CHAPTER 2

INVESTIGATIONS

A detailed description about the shock tube setup available in IITM used for experimental investigations and measurement of shock velocity and ignition delay time is illustrated in Figure 2.2 to 2.4. The various methods used to measure ignition delay time are collected from various sources along with evaporator unit and mixing unit used to prepare the mixture, measure shock velocity and ignition delay times in the present study is also explained.

2.1 SHOCK TUBE TECHNIQUES

A shock tube provides well-controlled test conditions for ignition studies. Basically, a shock tube is a cylindrical or rectangular cross-section tube, which is divided into two compartments by a diaphragm. One compartment holds high-pressure gas and is referred to as the “driver side”. The other compartment forms the combustible mixture and is called the “test section”. Initially both sides of the tube are at rest. At some point, the diaphragm is broken either by mechanical piercing or by exceeding its structural strength by using aluminium foil of different gauges through overpressurization of the driver side. A strong shock wave is thus created and subjects the combustible mixture to a temperature and pressure rise. After the shock wave hits the wall, it reflects and the reflected wave results in another step for temperature and pressure of the mixture. By controlling the pressures of both sides in the shock tube, a variety of shock strength can be created and thus leading to a range of test conditions. The pressures and temperatures that can be achieved are only constrained by the materials used. Ultimately, this technique is a unique means of heating gases instantaneously and it can be considered to be a “millisecond” high temperature furnace.
Both the incident and reflected shock wave can be used to create test conditions suitable for auto ignition studies. Because the reflected waves stagnate the gas, and through reinforcement of the shock strength, produce higher temperature conditions than incident waves, the reflected shock technique has been widely used in studies to elucidate the mechanism and kinetics of iso-octane oxidation reactions.

The movement of shock front, the contact surface and the rarefaction waves are shown in the x-t diagram of a single shock tube in Figure 2.1[21]. The variation of pressure and temperature along this tube at any instant of time \( \tau \) is also illustrated in the figure. In the ideal case the temperature shows an abrupt rise from the initial room temperature to a very high value as the shock front remains steady up to the contact surface, where it falls quickly to a value well below from room temperature and this slowly rises again to the initial temperature in the rarefaction wave. In practice there is some inter diffusion of gases at the contact surfaces, so that the temperature fall is less sudden than the ideal case.

2.2 CONCEPT OF IGNITION DELAY

In many practical steady combustion systems, ignition is simply a means of starting the system on its way to steady state. Performance and emissions are essentially independent of ignition in such systems as boilers, furnaces, and burners. However, in other practical problems, ignition has a great influence on performance, emissions, and other characteristics, and ignition can explain the performance of the entire system.

Ignition can depend on physical, chemical, mixing and transport features of a problem and in some cases on heterogeneous phenomenon. Excellent reviews of ignition can be found in sources [23,27,38&67] describing thermal feedback, chemical kinetics, chain-branching reactions, and
Figure 2.1. Conventional shock tube, pressure and temperature distribution diagram
other elements. However, ignition in general is an enormous subject. Spontaneous ignition is a process during which a combustible mixture undergoes chemical reaction accompanied by rapid evolution of heat and also emission of light. The induction period or ignition delay time can be defined as the period between the creation of a combustible mixture and the sustenance and onset of rapid reaction phase leading to the rise of temperature and pressure. The ignition delay times can be indicated by either a fixed temperature increase or an evolution of certain species. During the ignition delay period a number of chain branching reactions occur.

Ignition delay is strongly dependent upon the activation energy of the various reactions that comprise the reaction mechanism. Activation energy is the barrier that must be overcome for the initial decomposition reactions within a chemical kinetic mechanism. From the ignition delay expression it is visible that parameters like temperature, pressure, fuel concentration (or equivalence ratio) and oxygen concentration play a role in the process. Since activation energy varies with molecule type, fuel composition plays an important role as well. This finally leads to ignition or formation of a flame, marking end of the delay period.

Many criteria are available in literature to define the onset of ignition.

