LAMINAR FLAME SPEEDS AND AUTOIGNITION OF DIMETHYL ETHER
AT ELEVATED PRESSURES AND TEMPERATURE USING
NOVEL COMBUSTION TECHNIQUE

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NOVEL COMBUSTION TECHNIQUE

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ABSTRACT

Dimethyl Ether (DME) is a candidate fuel that has potential to be renewable and advantageous over diesel in terms of combustion and emission characteristics as well as suitable for use in stationary gas turbines. Further, it can be used neat as well as blended with diesel, gasoline or other fuels in conventional and advanced CI engines. The design of various types of engines that use DME as a fuel is greatly dependent on computational simulations which require validated chemical kinetic mechanisms that can reliably mimic the combustion and pollutant formation behavior of DME at physical conditions that are relevant to engines. The objective of this work is to contribute to a better understanding and validation of chemical kinetics of DME, particularly at elevated pressures. This is done by obtaining data for auto-ignition and laminar flame speed of DME, which is subsequently used to assess and refine existing chemical kinetic mechanisms.

To this effect, a novel optically accessible experimental facility, called DCF (Dynamic Combustion Facility), is first designed, fabricated, characterized and validated for laminar flame propagation studies. In this facility, the combustible mixture in the reactor cylinder is compressed to elevated pressures and temperatures by controlled motion of the reactor piston through a custom-designed hybrid cylinder arrangement. Spark is initiated after compression in the constant volume spherical chamber, yielding an outward propagating flame which is observed by Schlieren imaging technique. The procedures for data interpretation are developed and the experimental conditions under which piston motion
induced temperature non-homogeneity is avoided are delineated. The facility is validated by obtaining data for methane/air flame speed at atmospheric and elevated pressures and comparing with the literature data. Subsequently, flame speed data for DME is obtained over a range of pressures and compared with predictions from recent chemical kinetic mechanism.

The phenomenon of autoignition in the low-to-intermediate temperature region is of great practical importance in engines. Advanced combustion engines are based on low temperature combustion regime. Operation at these low temperature strategies is significantly kinetically-influenced by the complex low temperature chemistry of fuels. Therefore, autoignition of DME is investigated at low temperatures (630-785 K) and high pressures (8-38 bar) over a range of equivalence ratios (1-6) using a Rapid Compression Machine (RCM). In addition, the effect of CO\textsubscript{2} addition on ignition is investigated to gauge the effect of exhaust gas recirculation. Results show that DME is very reactive and there is significant kinetic activity during the compression stroke. Experiments using CO\textsubscript{2} show that there is no kinetic effect of CO\textsubscript{2} on ignition delay. The experimental data are compared with simulations from available detailed and skeletal chemical kinetic models. In general, there is good overall agreement and discrepancies are noted at low temperatures. The key reactions are identified through flux and sensitivity analysis.

The designed facility (DCF) is a novel approach and will be a substantial contribution to the existing arsenal of experimental facilities in combustion. The innovation can extend the range of experimental studies to higher pressures and temperatures, conditions beyond those attainable in existing facilities.
DEDICATION

To unknown HOPE and PASSION which has always triggered me!
To my family, relatives, friends and place for their care, courage, motivation and trust!

To my Grand-father: Chet Bhakta; Father: Shiva Prasad, and Bijay.
To my generous teacher, Dr. GAURAV MITTAL, for his knowledge and opportunity.
To my father-mother: Chandra Kant & Moti Maya Baral, and Surya Prasad Baral for their unconditional support.

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Few sweet memories: working late in tubular flames, GC, JSR, oil in floor from RCM, NASA droplet, problem in labVIEW, unforgettable sweets and food, Madam, Narayani, muffler of DCF, bursting of spark, >1000 numbers of test, frequent lab visit, blast and repair, again blast few more repairs, now next problem, hi! Bill & again repair, blast of oil in room, police, breaking of the piston, hopeless, it is impossible, and after 5 and half years, finally it worked. A genuine piece of theory, and the vigorous experiments. A dream, which came true with enormous possibilities.
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NOMENCLATURE

\( c_p \)  Specific heat (J/kg.K)

\( h_k \)  Specific enthalpy of the \( k \)th species (J/kg)

\( K \)  Flame stretch rate (1/sec)

\( L \)  Markstein length (cm)

\( Le \)  Lewis number (ratio of thermal diffusivity to mass diffusivity, dimensionless)

\( Ma \)  Markstein number (dimensionless)

\( P \)  Pressure (bar)

\( r_f \)  Flame radius (cm)

\( R_u \)  universal gas constant (J/K.mol)

\( S \)  Laminar flame speed (cm)

\( T \)  Temperature (K)

\( u \)  Speed (cm/sec)

\( W_k \)  Molecular weight of the \( k \)th species (g/mol)

\( \bar{W} \)  Mean molecular weight of the mixture (g/mol)

\( Y_k \)  Mass fraction of the \( k \)th species
Abbreviation

CC       Compression correction
CI       Compression Ignition
DCF      Dynamic Combustion Facility
DME      Dimethyl Ether
HCCI     Homogeneous Charge Compression Ignition
IC       Internal Combustion
OPF      Outward Propagating Flame
RCM      Rapid Compression Machine
ZOI      Zone Of Interest

Greek Symbols

\( \gamma \)  Specific heat ratio
\( \delta_D \)  Flame thickness
\( \phi \)  Equivalence ratio
\( \rho \)  Density
\( \lambda \)  Thermal conductivity
\( \dot{\omega}_k \)  Molar rate of production by chemical reaction of the \( k^{\text{th}} \) species per unit volume
Subscripts and Superscripts

\( b \) Burned conditions

\( c \) Conditions at the end of compression

\( i \) Conditions at the time of spark

\( o \) Upstretched conditions, standard state, initial conditions before the start of compression (for pressure and temperature)

\( u \) Unburned conditions
CHAPTER I

INTRODUCTION

1.1. Overview

Study of combustion characteristics of various fuels is important for sustainable energy. According to the data provided by the World Energy Resources (2013), energy due to the combustion of fossil fuels was 82%, leaving 11% for renewable, 5% nuclear and 2% for hydropower. A prediction for 2020 has been made in the same report, mentioning 16% increment in the renewable energy, while decrease in fossil fuels to 76%. However, it is clear that the consumption of fossil fuels will dominate for decades. Due to this fact, the byproducts like oxides of carbon and nitrogen (CO, CO$_2$ and NOx), particulate matters like soot and other pollutants of vehicles will continue to be a topic of concern. Moreover, the production of greenhouse gases, environmental hazards and future energy crisis are also concerning. To overcome these disasters in the future, focus is required on ideas based on sustainable fuel concepts for industries and transportation. In the current scenario, Dimethyl Ether (DME) is a promising alternative fuel with ease in production and application. It has shown a great potential to be a future fuel for IC (Internal Combustion) engines; as a replacement for diesel in the CI (Compression Ignition) engines as well as for stationary gas turbine engines. This dissertation is focused on understanding the combustion characteristics of DME at elevated pressures relevant to engine conditions.
1.2. Fossils Fuels

In the current scenario, fossil fuels are the major source of energy, catering to the wide range of transportation and industrial use despite of being limited.

1.2.1 Benefits of Fossil Fuels

(1) Ease of application and portability: The calorific value of fossil fuels is higher in comparison to other renewable fuels. Transportation of liquid fossil fuels is easy. For centuries, they have been serving as an easy, portable and reliable source of energy.

(2) Low cost and easy availability: In comparison to other sources of energy, extraction of fossil fuels is not so expensive. Due to their high consumption rate, it has been forecasted that the ratio of verified oil reserves to consumption makes them available for 40 more years (Olah, 2005). There are possibilities of discoveries of more sources and development of blends of fossil fuels with biofuels.

(3) Properly developed technology and infrastructure: Since the realization of fossil fuels as the foremost source of energy, ample studies and investment has been made for the process of extraction, purification and application, and considerable infrastructure exists. Development of infrastructure for any alternative fuel is a big challenge.
1.2.2 Challenges Facing Fossil Fuels

(1) *Energy crisis and security:* Fossil fuels are nonrenewable and rapid depletion of oil reserves is a problem. We may run out of fossils fuels in a few decades. Depletion of fossil fuels is a serious topic of concern as the economic activities today are so overwhelmingly dependent on the combustion of fossil fuels. Energy security is an important concern.

(2) *Environmental problem:* Air pollution from use of fossil fuels is a great concern for all natural and biological species. Carbon dioxide that is produced after burning is considered a greenhouse gas, which is a key factor in global warming. Melting polar ice, rising sea levels, flooding of low lying areas, acid rains, extinction of ecological species are the post effects of global warming which will create disorder in the ecosystem.

Fast depletion and environmental effects of fossil fuels have become crucial and problematic, making it necessary to pursue various alternatives to fossil fuels. One of the promising fuels in this regard is DME.

