in Fig. 3.4. The flow straighteners also flatten the inlet temperature profile as illustrated in Fig. 3.5.

The static pressure in the test section is measured upstream of the fuel injector on a Statham strain gauge pressure transducer. The transducer output is connected to a digital millivolt meter and is linear with pressure.

Test Length. As illustrated in Fig. 3.3 the test length is contained inside a larger pipe. The inner pipe is
Figure 3.3. Schematic diagram of apparatus used to measure ignition delay times.
Figure 3.4. The velocity profile at the inlet of the inner pipe.

Figure 3.5. The temperature profile at the inlet of the inner pipe.
supported in the center of the three-inch diameter outer pipe using two sets of three, circumferentially symmetric, legs. Along the length of the inner pipe are three wall-mounted thermocouples. These thermocouples are used to detect flashback and/or flame stabilization on the fuel injector. Originally they were located in the midstream of the inner pipe, but this led to premature autoignition and flashback in the flow recirculation zone created in the wake of the thermocouples.

The critical portions of the test section are the inlet, where the fuel is injected; and the exit, where the flame is detected. A cross-sectional cut at the injector is illustrated in Fig. 3.6. An enlargement of the test section is drawn in Fig. 3.7. The inner pipe is not drawn to scale, but the figure does indicate the geometries associated with the inlet and exit.

Fig. 3.6 shows the position of the blockage ring over the annulus between the inner and outer pipes. As illustrated, a slight gap between the blockage ring and the outer wall still allows flow in the annulus. The actual flow in the annulus is only twenty percent of the total flow. Originally the intention was to maintain the same bulk velocity on both sides of the inner pipe, and the inlet end of the inner pipe was flared to compensate for the blockage of the fuel injector. The blockage ring was installed after it became evident that to reduce the
likelihood of flashback some heat loss was necessary at the inner pipe surface. Greater blockage also aids in overcoming heater limitations since less flow is necessary to achieve the same velocity in the inner pipe.

The inlet air temperature is monitored using two shielded thermocouples. As illustrated in Fig. 3.6, one thermocouple is located at the tube axis while the other is 0.7 of the radius from the center. To determine the inlet air temperature the readings from the two thermocouples are averaged. The inlet fuel temperature is measured using a thermocouple pushed down inside of the fuel injector.

Figure 3.6. Cross-sectional view of test length inlet just downstream of fuel injector.
The exit end of the test section was designed to reduce the possibility of premature autoignition and flashback, as shown in Fig. 3.7. The water-cooled nozzle acts as a barrier against flashback in the boundary layer. It is 5.7 cm long, with diameter reducing from 3.4 to 2.2 cm. The nozzle acts to block flashback in two ways. First, it is made of copper with a water-cooled jacket, which lowers the wall temperature and increases the heat transfer from the fluid in the boundary layer. Lowering the boundary layer temperature in this manner increases the quenching distance and reduces the flame speed. Secondly, by raising the fluid velocity, the nozzle increases the velocity gradient at the wall.

The nozzle's abrupt expansion at the exit was frequently inspected visually for possible flame stabilization. At no time was any form of stabilization or autoignition in the recirculation zone detected. This is attributed to the large heat transfer associated with the copper end piece that seals the nozzle with the water cooling jacket. Also, the air entrained in the recirculation zone from the annulus is significantly cooler, thus acting as a quench.

The water used to cool the nozzle also serves to quench the combustible mixture downstream. Fig. 3.3 indicates that the water enters 20 cm downstream from the end of the inner pipe. It travels upstream through a quarter-
Figure 3.7. Schematic diagram of test section.
inch tube to the nozzle, cools the nozzle, and is then conveyed downstream in more tubing to the quench ring. The stainless steel ring is made of a loop of quarter-inch tubing with eight 1.54 mm holes drilled symmetrically around the ring. The water quenches the autoignition flame and also cools the back pressure valve.

The pressure in the test section is controlled with a pneumatically-operated Annin globe valve, which can withstand a maximum pressure of 1440 psig at 100°F. A 10 to 50 psig signal will open the valve under all operating conditions. The signal is controlled by a manual pressure regulator located in the control room.

**Flame Detector.** Autoignition is monitored with an ultraviolet sensitive phototube. The phototube and its housing are illustrated in Fig. 3.8. The detector is located directly above the end of the inner tube. The phototube is a Hamamatsu-type R334M UVtron. The tube requires a 350 to 490 V DC power source and emits a small signal when exposed to ultraviolet radiation at wavelengths between 160 and 290 nm. The signal is amplified with a LM 308 operational amplifier and is read on an Analogic digital DC mV meter located in the control room.

The detector is located six inches above the center-line of the test section. The housing is water-cooled to protect the phototube from the heat. The phototube is
Figure 3.8. The ultra-violet phototube flame detector.
separated from the flame by a sapphire window with a transmissivity of 60% in ultraviolet radiation. Two nitrogen jets keep the sapphire clear and prevent the housing tube from filling with combustible mixture which might ignite.

The flame detector works only in the on/off mode. If the phototube "sees" a flame the mV meter jumps to a non-steady value between 20 and 200 mV. At the test section centerline the detector can see a length of approximately two inches. This range does introduce some error in determining the actual position of the autoignition flame.