The entities noted in theoretical analysis are the following [44]:

1. Time for OH concentration to reach a value of $1 \times 10^{-9}$ moles / cm$^3$
2. Based on location of the intersection of the slopes of the tangents from the initial and sudden change of pressure rise
3. Time required to reach a temperature of fixed percent (2 to 5%) higher than initial temperature
4. An interpolation procedure based on the location of intersection of slopes of initial and maximum temperature rise
5. Time for the product of the concentration of C and CO to reach a maximum value
6. The inflection point in the temperature profile [59]
7. Time for maximum CH concentration

In the experimental investigations the following technique have been used, to mark the onset of ignition or end of ignition delay period in Shock – Tube Techniques.

1. From pressure records, when the pressure suddenly rises or the slope changes marked due to this onset of ignition [43]
2. From emission of visible light detected by photosensitive element
3. Time resolved spectroscopic measurement of chemical luminescent emission or absorption of various species like OH, CH₄, CO₂, CH₃, CO, CH, C₂ etc generated during the induction period
4. From heat mixtures, when there is a sudden rise from their normal increase or a marked change in their slopes caused by the onset of ignitions

Each of the criteria mentioned above gives slightly different absolute values of induction period, but their general trends are similar and errors are negligible.

2.2.1 Ignition Delay Time Correlation

A number of different methods have been employed in analyzing ignition time measurements. Perhaps the most useful method involve performing a regression analysis on the experimental data, and using the resultant empirical regression coefficients to express the ignition time as a function of key parameters. The developments of correlation facilitate the comparison of ignition time data among studies, and enable the ignition time sensitivity to a particular parameter to be explicitly stated. However, a variety
of correlation forms have been previously employed, making it difficult to compare directly the results from different studies. Listed below are examples of some of the correlation forms found in the literature.

\[ \tau = Z \left[ F \right]^a \left[ O_2 \right]^b \rho^r e^{B/T} \] [51]

\[ \tau = Z \left[ F \right]^a \left[ O_2 \right]^b \left[ Ar \right]^c e^{E/RT} \] [9]

\[ \tau = (P/RT)^y e^{(A+B/T)} \] [60]

\[ \tau = Z \Phi^k P^n e^{E/RT} \] [11]

where \( Z \) is simply a scaling constant, \( T \) is the mixture temperature, \( \Phi \) is the mixture equivalence ratio, \( \rho \) and \( P \) are the total mixture density and pressure respectively, \( R \) is the universal gas constant, and \( a, b, c, r, B, E, y, A, k, \) and \( n \) are the empirically determined regression coefficients.

Another application for correlation is that they provide a method of scaling time data to different conditions. This is especially useful when attempting to compare ignition time results that have been obtained at different conditions. For example, ignition time measurements obtained at low pressure may be scaled to high pressures using the empirically determined pressure sensitivity. However, the uncertainty inherent in scaling ignition time data becomes more problematic if the ignition time sensitivity to a given parameter does not follow a simple mathematical relationship. This may not be explicitly apparent from the results of a regression analysis, and therefore the accuracy of correlations should be analyzed with respect to the experimental data that was utilized to derive them. Ignition time correlations may also be useful in the development of reduced chemical mechanisms.

2.3 UNCERTAINTIES IN SHOCK TUBE STUDIES

In order to improve the accuracy of the ignition time measurements for the present study, a sensitivity analysis was performed to determine which
uncertainties are likely to be most problematic in obtaining high quality ignition time measurements. These uncertainties have been subdivided into two general classes parametric uncertainties and measurement uncertainties. Parametric uncertainties are defined as those due to uncertainties in the relevant test parameters (i.e. pressure, temperature, and mixture composition) while measurement uncertainties are associated with the inaccuracies inherent in measuring and quantifying the ignition time.

2.3.1 Parametric Uncertainties

The key parameters that determine the ignition time of a combustible mixture are its composition and the local conditions (i.e. pressure and temperature). Based on the results of numerous ignition time studies, it is readily apparent that the ignition time is far more sensitive to temperature than any of the other parameters. Hence, it is concluded that the largest source of error in shock tube ignition time measurements is due to the uncertainty in the post-shock temperature. The ignition time temperature sensitivity is typically specified in terms of global activation energy, which for many hydrocarbons is in the range of 142 – 210 kJ/mol. Most previous shock tube studies base the uncertainty of the reflected shock temperature on the errors associated with determining the incident shock speed at the shock tube endwall. The reflected shock temperature is also depending on the initial temperature of the test gas and the incident shock velocity. Fortunately, the reflected shock temperature is relatively insensitive to the initial temperature of the mixture. For example, 1% uncertainty in the initial temperature (i.e. 3K) will result in an uncertainty of about 1K in the reflected shock temperature. However, uncertainties in the shock velocity are much critical, and therefore most shock tubes are designed to measure the incident shock velocity to a very high degree of accuracy. For reflected shock measurements, the velocity of the incident shock at the endwall is achieved by utilizing a series of pressure transducers spaced axially
along the shock tube wall to determine the velocity profile of the incident shock.