1.3. DME as a Prospective Alternative Fuel

DME is the simplest ether and has several properties similar to the diesel fuel. It is colorless, non-toxic and highly flammable. Its molecular structure is shown in Fig. 1.1.
1.3.1 Properties of DME

Table 1.1 - Properties of DME vs Diesel fuel (Park et al., 2013; Arcoumanis et al., 2008)

<table>
<thead>
<tr>
<th>Properties</th>
<th>DME</th>
<th>Diesel</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Structure</td>
<td>CH₃OCH₃</td>
<td>C₁₂H₂₃</td>
<td></td>
</tr>
<tr>
<td>Carbon content</td>
<td>52.2</td>
<td>86</td>
<td>Mass%</td>
</tr>
<tr>
<td>Hydrogen content</td>
<td>13</td>
<td>14</td>
<td>Mass%</td>
</tr>
<tr>
<td>Oxygen content</td>
<td>34.8</td>
<td>0</td>
<td>Mass%</td>
</tr>
<tr>
<td>Carbon-to-hydrogen ratio</td>
<td>0.334</td>
<td>0.521</td>
<td></td>
</tr>
<tr>
<td>Critical temperature</td>
<td>400</td>
<td>708</td>
<td>K</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>5.37</td>
<td>3.00</td>
<td>MPa</td>
</tr>
<tr>
<td>Critical density</td>
<td>259</td>
<td>-</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Liquid density</td>
<td>667</td>
<td>831</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Relative gas density with air</td>
<td>1.59</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Molar mass</td>
<td>46</td>
<td>170</td>
<td>g/mol</td>
</tr>
<tr>
<td>Cetane number</td>
<td>&gt;55</td>
<td>40-50</td>
<td></td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>508</td>
<td>523</td>
<td>K</td>
</tr>
<tr>
<td>Stoichiometric air/fuel mass ratio</td>
<td>9</td>
<td>14.6</td>
<td></td>
</tr>
<tr>
<td>Boiling point at 1 atm</td>
<td>248.1</td>
<td>450-643</td>
<td>K</td>
</tr>
<tr>
<td>Enthalpy of vaporization</td>
<td>467.13</td>
<td>300</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>Lower heating value</td>
<td>27.6</td>
<td>42.5</td>
<td>MJ/kg</td>
</tr>
<tr>
<td>Gaseous specific heat capacity</td>
<td>2.99</td>
<td>1.7</td>
<td>kJ/kg K</td>
</tr>
<tr>
<td>Ignition limits</td>
<td>3.4-18.6</td>
<td>0.6-6.5</td>
<td>Vol% in air</td>
</tr>
<tr>
<td>Modulus of elasticity</td>
<td>6.37e+08</td>
<td>14.86e+8</td>
<td>N/m²</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>&lt;0.1</td>
<td>3</td>
<td>cSt</td>
</tr>
<tr>
<td>Surface tension (at 298 K)</td>
<td>0.012</td>
<td>0.027</td>
<td>N/m</td>
</tr>
<tr>
<td>Vapor pressure (at 298 K)</td>
<td>530</td>
<td>&lt;&lt;10</td>
<td>kPa</td>
</tr>
</tbody>
</table>
Figure 1.1 - Molecular structure of DME

DME has combustion characteristics similar to diesel fuel, and, therefore, it came into frontiers as a possible alternative fuel. A comparison of the important properties of DME and diesel is made in Table 1.1. DME can be produced from fossil fuels like natural gas and coal as well as from renewable, biodegradable waste (Oberon partnership, 2013). High cetane number of 55-60 makes DME autoignite easily and suitable for CI engines (Semelsberger et al., 2006). The bond breaking energy for DME, which has C-O bond, is less than the C-C and C-H bonds in diesel, which causes shorter autoignition delay (Teng et al., 2001 & 2004). Absence of C-C direct bond in the molecular structure, low carbon-to-hydrogen ratio and higher oxygen content (34.8%) in DME yield almost zero particulate matter (PM) emissions at all engine speeds and loads (Semelsberger et al., 2006). In essence, DME is suitable for combustion in the CI engines that use diesel with the added advantage that soot formation is avoided.

Vapor pressure of DME is greater than 5 bar at 298 K. Due to its high vapor pressure, the injected DME exists in superheated vapor phase in combustion chamber and

---

H₃C – O – CH₃

---

O

---

CH₃
mixes relatively rapidly. DME also has higher latent heat of vaporization than diesel. As a result, evaporation of DME in a CI engine results in lower charge temperature after injection of fuel (Park et al, 2013).

1.3.2 Challenges Regarding Use of DME in CI engines

Although DME shows potential for replacing diesel fuel, one of the problems with DME is due to its low viscosity and energy density in comparison to diesel.

It is well established that DME cannot be used in current diesel engines without modification of various fuel injection system parts. Due to low viscosity and high vapor pressure of DME, development of proper fuel injection system is necessary. Some of the challenges and modifications required for use of DME in CI engines are discussed below.

1) Fuel storage and supply

For operation on DME, different fuel storage and fuel delivery system is required, though it does not require engine modifications. Boiling point of DME at normal atmospheric pressure is ~248K, and DME exists in gas phase at normal pressure and temperature. Therefore, a technique used to store LPG (Liquefied Petroleum Gas) can be used for DME due to similarity in physical properties (Zhang et al., 2012). Fuel tank size of DME should be double than diesel fuel owing to lower energy density. Fuel line from fuel tank to the engine can also be similar to the supply system of LPG based engine.
2) Cavitation in the injection system

The low boiling point of DME necessitates higher pressure in the injection system to avoid cavitation (Edgar et al., 1997). Frequent cavitation at higher loads can lead to engine knocking and emission problems. Prevention of cavitation helps stable fuel injection. DME remains in liquid state under normal temperature if pressurized above 0.5 MPa.

3) Lower injection pressure

However, due to low boiling point, DME evaporate immediately when injected as a liquid. Low injection pressure of 20 -30 MPa is sufficient for DME in comparison to the current modern diesel engines which require pressure of 50 – 150 MPa.

4) Leakage

Low viscosity of DME causes problem of leakage in the injection system, making current system of diesel engines unsuitable for DME. Even up to 40-50% of fuel leakage has been reported (Edger et al., 1997). Conventional sealing materials used in diesel injection system cannot prevent leakage of DME. Application of Teflon and PTFE compounds can solve the problem of leakage (Sorenson, 2001). The fluorocarbon based polymer named EPDM and KalRez have also been tested successfully.

5) Low lubricity

Wear of fuel injection system parts is caused by low lubricity of DME. The problem worsens in case of parts which have to be operated in very less clearance. In order to make DME a suitable fuel, blends with other hydrocarbon fuels have been
considered. Nielsen and Sorenson (1999) studied DME fuel with additives to investigate the wear characteristics of DME in diesel engine. Various roughness measurements and photographic techniques were used to characterize the wear of the pump plunger and they concluded that the additives in DME may not solve long term problem of wear.

Sivebaek et al. (2013) measured viscosity of pure DME as well as blends with other diesel, biodiesel, vegetable oil, in order to get viscosity similar to conventional diesel. It was shown that it is impossible to reach the level of viscosity by addition of these additives. Blending of Castor oil (C12 fatty acid) by 1% weight significantly improved lubricity in comparison to pure DME, though it may lead to emission problems (Teng et al., 2002). This problem creates vulnerable engine parts jeopardizing the durability of the expensive injection system.

6) Longer injection duration

Heating value and density of DME are 64.7% and 80% of diesel. To achieve similar engine energy input, 1.8 times more DME (by volume) should be injected than diesel fuel. DME also has lower bulk modulus, which slows the propagation of pressure wave and lengthens injection delay and duration (Sheng et al., 2012). This requires modifications in the injection period and timing.

7) Higher compression work

Due to higher compressibility and lower density, the amount of work required to compress the fuel in pump will always be higher than diesel fuel (Sorenson et al.,
At higher temperature, fuel heating occurs which results in further increase in compressibility and decrease in density.

In order to retrofit current diesel injection systems to use DME, still more research has to be done. Regardless of these challenges, Volvo had announced to commercialize DME powered vehicles in North America by 2015 (Oberon partnership, 2013).

1.4. Synthesis of DME

In 1929, Brown and Galloway first published a paper on the direct synthesis of DME; although commercialization of direct DME production started after 1990 (Sofianos and Scurrell, 1991). DME can be produced from natural gas and other sources like biomass and coal. There are mainly two methods for the production of DME. An indirect route produces methanol which is dehydrated into DME, and a direct route in which DME is produced using single bi-functional catalyst unit directly. There are lots of production companies like Haldor Topse, Air products, MGC, JFC Holding, Toyo, MGC, Lurgi etc which are working using the basic or self-developed direct route. A main step in the synthesis of DME is production of synthesis gas from the feedstock (Azizi et al., 2014).
1.4.1 Indirect Method

Kabel and Johnson (1962) proposed that ether is formed from ethanol at very low temperature without any kind of branching reactions to olefins. Later on, Gates and Johnson (1971) proposed that similar mechanism can be used to make DME. This indirect method occurs in two steps. First, methanol is produced by synthesis gas (syngas) and purified, and then it is converted into DME by the process of dehydration as below

\[
2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}; \quad \Delta H_{298K}^{\circ} = -23.5 \text{ kJ/mol}
\]

In theory, dehydration of methanol occurs at low temperature, but due to the exothermic nature of the reaction, products like ethylene, carbon monoxide, hydrogen and coke formation is significant (Aziz et al., 2014).

1.4.2 Direct Method

Direct synthesis of DME from syngas (H\textsubscript{2}, CO and CO\textsubscript{2}) occurs via reactions (1) or (2) below. The first reaction occurs in three consecutive steps; (i) methanol synthesis from syngas (reactions a, a*), (ii) dehydration of methanol (reaction b) and (iii) water gas shift reaction (reactions c). These three steps are simultaneously executed in a one-step process using bi-functional catalyst. Reactions (a) and (c) are catalyzed by methanol synthesis
catalyst (CUO-ZnO-Al₂O₃) and reaction (b) by HZSM-5 (Gądek et al., 2013; Peng et al., 1997).

\[
\begin{align*}
3\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2 \quad -246.0 \text{kJ/mol} \quad (1) \\
2\text{CO} + 4\text{H}_2 & \leftrightarrow 2\text{CH}_3\text{OH} \quad -182 \text{kJ/mol} \quad (a) \\
\text{CO}_2 + 3\text{H}_2 & \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad -49.4 \text{kJ/mol} \quad (a^*) \\
2\text{CH}_3\text{OH} & \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad -23 \text{kJ/mol} \quad (b) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad -41 \text{kJ/mol} \quad (c) \\
2\text{CO} + 4\text{H}_2 & \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad -205.0 \text{kJ/mol} \quad (2)
\end{align*}
\]

Reaction (2) occurs without interference of water gas shift reaction. Water produced in reaction (a*) and (b) is removed via water-gas-shift reaction to produce hydrogen which kinetically favors the production of methanol.