Fuel Injector. The fuel injector, as illustrated in Fig. 3.6, was designed to keep the mixing time as short as possible. It comprises a ring-shaped piece of 4.76 mm stainless steel tubing of 2.02 cm mean diameter. Drilled through its downstream face are eight evenly-spaced 1.52 mm holes. The inlet stem of the injector is attached to the fuel supply with an AN fitting welded to the outer pipe.

The mixing characteristics of the fuel injector were tested by studying the thermal diffusion of warm air issuing from the injector into a cooler air stream. Temperature profiles were taken at different axial locations and the standard deviation factor (SDF) was calculated.
SDF is defined as indicated below

\[
SDF = \sqrt{\frac{\sum (T_L - T_M)^2}{T_H - T_M}}
\]  

(3.1)

where \( T_L \) is the local temperature, \( T_M \) is the mean temperature of the profile, and \( T_H \) is the temperature of the warm air issuing from the injector. As the temperature profile flattens with axial distance SDF goes to zero. Fig. 3.9 is a graph of SDF versus axial distance taken with this injector at the indicated conditions. Here the fuel to air ratio (F/A) is the mass ratio of warm air from the injector to the cool air in the main air stream. The flow conditions were selected to be representative of those during actual test runs. The standard deviation factor does not fall to zero as predicted because of non-adiabatic conditions at the tube wall. The key factor in this graph is that the slope of the curve drops to zero. The slopes in Fig. 3.9 reduce to zero in one to two pipe diameters from the injector, indicating that the fluids are effectively mixed in less than 6% of the total test length.

For fuel injected into air, thermal diffusion is not as important as is mass diffusion. Work has been done by Forestall and Shapiro [31] on the mixing of a jet in a coaxial stream. The jet contained small concentrations of helium. Concentration profiles were determined at various velocity ratios. They concluded that temperature and
Figure 3.9. Mixing characteristics of the fuel injector as determined by the standard deviation factor of the temperature profile.
concentration profiles have the same shape, and that turbulent Schmidt number is equal to the turbulent Prandtl number. They also noted that turbulent Prandtl and Schmidt numbers are independent of experimental conditions. Their results suggest that the concentration profile varies as the temperature profile with axial distance from a jet source in a coaxial stream. Thus, it is considered that the injector provides complete thermal and mass mixing in less than 6% of the total test length.

**Experimental Procedure**

Successful operation of the test apparatus described in the previous section requires setting the pre-calculated flow conditions, establishing a pre-heat period, and the attainment of an autoignition flame. Each of these requirements are described in this section.

**Pre-Calculations**

With so many independent variables, acquiring useful data requires the calculation of flow conditions before the test rig is operated. Autoignition delay time is sensitive to fluid velocity, pressure, fuel concentration, and temperature. The experimental procedure adopted was to set the pressure, fluid velocity, and fuel concentration; and then measure the mixture temperature at which autoignition occurred. A computer program was written to perform the calculations needed to determine the test conditions.
The calculations performed in the program provide orifice plate pressure drop in inches of water and the fuel flow meter scale readings over a range of equivalence ratios. The program is run for each rig pressure at which data are to be taken. The inputs required are the pressure and temperature at the orifice plate, the fuel density and viscosity at the flowmeter, the stoichiometric fuel/air ratio based on mass, and an approximate inlet air temperature to calculate the fluid velocity.

Pre-Heating

Depending on the type of fuel used and the air flow rate required, the test apparatus can require up to three hours to attain the desired temperature. This long heating period is necessary because of the thermal lag of the piping and insulation connecting the twenty-atmosphere heater to the test cell. The 15 kW electric heater is limited by an 860°C sheath temperature at low flow rates, and by the 15 kW maximum power rating at high flow rates. Typically, the electric heater can raise the air temperature no more than 200°C above the temperature of the air supplied from the twenty-atmosphere heater. The piping, flanges, and insulation around the test section require an hour to heat to steady state temperature. The fuel heater requires thirty minutes to reach a steady temperature.
Establishing Autoignition

After the air flow rate and test pressure have been set, the fuel may be introduced in an attempt to establish autoignition. The inlet air temperature is set below the anticipated autoignition temperature, and the fuel injector is cooled with a nitrogen purge for ten to thirty seconds. The fuel is then injected and allowed to flow for about one minute to allow its temperature to stabilize. As the temperature is below the autoignition value flame is not detected anywhere. The fuel flow is then terminated and the inlet air temperature increased by 10°C. This procedure is continued until an autoignition flame occurs somewhere along the test length.

The combustible mixture can ignite anywhere along the 97 cm length from the fuel injector to the water quench ring. As mentioned earlier, the flame detector is located 81 cm downstream of the fuel injector at the exit of the inner pipe. This is the desired point of autoignition, and the temperature is adjusted until autoignition occurs here.

If the mixture temperature is too high, autoignition will occur inside the inner pipe; and the flame will flashback along the boundary layer to the fuel injector. Should a flame stabilize on the injector the temperature indications from the wall-mounted thermocouples along the inner pipe rise drastically, and the flame detector no longer
indicates flame because all the fuel has been consumed upstream. Thus, a flame stabilized on the injector is detected by the wall-mounted thermocouples only. When this occurs the fuel flow is terminated and the temperature decreased by 10°C.

Autoignition can occur downstream of the inner pipe exit, but it cannot be detected unless it is seen by the flame detector. Whenever an autoignition flame is detected by the flame detector it is considered a valid data point.