The interaction of the reflected shock wave with the incident shock boundary layer may cause the reflected shock temperature to increase slowly throughout the test period, and thus this temperature rise becomes more significant at longer test times. Also, since viscous effects lead to a deceleration of the incident shock velocity, the increase in the reflected shock temperature during the test period is more rapid under conditions in which the shock attenuation rate is high. Another potential source for error when measuring ignition times is the effect of impurities. It is advisable that prior to each test the shock tube be thoroughly evacuated to minimize the presence of residual gases from previous tests, and that the shock tube be cleaned on a regular basis to remove any stary diaphragm particles that might accumulate.

2.3.2 Measurement Uncertainties

Shock tube measurements are typically obtained in the reflected shock region, where the ignition delay time may be defined as the time interval between the passing of the reflected shock wave and the onset of ignition. For highly exothermic mixtures, in which ignition leads to an abrupt increase in pressure, the ignition time may be accurately measured from the pressure trace alone. However, for relatively dilute mixtures, the rise in pressure at the time of ignition is very gradual, which prevents an unequivocal determination of the ignition time. In order to measure the ignition delay times of highly dilute test mixtures, a variety of diagnostics have been employed to record the time history of a select intermediate combustion species such as OH [13] or the intersection between a line corresponding to the maximum slope and the initial OH or CH concentration [35]. However these diagnostics are usually positioned along the shock tube sidewall, which may lead to severe errors in the ignition time measurement. Specifically, it has been shown that ignition
time measurements recorded at the shock tube sidewall may be significantly shorter than those measured at the endwall due to perturbations caused by the energy release of the reaction [47]. Thus, the correct ignition delay is that which occurs at the shock tube endwall, where the ignition process proceeds in an essentially quiescent reaction zone until the time of ignition. In contrast, the ignition delay measured at the sidewall is affected by the energy release and resulting gas dynamics of the combustion wave as it propagates from the endwall and causes an acceleration of the ignition process. The magnitude of the sidewall measurement error has been shown to be significant for highly energetic mixtures, even when the sidewall location is positioned very close to the shock tube endwall. In addition, at lower temperatures, for which the ignition time becomes relatively long, the ignition process may originate as one or more distinct flame kernels, formed at some distance from the shock tube endwall, thereby causing a misinterpretation of the endwall ignition time. Therefore, when employing the reflected shock technique, a method should be utilized that enables the endwall ignition time to be accurately measured.

2.4 METHODS OF IGNITION DELAY MEASUREMENT

A large number of experimental techniques have been developed in the past for the measurement of ignition delay. Some of them are listed below.

2.4.1 Hot air stream technique

Hot air stream technique developed by Mullins [45] in which liquid fuel is injected into a stream of hot air whose velocity and temperature is known. Measuring the distance between the point of ignition of fuel and the point at which ignition occurs, the ignition delay time of fuel is computed.
2.4.2 Adiabatic compression method

In adiabatic compression method, the fuel air mixture under study is compressed suddenly by a falling piston. This results in sudden heating of mixture and the reaction is followed either by noting the pressure rise or by a photovoltaic cell. This method can be used for fuels whose ignition delay is greater than the time of compression.

2.4.3 Shock tube technique

Shock tube technique, in which a shock wave is used to heat the mixture. The shock wave is an ideal device, which has a short compression time and no wall effects. This method is most suitable for the study of ignition delay characteristics of fast reacting fuels.

2.5 REFLECTED SHOCK WAVES

If the end of the test section is closed, the incident or primary shock reaching the end of the shock tube gets reflected back into the gas, which has already been heated by the passage of incident shock. This results in further increase in pressure, temperature and density of gas. The reflected gas thus affords a convenient means of obtaining elevated temperatures and pressures. To obtain the same condition in an incident shock, extremely high diaphragm pressure ratios and mach numbers would be required.

