CHAPTER 1

INTRODUCTION

1.1 GENERAL

Among the present problems of the affluent countries, the pollution due to the ground traffic is a major concern. The increasing number of vehicles, especially in the urban areas, as long as carbonated fuels are used, is responsible for the dramatic increase in atmospheric pollution. The pollution due to the vehicles exhaust (NO\textsubscript{X}, CO\textsubscript{X}, HC etc) has a direct effect on human health as well as on the climate change. During the last decade an improvement of the engine efficiency was obtained by redesigning it, but another away to look at the problem is to come up with a reformulated gasoline. Gasoline is a complex mixture of a large number of different hydrocarbons that can be divided in different families. Out of this iso-octane is the major component. The fuel reformulation, for a lower pollutant emission and a sufficient knock rating, requires understanding of the hydrocarbon oxidation as a mixture. Pure hydrocarbon oxidation has been the subject of an increasing number of studies, but only limited data about the interaction between those heavy hydrocarbons are available. Experimental database are of great interest in order to develop and validate detailed kinetic models. For the high temperature side, auto-ignition delay time constitutes an over-all parameter that characterizes the oxidation of the mixture and helps in the detailed kinetic model assessment.

Investigations on Hydrocarbon ignition and kinetic studies are used in modeling of practical combustion systems and prediction of emissions such as in internal combustion engines, jet and rocket propulsion, detonations, pulse combustors and flame initiations. Although the factors like the volatility of
energy prices and the growing concern for pollution control have motivated the development of alternative energy sources, the combustion of fossil fuels remains the primary source of energy throughout the world. In an effort to improve energy efficiency and reduce pollutant emissions, substantial investments have been made in research related to development and implementation of advanced combustion technologies. To ensure high efficiency and better operational performance the new combustion systems must be compatible with desired operating fuel, which is largely dependent on the ignition characteristics of the fuel. The present studies aim at augmenting the above.

As the iso-octane and hydrocarbon mixtures are commonly used for high speed combustion such as in automobile propulsion, the above fuel has been chosen for the present studies. Even though many studies have been done in pure hydrocarbons, the available kinetic and emission data on mixtures of hydrocarbon fuels for automobile propulsion is scarce.

The ignition characteristics of a combustible mixture may be quantified by its ignition delay time, which is defined as the time interval required for the mixture to spontaneously ignite at some prescribed set of conditions. Spontaneous ignition, also referred to as auto ignition, is an important parameter in many combustion applications, which results when the chemical inter reaction of a fuel and oxidizer rapidly accelerates, thereby causing the mixture to ignite. The ignition delay time can be defined as the period between the creation of a combustion mixture, as by injection of fuel in to the oxidizing environment, and the sustenance and onset of the rapid reaction phase leading to the rise of temperature and pressure as well as visible light. It can also be indicated by either a fixed temperature increase or an evolution of certain species. The ignition delay time is essentially a macroscopic measurement of the ignition process, which may be readily obtained by number of methods. By
varying the parameters like pressure, temperature, diluents, equivalence ratio and fuel composition, the ignition delay time sensitivity to each parameter may be ascertained, thus enabling the ignition delay time of a specific fuel to be determined and regulated over a range of conditions. When any combustible fuel-oxygen-nitrogen mixture is suddenly heated by a shock wave nothing happens for a while (Induction period) after which there will be an abrupt increase in rate of reaction coinciding with substantial temperature and pressure changes. The rate of reaction increases almost exponentially towards the end of ignition delay period. The measurement of the dependence of ignition delay on temperature and reactant composition provides a powerful tool for modeling and understanding of combustion.

The efficient use of any fuel necessitates detailed knowledge of high temperature chemical kinetics relating to the formation and subsequent pyrolysis and oxidation of intermediate species. When a higher order hydrocarbon fuel is heated above its ignition temperature, it first decompose to lower hydrocarbons, which in turn start decomposing and reacting to yield final products like carbon dioxide and water. The liquid fuels like petrol and diesel are widely used in automobile and other industrial applications. The pollutants generated through the combustion of liquid fuels are comparatively more.