When the temperature of the fuel-air mixture is known to be within 10°C of the autoignition temperature, the fuel is injected continuously and the air temperature gradually increased. The autoignition flame moves upstream with rise in air temperature until the flame is beneath the flame detector. At this condition the inlet air temperature, inlet fuel temperature, air flow rate, the air pressure, and fuel flow rate are recorded. The autoignition flame in this position is usually unstable and flashback generally follows.

This test procedure was used to collect data for different fuels over mixture temperatures from 400°C to 750°C, pressures from 1 to 10 atmospheres, bulk fluid velocities from 6 to 30 m/s, and equivalence ratios of 0.2 to 0.7. The procedure employed for data reduction, and the results obtained, are described in the following chapter.
DATA REDUCTION AND RESULTS

Autoignition delay times were measured for propane, ethylene, methane, acetylene, vaporized n-heptane, and vaporized Jet-A. The influence of pressure, temperature, and fuel concentration on delay time were the main focus of the experimentation. When possible, visual observations of the autoignition flame were made and are reported for each fuel. The procedure for data reduction is presented prior to the results.

Data Reduction

Once an autoignition flame has been established, the mixture velocity and test section length are all that are needed to determine the delay time. The test length remains constant at 81.26 cm. The mixture velocity is dependent on the air flow rate, the mixture temperature, and the static pressure. The pressure is the only property that is recorded directly.

The air flow rate is determined using standard orifice plate calibration equations taken from Holman [33]. The orifice plate pressure, temperature, and pressure drop are recorded to determine the air flow rate. The fuel flow
rate is calculated using calibration equations provided by the Gilmount Company. The fuel temperature and pressure at the flow meter are recorded during the experiment. Using these properties the viscosity and density are obtained from Vargaftik [34] for all fuels except Jet-A.

As the mixture temperature along the test length is not constant, the question arises as to what temperature should be used to correlate the delay time. Using the mixture temperature at the fuel injector provides the most consistent results, and has been the approach adopted by most previous workers. This temperature may be calculated at the injector plane using a thermodynamic energy balance. The principle is that the energy contained in the inlet fuel and air is equal to the energy in the exiting mixture, assuming no heat loss across the injector. This energy balance can be solved for the initial mixture temperature as

\[ T_m = \frac{T_A C_{PA} + \text{FAR} T_F C_{PF}}{\text{FAR} C_{PF} + C_{PA}} \]  

(4.1)

where the subscript A denotes air, the subscript F denotes fuel, and FAR is the fuel-air ratio. Specific heats are calculated with empirical expressions that are a function of inlet fuel temperature [36].
The mixture velocity may be calculated from an ideal gas assumption and continuity as

\[ U = \frac{m_m R_m T_m}{P A_p} \]  \hspace{1cm} (4.2)

where the subscript \( m \) denotes mixture, and \( A_p \) is the cross-sectional area of the inner pipe. The ideal gas constant of the mixture, \( R_m \), is a mass averaged gas constant for the fuel and air. The delay time is then calculated quite simply as

\[ \tau = \frac{L}{U} \]  \hspace{1cm} (4.3)

where \( L \) is the length of the test section.

Results

Results are presented for each of the fuels studied to show the effect of temperature, pressure, and fuel concentration on delay time. Comparisons between the various fuels are made, followed by a comparison between the results of this study and those of previous workers.

The relationships for temperature, pressure, and fuel concentration with delay time are based on global reaction theory. The temperature dependence is expressed graphically as the log of delay time versus the reciprocal of mixture temperature for different pressures and fuel concentrations. The correlation should be a straight line whose slope is proportional to activation energy.
The activation energy is determined as

\[ E = \frac{1.9858 \ln \frac{T_1}{T_2}}{T_{m_1} - T_{m_2}} \]  \quad (4.4) 

Pressure dependence is obtained as the log of delay time versus the log of pressure in atmospheres. The slope of the line represents the pressure exponent.

The fuel concentration effect is presented as the log of delay time versus the log of equivalence ratio. The slope of this line is the fuel concentration exponent. As in the case of pressure, the data points shown in these graphs are extrapolated from the temperature dependence graphs at constant temperature with varying fuel concentrations.

In all test runs the fuel temperature was maintained at between 300° and 400°C. Visual observations of the autoignition flame were made at equivalence ratios of 0.3 and 0.4. All observations were made by removing the flame detector and looking down through the sapphire window to the end of the test section. A distance of approximately 5 cm was visible from the nozzle exit along the center line of the inner pipe. For all fuels the flame was intermittent when first observed, but as the temperature was increased it became more stable. Usually it oscillated through several centimeters around a mean position. These
fluctuations are attributed to slight irregularities in velocity, temperature, and fuel concentration, although none could be detected. When the flame started to jump inside the nozzle of the inner pipe, flashback to the injector would ensue. Observations were made at higher equivalence ratios, but the flame was very short-lived. Flame stability worsened as the pressure was increased.

It should be kept in mind that an autoignition flame does not stabilize on any flow disturbance, as is normally associated with flame stabilization. Rather, it is constantly re-lighting at the same point. This consistent ignition at one point denotes the autoignition flame's stability.