1.4.3 Economic Analysis of DME Synthesis

The most common method for production of DME is by dehydration of methanol; so it seems that it will be more expensive than methanol. Lots of research is going on in order to directly get DME, and the methods are still in the process of economic and feasibility analysis. A study was done by Huisman et al. (2011) to estimate the cost of biomass-to-fuel plant producing methanol, DME or hydrogen. It was found that bio-methanol production cost was in the range of ethanol production cost, while DME production cost was lower than the current market price for RME (Rapeseed Methyl Ester).
Production of DME may be commercially attractive and reduction in cost can be achieved by using cheaper feedstock or large scale production facilities. Based on vapor phase DME synthesis by Hysys process simulation software, Tavan et al. (2013) studied that the capital investment in conventional DME is greatly affected by distillation tower and operating cost. Dividing Wall Column (DWC) technique leads to significant reduction in operational cost. Oberon Fuels has been focusing on converting abundantly found and inexpensive natural gas into DME as a high valued transportation, construction and household fuel in North America. DME is also being promoted as a second generation synthesis biofuel for significant use in European Union vehicles by 2030 (Bio-fuel Research Advisory Council).

1.4.4 Well-to-Wheel and Wood-to-Wheel Analysis for DME

Economics of well-to-wheel in diesel fuel can be changed into wood-to-wheel in case of DME, though DME can also be produced from fossil fuels. Efforts on production of DME through the process of gasification from multiple feedstock is an attractive direction. To implement this idea, Chemrec in Sweden has built and has been operating the world’s first DME production plant since 2008 (Law et al., 2013). This concept entirely works on the renewable methanol pathway and relies on gasification of black liquor which is a byproduct of paper mills. At the demonstration and research scale, 140,000 tons (47 million gallons) of renewable methanol is produced annually.

The most effective route for the production of DME is by using century-old sulfur based chemical process called kraft pulping. Biomass is fed and processed at higher temperature and pressure in a digester and transformed into pulp called black liquor (Ekbom et al., 2005). Black liquor containing around 15% of solid organic particles from
Biomass is further oxidized to produce syngas for making bio-DME. Bio-DME project was tested in Sweden by major DME research companies, including test in DME fueled vehicles.

![Figure 1.3](image)

Figure 1.3 - Comparison between well-to-wheel and wood-to-wheel efficiency; and Green House Gas production. (Source: Volvo Technology Corporation)

The production plant was constructed, brought into operation and successfully tested in Volvo truck (Landälv et al., 2014). Volvo has estimated and compared well-to-wheel and wood-to-wheel analysis as presented in the Fig. 1.3. The estimation is based on production, transportation and end use greenhouse gas emissions. DME from Biomass has 25% more energy efficiency than synthesis diesel and has the lowest tendency of producing greenhouse gas (Volvo Technology Corporation).
1.5. DME Use in CI Engines

DME use in CI engines is being explored in several European and Asian countries including Sweden, South Korea, China, Japan and Israel, however, research in USA is comparatively less. In August 2007, Volvo trucks unveiled seven demonstration trucks, each tailored to run on various biofuels, including DME. Volvo is the first truck manufacturer to carry out comprehensive customer based field tests involving bio-DME fuel and has intended to install its plant in North America by 2015 (Brandon et al., 2013). Oberon is the first company to announce plans for the production and commercialization of DME in North America with small scale cost effective production facilities.

Conventional diesel engines are known as high emitter of NOx and particulate matter. Any strategy to minimize soot in conventional diesel engine results in an increase in NOx. This is called soot-NOx tradeoff. Therefore, in the after-treatment system of diesel engines, a diesel particulate filter and NOx reduction system (for example by using Urea) is required to get rid of PM and NOx, both of which increase capital and operational cost. DME is mostly a non-sooting fuel and the soot-NOx tradeoff is not applicable.

Therefore, there is room to play with the injection strategy and Exhaust Gas Recirculation (EGR) to minimize NOx without incurring an increase in soot emissions. However, methods to decrease in-cylinder NOx production can deteriorate combustion efficiency and increase CO and hydrocarbon emissions. Therefore, research is required to optimize DME based engine operation at various loads in terms of efficiency and emissions. Some of the prominent studies in this regard are summarized in Table 1.2.

Apart from using neat DME in engines, there is also potential for blending it with other fuels and, thereby, partially realizing the benefits of DME while avoiding the
challenges associated with it. As noted in Table 1.2, a number of studies have been done with blended fuels (e.g. Ying et al., 2005 and 2008; Chen et al., 1998; Wang et al., 2010). Chen et al. (1998) studied blends of diesel and DME in a single cylinder test engine. Blended fuels achieved mutual solubility at any ratio and satisfactory lubricity and atomization, which contributed to an improvement in the leakage and spray characteristics as well as decrease in soot emissions by 30% with 10% DME addition.

Several investigators (e.g. Shudo et al., 2003; Zheng et al., 2004; Wang et al., 2009; Komatsu et al., 2011) have also pursued use of DME in HCCI (Homogeneous Charge Compression Ignition) engine. Zheng et al. (2004) concluded that stable HCCI operation of DME/methanol can be obtained for broad speed and load range. NOx emissions were very low, though hydrocarbon and CO emissions were higher than diesel operation.

A study done by Komatsu et al. (2011) using blends of two distinct type of fuels, DME which has high cetane number and methane with very low cetane number, in HCCI engine showed that engine operation was possible in the high load region while avoiding the occurrence of knocking.

Due to its high reactivity, DME also holds great potential for the novel RCCI (Reactivity Controlled Compression Ignition) concept in which two fuels, a low reactivity fuel and a high reactivity fuel, are used to achieve high efficiency and minimum emissions over a wide range of engine operating conditions.
Table 1.2 - Summary of various works on DME engine performance and emission

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year / modes</th>
<th>Fuel type</th>
<th>Engine type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kozole et al.</td>
<td>1988</td>
<td>DME/methanol</td>
<td>1 cylinder; CR:12; Methanol fueled SI engine</td>
</tr>
<tr>
<td>Green et al.</td>
<td>1990</td>
<td>DME/Methanol</td>
<td>4 stroke CI engine</td>
</tr>
<tr>
<td>Karpuk et al.</td>
<td>1991</td>
<td>Diesel and Methanol/DME</td>
<td>1 cylinder; DI; high speed diesel engine</td>
</tr>
<tr>
<td>Marayama et al. &amp; Guo et al.</td>
<td>1992/Direct Injection (DI) and 1994/DI</td>
<td>Methanol/DME</td>
<td>CI diesel engine</td>
</tr>
<tr>
<td>Fleisch et al.</td>
<td>1995</td>
<td>Neat DME</td>
<td>Non turbo small diesel engine</td>
</tr>
<tr>
<td>Chen et al.</td>
<td>1998/DI</td>
<td>DME / Diesel</td>
<td>1 cylinder engine; diesel engine</td>
</tr>
<tr>
<td>Sato et al.</td>
<td>2000/DI</td>
<td>Neat DME</td>
<td>1 cylinder; diesel engine; displacement 1.05 ltr; CR 18:1</td>
</tr>
<tr>
<td>Ying et al.</td>
<td>2005/DI</td>
<td>DME / diesel</td>
<td>Light duty; diesel engine; 4 stroke; 4 cylinder; CR:17</td>
</tr>
<tr>
<td>Salsing et al.</td>
<td>2007/DI/EGR</td>
<td>Neat DME</td>
<td>Volvo heavy duty; 1 cylinder; CR:17</td>
</tr>
<tr>
<td>Hansen et al.</td>
<td>2008/DI</td>
<td>Neat DME</td>
<td>2 stroke; Diesel engine; CR:19; DI pressure:100bar</td>
</tr>
<tr>
<td>Liu et al.</td>
<td>2008/CIDI;HCCI;</td>
<td>Neat DME</td>
<td>2-cylinder; 4 stroke; DI diesel engine; CR: 16.5</td>
</tr>
<tr>
<td>Salsing et al.</td>
<td>2008/DI/EGR</td>
<td>DME/Methanol/Water</td>
<td>6 cylinder; heavy duty; CR:18</td>
</tr>
<tr>
<td>Wang et al.</td>
<td>2008/DI</td>
<td>DME / Bio-diesel</td>
<td>4 stroke; Diesel engine; CR:17; DI pressure:100bar</td>
</tr>
<tr>
<td>Wang et al.</td>
<td>2010/DI</td>
<td>DME / Bio-diesel</td>
<td>2 Stroke; 2 cylinder; CR: 16.5</td>
</tr>
<tr>
<td>Hansen et al.</td>
<td>2011/DI</td>
<td>Neat DME</td>
<td>2 stroke; Diesel engine; CR:22; DI pressure:150bar</td>
</tr>
<tr>
<td>Jeon et al.</td>
<td>2013/PCCI</td>
<td>DME / H₂</td>
<td>1 cylinder; CR:17</td>
</tr>
<tr>
<td>Yoon et al.</td>
<td>2013/DI</td>
<td>DME</td>
<td>1 cylinder; 1200rev/min; injection pressure 60MPa;</td>
</tr>
</tbody>
</table>
1.6. DME Use in Gas Turbines

DME has also been explored as a fuel for gas turbines. Hitachi developed a 25 MW scale DME burner, which is a full size multi-cluster burner (Kobayashi et al., 2003). The Tokyo Electric Power Company conducted a study on the application of DME to an LPG micro-gas turbine. They obtained equivalent or superior operational performances with DME than with LPG (Tsuchiya and Okamoto, 2005). General Electric conducted a combustion test on a mixed solution of DME, methanol, and water by means of a bench-scale burner and got a patent on the usage range of the fuel mixture (Basu et al., 2001). They reported that the mixture could be utilized in a commercialized gas turbine. Gokalp and Lebas (2004) also demonstrated the superior features and the physical and chemical properties of DME as a fuel for gas turbines.