Iso-octane is an important component of practical fuels. It is also used as a high octane number primary reference fuel in the development of surrogate fuel mixtures for gasoline engine chemistry modeling. The activation energies of iso-octane are higher than n-octane. Hence iso-octane is widely used for combustion simulations. Iso-octane (2,2,4-trimethylpentane), a primary reference fuel for branched alkane components found particularly in gasoline[48], but also are found in diesel [19] and jet fuels [14]. Due to this relevance to practical liquid fuels, iso-octane has been the subject of many
experimental and kinetic modeling studies. Experimental investigations of iso-octane oxidation and ignition have been carried out in shock tubes, rapid compression machine, jet stirred reactors and flow reactors. The important properties of iso-octane are listed in Table 1.1.

The ignition delay periods of iso-octane are short (fraction of milliseconds). In the measurement of such short ignition delay periods, in order to ensure accuracy of the results, the time of the compression process to bring the reactant mixture from the room conditions should be as short as possible relative to the ensuing delay period, so that the reactions occurring during the period become negligible when compared to the reaction process. Therefore, the speed of the compression process must be high and the heat transfer is low so as to measure such short ignition delays. The shock tube technique has the advantages of instantaneous energy input, reduced dependence on transport phenomena, the capability for producing a one dimensional reaction profile where distances behind the shockwave can be related to progress of reaction and the ability to provide such reaction profiles under various conditions like temperature, density and stoichiometry, where stable flames cannot be achieved.

The time available for making measurements on the test gas after the passage of the shock wave is called observation time. This time is usually very short (order of milliseconds) and depends on the shock Mach number and the distance of the observation station from the diaphragm. For measurements
## Table 1.1. Properties of Iso-octane

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>2,2,4-Trimethylpentane</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C8 H18</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>114.23 g mol⁻¹</td>
</tr>
<tr>
<td>Exact mass</td>
<td>114.14 g mol⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>692 mg mL⁻¹</td>
</tr>
<tr>
<td>Melting point</td>
<td>165.71-165.83 K</td>
</tr>
<tr>
<td>Boiling point</td>
<td>372.2 -372.6 K</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>5.5 kPa (at 21 °C)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.391</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Std enthalpy of combustion</td>
<td>-5462.6 – -5460.0 kJ mol(^{-1})</td>
</tr>
<tr>
<td>Std enthalpy of formation</td>
<td>-260.6 – -258.0 kJ mol(^{-1})</td>
</tr>
<tr>
<td>Std entropy</td>
<td>328.03 J K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>242.49 J K(^{-1}) mol(^{-1})</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colorless, transparent liquid</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
</tbody>
</table>
behind the reflected shock waves, it is advantageous to have the measuring station as close to the end flange as possible. The observation time in this case will be the time interval available between the reflection of the incident shock on the end flange and arrival of the reflected wave with the contact surface [20].

The mechanism of combustion of all hydrocarbons is highly complex, involving many species and a number of elementary reactions. After the development of a suitable reaction mechanism, consistent with the available kinetic data, one can obtain the concentration-time profiles of all the intermediate species, ignition delay times, pressure and temperature variations, and other parameters by numerically integrating the kinetic model. Direct quantitative measurements of the above parameters pose greater problems, even with advanced techniques. When ignition data obtained from experimental techniques are complemented by analytical studies, an insight into the mechanism is obtained.

The overall reaction of a fuel-oxidant mixture can be subdivided into many elementary steps. This introduces many complexities. Many intermediate species are formed and consumed during the course of the reaction. Most of these are highly reactive, of fleeting existence and of very small concentrations, yet they determine the overall reaction rate.

Two types of chemical kinetic experiments are available in the field of combustion. The first type may be termed as “reaction specific” and consists of experiments, which are designed to isolate and measure rate coefficients for particular elementary reaction steps. The second type “non-reaction specific” or global which provides information only about the macroscopic behavior of the fuel-oxidizer mixtures. Such experiments include composition profiles in the low-pressure flames, flame speed measurements and shock tube measurements of parameter like induction time. The interpretation of the latter
type of experiments usually requires a complex chemical kinetic model. The measurement and modeling of ignition delay times of fuel is a very powerful tool for exploring the chemical kinetic behaviour of mixtures.

The important applications of chemical kinetic modeling are in the following fields

1. Design of high intensity combustion devices.
2. Control of knocking of I.C. Engines.
3. Prevention of detonation hazards in the flow of explosive fluids through pipes.
4. Control of combustion generated pollutants like PCAH (Poly Cyclic Aromatic Hydrocarbons), UHC (Unburned Hydro Carbons), CO, CO$_2$, Soot etc.
5. Ignition of lean mixtures in I.C. Engines.