Propane

Propane was used as the baseline fuel mostly because of the large quantity available, but also because its behavior was known from previous work at atmospheric pressure (see Freeman [4]). As the baseline fuel, propane was used to calibrate the flame detector and refine the experimental technique.

Autoignition flames were observed at all pressures. The flame was pale blue and burned slightly brighter at higher pressures. Prior to the autoignition flame a cool flame was observed. Cool flames are characterized by a faint luminosity and relatively low temperature rise.
The temperature dependence of propane is illustrated in Fig. 4.1. The test runs were conducted with a variation in mixture velocity from 7 to 27 m/s, temperatures from 560° to 727°C, and pressures from 1 to 10 atmospheres. The activation energy is estimated as 38.2 kcal/kg-mol and is constant with pressure.

Delay time is inversely related to pressure, as illustrated in Fig. 4.2. For this figure the data points were extrapolated from Fig. 4.1 at a mixture temperature of 635°C. The pressure exponent is 1.21.

Fig. 4.3 shows the fuel concentration effect of propane. The fuel concentration exponent is 0.3 and is constant with pressure from 2 to 5 atmospheres.

As expected from global reaction theory, temperature has the strongest influence on delay time. Pressure exerts a moderately strong influence on delay time, while the fuel concentration effect is relatively weak.

Ethylene

Ethylene requires much lower temperatures for autoignition than does propane. The ethylene autoignition flame is less stable. Velocity was varied between 7 and 30 m/s, and pressures from 1 to 10 atmospheres to give autoignition temperatures from 670° to 540°C. As pressure is increased the stability worsens, as it did with propane, but the
Figure 4.1. Influence of temperature on ignition delay times of propane/air mixtures.
Propane–Air Mixtures

$T_m = 908 \text{ K}$

$\tau \propto P^{-1.21}$

Figure 4.2. Influence of pressure on ignition delay times of propane/air mixtures.
Figure 4.3. Influence of fuel concentration on ignition delay times of propane/air mixtures.
difference in stability over the pressure range is not as noticeable. Ethylene flames are slightly bluer than propane flames. Again a cool flame was observed prior to ignition.

The temperature dependence for ethylene is illustrated in Fig. 4.4. The activation energy is estimated as 37.2 kcal/kg-mol and is independent of pressure.

The pressure dependence is shown in Fig. 4.5. The points were extrapolated from Fig. 4.4 at a temperature of 589°C. A scatter between the data and global reaction theory is indicated at pressures of 9 and 10 atmospheres. At these pressures the flame is very unstable, but the results were repeatable. At lower pressures the theory applies very well and the pressure exponent was determined to be 0.75. Pressure exerts less of an influence on ethylene than on propane.

The most surprising results are shown in Fig. 4.6. The plot of fuel concentration versus delay time illustrates an influence of pressure on the fuel concentration exponent, which increases from 0.27 at 1 atmosphere to 0.55 at 5 atmospheres. The sharpest increase is between 1 and 2 atmospheres, with decreasing difference in exponent between subsequent pressure levels. This suggests that the fuel exponent attains a constant value with pressure. The best explanation for these results is a change in the dominant
Figure 4.4. Influence of temperature on ignition delay times of ethylene/air mixtures.
Figure 4.5. Influence of pressure on ignition delay times of ethylene/air mixtures.
Figure 4.6. Influence of fuel concentration on ignition delay times of ethylene/air mixtures.
reactions with pressure of the reacting ethylene-air mixture. If this is true, Fig. 4.4 becomes more interesting owing to the absence of change in activation energy with pressure that might be expected as the dominant reactions change. This would suggest that the dominant reactions at high pressures have nearly the same activation energy as those occurring at lower pressures.

Methane

Methane has a higher autoignition temperature than other fuels. Due to temperature limitations on the heater sheath, data could only be taken over pressures from 7 to 10 atmospheres, mixture temperatures from 727° to 650°C, and velocities from 5 to 13 m/s. A very faint cool flame was observed for methane, even though previous workers have never reported any. This cool flame may be due to the other alkanes present in the fuel, as indicated in Table 4.3. The autoignition flame was paler than for both propane and ethylene flames. The autoignition flames of methane appear to be very stable, even at a pressure of 10 atmospheres.

The delay time-temperature dependence is illustrated in Fig. 4.7. The activation energy for methane is estimated as 25.0 kcal/kg-mol, which is considerably lower than for either propane or ethylene. The activation energy is independent of pressure.
The pressure relationship is shown in Fig. 4.8. The data was extrapolated at a mixture temperature of 690°C. The methane pressure exponent is 0.99, which is closer to the value exhibited for propane than for ethylene.

Fig. 4.9 illustrates the fuel concentration influence on delay time. The stability of the methane autoignition flame at high pressures made it possible to record data up to 10 atmospheres at equivalence ratios greater than 0.4. The effect of fuel concentration is very weak with an exponent of 0.19 and no variation with pressure.