Lee et al. (2008) conducted a study to verify the combustion performance and to identify potential problems when DME is fueled to a gas turbine. Combustion tests using DME were compared with methane in terms of combustion instability, NOx and CO emissions. The results of their performance tests showed that DME combustion is very clean but hard to control. The CO emission levels of DME were lower than that of methane, while the NOx emission levels of DME were as low as that of methane. When firing DME, the pressure fluctuations in the combustion chamber caused by combustion instability were also lower than that occasioned when firing methane. However, they also ascertained that DME combustion is more likely to flashback than methane combustion and this property should be considered when operating a gas turbine and retrofitting a burner.

Lee et al. (2009) selected the GE7EA gas turbine of the Pyong-tak power plant in Korea as a target for DME application. Combustion performance tests were conducted by
comparing DME with methane. Most results of the combustion performance tests showed that DME is very clean and efficient fuel for gas turbines. In their study, flashback phenomena was not observed to occur, because the GE7EA gas turbine uses partially premixed combustion method, which means that the GE7EA machine is highly suited to DME fuel. However, they also showed that it is necessary to retrofit a fuel nozzle to the combustor in consideration of the combustion properties of DME, in order to enhance the reliability of DME fired gas turbines. They concluded that DME can be applied to the GE7EA gas turbine with only a small modification, and it is expected to ensure clean and stable operation upon application.

1.7. Relevance of the Present Work

It is apparent that DME is a candidate fuel that has potential to be renewable and advantageous over diesel in terms of combustion and emission characteristics as well as suitable for use in land based gas turbines. Further, it can be used neat as well as blended with diesel, gasoline or other fuels in conventional and advanced CI engines such as HCCI and RCCI. The design of various types of engines that use DME as a fuel is greatly dependent on computational simulations which require validated chemical kinetic mechanisms that can reliably mimic the combustion and pollutant formation behavior of DME at physical conditions that are relevant to engines. In fact, investigations of rates and mechanisms of combustion reactions has been in the mainstream of combustion research after the recognition that tackling of practical combustion problems requires detailed understanding of chemical kinetics.
The development of a kinetic mechanism is largely dependent on the continued collection and evaluation of experimental data. Determination of kinetic data over the range of pressures and temperatures relevant to engines requires use of several experimental facilities. These facilities are generally homogeneous or 1-D systems, in which complicated fluid mechanical effects are avoided so that the chemistry of interest can be isolated and probed with confidence. These types of simpler experimental configurations include static reactors, flow reactors, well-stirred reactors, shock tubes, rapid compression machines (RCMs) and flame configurations such as counter-flow burner, flat flame burner and Bunsen burner.

In the present work, experimental data for autoignition and laminar flame propagation of DME is obtained to contribute to a better understanding and validation of chemical kinetics of DME, particularly at elevated pressures. Specifically, autoignition is investigated in the low temperature range (T < 800 K) at elevated pressures (up to 36 bar) and laminar flame propagation at atmospheric and elevated pressures. These two phenomenon, namely the low temperature autoignition and flame propagation, are very different in terms of controlling chemistry. Therefore, the data obtained in this work is valuable for evaluating and refining chemical kinetics at low as well as high temperature.

The phenomenon of auto-ignition in the low-to-intermediate temperature region is of great practical importance in engines. For example, it is the desired way of achieving combustion in HCCI engines, while it can produce undesirable ‘knock’ in the Spark Ignition (SI) engines. Even though significant research effort has been expended on HCCI, the concept is problematic due to lack of direct means to initiate combustion and power densities are lower for naturally aspirated HCCI engines (Hiltner et al, 2002), due to highly
diluted or fuel lean operation. At high loads, HCCI becomes especially problematic due to excessive pressure rise rates. Turbocharging or supercharging is applied to overcome low power density (e.g. Olsson et al., 2001; Christensen and Johansson, 2000) and efforts have been made to extend the high load limit through external EGR, charge stratification, RCCI, and use of an external ignition source, such as a spark plug or laser (Yang et al., 2012) The last strategy is called SACI (Spark Assisted Compression Ignition) and involves an initial deflagrative phase which triggers HCCI of the unburned charge. All these strategies have been shown to increase the load limits and stability. These strategies share the common denominator of dilute, high pressure combustion. This combustion regime is different from the traditional SI and CI engines and is referred to as advanced combustion regime or low temperature combustion. Operation at these low temperature strategies is significantly kinetically-influenced by the complex low temperature chemistry of fuels. Therefore, an important ingredient in the design of clean and efficient engines is the need for understanding the chemical kinetic mechanisms of fuels at high pressure and low temperature conditions.

Study of autoignition is also relevant from safety point of view. For example, premixed fuel and oxidizer may be present in the inlet manifolds of gas turbine combustor, and if the autoignition delays are shorter than the residence time, ignition can occur in the manifold rather than as desired in the combustor. In particular, in lean premixed combustion systems operating at high pressure and temperature ranges, the phenomena of autoignition and flashback in the premixing ducts can be a serious issue.

Since combustion in practical engines takes place at elevated pressures and temperatures, study of flame propagation at elevated pressures and temperatures is also
very relevant (Law et al., 2003; Qin et al., 2005). The importance of investigating high pressure flame propagation and associated chemical kinetics is amply recognized for the development of comprehensive chemical kinetic mechanisms (Qin et al., 2005; Rozenchan et al., 2002; Sun et al., 2007). As pressure increases, the controlling chemistry changes. It is expected that the combustion in advanced IC engines will be in mixed-mode operation; where along with chemical kinetics, diffusive and transport phenomenon will also be important. Therefore, available chemical kinetic mechanisms must be based on experimental data obtained in well-characterized homogeneous as well as transport dominated environments, such as flames. For the use of DME in industrial gas turbines, study of laminar flame propagation is important for predicting flashback, blow-off and combustion instabilities. In addition, laminar flame speeds are very useful target data for development of kinetic mechanism.

In the light of above-mentioned considerations, in this work, laminar flame speed propagation and autoignition of DME is investigated.

1.8. Specific Objectives

In order to obtain experimental data for validation of chemical kinetics, well characterized experimental facilities are required. The first objective of this work is to design a novel experimental facility, called DCF (Dynamic Combustion Facility) for studying laminar flame propagation at elevated pressures and temperatures. The DCF is to be designed, properly characterized through CFD simulations and validated by comparison with literature data on flame speed. In addition, various procedures and codes for the interpretation of data from the newly designed facility are to be implemented. Following
the design and characterization of the facility, the second objective is to measure laminar
flame speeds of DME and compare the data with predictions from various chemical kinetic
models.

The third objective is to study autoignition of DME in an RCM. Experiments are to
be conducted over a range of compressed pressures, temperatures and equivalence ratios.
Finally, the experimental data will be compared with simulations from detailed chemical
kinetic models and potential refinements to kinetic mechanism will be undertaken.

1.9. Structure of the Dissertation

Chapter II discusses background on laminar premixed flames and the existing
facilities for measuring flame speeds. Thereafter, the unique concept behind the newly
design DCF is presented.

Chapter III delineates the design and key features of the DCF. The methods used
for data interpretation are also discussed in detail. The modeling for determination of
laminar flame speed is described in Chapter IV.

Chapter V presents the results of validation experiments for DCF in static as well
as dynamic mode. Computational investigations on the flow and temperature field inside
the DCF as well as the accessible physical conditions are also properly delineated. Finally,
experimental data and analysis for laminar flame speed of DME is presented.

In Chapter VI, results of detailed investigations of DME autoignition are presented.
Experimental measurements are compared with several kinetic mechanisms. These
comparisons are shown to highlight the deficiencies in the present understanding of DME
oxidation at high pressure and low temperature. Refinements to existing kinetic mechanisms are also presented.

In Chapter VII, results are summarized and recommendations for further studies are discussed.
CHAPTER II

MEASUREMENT OF LAMINAR FLAME SPEED AND THE CONCEPT OF
DYNAMIC COMBUSTION FACILITY

2.1. Laminar Flame Speed

Laminar flame speed is one of the most important fundamental characteristics of a combustible mixture. It is a combined metric of mixture’s reactivity, exothermicity and transport properties (Law, 2006). It is defined as the propagation speed of a planer, one dimensional and adiabatic flame-front relative to the unburned gas mixture. Laminar flame speed is dependent on the physical properties like temperature, pressure and mixture composition. There are numerous studies that demonstrate that laminar burning speed is an important variable in theoretical studies of minimum ignition energy, flashback, and flame instabilities. Laminar flame speed data can be used in empirical formulations predicting turbulent flame speed, flash back, and blow-off (Rallis et al., 1980). In addition, such data constitutes important target in validation and refinement of chemical kinetic mechanisms.

In this work, a novel facility was designed to measure laminar flame speeds. In order to put the present work in proper perspective, various existing experimental facilities that are used to measure laminar flame speeds are briefly reviewed below.
2.2. Flame Speed Measurement Techniques

From a very basic flame measurement techniques like soap bubble method to the recent and innovative novel concept named DCF, which is the main objective of this dissertation, has been summarized below.

2.2.1 Bunsen Burner

In a Bunsen burner, premixed fuel-air mixture is flown in a sufficiently long and constant cross-section tube, and burned at the circular opening. However, this leads to a parabolic velocity profile at burner exit. In order to get a uniform velocity profile at exit, nozzles are often used. The shape of the flame is determined by the combined effect of the velocity profile and heat loss to the burner lip. The laminar flame speed is equal to the component of the unburned gas velocity normal to the flame. Flame speeds in Bunsen burners are determined in two ways, Angle method and Average method.