For example the thrust of a rocket motor will depend on the state of the combustion products, and a knowledge of the ignition delay times may help to predict this state. Eventhough intermediate species can be observed in situ, their occurrence in the reacting mixture contributes markedly to the macroscopic behavior of the system and their presence cannot be ignored.

Kinetic modeling is extremely useful, as actual experiments of this kind are difficult and very expensive, many times impossible in developing countries.
1.2 MOTIVATION

Combustion of fossil fuel is the major energy source in today’s society. While the use of fossil fuel is a necessity for our society to function, there has been an increasing concern on the emission. Global warming and climate changes have received much attention in recent years. There is a broad consensus that the increase in IC engine emission is directly related to the climate changes we experience today. About 80% of the hydrocarbon emissions resulting from human activities are linked to the energy sector which is mostly related to combustion of fossil fuels. As the world energy demand is increasing, it is a formidable task to achieve a reduction in hydrocarbon emissions.

Although numerous ignition delay and emission studies have been previously conducted, many hydrocarbon species relevant to practical fuels have not been extensively studied. Due to the large number of hydrocarbons that exists in practical fuels, it is clearly advantageous to develop a method that will reduce the number of experimental studies needed to determine the ignition delay characteristics of hydrocarbons. When performing experimental studies, it is necessary to compare current results to past measurements in order to assess the agreement among studies and build upon knowledge base. However, there is often very little overlap among ignition time studies regarding the experimental conditions at which measurements were obtained, making it difficult to compare results directly.

Also, there is currently no standard method employed to develop a correlation that expresses the ignition time of a particular fuel as a function of the relevant parameters. However, the choice of parameters is arbitrary, leading to variety of different correlation forms, and making it difficult to compare these studies. Establishing a method that enables ignition time
measurements to be directly compared when obtained over different conditions would clearly be beneficial.

While ignition time and emission measurements are useful in characterizing the ignition process from a macroscopic perspective, a more detailed understanding of the complex reaction mechanism by which fuel oxidizers is also necessary. This may be provided by detailed chemical kinetic mechanism, which enables the combustion process to be analyzed on a macroscopic level. These mechanisms may include thousands of elementary reactions and hundreds of individual species, and thus temporal measurements of key species are needed to aid in the development and refinement of these mechanisms. Such measurements also enable a more rigorous validation of these mechanisms than those provided by ignition times alone.

1.3 SUMMARY OF PREVIOUS WORK

D. F. Davidson et al [16]. measured the ignition times and OH radical concentration time histories behind reflected shock waves in Iso-octane/O₂/Ar mixtures. Initial reflected shock conditions were in the ranges 1177 to 2009 K and 1.18 to 8.17 atm, with various fuel concentrations and equivalence ratios from 0.25 to 2. They reported the ignition time data with a variety of current Iso-octane oxidation mechanisms revealed that these mechanisms replicate some of the features of the ignition time data reasonably well, but do not accurately capture the temperature dependence of the ignition time or the roll of behavior with rich equivalence ratios.

Hsi – Ping S. Shen et al [33]. studied the ignition of Iso-octane/air/ and Iso-octane/O₂/Ar (~20%O₂) mixtures in a shock tube at a temperatures of 868-1300 K, pressure of 7-58 atm, and equivalence ratios PHI = 1.0, 0.5 and 0.25. Ignition times were determined using endwall OH emission and sidewall piezoelectric pressure measurements. They reported sensitivity analysis
exhibits the importance of HO$_2$ creation and removal for predicting ignition times and the comparison of measurements made for mixtures containing nitrogen and argon as the diluent gas allow for an assessment of the influence of diluent gas on ignition time.

Youngchul Ra et al [65]. presented a reduced kinetic model for IC engine combustion simulation with primary reference fuels like n-heptane and iso-octane. The final version of primary reference fuel mechanism consists of 41 species and 130 reactions. They noted the ignition delay curve sensitivity analysis allows an understanding of effects of individual reactions on ignition delay behavior over a wide range of temperatures and compositions, and was useful in the optimization of the reaction rate constants of important reactions. Based on the validation results they concluded that the reduced primary reference fuel mechanism not only performs reliably as a reaction kinetics model in multidimensional CFD simulations.