Acetylene

Acetylene is the least stable, and most easily ignited of the fuels examined. Tests were conducted for mixture temperatures from 514°C to 546°C, velocities from 11 to 20 m/s, and pressures from 1 to 3 atmospheres. The tests were conducted at a baseline equivalence ratio of 0.2. The equivalence ratio was lowered to improve stability, and also to prevent coking inside of the fuel injector. Attempts to take data at an equivalence ratio of 0.4, clogged the fuel injector with coke after only eight hours of operation. Stability was also improved by not pre-heating acetylene in the fuel heater. However, acetylene was still heated to between 150°C and 250°C when it passed through the fuel supply tubing adjacent to the test section.
Figure 4.7. Influence of temperature on ignition delay times of methane/air mixtures.
Figure 4.8. Influence of pressure on ignition delay times of methane/air mixtures.
Figure 4.9. Influence of fuel concentration on ignition delay times of methane/air mixtures.
Intermittent pale blue flashes of flame appeared just before the occurrence of flashback. Due to the low equivalence ratio, the flame could not always be detected until the flame flashed back. Observations made at equivalence ratios of 0.3 and 0.4 revealed no blue flame. Instead a brief cool flame followed by a bright yellow flash was observed, and then a flame stabilized on the fuel injector. To correlate the effect of fuel concentration on delay time these flashes were assumed to occur at the end of the test length.

Fig. 4.10 illustrates the temperature and delay time relationship for acetylene. The activation energy is estimated at 30.6 kcal/kg-mol and is constant with pressure. The scatter illustrated is attributable to the two points made earlier. First, acetylene is a very unstable fuel; and secondly, the flame detector loses sensitivity at low equivalence ratios.

The pressure and delay time relation illustrated in Fig. 4.11 shows considerably less scatter. The data points shown were extrapolated from Fig. 4.10 at a mixture temperature of 533°C. The pressure exponent is lower than for other fuels, having a value of 0.66.

Fig. 4.12 illustrates the influence of fuel concentration on delay time. The fuel concentration exponent of 0.75 is the highest of all fuels tested. Although at
Figure 4.10. Influence of temperature on ignition delay times of acetylene/air mixtures.
Acetylene – Air Mixtures

\[ T_m = 806 \text{ K} \]

\[ \tau \propto P^{-0.66} \]

Figure 4.11. Influence of pressure on ignition delay times of acetylene/air mixtures.
Figure 4.12. Influence of fuel concentration on ignition delay times of acetylene/air mixtures.
equivalence ratios from 0.3 to 0.4 stable autoignition flames were not achieved, the data points seem reliable and consistent.

Acetylene was the only fuel tested for which the influence of fuel concentration on delay time is greater than that of pressure. Acetylene exhibits characteristics very similar to those of ethylene, with a slightly smaller pressure influence and a stronger fuel concentration effect. Acetylene flames are much less stable.

n-Heptane

The n-heptane was supplied by Phillips Petroleum Co. This gasoline is rated as 99% pure n-heptane. The liquid fuel was vaporized in the fuel heater prior to injection. This process could only be successfully accomplished at pressures below 2 atmospheres. At higher pressures and vapor temperatures of 350°C, n-heptane should still be in the vapor state, but the results obtained were erratic. Also, when flashback occurred the flame burned as a heterogeneous flame with a yellow streaky appearance and glowing carbon particles.

The autoignition flames observed were extremely intermittent and could be detected a long time before the flame became consistent enough to be considered for a data point. The flames were pale blue and quite stable at low pressures. Cool flames were again observed.
As expected, n-heptane has autoignition temperatures in the same range as propane. Data were taken at pressure levels of 1 and 2 atmospheres, mixture temperatures from 636°C to 707°C, and velocities between 12 and 24 m/s.

The temperature dependence for n-heptane is illustrated in Fig. 4.13. The data were taken at an equivalence ratio of 0.3, which is lower than for most other fuels, in an attempt to obtain data at pressures above 2 atmospheres. The activation energy is estimated as 37.8 kcal/kg-mol, regardless of pressure.

The pressure and delay time relationship is shown in Fig. 4.14. The points were extrapolated at a mixture temperature of 670°C. The pressure exponent is equal to 0.85. This value lies between the values of the exponents for methane and ethylene.

Fig. 4.15 illustrates the influence of fuel concentration on delay time. The fuel concentration exponent has a value of 0.425, thus n-Heptane exhibits the strongest effect of fuel concentration for all the alkanes. The fuel concentration exponent is independent of pressure.

With its large fuel concentration exponent and low pressure exponent, n-heptane behaves in a more similar manner to the alkenes than the alkanes.
Figure 4.13. Influence of temperature on ignition delay times of vaporized n-heptane/air mixtures.

Vaporized n-Heptane–Air Mixtures
$\phi = 0.3$
Figure 4.14. Influence of pressure on ignition delay times of vaporized n-heptane/air mixtures.
Figure 4.15. Influence of fuel concentration on ignition delay times of vaporized n-heptane/air mixtures.
Jet-A was obtained from the Rock Island Refinery in Indianapolis, IN. This company produces fuel that follows the ASTM specifications for aviation gas turbine fuels listed in ASTM D 1655. Unfortunately, data could only be taken at pressures up to 2 atmospheres, while still insuring a homogeneous mixture. The velocity was varied from 13 to 21 m/s at mixture temperatures from 620°C to 690°C.

Jet-A autoignition flames are more stable than n-heptane flames and are pale blue. Flames are observable over a range of 6°C between the first sighting and the onset of flashback. Cool flames are observed at temperatures around 10°C below the autoignition temperature.