The advantages and disadvantages of shock tube techniques are listed below,

**Advantages**

1. It guarantees that surface effects won’t contribute to the process since the gas is not heated by hot surfaces and the ‘event’ time is too short for molecules to diffuse to or from the cold wall.
2. It can provide much higher temperature ranges than an electrical heater. Michael and Lim [43] pointed out that “the only reliable method available at present is shock tube technique” for very high temperature chemical kinetic studies.

3. Unlimited choice of temperature. Any required temperature can be instantaneously achieved through the suitable adjustment of present ratio across the diaphragm.

4. Instantaneous heating, which enables study of fast, processes such as relaxation effects.

5. Any gas can be used for study and homogenous heating of the gas at any section is obtained.


Disadvantages

1. The observation time is short (order of microseconds) and hence slow reaction cannot be studied.

2. Suitable only for studies involving gases and vapours.

3. Instrumentation is very expensive. Sophisticated measuring instruments such as electronic counters, photo multipliers, oscilloscope and sensitive probes like piezoelectronic pressure transducers are needed.

2.6 REFLECTED SHOCK TECHNIQUE

Ignition delay technique in shock tube can be made behind incident or reflected shock wave. But most of ignition delay studies are conducted behind reflected shock waves. This is because of advantages of the reflected shock waves over incident shock waves.
The main advantages are

1. For the same diaphragm pressure ratio the temperature behind a reflected shock wave is roughly twice of that behind the incident shock wave.

2. The reflected shock may be used for studying highly exothermic reactions, which cannot be observed behind the incident shock. This is because the bursting of diaphragm causes spontaneous shock and the incident shock accelerates due to the reaction, make it difficult to interpret velocity data.

3. The gas behind the reflected shock is almost stationary so that their time resolution is greater than that behind an incident shock wave.

Even though reflected shock wave techniques have been universally accepted, but Strehlow et al. [55] have pointed out some of its limitations. The main disadvantages of the reflected wave technique is the non-ideal behavior of reflected shock waves. This is due to the interaction of boundary layer created by the incident shock and reflected shock waves.

The above factors posed serious objections to determination of conditions behind the reflected shock from incident shock velocity measurement, using the ideal one-dimensional shock theory. Of the various reflected shock properties, temperature is the only one that cannot be measured accurately and errors in temperature are liable to introduce serious errors in kinetic studies. A number of workers have measured reflected shock velocities and generally have found them to be low compared to the ideal. Strehlow et al [55] have reported experimental reflected shock temperatures to be 4% below the theoretical value in the range of 1500-3000K. Skinner [53] presents evidence that the uncertainty in the temperature calculated from the incident shock velocities is much less than the above. His conclusion from density and pressure measurement is that the region where the reflected shock temperature
would be 1500-3000K for shock waves in Argon, the actual temperature would be 30-60K lower than that calculated from the ideal theory. Measurements of pressure have shown it to be normal, within the experimental error just behind the reflected shock and to increase slowly after the shock. This is because the reflected shock is little weaker than that is required to bring the gas to rest. Subsequently as the gas is brought to rest, the pressure rises.

The best place to observe a reaction in a reflected shock wave would be the center of reflected surface. Here the gas does not spend any time in getting heated to the intermediate shock temperature. The centre of end wall is made likely to experience the expected shock temperature as it is farthest from boundary layer on the walls and the gas is indefinitely at rest at this point. This is supported by previous investigations of chemical reactions behind the reflected shock waves, in which the calculated temperature allowed a sensible interpretation of the results. When a chemically reacting system has been allowed to come to equilibrium behind the reflected shock wave, the final composition has always agreed with calculations based on the ideal reflected shock temperature. The only disadvantage in making observation at the reflecting surface is that cooling by the end plate would be appreciable during the normal period of observation. This could be avoided if the shock wave could be reflected from another shock wave.