Y-H. Chen et al [64]. developed two Iso-octane skeletal mechanisms based on LLNL detailed mechanism, one with 259 species and the other with 291 species. Both the mechanisms predicted the SOC in good agreement with those from LLNL detailed mechanism over a wide range of conditions.

M. Yahyaoui et al [63]. studied the oxidation of gasoline fuel type hydrocarbons. The ignition delay times of several fuel/O$_2$/Ar mixtures have been investigated behind reflected shock waves. As typical representatives of dominant gasoline families, iso-octane, 1-hexene and toluene were chosen. The experiments were carried in the temperature range 1380-1732 K, at pressure around 200 kPa, with 0.05% - 0.4% initial fuel concentrations. The equivalence ratio was varied from 0.25 to 1.5. They reported that the auto-ignition delay time in the case of a bi-component fuel mixture was not a linear combination of the pure fuel auto-ignition delay time but one had to take
into account the interaction between the fuels and their primary oxidation products.

X. He et al [32] examined using a rapid compression facility with iso-octane, oxygen, nitrogen and argon mixtures. They studied the iso-octane ignition characteristics over a range of equivalence ratios (PHI = 0.25-1.0), pressures (P = 5.12-23 atm), temperatures (T = 943-1027), and oxygen mole fractions (O2 = 9-21%), and with addition of trace amounts of combustion product gases. They found carbon dioxide have no chemical effect on ignition delay time. Water was found to systematically decrease ignition delay time by a small amount. The maximum uncertainty in the measured ignition delay time is ± 12% with an average uncertainty of ± 6%.

S. M. Walton et al. [61] investigated the ignition phenomena of iso-octane/air mixtures. The results indicated the existence of two ignition regimes. In one domain, ignition was rapid and ignition occurs simultaneously throughout the test volume. In other domain, reaction fronts form and propagates within the test volume prior to volumetric ignition. The data span equivalence ratios from PHI = 0.20 to 1.98, with inert/O2 gas ratios from 1.38 to 5.89, pressures from 8.7 to 16.6 atm, and temperatures from 903 to 1020 K. They found the ignition delay times for both ignition regimes are well reproduced using a homogeneous simulation with detailed reaction chemistry, when the state conditions were modified to account for the presence of the reaction fronts.
1.4 OBJECTIVES OF THE RESEARCH

High temperature oxidation studies on iso-octane have been carried out by several investigators, but so far, the ignition and emission studies have been mostly confined to a single hydrocarbon or a hydrocarbon with additives. Investigations on the ignition of fuel mixtures are very scarce. The objective of the present work is to investigate analytically the ignition characteristics of iso-octane mixtures and the prediction of emissions at shock tube conditions and IC Engine conditions. [76]

The complete reaction mechanism (994 reactions and 201species) which involve in the combustion of iso-octane is proposed & validated with LLNL (Lawrence Livermore National Laboratory) detailed mechanism. Initially 3606 reactions and 857 species have been compiled and reduced to 994/201. In building up a chemical kinetic model, a number of assumptions have to be made. In fact the assumptions are made so that the conditions simulated correspond to the conditions that prevail in the experimental side. This program has been developed in MATLAB for the calculation and prediction of the concentration of 201 species of iso-octane chemistry for various temperatures, pressures and equivalence ratios. Nitrogen is considered as the diluent. The diluent percentage is assumed as 79% to simulate atmospheric condition. Cantera (an object oriented software for reacting flows) software is used in these studies.

The model of predictions in each case thus provides information pertaining to concentration profiles of species, temperature and pressure rise during and after ignition. The analytical results were compared with the recently reported data of other investigators. Detailed sensitivity analysis and parametric studies were conducted on individual reactions in the kinetic scheme and significant reactions were identified and the simplified scheme is proposed.
Numerical computations were performed to simulate the emissions during the combustion of iso-octane mixtures related to some typical IC Engine conditions at varying equivalence ratios, temperatures and pressures. The results of the present investigations on hydrocarbon ignition and combustion kinetic studies can be used in modeling of practical combustion systems and prediction of emissions such as in internal combustion engines, jet and rocket propulsions.