The temperature dependence of delay time is shown in Fig. 4.16. The activation energy is estimated at 29.6 kcal/kg-mol and is constant with pressure. This value is well below the commonly accepted value associated with gas turbine fuels of around 40 kcal/kg-mol. The effect of fuel vaporization on the autoignition characteristics of such a complicated fuel are unknown. Jet-A has a distillation range of 100°C, so the light fractions boil off first, possibly producing slightly different fuel characteristics. Of course, for fuel vapor to actually differ from the liquid fuel, some component would have to be left behind in the fuel heater. The heater is mounted vertically and fuel
Figure 4.16. Influence of temperature on ignition delay times of vaporized Jet A/air mixtures.
enters from the bottom and exits at the top. So, a small portion of the fuel may not pass through, although no evidence was found to support this hypothesis.

Fig. 4.17 illustrates the pressure-delay time relationship. The data points were extrapolated at a temperature of 670°C. The pressure exponent is 0.98.

The influence of fuel concentration on delay time is illustrated in Fig. 4.18. The fuel concentration exponent is 0.37 and is constant with pressure.

Effect of Fuel Chemistry

The fuels tested in this study can be divided into three groups: the paraffins - methane, propane, and n-heptane; the olefins - acetylene and ethylene; and a commercial kerosine - Jet-A.

The fuels are listed in order of decreasing autoignition flame stability in Table 4.1, with their respective carbon to hydrogen ratios (C/H) and maximum laminar flame speeds [34].
Figure 4.17. Influence of pressure on ignition delay times of vaporized Jet-A/air mixtures.
Figure 4.18. Influence of fuel concentration on ignition delay times of vaporized Jet-A/air mixtures.

Vaporized Jet-A-Air Mixtures

\[ T_m = 926 \text{ K} \]

\[ \tau \propto \phi^{-0.37} \]
Table 4.1 Fuels Listed by Decreasing Flame Stability, C/H Ratio, and Laminar Flame Speed

<table>
<thead>
<tr>
<th>Fuel</th>
<th>C/H</th>
<th>$S_L$(cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.25</td>
<td>34</td>
</tr>
<tr>
<td>Jet-A</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>Propane</td>
<td>0.38</td>
<td>39</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.44</td>
<td>39</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.50</td>
<td>68</td>
</tr>
<tr>
<td>Acetylene</td>
<td>1.00</td>
<td>158</td>
</tr>
</tbody>
</table>

Table 4.1 suggests autoignition flame stability is a strong function of flame speed. Methane exhibits the most stable characteristics with the lowest flame speed, while acetylene has a flame speed five times higher and is very unstable. This observation is not surprising, since the stability of autoignition flames depends on its flashback characteristics, and flashback is a function of flame speed. A similar relation can be made between C/H ratio and autoignition stability. Fuels with lower C/H ratios exhibit greater stability.

Fig. 4.19 illustrates the temperature-delay time relationship for all the fuels tested. For purpose of comparison the methane data has been multiplied by pressure with an exponent of 0.99. This is the value of the exponent determined for methane. All the data shown are at one atmosphere for each fuel except methane, which is at 7
atmospheres. By using the pressure exponent for methane and comparing it with the other fuel's relationships at one atmosphere, the variation in pressure exponent with fuel type is made inconsequential.

As illustrated in Fig. 4.19, Olefins exhibit lower autoignition temperatures than paraffins over this range of temperatures. This is because the carbon to carbon double bond makes olefins more reactive. As C/H ratio increases the autoignition temperature decreases. The activation energies of the fuels are expected to behave in a similar manner. The olefins, being more reactive, should also have lower activation energies than the paraffins. However, methane and Jet-A exhibit the lowest values, and propane shows the highest. With these results no correlations between fuel type and activation energy can be made.

Fig. 4.20 provides a summary of the pressure and delay time data for all the fuels tested. The relationships were transferred directly from the pressure versus delay time figures presented earlier for various fuels, and are at the same mixture temperatures shown there. Olefins exhibit a smaller pressure dependence than paraffins. Of the two olefins listed, acetylene has the lowest pressure exponent and the highest C/H ratio. No relation can be drawn between C/H ratio and pressure influence within the paraffins. Jet-A exhibits a pressure influence similar to the paraffins.
Figure 4.19. Comparison of temperature effect on ignition delay times for all fuels.
A summary of the fuel concentration influence on delay time is contained in Fig. 4.21. The influence of fuel concentration is generally weak. Ethylene shows a pressure influence on the fuel concentration exponent. As the C/H ratio increases so does the fuel concentration exponent for all fuels except ethylene.

Comparison with Previous Work

Most of the previous work using continuous flow systems employed heterogeneous mixtures. Results are available for comparison for all the fuels studied except ethylene.

In past work Mullins [6] took the most data employing homogeneous mixtures. He found an activation energy for methane of 29 kcal/kg-mol and for acetylene of 31 kcal/kg-mol, which compares very well with the values found in this study of 25 and 30.6 kcal/kg mol, respectively.

Fig. 4.22 is a summary of the results obtained by previous researchers for gas turbine fuels. Results for propane and vaporized Jet-A are included from this study. Propane data were obtained by Lezberg [12] and Freeman [4]. Both estimated activation energies of 38 kcal/kg-mol, which is the same value found in this study. The slight shift between their ignition delay times and those of the present study might be attributable to differences in flame detection. They conducted experiments at atmospheric pressures
Figure 4.20. Comparison of pressure effect on ignition delay times for all fuels.
Figure 4.21. Comparison of fuel concentration effect on ignition delay times for all fuels.
only with visual flame detection.