As shown in Fig. 2.1, in the Angle method $S_u = u_0 \sin \alpha_u$ is used where $\alpha_u$ is the half cone angle and $u_0$ is local mixture velocity and $S_u$ is the laminar flame speed. If the velocity profile at exit is non-uniform, the flame will have curvature, introducing uncertainty in the determination of the cone angle. In the Average method, the flame speed is calculated using the relation $S_u = \frac{\dot{m}}{\rho_u A_f}$, where $\rho_u$ is the unburned density of the mixture, $\dot{m}$ is the mass flow rate and $A_f$ is the flame surface area (Law, 2006).
The definition of flame surface area has some ambiguity as depending on the method used (Visible, Schlieren and Shadowgraph) different surfaces are identified. Due to variation of flame surfaces, there is inconsistency in the reported data. In summary, flame speed measurements using Bunsen burner is simple but complicated due to flame curvature and thickness.

2.2.2 Flat Flame Method

In order to overcome the problem of identification of flame surface in the Bunsen burner method, Pawling (1949) developed a new concept of flat flame, which is easily
established as a planar flame over a porous surface as shown in Fig. 2.2. However, flat flames established above a burner are non-adiabatic due to heat loss to the burner. So, various extrapolation methods are used to calculate adiabatic laminar flame speed, which can introduce much uncertainty.

Heat flux method is a modification of the flat flame method (Goey et al., 1993). The physical parameters are similar to the flat flame, and adiabatic flame is achieved when burner plate temperature is above the unburnt mixture temperature, making no heat transfer from flame to burner (Mareen and Goey, 1994).

![Figure 2.2 - Flat flame burner](image_url)

2.2.3 Soap Bubble Method

An outward propagating spherical flame can be generated inside a soap bubble. Soap bubble is a capsule which prevents diffusion of inner gas to outer surrounding. This has been used as a low solubility boundary because when flame is propagated inside the
bubble, the inner part is exposed to high temperature and bubble ruptures immediately due to a reduction in the surface tension force (Takeno, 1985).

Figure 2.3 - Soap bubble method

The problem with this method lies in the uncertainties of chemical effect of soap in the mixture and diffusion of gases from the surface of the bubble. Thermodynamically the process is isobaric, and temperature, density and composition remain constant for burned gas and unburned mixture.

2.2.4 Counterflow Burner

In this method, twin flames are generated from premixed mixtures issuing from opposing nozzles as shown in Fig. 2.4. The flow field is characterized by a method such as PIV (Particle Image Velocimetry). Due to symmetry and being away from the nozzle, the flame is adiabatic. However, the flame is stretched due to tangential velocity gradient. A general definition of stretch at any point on the surface is the Lagrangian time derivative of the area A of an infinitesimal element of the flame surface (Williams, 1985)
\[ K = \frac{1}{\frac{dA}{dt}} \]  

(2.1)

Figure 2.4 - Twin flames from counter-flow burner

For a counter-flow burner, stretch is obtained from the velocity field measured by PIV. Experiment is conducted over a range of stretch values by varying the flow through the nozzles, and extrapolation to zero stretch has to be done to obtain unstretched laminar flame speed. A variation of this method is stagnation method in which only one flame is stabilized by a single nozzle directed at a stagnation surface.

2.2.5 Spherical Outward Propagating Flame

The Bunsen burner, flat flame burner and counter-flow burner employ stationary flames, whereas the spherical outward propagating flame method is based on a freely propagating flame. In this method, a flame is initiated by spark in the center of a closed chamber that is filled by the combustible mixture. A flame propagates spherically outward
and its radius-time history is captured by some technique. Flame propagation in a closed spherical chamber also leads to rise in pressure.

However, there are methods to minimize or avoid the rise in pressure and observe a flame under isobaric conditions. These methods include (a) use of a bigger chamber in which pressure rise is negligible until flame radius reaches up to 25% of the chamber radius, (b) use of dual chamber, pressure release type apparatus in which flame is generated in an inner chamber and flow of gases from the inner to a larger outer chamber after flame initiation avoids rise in pressure (Law et al., 2000; Qin and Ju, 2005). In the schematic of a spherical outward propagating flame, Fig. 2.5, the burned gas behind the flame is stationary when pressure rise is negligible. Therefore, the rate of change of flame radius is the velocity of the burned gas relative to the flame, or

\[
S_b = \frac{dr_f}{dt}
\]  

(2.2)

Figure 2.5 - Spherical outward propagating flame
The velocity of the unburned gas relative to the flame is obtained by using continuity across the flame

\[ S_b \rho_b = S_u \rho_u \]  \hspace{1cm} (2.3)

This \( S_u \) is the laminar flame speed. Density ratio across the flame is easily obtained by thermodynamic calculations. Thus, simply by observing flame radius history, \( r_f(t) \), laminar flame speed can be determined. However, the flame is stretched and the stretch here is given by

\[ K = \frac{1}{A} \frac{dA}{dt} = \frac{2}{r_f} \frac{dr_f}{dt} \]  \hspace{1cm} (2.4)

Stretch decreases as flame radius increases and from a single experiment one can get \( K \) vs \( S_u \) data, which has to be extrapolated to zero stretch to obtain unstretched laminar flame speed.

Asymptotic analysis and detailed modeling (Dowdy et. al. 1991) show a linear relation between flame speed and stretch at low stretch rates.

\[ S_u^0 = S_u + L_u K \]  \hspace{1cm} (2.5)

Where superscript ‘o’ indicates unstretched flame speed and \( L_u \) is called the Markstein length, which characterizes the sensitivity of flame speed to stretch. However, this linear extrapolation is not valid if stretch or \( L_u \) is large, and nonlinear extrapolation is required. Various nonlinear methods of extrapolation are reviewed in Chapter III.

The non-dimensional parameters, Karlovitz number \((Ka)\) and Markstein number \((Ma)\) are often used to characterize stretch and sensitivity to stretch.
\[ Ka = K \frac{\delta_B}{S_u}, \]  

\[ Ma = L_u / \delta_D \]  

Where, \( \delta_D \) is the flame thickness. This gives

\[ \frac{S_u^0}{S_u} = 1 + MaKa \]  

When the Karlovitz numbers is small, the accuracy of linear extrapolation improves (Vagelopoulos et al., 1994).

2.3. Effect of Stretch on Flame Speed

The phenomenological effect of stretch on flame response is most easily understood by considering a stagnation surface flame, Fig. 2.6. The following discussion is based on the review by Law and Sung (2000). For mixtures with unequal diffusivities, flame response is strongly influenced by stretch. There are 3 diffusivities of interest for an inert-abundant mixture, namely those associated with heat diffusion \( D_T \), the deficient reactant diffusion \( D_i \), and the excess reactant diffusion \( D_j \). When these diffusivities are unequal, two parameters, namely Lewis Number ( \( Le = D_T / D_i \) ) and \( D_i / D_j \) are used to explain the effect of non-equidiffusion for stretched flames.
Considering flame response in stagnation flow, as shown in Fig. 2.6, a control volume enclosing the transport zone and divergent streamlines is shown. Since the diffusive transport is normal to the reaction surface, then with the nonunity Lewis number, the control volume loses thermal energy to the external streamlines while it gains chemical energy from them due to the diffusion of deficient reactant across the streamline. The flame response depends on relative heat and mass diffusion. If the diffusivities are equal such that $Le = 1$, then total energy is conserved and the flame temperature is the adiabatic flame temperature. However, if $Le > 1$, heat loss exceeds mass gain and flame temperature becomes less than the adiabatic flame temperature.

Next consider the effect of $D_i/D_j \neq 1$. If the leaner reactant is also the more diffusive, then the reactant concentration in the reaction zone will become more stoichiometric such that the flame temperature will increase and the burning will be more
intense. The converse holds if the leaner reactant is less diffusive. For off-stoichiometric burning, nonunity Lewis number effect is more prevalent. Therefore, for flames with $Le > 1$, the flame becomes weaker as stretch increases, the burning speed decreases and eventually it extinguishes.

On the other hand, for a $Le < 1$ flame, increasing stretch elevates temperature and therefore extinction cannot occur until the downstream boundary of the reaction zone is pushed onto the stagnation surface and the flame movement becomes restrained. With further stretching, reaction cannot be completed because of the reduced residence time. Only then will the flame temperature start to decrease, leading eventually to extinction (Law and Sung, 2000). In any case, the linearized results, equation 2.5 or 2.7, cannot exhibit the intrinsically nonlinear phenomena of extinction. The response of flame to stretch is nonlinear, and nonlinear models are presented in Chapter III.

As shown in Fig. 2.7, apart from stretch, a spherically propagating flame is influenced by spark initiation, chamber effects and buoyancy. The effect of spark dies after some period and chamber effect becomes important as flame approaches 40% of the chamber radius for a cylindrical chamber. This is due to the lack of symmetry in cylindrical confinement (Burke et al., 2009). Buoyancy becomes important only for weak flames. Therefore the usable flame radius data, $r_f(t)$, is carefully chosen between a lower and upper radius so that the effect of spark and chamber are avoided in data interpretation. The data is also influenced by flame unsteadiness, curvature and finite flame thickness. However, these influences can be neglected for $\delta_D/r_f \ll 1$ (Tseng et al., 1993).
Figure 2.7 - Various factors influencing spherically propagating flame

2.4. Importance of Flame Speed Data at Elevated Pressures and Temperatures

The new facility designed in this work is guided by the motivation to provide flame speed data at elevated pressures and temperatures. Therefore, the importance of such data is elaborated upon here before describing the concept behind the new facility.