1.5 COMBUSTION

Combustion or burning is a complex sequence of chemical reactions between a fuel and an oxidant accompanied by the production of heat or both heat and light in the form of either a glow or flames. Each term in the definition requires a further clarification, which explains the complexity of the phenomenon. In simple terms, it is defined as the burning of a fuel and oxidant to produce heat and/or work. Combustion includes thermal, hydrodynamic, and chemical processes. It is the major energy release mechanism on Earth and is the key to humankind's existence, thus explaining its significance. Combustion processes are involved in engines, reactors, thermal plants and a gamut of energy generating units. The post-combustion products now have become a crucial concern for environment. Efficient and responsive use of our energy sources has become a primary concern for human society. Thus, it becomes imperative to have detailed analysis of this complex process. Advanced measurement and control equipment has traditionally been used as a tool for the analysis of a combustion system. The analysis can lead to lower energy use and pollutant emissions. However, when looked in depth, each combustion phenomenon is governed by a chemical reaction or an endless set of them. So calculations and computations become an integral part of combustion analysis, which not only involves certain set of chemical reactions, but a wide variety of
engineering aspects including heat transfer, fluid dynamics, design and thermodynamics.

1.6 AUTO-IGNITION THEORY

Auto-ignition is the spontaneous combustion of a mixture of fuel and oxidizer in the absence of any ignition source. The ignition occurs after some period of mixing between the fuel and oxidizer. It is the initiation of overall chemical reaction. The ignition delay time can be defined as the period between the creation of a combustible mixture, as by injection of fuel into an oxidizing environment, and the onset of the rapid reaction phase leading to the rise of temperature and pressure. The ignition delay times can also be indicated by either a fixed temperature increase or an evolution of certain species.

1.7 FACTS ABOUT POLLUTION

The Environmental Protection Agency (EPA) imposes regulations on NO$_x$ but not on CO or UHC. These standards are typically expressed in parts per million by volume (ppmv) and are referenced to 15% oxygen on a dry basis. The correction formula for NO$_x$ is as follows.

(NO$_x$)$_{\text{ref 15\% oxygen}} = [(5.9) (\text{NO}_x \text{ measured})] / [20.9 – \text{O}_2 \text{ measured}]

Where O$_2$ is expressed in % by volume on a dry basis.

Additionally, CO is referenced to 15% oxygen on a dry basis similar to that of NO$_x$. The correction formula for CO is as follows.

(CO)$_{\text{ref 15\% oxygen}} = [(5.9) (\text{CO} \text{ measured})] / [20.9 – \text{O}_2 \text{ measured}]

Where O$_2$ is expressed in % by volume on a dry basis.

These conditions fall within the high power operating realm where CO and UHC pollutant formations are negligible. Recent advancements to
decrease NO\textsubscript{x} pollutants (i.e. lean direct injection combustors) have decreased the reaction-rate temperatures, which in turn, decrease the formation of NO\textsubscript{x}. Although this method is effective for decreasing NO\textsubscript{x}, decreasing the reaction temperature promotes the formation of CO and UHC. Therefore, the implementation of a low NOx pollutant forming combustor may increase CO and UHC to unacceptable levels and the addition of regulations by the EPA on those pollutants may become necessary.

**1.8 KINETIC MODELING**

Kinetic modeling is the process by which the combustion process can be formulated mathematically. It can be regarded as a tool to analytically describe the complex processes taking place during the combustion process. As a combustion process is completed within a few microseconds, explanation of various developments taking place cannot be explained without an analytical tool. A chemical kinetic model consists of a reaction mechanism, which provides us with a path through which a process moves to attain the final products. Thus using such a model, the effect of various species on the overall performance can also be measured. Furthermore, an analytical tool can also be used to simulate the effect of different conditions on the fuel without conducting the experiments for the same.

In fact good chemical kinetic model should not only predict the behavior of the fuel under specific conditions, but should be able to do so for a wide range of prescribed conditions. The basic limitation to this is the unavailability of sufficient kinetic data. The lack of data to anyone of the elementary reactions considered can produce erroneous results. The rate constant is the most important characteristic of an elementary reaction, which determines the reaction rate.
1.9 REACTION MECHANISM

Reaction mechanism forms the core of the kinetic model. It provides us with a description of the elementary steps, which occur during the conversion of the fuel and oxidizer into the final products. An overall chemical reaction indicates the initial reactants and the final products only. Actually a chemical reaction occurs through a number of reaction steps referred to as the reaction mechanism. It involves almost all the reactions occurring amongst the different species evolved. The reaction mechanism consist of three different types of reaction namely Initiation reaction, Propagation reaction and the Termination reactions.