Correlations for Jet-A were made by Freeman and Marek et al. [11]. Marek studied heterogeneous mixtures and found an activation energy of 16.5 kcal/kg-mol, while Freeman used vaporized fuel and obtained a value of 40.9 kcal/kg-mol. The activation energy measured in this study of 29.6 kcal/kg-mol lies between these two findings. The temperature relationship also lies between their values, but closer to Freeman's results. This shift and change in activation energy may be attributed to two possible causes. First, it might be an effect of pressure on the activation energy. More likely, the shift might be caused by differences in experimental technique and flame detection.

Fig. 4.23 is a summary of the pressure and delay time results of previous work on homogeneous mixtures. The relationships obtained in this study are labeled directly. The numbers in parentheses are the corresponding pressure exponents. As different temperatures were used, the pressure exponents should be compared rather than the positions of the relationships.

Mullins tested methane and acetylene at sub-atmospheric pressures. For acetylene good agreement exists between his study and the present work, but for methane a larger discrepancy is found. The difference between Brokaw and Jackson's [7] pressure exponent for propane and the
Figure 4.22. Summary of results obtained by different workers on the effect of temperature on ignition delay times for gas turbine fuels.
value obtained in this study is appreciable. This difference is attributed to differences in experimental technique. Brokaw and Jackson used the pressure rise associated with autoignition to detect ignition and measured the time directly from fuel injection to ignition. Correlations for n-heptane and ethylene also appear in Fig. 4.23. The exponents for these fuels are within the range of values obtained in other studies.

A summary of the pressure dependence of ignition delay time for gas turbine fuels appears in Fig. 4.24. The pressure correlations for propane and vaporized Jet-A from this research are labeled. The propane pressure exponent is within the range of exponents shown in this figure.

The pressure exponent obtained for vaporized Jet-A agrees very well with the values of Marek et al. and Stringer et al. [16]. Spadaccini and TeVelde [10] have correlated their data using two different pressure exponents. The smaller pressure exponent (1.0) agrees with this study very well. All these studies employed heterogeneous mixtures.

The effect of fuel concentration is contested between different workers. In this study a weak fuel concentration dependence ($m < 0.5$) was observed for all fuels except acetylene. Many previous researchers concluded that fuel concentration exerts no influence on ignition delay
Figure 4.23. Summary of results obtained by different workers on the effect of pressure on ignition delay times for homogeneous mixtures.
Figure 4.24. Summary of results obtained by different workers on the effect of pressure on ignition delay times for gas turbine fuels.
Freeman found no effect for propane and vaporized Jet-A, but recorded a small fuel concentration effect for n-heptane. He found an exponent of 0.23 compared to the value of 0.4 obtained in this work.

In general, good agreement with recent studies was observed for most fuels. In particular, the propane and n-heptane data agrees well with those of Freeman. The vaporized Jet-A data taken in these two studies also agrees quite well. Agreement between these studies is important since one is building on the work of the other.
CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The apparatus described earlier provided consistent and repeatable autoignition data for the six fuels studied. Delay times were successfully correlated with pressure, temperature, and fuel concentration for homogeneous mixtures using global reaction theory whereby

$$\tau \propto \exp \left( \frac{E}{RT} \right) [\text{fuel}]^{-m} [\text{p}]^{-n}. \quad (5.1)$$

Table 5.1 presents a summary of the global activation energies, fuel concentration exponents, and pressure exponents for all fuels tested.

Autoignition flames were located in a controlled position for all fuels except acetylene at higher fuel concentrations. All autoignition flames were pale blue, and variations between fuels were slight. Cool flames were observed for all fuels.

Olefins are more reactive and have lower autoignition temperatures than paraffins. They are influenced more strongly by differences in fuel concentration than are the
paraffins, but show a smaller pressure effect on delay time. The paraffins show a weak fuel concentration influence on delay time.

Table 5.1 A Summary of the Ignition Delay Time Parameters

<table>
<thead>
<tr>
<th>Fuel</th>
<th>E (kcal/kg-mol)</th>
<th>n</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>25.0</td>
<td>0.99</td>
<td>0.19</td>
</tr>
<tr>
<td>Propane</td>
<td>38.2</td>
<td>1.21</td>
<td>0.30</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>37.8</td>
<td>0.87</td>
<td>0.40</td>
</tr>
<tr>
<td>Acetylene</td>
<td>30.5</td>
<td>0.66</td>
<td>0.75</td>
</tr>
<tr>
<td>Ethylene</td>
<td>37.2</td>
<td>0.75</td>
<td>0.27-0.55</td>
</tr>
<tr>
<td>Jet-A</td>
<td>29.6</td>
<td>0.98</td>
<td>0.37</td>
</tr>
</tbody>
</table>

The global activation energy is lower than expected for Jet-A, but lies in the range of results obtained by previous workers. The agreement between Freeman and this study for propane and vaporized n-heptane is very good, while the results for vaporized Jet-A agree slightly less well. Such good agreement suggests that for homogeneous mixtures apparatus effects are not so great as to preclude the possibility of describing the autoignition characteristics with a delay time equation derived from global reaction theory.
Recommendations

Recommendations are made on designing an apparatus for studying autoignition, and suggested for further studies on autoignition characteristics of hydrocarbon fuels.