The phenomenon of flame propagation and flame structure are significantly influenced by mixture pressure and preheating. Since combustion in practical engines takes place at elevated pressures and temperatures, study of flame propagation at simultaneously
elevated pressures and temperatures is particularly relevant. As pressure increases, the controlling chemistry changes due to the increased importance of the three-body termination reactions. Investigations with methane and H₂ flames at elevated pressures have revealed that the overall reaction order shows a non-monotonic behavior with pressure, which is analogous with the three explosion limits of hydrogen/oxygen mixtures (Rozenchan et al., 2002). The overall reaction order initially decreases with increase in pressure due to the increased importance of the termination, H+O₂(+M) → HO₂(+M), over branching reactions, H+O₂ → OH+O etc., and then it increases again due to the branching pathways from HO₂ at higher pressures. Consequently, the chemical kinetics in high pressure flames is significantly influenced by HO₂ pathways which are poorly understood in comparison to the high temperature chain branching pathways.

In order to illustrate the change in controlling-chemistry with pressure, Fig. 2.8 shows sensitivity coefficients of mass burning flux for stoichiometric hydrogen-air mixtures at various pressures by using the mechanism of O’Conaire et al. (2004). It is noted that as pressure is increased from 1 bar to 25 bar, the sensitivity to various elementary reactions increases substantially. This increase in sensitivity is due to the increased importance of termination and recombination reactions at higher pressures. There are following two messages from this observation: (1) The chemical kinetics of the reactions involving HO₂ needs to be better understood to accurately predict the flame speeds at higher pressures. (2) A given uncertainty in kinetic parameters of elementary reactions will result in larger uncertainty in flame speed predictions at higher pressures due to increased sensitivity of flame speed to rate parameters at elevated pressures. Consequently, the validation of kinetic mechanisms against high pressure flame speed data will impose
stronger constraints on kinetic model parameters and will be highly beneficial for the validation and development of kinetic models (Burke et al., 2010).

Figure 2. 8 - Sensitivity coefficients $\partial \ln m^o / \partial \ln k_i$ for mass burning flux for stoichiometric hydrogen-air flames. Unburned gas temperature = 300 K

Apart from the importance of high pressure flame speed data, as highlighted above, there is also significant interest in studying flame propagation with preheating. With preheating, the rates of some elementary reactions increase while of others decrease, and transport properties are modified. These changes could affect the flame structure. Consequently, mixture preheating is recognized as an important parameter in flame studies from both fundamental and practical considerations (Natarajan et al., 2007; Kumar et al., 2007 and 2008). Various investigations have shown that while the chemical kinetic
mechanisms could predict the laminar flame speeds at room temperatures reasonably well, the discrepancy became larger with increasing preheat.

The most popular techniques for flame speed measurements are counterflow/stagnation flames and spherically outward propagating flames (OPF). Flat flame and Bunsen burner have also been successfully used. Counterflow burners offer an excellent configuration for determination of stretch-corrected flame speeds, but typical pressures are below 7 atm due to transition to turbulence with increasing pressure. OPFs in optically accessible combustion chambers have been widely used for investigations at elevated pressures, up to 60 atm for gaseous fuels at room temperature (Rozenchan et al., 2002). It is noted that experiments for constant pressure OPFs for liquid fuels at elevated pressures are rarely conducted, such as by Bradley et al. (1998) up to 10 atm for isooctane and n-heptane, and by Jerzembeck et al. (2009) up to 25 bar for primary reference fuels and gasoline. This lack of data is due to associated experimental difficulties with liquid fuels.

Recognizing the importance of investigating flame propagation at elevated pressures and temperatures, and the voids in experiments at such conditions, in the following a novel experimental methodology is proposed that is capable of providing experimental conditions of elevated pressures and with simultaneous preheating. The facility is based on the OPF method but combines it with a compression stroke as discussed below.
2.5. Concept of the DCF

An innovative optically accessible large bore dynamic combustion facility (DCF) is proposed, as shown in Fig. 2.9. The facility will enable generation of OPF in a well-characterized atmosphere at elevated pressures and temperatures, attained through slow compression of reactive mixtures in a carefully designed combustion chamber. The basic idea is to compress the combustible mixture in the reactor cylinder to elevated pressures and temperatures by controlled motion of piston through pneumatic and hydraulic arrangements. After compression, the piston does not rebound due to the thrust of high pressure driving air and the reaction chamber assumes a near-spherical shape (slightly off-spherical due to optical accessibility). Spark is initiated after compression in the constant volume spherical chamber, yielding an OPF whose radius-time history is recorded by Schlieren imaging using a high speed camera. The uniqueness of the facility lies in the use of compression stroke to achieve elevated pressures and temperatures.

There are two important considerations to be fulfilled at the time of initiation of spark by careful design of the facility: (1) Homogeneous temperature field with known temperature (2) Quiescent atmosphere without significant piston induced gas motion. These objectives can be achieved by (a) slow compression (~ 5-20 s) (b) incorporation of a crevice/recess on the periphery of the piston to dampen fluid motion and (c) designing a compression chamber with large volume to surface area ratio.
In the following, by taking example of a representative fuel (n-decane), the utility of the proposed approach is shown in acquiring data at conditions which are not easily attainable in existing facilities. n-decane has low vapor pressure. In conventional spherical combustion vessels, experiments with n-decane are made difficult because of the requirement of preheating to increase the fuel vapor pressure, which also makes the mixture prone to autoignition. Figure 2.10 and 2.11 illustrates the range of experimental pressure-
temperature conditions that could be accessible to conventional spherical combustion vessels for stoichiometric n-decane/air mixtures. In Fig. 2.10, the left curve is dictated by the requirement of preheating to obtain sufficient vapor pressure. For pressure-temperature conditions to the left of this curve, vapor pressure is insufficient for mixture preparation. The right curve is dictated by the autoignition temperature. Autoignition will happen if mixture state is to the right of this curve. Only the region marked ‘accessible region’ is accessible in conventional spherical chambers.

Figure 2.10 - Illustration of pressure-temperature conditions accessible in conventional spherical vessel for stoichiometric n-decane/air mixtures. The autoignition temperature curve is offset by 30 K from safety point of view and vapor pressure curve is drawn such that the required fuel partial pressure is 80% of the fuel vapor pressure to avoid condensation.
An extension of accessible conditions in DCF is possible in the following way. First, a homogeneous mixture can be prepared at a much lower temperature and pressure within the ‘accessible region’, such as any green circle in Fig. 2.11. The mixture could then be compressed in the DCF along the corresponding compression curve from that point, which is also shown in Fig. 2.11. The end state of the mixture could fall into the ‘autoignition’ region and will depend on the compression ratio used. Such thermodynamic states cannot be reached in static spherical vessels because of long mixture preparation and homogenization time which will lead to autoignition. However, in the DCF, such states could be reached within few seconds. If ignition delays at the resulting elevated...
temperature and pressure states are greater than few seconds and the chemical activity during compression is also negligible, an OPF could be generated and observed after compression, without the problem of autoigniting the mixture.

The details of this basic concept along with its design, characterization and validation are presented in the subsequent chapters.
CHAPTER III
EXPERIMENTAL FACILITY FOR FLAME STUDIES

3.1. Introduction

One of the objectives of this thesis was to develop a novel experimental facility, referred to as Dynamic Combustion Facility (DCF), for investigating flame propagation at simultaneously elevated pressures and temperatures and, subsequently, use the facility for studying laminar premixed flames.

An experimental facility was successfully designed and fabricated for studying outward propagating spherical flames at elevated pressures and temperatures. This included the computational fluid dynamics (CFD) based optimization of the geometry of the combustion chamber, determination of the pneumatic and hydraulic arrangements for controlled compression, stress analysis of the components, preparation of the 3-D drawings for fabrication, fabrication of necessary parts, working out the details of the optical imaging set-up, ignition system, synchronization, image processing and model for data interpretation. The overall layout of the facility is shown in Fig. 3.1 and detailed description of each component is provided below.

3.2. Experimental Facility

For a novel facility to be introduced, importance and challenge are two aspects to be considered regarding concept and design of proposed experimental system. To modify
the concept in to workable experimental setup, lot of procedures are encountered. Following systems have been considered to revive the concept into real feasible experimental model.

3.2.1 General Hardware

The picture of the facility and cross-sectional view are shown in Figs. 3.2 and 3.3, respectively. It consists of a reactor cylinder of inside diameter of 10.16 cm with nearly hemispherical reactor piston and cylinder head.

![Diagram of experimental facility](image)

**Figure 3.1 - Layout of the experimental facility**
The combustible mixture in the reactor cylinder is compressed to elevated pressures and temperatures by controlled motion of the reactor piston through a custom-designed hybrid cylinder (pneumatic drive and hydraulic damping) arrangement. The hybrid cylinder has a bore of 20.32 cm and adjustable stroke up to 50.8 cm. Stroke is easily adjusted by using a screw that sticks out of the rear side of the cylinder. The position of the screw sets the initial position of the piston. The only moving part in the facility is the piston assembly that includes the driver piston and reactor piston connected by the piston rod. For driving the piston assembly, compressed air to the air side of the hybrid cylinder is supplied by a 90 L air receiver rated to 200 psi. Pressurized oil is supplied to the other side of the driver piston by a hydraulic pump.
Before the start of compression, the piston assembly is held in the initial retracted position by oil pressure. The piston begins to move under thrust of the compressed air when oil pressure is released and oil is allowed to flow out of the cylinder. The speed of the piston assembly can be controlled by the venting rate of oil. At the end of stroke, the piston assembly comes to a smooth stop due to a built in cushion in the hybrid cylinder. Since the hybrid piston is connected to the piston in the combustion chamber by the piston rod, the gas in the combustion chamber is compressed to higher pressure and temperature. After compression, the reaction chamber assumes a nearly spherical shape. The details of the reactor piston are shown in Fig. 3.4. It incorporates a crevice for suppression of the roll-up vortex during compression and a flat surface on which a 5 cm diameter mirror is mounted for Schlieren imaging.
The near-spherical chamber at the end of compression is equipped with an end optical window of 5 cm diameter and 6.35 cm thickness, and ports for pressure transducer (Kistler 6052C) and temperature transducer, a rupture diaphragm for safety, and electrodes for initiating a flame by spark. Details of various ports are shown in Fig. 3.5.