Initiation reaction involves the reaction in which the fuel breaks down into the various radicals. The fuel molecule gets split up into ethyl radical and methyl radical respectively. This is one of the reactions that occur. Many more reactions of this sort occur. In fact it is these types of equations that start up the process and hence are called the initiation reactions.

Propagation reaction consists of equations between various radicals generated in the initiation reaction. The operation proceeds due to these sets of equations. Equations of this sort may also occur between radicals and molecules, say like $O_2$ reacting with $CH_3$ producing OH etc.

Termination reaction includes reaction that end up in the final products such as Carbon dioxide and water. These are the reactions responsible for the cessation of the process.

1.9.1 Selection of Species

This step involves the inclusion and exclusion of different species, which may involve during the reaction process, based on the theoretical as well as experimental data available.
1.9.2 Kinetic data and thermo chemical data

Kinetic data refers to values such as the forward rate coefficients and the backward rate coefficients of the various reactions that have been chosen in the reaction mechanism. These data have to be collected from recent publications and the experimental data available. The values for the determination of specific heats, enthalpies, entropies and Gibb’s energy called as thermo chemical properties have been collected from the JANAF tables. It is from these values that equilibrium constants and the temperature rise or drop is measured.

1.9.3 Arrhenius equation

The temperature dependence of the rate constant is given by the Arrhenius equation as given below.

\[ K_f \text{ or } K_b = AT^n \exp\left(-\frac{E_a}{RT}\right) \]

Where A is Arrhenius constant, \(E_a\) is activation energy, which is the minimum amount of energy required by a molecule in order to undergo chemical reaction, \(n\) is a constant and is normally equal to zero. The exponential nature of the expression indicates that, with increase in temperature, the rate of reaction increases exponentially. The large increase in the rate is due to more molecules acquiring the activation energy at higher temperature.

1.9.4 Stiff equations

In recent years, the equations of chemical kinetics have been of interest of numerical analyst as they are of combustion engineers. The reason is that the individual equations proceed with vastly differing time scales, which on mathematical modeling give rise to situation called stiffness. The system of equation are called stiff if more than 100 steps are taken over an interval
during which the solutions change by less than 1% only. The differential equations or rate equations become stiff because so many of the terms change very rapidly, at the same time other terms are hardly changing at all. These involve the extremes of very fast and very slow reactions. In chemical kinetics such cases arise and the differential equations denoting the concentration change exhibits the stiffness behavior and are hence called stiff differential equations.

Since the process of combustion of hydrocarbons resulting in final products, carbon dioxide and water, is a very fast process (in the range of few microseconds) which also involves a number of intermediate species, the ignition delays can only be measured accurately by experimental setup such as those conducted using shock tube or flow reactors. Moreover, an experimental set up will also have to be preceded by a theoretical analysis in order to study the process completely. In an experimental study, we cannot measure or examine the study of intermediate species involved. As the process is instantaneous, the only measurable properties are the macroscopic properties such as pressure, temperature and in turn ignition delay period.

The ignition delays of such fuels under different conditions can also be determined experimentally. It is in this context, that the chemical kinetic modeling comes into play. The chemical kinetic modeling opens the door for the theoretical analysis of particular process. For example, if the different reactions leading to the formation of the final products are known, then we could develop a particular model, in which the concentration, temperature, pressure and other properties of the combustion process can be predicted. Stiff equations can be developed and solved using various numerical techniques available like Runge – Kutta or Hamilton method, Gears method, Chemkin, Cantera etc. Availability of large amounts of elementary kinetic data, improved techniques for estimating specific reaction rates, and moreover the
continual growth in size, speed and availability of computers have contributed to the increasing application of the detailed chemical kinetic modeling.

1.9.5 Building up a chemical kinetic model

The basic building block of a chemical kinetic model is the reaction mechanism. The reaction mechanism provides a description of elementary steps which occur during the conversion of fuel and oxidizer into final products. The term “elementary” is used, since any mechanism is really an approximation in which all intermediate states with characteristic lifetimes too small to be resolved or to effect the observable features of the combustion are usually neglected. Often the mechanism to be used can depend upon the combustion environment or on the types of results which are needed from the model.