Test Apparatus

The test apparatus used in this study provided reliable data, but several improvements could be made. These improvements apply to both homogeneous and heterogeneous studies.

The temperature limitations on the system decrease the range of data that can be taken. The maximum sheath temperature of the electric heater is 860°C. At lower flow rates this temperature is reached quite rapidly, while providing an outlet temperature of less than 750°C. One reason for this inefficient heating is that the diameter of the pipe currently housing the heater is too large. A smaller pipe would increase the heat transferred to the air providing an outlet temperature of 800°C. The procurement of a heater with a higher sheath temperature would be even more advantageous.

Another way to increase the range of data would be by increasing the length of the test section. The current test section is 81 cm long. A length of 120 cm would increase the residence time and lower the temperature
requirements. The only concern with a longer test section is the effect of additional heat loss.

In Fig. 5.1 are two schematics of alternate test apparatus designs. Both designs feature the ability to control the test section wall temperature. Such control is advantageous in two ways. A relatively cool wall deters flashback, while a warm wall minimizes the temperature drop along the test length. Obviously there is an optimum compromise temperature, but this temperature changes depending on the fuel type, flow rate, fuel concentration, and static pressure. An uninsulated, electrically-heated wall with a variable power supply would provide sensitive control of wall temperature. Electrical "strap-on" heaters are available in the temperature ranges of interest.

Also common to the two designs are windows located at the fuel injector. For heterogeneous mixtures windows at the injector plane are required for drop sizing. In homogeneous mixtures these windows could be used for mixing studies, and examining flashback at the injector.

The difference in the two illustrations in Fig. 5.1 lies in the method of flame detection. Fig. 5.1(a) shows a flame detector scheme similar to that used in these studies. It provides a strong signal and is very sensitive. The sensitivity is limited by the transmissivity of the sapphire window. Sapphire only transmits 60% of the
Figure 5.1. Two alternative continuous flow ignition systems.
(a) using remote flame detection
(b) using visual flame detection
ultra-violet radiation. Using a window made of lithium fluoride with a transmissivity of 90% would increase the sensitivity. The detector provides a very erratic signal, and determining the precise flame location within the detector's range of "sight" is impossible. A time-averaging signal processor could be used to measure flame intensity, which would increase as the flame moved closer to the test section exit and became more consistent.

Another method for flame detection is illustrated in Fig. 5.1(b). In this design the end of the test section is fitted with an observation window. Visual observations of autoignition flames have several advantages. Most important is the additional knowledge acquired on the characteristics of autoignition flames at higher pressures. Direct observations would also provide greater accuracy over the current design. The window would be cooled and kept clean with nitrogen jets. The recirculation zone at the sudden expansion of the test section would be quenched with either nitrogen or cool air preferably in coaxial flow with the air fuel mixture. A video camera may be used for flame monitoring in the control room during experiments.

Either design in Fig. 5.1 represents an improvement on the current design. The apparatus illustrated in Fig. 5.1(a) is less expensive, but provides less information on autoignition than the alternate design.
Autoignition Characteristics

The next step in these studies is to add the physical effects to the autoignition model. In heterogeneous mixtures the additional physical variables that influence delay time are initial drop size, fuel temperature, and fuel evaporation rate. Once the effects of these properties are defined, a complete model of the delay time can be developed including both the physical and chemical components.

Several characteristics of the autoignition phenomenon have received little or no attention, such as the effect of mixing time and turbulence on the delay time. The influence of mixing could be studied by using homogeneous mixtures and varying the mixing length with different injector configurations. This would involve first measuring the characteristic mixing length at certain flow conditions, and then measuring the autoignition delay time at the same flow conditions.

The effect of turbulence influences delay time by changing mixing time as well as temperature and velocity profiles. Experiments would also be conducted using homogeneous mixtures, and autoignition delay times measured for various values of turbulence intensity and scale while maintaining other flow conditions constant.
These are just two areas that require more study. Previous workers have assumed that these effects are small. Until the proposed studies are carried out the validity of that assumption is questionable.
REFERENCES


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### Title and Subtitle

Spontaneous Ignition Delay Characteristics of Hydrocarbon Fuel/Air Mixtures

### Author(s)


### Performing Organization Name and Address

Purdue University  
School of Mechanical Engineering  
West Lafayette, Indiana 47907

### Sponsoring Agency Name and Address

National Aeronautics and Space Administration  
Washington, D.C. 20546

### Abstract

The influence of pressure on the autoignition characteristics of homogeneous mixtures of hydrocarbon fuels in air is examined. Autoignition delay times are measured for propane, ethylene, methane, and acetylene in a continuous flow apparatus featuring a multi-point fuel injector. Results are presented for mixture temperatures from 670K to 1020K, pressures from 1 to 10 atmospheres, equivalence ratios from 0.2 to 0.7, and velocities from 5 to 30 m/s. Delay time is related to pressure, temperature, and fuel concentration by global reaction theory. The results show variations in global activation energy from 25 to 38 kcal/kg-mol, pressure exponents from 0.66 to 1.21, and fuel concentration exponents from 0.19 to 0.75 for the fuels studied. These results are generally in good agreement with previous studies carried out under similar conditions.