From the above discussions, it can be noted that the advantages of reflected shock technique outweigh its limitations. This is also supported by the fact that many investigators have successfully used the technique as reported in previous chapter.
2.7 OXIDATION IN SHOCK TUBE

For hydrocarbon oxidation in shock tube, the entire reaction is divided roughly into three phases: initiation, fuel consumption, and finally CO oxidation. The first two phases may overlap, depending on the fuel considered and initial pressure and temperature. However, the CO oxidation phase is usually distinct. Most of the heat release of overall reaction is associated with the CO oxidation. Thus, the rapid temperature and pressure transients, which are often used to define the end of the ignition delay period, also indicate the onset of CO oxidation. The duration of the overall reaction consists almost entirely of the time required for initiation and fuel consumption, with CO oxidation usually taking less than 1-5% of the total ignition delay time. The rates of reactions between radicals and intermediate hydrocarbon species are much higher than the reactions with CO. Thus, CO oxidation is effectively inhibited until most of these hydrocarbons have been consumed. For the same reason, O, OH, and H concentrations remain low until hydrocarbon species are gone, whereupon they rise rapidly to levels characteristic of CO oxidation.

Experimental Studies

The Ignition delay characteristics of the fuel iso-octane have been studied under reflected shock conditions in the nitrogen heat bath for the range of initial conditions viz. P = 10 to 40 atm, Φ =0.5 to 2.0, N₂ = 79 to 95 %. The temperature ranged from 600 to 1200 K by many researchers.

Apparatus

The shock-tube used in IITM consists of a conventional stainless steel tube of 71mm inside diameter and 14 mm wall thickness. The high-pressure section or driver section is 3 meters long and low pressure or test section is 5 meters long. The full view of the shock-tube is shown in Figure 2.2.
**High-pressure section**

The driver section consists of 3m long stainless steel pipe with steel flanges of 50mm thickness at the ends. The flanges on the diaphragm end has provisions for an ‘O’ ring and for fixing a vacuum nipple, through which the driver section can be evacuated. The other end of the tube is closed by a blind flange, to which the driver gas connections and the pressure gauges have been provided. Figure 2.3. shows the driver section and the diaphragm station.

**Low-pressure section**

The low-pressure section is made up of two tubes of 2 and 3 meters in length, the latter is called the test section. Figure 2.4. shows the test section with instrumentation. The inside of the pipes have been honed to an H8 finish. The two pipes are joined by flanges. The flange at the diaphragm end has a nipple through which the test section can be evacuated.

The other end of the test section is closed by a blind flange with provision for fixing pressure transducers. The test section has provisions to fix four pressure transducers at 30 cm interval for measuring shock velocity. There are two observation windows, one at the end of the test section and the other located 8 cm from the end flange.
Diaphragm station

The diaphragm material used was Aluminium foil of 0.1 mm, 0.15 mm and 0.2 mm thick in order to maintain the desired reflected shock pressure. The diaphragm material is fixed between the flanges of high and low pressure sections. The foils used are collapsible type. The ‘O’ ring on the test section flange ensures a leak proof diaphragm assembly. After each run, the ruptured diaphragm pieces are blown out from the low-pressure section by compressed air.

Vacuum system

A Leybold vacuum pump of 12 m³/hr capacity, single stage, and oil sealed is used to evacuate the H.P and L.P sections of the shock tube. The pump is capable of giving a vacuum of 1E⁻⁰² mm of mercury (1.32 Pa).
Figure 2.3. Driver section and the diaphragm station of the Shock Tube
The vacuum lines from the H.P and L.P sections, mixing chamber, manometers etc. are connected through Leybold vacuum valves to a stainless steel tube, which in turn is connected to the pump. The leak rate of the tube was below $1 \times 10^{-03}$ mm of mercury / min (0.132Pa)

**Exhaust system**

The possibility of using the explosive gases in experiments demands the provision of a proper exhaust system to ensure safety. All the exhaust connections from the shock tube as well as the vacuum pump are connected to an enclosed duct with an exhaust fan, leading to outside atmosphere. In addition to prevent any hazards due to the leakage of explosive gases, the room itself is provided with a good ventilation system.
Preparation of test gas mixtures

Test gas mixtures were prepared by first evacuating a mixing chamber, and then introducing the molar quantities of the constituent gases, and were controlled by the method of partial pressures and stored in mixing chamber at 5 atm pressures. The mixtures were prepared at least 24 hours prior to use, to ensure thorough mixing of the gases. The following table gives the composition of the test gas mixtures for various mixtures.