It is desirable to have a large and spherical combustion chamber for studying outward propagating flames. A spherical chamber avoids undue distortion of the flame, which happens in the case of cylindrical confinement (Burke et al., 2009), and a large chamber allows constant pressure flame propagation up to a larger radius (and consequently smaller stretch) so that the extrapolation to zero stretch can be done with increased confidence.
Figure 3.5 - Reaction chamber (head side) showing various ports

- Pressure transducer
- Rupture disc
- Fixed electrode
- Inlet/outlet port
- Adjustable electrode
- Temperature sensor
In the present design of the facility, the combustion chamber is nearly spherical in shape, however, after careful considerations, the diameter of the chamber is taken as 10.16 cm and the maximum compression stroke length of the facility is 50.8 cm. An increase in the diameter of the combustion chamber requires a proportionate increase in the length of the compression stroke and exacerbates the possibility of reaction and turbulence during compression. With a combustion chamber diameter of 10.16 cm, the flame radius-time data up to the flame radius of 2.5 cm (half of the radius of the combustion chamber) may be used for extrapolation (Chen et al. 2009). It is noted that at this flame radius, pressure in the combustion chamber may rise by about 15% and temperature also by 5%. However, the influence of these factors on flame speed is typically less than 2% and the experimental data can be extrapolated to zero stretch with confidence when compression correction is taken into account. In literature, most of the experimental data from outward propagating flames is based on flame radius less than 2.5 cm (Burke et al. 2010 and 2011; Jerzembeck et al., 2009).

The combustion chamber includes a rupture diaphragm for safety. A schematic of the rupture diaphragm holder is shown in Fig. 3.6. Aluminum foils of various thicknesses corresponding to different burst pressures are mounted on the diaphragm holder. Even though the facility is designed to withstand pressure greater than 120 bar, the diaphragms of burst pressure around 15-20 bar are used for safety. The flow of combustion chamber gases after the rupture of diaphragm can be unbearably loud. Therefore, a silencer (Allied Witan, Model # 44AW56M20) is mounted on the outside of the holder which leads to up to 85% reduction in the perceived noise. An image of the diaphragm holder along with the silencer is also shown in Fig. 3.6.
Figure 3. 6 - Rupture diaphragm holder and silencer

3.2.2 Ignition System

Spark is initiated after compression in the constant volume spherical chamber, yielding an outward propagating flame. The ignition energy for the spark is provided by discharging an automotive coil, saturated through a constant current power supply (GW
Instek GPR 1810HD) using an inductive circuit. The ignition energy is easily adjusted by adjusting the current on the power supply. One of the electrodes is modified from a standard spark plug by removing the ground electrode and welding a stainless steel tube and wire to it. The other electrode has threads and an O-ring and, therefore, is easily adjustable. It allows for fine adjustment of the spark gap. The electrodes are shown in Fig. 3.7 and the ignition system in Fig. 3.8 (a). When higher ignition energy is required (for example when He is used in experiments), a different system as shown in Fig. 3.8(b) is used along with the power supply BK Precision, 1694.

Figure 3.7 - Electrodes for spark generation
Figure 3.8 - Ignition system

(a) Low energy ignition system

(b) High energy ignition system
3.2.3 Optical System

Radius-time history is recorded by Schlieren imaging using a high speed camera. A single window coincident optical layout is selected for Schlieren imaging. This arrangement, as shown in Fig. 3.9, requires only one window and minimizes the distortion of the spherical geometry of the combustion chamber. A 48 W halogen lamp source is focused through a condenser lens on a pinhole to provide intense illumination. A 400 mm focal length achromatic doublet lens provides collimated beam through the 5 cm diameter window. A quartz substrate front surface mirror is mounted on the face of the piston, which reflects the light. The reflected light is focused by the lens and beamsplitter on a knife edge. The Schlieren image is acquired by a high speed camera (Photron Fastcam SA 3) with a 50 mm Nikon lens.

Figure 3.9 - Set-up of the Schlieren imaging system
3.2.4 Data Acquisition

A schematic of the data acquisition and control system is shown in Fig. 3.10. The pressure in the chamber is measured using a Kistler piezoelectric (6052C) sensor and a charge amplifier (Kistler 5010B). The voltage output of the sensor is recorded using a data acquisition card (National Instruments PCI 6036E). The pressure signal is used to synchronize the spark generation and image acquisition through a time delay program in LabVIEW. After the start of compression, pressure is continuously recorded and compared with a preset trigger pressure in LabVIEW. When pressure exceeds the trigger pressure, image acquisition is triggered after a preset camera delay in LabVIEW. Following the initiation of the image acquisition, spark is initiated after a preset spark delay by triggering the spark relay.

Figure 3.10 - Data acquisition and control
The set up allows for synchronization and control of the entire system along with recording of flame images and pressure data. The LabVIEW-vi interface is shown in Fig. 3.11.

![LabVIEW vi interface](image)

**Figure 3.11 - LabVIEW vi interface**

The developed facility can be used in the static or dynamic mode. In the dynamic mode, the desirable conditions of elevated pressure and temperature are attained by compression of homogeneous reactive mixture. In the static mode, the experiment is conducted without compression.
3.2.5 CFD Analysis of the Combustion Chamber

In order to optimize the geometry of the reaction chamber, CFD simulations were conducted on an axisymmetric grid by using the Fluent CFD package. Computations were performed from the beginning of the compression stroke. Initially, before the compression stroke begins, the gas mixture at rest is specified with a uniform temperature and known pressure. A fixed temperature and no slip conditions are specified at the cylinder wall boundary and the piston surface. Simulations use the PISO (Pressure-Implicit Split-Operator) algorithm for the pressure–velocity coupling, and the second-order upwind discretization for density and momentum.

Figure 3.12 shows the temperature and velocity fields at the end of compression for a representative case. Except for the boundary layer, the temperature in the bulk gas remains uniform. Furthermore, due to the incorporation of an optimized crevice, gas inside the chamber is practically quiescent. The crevice on the periphery of the combustion chamber piston was based on these simulations. These simulations were conducted at the time of design of facility and are for a perfectly spherical geometry. Further simulation results for the actual geometry are presented in detail in Chapter V.
Figure 3.12 - Temperature and velocity fields from the CFD simulations. Gas: Air. Stroke = 44.6 cm. Initial pressure and temperature = 3 bar, 300 K; Compressed pressure and temperature = 33.8 bar, 600 K.

3.3. Data Analysis

As discussed in Chapter II, in the past 50 years, several experimental approaches have been used for the determination of laminar flame speed. These include Bunsen burner and flat flame burner (Natarajan et al., 2007 and 2009), outward propagating spherical flame (Rozenchan et al., 2002; Tse et al., 2000; Sun et al., 2007) and counterflow or stagnation flame (Wu and Law, 1985; Egolfopoulos et al., 1989; Dong et al., 2002; Zhao et
al., 2004; Huang et al., 2004). Despite the simple geometry, spherical flames are subjected
to positive stretch, causing the flame speed to be modified by non-equidiffusion of heat
and mass, which is characterized by non-unity Lewis number and preferential diffusion
between fuel and oxidizer (Wu et al., 2015). Therefore, the effect of stretch needs to be
eliminated by extrapolation to zero stretch. In the following, first the data obtained from
the experiments is described, followed by a discussion of various extrapolation techniques
that can be used to obtain the unstretched laminar flame speed.

3.3.1 Image Processing

The experimental data consists of pressure trace and images of the propagating
flame that are acquired by the high speed camera. Sample images for CH$_4$/air flame at unity
equivalence ratio and 1 atm initial pressure are shown in Fig. 3.13. These images are
processed to obtain flame radius vs time data. A Matlab code was written for image
processing and the method is explained through Fig. 3.14. In any image, a point (O) inside
the flame is first taken and the flame boundaries in the horizontal and vertical direction are
determined based on intensity. These boundaries are identified as H$_1$, H$_2$, V$_1$ and V$_2$ in Fig.
3.14.

The center coordinates are identified as the midpoints of H$_1$H$_2$ and V$_1$V$_2$ in the
horizontal and vertical direction, respectively. The process for identification of boundaries
and center coordinates is repeated until the convergence is obtained. Thus the flame center
is clearly identified at which point OH$_1$ and OH$_2$ are not different by more than one pixel
and similarly OV$_1$ and OV$_2$. The difference between the horizontal and vertical radii was
not more than 2 pixels, and the flame radius is taken as an average of the horizontal and vertical radii.

Figure 3. 13 - Images for CH₄/air, φ=1 at Pi=1 atm and Ti= 296 K. Successive images are 0.2 ms apart. Exposure time=33 microsecond
Figure 3. 14 - Method for determination of flame radius

Figure 3. 15 - Vertical position of flame center, CH$_4$/air, $\phi$=1 at Pi= 1 atm and Ti= 296K
The effect of buoyancy is negligible as indicated by the change in the vertical position of the center in Fig. 3.15. The flame radius data along with pressure is shown in Fig. 3.16. This time, radius, pressure data is used to obtain unstretched flame speed as explained next.