In practical terms, the mechanism consists of all the chemical species which effect a given combustion event, together with elementary reactions among those species. At first glance this might seem to require an enormous number of reactions. For N species there would be $N^2$ reactant pairs, and for each pair there would be a number of possible products. Fortunately such a situation does not actually prevail. Many reactions that are mathematically possible either do not occur at all chemically or with rates which are vanishingly small. Therefore the construction of a realistic reaction mechanism involves principally the identification of those reactions which rapidly occur and are rapid enough to have an impact on the overall progress of the combustion event.

The combustion of Hydrocarbon fuel consists primarily of the sequential fragmentation of the initial fuel molecule into smaller intermediate species which are ultimately converted into final products usually dominated by water and carbon dioxide. In many cases, the intermediate species can be
fuel themselves. For e.g Ethylene (C$_2$H$_4$) is an important intermediate species in the combustion of Propane and other higher hydro carbons, but it can also be a primary fuel. Carbon monoxide and H$_2$ are common species that are observed during the oxidation of all hydrocarbons. H, OH, O$_2$, HCO etc. are other common species to all Hydrocarbon combustion.

A mechanism can be developed systematically beginning with simplest species and reaction which are common sub-elements in the combustion of more complex species, and sequentially constructed by incorporating new species and reactions in the order of increasing complexity.

1.9.6 The mathematical model

A mathematical model has been formulated to stimulate the ignition process of iso-octane mixtures oxidation under reflected shock conditions. In order to approximate the conditions during the self ignition process behind a reflected shock, the following assumptions were made

1. Constant volume, adiabatic combustion
2. The gases obey the ideal gas laws
3. The test gas mixture behind the reflected shock is at rest and homogeneous
4. Heat losses by conduction, convection or radiation are negligible
5. No wall effects
6. No diffusion of species
7. All species are assumed to be present in gas phase only

With the above assumptions the self ignition process behind the reflected shock wave reduces to a purely kinetically controlled problem. But in spite of the impressive list of assumptions, the greatest uncertainty is in the published experimental rate constant values used. This is a complicated matter since an error in the rate of one reaction may or may not have a vital effect on
the computed ignition delay times, depending on the importance of that reaction.

1.10 NEED OF COMPUTATION

The mathematical analysis of the combustion phenomenon is however, almost impossible without the aid of a computational machine, due to the intricacy of the process. Therefore, in recent years, computational codes, including kinetics and fluid dynamics codes have been used as an added tool for combustion analysis. These methods involving computational codes, however, require a prior knowledge and background of programming languages, thus restricting their application to some extent. In other words, they cannot be implemented in classroom teaching and are much difficult to be used in general combustion calculations. Moreover, the process of writing codes is time-consuming, and in some cases, also requires a lot of computational time and power. To overcome these shortcomings of computational codes, and to make the computations more fluent, some combustion computational tools have been developed in the recent past.

Two of such software or tools, are Cantera and Chemkin. But before putting to practical applications, it becomes necessary to understand the working of the tool, and then validating its solutions either against experimental results or with the standard results available. Thus the project aims at i) understanding the working of the two software in detail ii) observing whether Cantera can be implemented in the regular course curriculum and iii) comparison of solution of selected combustion problems amongst the two as well as with the standard results available.
1.10.1 CANTERA

Cantera is an object-oriented, open source suite of software tools for reacting flow problems involving chemical kinetics, thermodynamics and transport processes. It can be used to conduct kinetic simulations with large and complex reaction mechanisms, to compute chemical equilibrium, to evaluate thermodynamic and transport properties of mixtures, to evaluate species chemical production rates and to create process simulators using networks of stirred reactors. Cantera is a multi-platform combustion tool and can be used on Windows, Mac, Linux and Unix platforms. Moreover, it can be used with the help of various programming languages such as C, C++ and Fortran 90. The most convenient feature is its ability to be operated from interactive/scripting environments such as MATLAB and Python for rapid problem solution. Cantera consists of a kernel written in C++, and a set of language interface libraries that allow using Cantera from other programming languages. The kernel is object-oriented, and defines a set of classes that represent important entities for a reacting-flow simulation. A great advantage of an object-oriented framework is that, objects can be combined together to build more complex dynamic systems and process models. For example, it is a simple matter to quickly put together a complex network of stirred reactors. Throughout this project, various problems of different aspects of combustion have been solved using the user-friendly Matlab interface. Cantera can be easily linked to Matlab, through its toolbox, which is further linked to the kernel of the software. All the links and how cantera operates through Matlab is explained clearly in Figure 1.1. Being an object oriented software, cantera uses a gamut of objects for various purposes.