<table>
<thead>
<tr>
<th>Mix No</th>
<th>Fuel % mole</th>
<th>O₂ % mole</th>
<th>N₂ % mole</th>
<th>Equi:ratio(Φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.42</td>
<td>20.90</td>
<td>78.68</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.86</td>
<td>20.66</td>
<td>78.48</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1.65</td>
<td>20.68</td>
<td>77.67</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>1.95</td>
<td>20.45</td>
<td>77.60</td>
<td>2</td>
</tr>
</tbody>
</table>

2.8 COMPUTATION OF SHOCK PARAMETERS

A direct measurement of the pressure and temperature behind reflected shock wave is rather complicated, owing to the very short time interval (fraction of a millisecond) during which the measurements must be completed. So a measurement of reflected shock parameters is avoided. They are computed from the knowledge of the mixture’s incident shock velocity and molar composition. With the thermodynamic functions of the constituent gases the test mixtures are employed. It is done with the laws of conservation of mass, momentum and energy and the normal shock equations [20]. A computer program developed based on this, assuming no chemical reaction before shock reflection, can be used to compute the reflected shock parameters. The details of calculation are available in literature [21, 25]. The molar enthalpies of iso-octane, oxygen and nitrogen are available in JANAF thermo chemical tables [56].
The test mixture is to be prepared and stored in the mixing chamber at least 24 hours prior to the starting of a series of experiments. After opening the diaphragm station, both L.P and H.P sections of the shock tube are cleaned and flushed with compressed air. The aluminium foil of desired gauge is used depending on the magnitude of the reflected shock pressure (P5) required. The two sides are evacuated to a vacuum of $10^{-2}$ torr, the H.P section is then closed and the test section alone to be continued to evacuate for some more time to get ultra high vacuum. The tube connections leading from mixing chamber to the test section also are evacuated to ensure absence of entrapped air. A McLeod gauge is used to measure the vacuum.

Test mixture is then admitted to the L.P section up to the desired pressure (P1), depending on the value of the temperature required behind the reflected shock (T5). The H.P section is then filled with hydrogen up to the pressure (P4) required to rupture the aluminium foil.

A lower value of P1 will give a higher temperature, as P4/P1 will be more, for a particular value of P4, which in turn depends on the foil thickness. All the measuring instruments like Electronic timers, Charge amplifiers, Oscilloscope etc. are adjusted to proper signal levels depending on the expected shock strength (P4/P1) and mach number (M1), which in turn reads the shock velocity and ignition delay time.

When the diaphragm bursts with increasing the driver gas pressure (P4), the driver gas rushes in to the test section serving as a piston to drive a pressure pulse into the test gas. Since plane normal shock wave front is the stable state, the flow conditions rapidly adjust themselves to conform to this configuration. The incident shock wave heats the mixture to high pressure (P2) and temperature (T2) and the reflected shock wave up to the level of very high
pressure (P5) and temperature (T5). The time duration is of the order of milliseconds, and so it can be assumed that adiabatic conditions prevail.

After each run the gases are evacuated and the shock tube is cleaned using compressed air to flush out the ruptured foil pieces and to ensure that no burnt gases or deposits remain in the shock tube.

2.10 MEASUREMENT OF SHOCK VELOCITY

The incident shock velocity is measured by two kisler pressure pick-ups kept 30 cm apart flush with the walls of the tube. The leads from the pressure pick-ups are connected to an electronic timer through the charge amplifier. The first and the second pressure pick-ups are respectively connected to the start and the stop terminals of the electronic timer. Transient time between stations is measured to an accuracy of ±1µs. The time recorded gives the time taken for travel of the incident shock wave for 30 cm from which the incident shock velocity can be calculated. The reflected shock parameters have been computed from the measured value of the shock velocity.

2.11 MEASUREMENT OF IGNITION DELAY TIME

The duration of the induction period is determined from pressure observations with the aid of a pressure transducer located at the centre of the end plate of the test section. Ignition delay is taken as the time interval between the reflection of the shock wave from the end plate (start signal) and the onset of ignition sensed by a photomultiplier tube (stop signal). The induction times are also read from the oscilloscope with an accuracy of ~5%.