![Figure 3.16 - Flame radius (circle) and pressure history (square). CH₄/air, ϕ=1 at Pi = 1 atm, Ti = 296 K](image)

3.4. Models for Unstretched Flame Speed

Accurate determination of laminar flame speed is important which is given by concept of stretch in flames. Large discrepancy has been reported without considering stretch effect in laminar flame speeds. Presented are the few models which has been helpful in adding stretch effect comparable to experimental data.
3.4.1 Linear Stretch Model

The flame stretch for a spherical outward propagating flame is given as

\[ K = \frac{1}{A} \frac{dA}{dt} = \frac{2}{r_f} \frac{dr_f}{dt} \]  \hspace{1cm} (3.1)

A linear model based on stretch is given by

\[ S_b = S_b^o - L_b K \]  \hspace{1cm} (3.2)

where \( L_b \) is the burned Markstein length and \( S_b^o \) is the unstretched burned flame speed. This model is based on near unity Lewis number and weakly stretched flame, and has been extensively used in the literature. The flame speed and Markstein length with respect to the unburned gas can be obtained by using the density ratio across the flame.

\[ S_u^o = \frac{\rho_b}{\rho_u} S_b^o \]  \hspace{1cm} (3.3)

And,

\[ L_u = \frac{\rho_b}{\rho_u} L_b \]  \hspace{1cm} (3.4)

When pressure rise in the chamber is negligible, the burned gas behind the flame front is stationary and \( S_b = \frac{dr_f}{dt} \). However, for non-negligible pressure rise, the effect of flow compression needs to be taken into account (Chen et al., 2009).
3.4.2 Linear Stretch Model with Compression Correction

Flame radius and pressure history can be used to deduce the laminar flame speed with compression correction as follows. For an outward propagating flame, the mass of the burned gas, \( m_b \), is described as

\[
\frac{dm_b}{dt} = \frac{d}{dt} \left( \frac{4}{3} \pi r_f^3 \rho_b \right) = 4\pi r_f^2 \rho_u S_u
\]  
(3.5)

where \( r_f \) is flame radius and \( \rho_b \) is the mass averaged density of the burned gas. A rearrangement of the terms gives –

\[
S_u = \rho_u \left( \frac{dr_f}{dt} \right) + \frac{r_f}{3\rho_u} \frac{d\rho_b}{dt}
\]  
(3.6)

In this equation, the second term accounts for compression induced flow velocity in the burned gas. The burned gas velocity behind the flame is given by

\[
U_b = \frac{r_f}{3\rho_b} \frac{d\rho_b}{dt}
\]  
(3.7)

The unstretched laminar flame speed, \( S_u^o \), can be obtained by linear extrapolation of the stretched flame speed to zero stretch.

\[
S_u = S_u^o - L_u K
\]  
(3.8)

In order to deduce, Markstein length and \( S_u^o \) from the experimental data, it is better to work with the integrated form of the above equation, which avoids amplification of
random experimental scatter during differentiation to get \(\frac{dr_f}{dt}\). An integration of the equation gives

\[
\int_{r_i}^{r_f} \left( \frac{\rho_b}{\rho_u} \frac{dr}{dt} + \frac{r_f}{3\rho_u} \frac{d\rho}{dt} \right) dt = S_u^o (t - t_0) - 2L_u \ln \left( \frac{r_f(t)}{r_0} \right) \quad \text{(3.9)}
\]

Experimental data of pressure and radius can be used to evaluate the integral in the above equation, and \(S_u^o\) and \(L_u\) can be determined from a linear regression. Note that \(\rho_b\) and \(\rho_u\) are time dependent. Determination of \(\rho_u\) is straightforward from isentropic compression of the unburned gas by using

\[
\int_{T_i}^{T_f} \frac{\gamma}{\gamma - 1} \frac{dT}{T} = \ln \left( \frac{P(t)}{P_i} \right) \quad \text{(3.10)}
\]

Where, subscript \(i\) denotes initial conditions at the time of spark discharge and \(\gamma\) is temperature dependent specific heat ratio of the unburned gas mixture.

In order to determine \(\rho_b\), a multi-zone model is used that utilizes the experimental time-radius-pressure data. In the multi-zone model, flame propagation is taken as the consecutive consumption of unburned gas mixture within the zones. The number of zones equals the number of time-radius-pressure data points that are available from the experiment.
After ignition, the flame front consumes zone I first. The post combustion radius of zone I at this instant, time=t₁, is taken as the first radius point available from the experimental data and its temperature is deduced by first calculating the isobaric equilibrium temperature of the burned gas based on initial temperature and pressure, \( T_i \) and \( P_i \), and then correcting for the isentropic compression of the burned gas from \( P_i \) to \( P_1 \). This gives the burned gas temperature and density of Zone I at time=t₁. Mass of the burned gas in zone I is also calculated.

After the combustion of the first zone, combustion of the second zone occurs at a higher unburned gas pressure, \( P_1 \), and temperature, which is determined from isentropic compression of the unburned gas. After the combustion of zone II, the outer radius of the zone II is taken as the next available time-radius-pressure data points. The temperature of the zone II is deduced by first calculating the isobaric equilibrium temperature of the burned gas based on temperature and pressure of the unburned gas after the consumption of zone I and then correcting for the isentropic compression of the burned gas. Combustion of zone II also leads to compression of zone I, and its temperature can be calculated from isentropic assumption. Also, since the mass of gas in zone I is already known, its radius at the present time step can also be updated. This process is followed for the subsequent zones. Note that in this model, every zone is considered adiabatic even though temperature gradients are established in the burned gas. NASA chemical equilibrium program from Gordon and Mcbride (1971) is used to evaluate the burned gas temperature, molecular weight and specific heat ratio.

Figure 3.17 shows an example of output from the model. It is noted that there is a small increase in the unburned gas temperature and density. The burned gas density also
increases due to compression, and temperature gradient is present in the burned gas temperature profile.

Based on this model, flame speed vs stretch rate and linear interpolations are plotted in Fig. 3.18. For linear interpolation, only flame radius from 0.7 to 2 cm is taken to avoid the effect of initial spark-induced flame acceleration. Figure 3.18 also shows a comparison of data interpretation by including and excluding the effect of compression induced flow velocity and variable density ratio. When these effects are excluded, \( \frac{d\rho_b}{dt} \) term in equation 3.9 is neglected and the density ratio \( \frac{\rho_b}{\rho_u} \) is determined based on the initial unburned gas temperature and pressure. An underprediction of \( \approx 5\% \) in \( S_u^0 \) is noted when these effects are excluded.
Figure 3.17 - Time evolution of a) Unburned gas density b) Burned gas density c) Unburned gas temperature. d) Temperature profile of burned gas at flame radius of 2 cm.

Calculations from the Multi-zone model.
The model described above for compression correction was implemented in Matlab. It requires extensive equilibrium calculations for each experimental condition in order to do compression correction. An easier approach is to express the gas velocity behind the flame front as

$$U_b = \frac{r_f \ d\rho_b}{3 \rho_b \ dt} = \frac{r_f \ dP}{3 \gamma P \ dt} = \frac{r_f \ dP \ dr_f}{3 \gamma P \ dr_f \ dt}$$ \hspace{1cm} (3.11)

Then the linear stretch model $S_b = S_b^0 - L_b K$ can be expressed as

$$\frac{dr_f}{dt} \left(1 + \frac{r_f \ dP}{3 \gamma P \ dr_f}\right) = S_b^0 - L_b K$$ \hspace{1cm} (3.12)

The integration of the equation yields
\[ r_f + \frac{1}{3\gamma} \int \frac{r_f \, dP}{P \, dr_f} \, dr_f = S_b^0 t - 2L_b \ln r_f + C \] (3.13)

In the above expression \( \frac{dP}{dr_f} \) is evaluated after fitting a cubic polynomial to the experimental pressure-radius data. A regression on the equation 3.13 provides \( S_b^0 \) and \( L_b \).

Experimental pressure vs radius along with the fitted curve and compression induced velocity in the burnt gas for \( \text{CH}_4/\text{air}, \phi=1, 1 \text{ atm}, 296 \text{ K} \) are shown in Fig. 3.19

3.4.3 Nonlinear Model 1 - Linear Curvature Model

The linear stretch model described above is easy to use and has been used most extensively. However, linear extrapolation is reasonable when the non-dimensional stretch, expressed as Karlovitz number, is sufficiently small so that the deviation of the measured flame speed from the unstretched value is small (Kelley and Law, 2009). The deviations
can be substantial due to high stretch (large Karlovitz number) and/or strong non-equidiffusion.

![Figure 3. 19 - Experimental pressure vs radius along with the fitted curve (solid line) and compression induced velocity in the burnt gas (dashed line). CH4/air, φ=1, 1 atm, 296 K](image)

In such situations, the behavior could be nonlinear and a linear extrapolation is not justified. Wu et al. (2015) compared various linear and nonlinear models with direct numerical simulations of spherical expanding flames and derived a relation between extrapolation uncertainties and the product of Markstein number and Karlovitz number.

A nonlinear stretch vs flame speed model was derived by Chen and Ju (2007) by including the effect of stretch and general Lewis number. The model is linear in terms of curvature and is expressed as
\[ S_b = S^0_b - L\kappa = S^0_b - \frac{2L}{r_f} \]  \hspace{1cm} (3.14)

Where \( \kappa = \frac{2}{r_f} \) is the curvature. This expression was proposed empirically by Markstein (1951). This model also showed close agreement with the numerically simulated methane flames, especially for \( Le > 1 \) (Chen, 2011).

When compression correction is included, this model is expressed as

\[ \frac{dr_f}{dt} \left( 1 + \frac{r_f}{3\gamma P} \frac{dP}{dr_f} \right) = S^0_b - \frac{2L}{r_f} \]  \hspace{1cm} (3.15)

and the integrated form is

\[ \frac{r_f^2}{2} + \frac{1}{3\gamma} \int \frac{r_f^2}{P} \frac{dP}{dr_f} \, dr_f = S^0_b \int r_f \, dt - 2Lt + C \]  \hspace{1cm} (3.16)

A regression on the above equation gives \( S^0_b \), \( L \) and \( C \). It is to be noted that \( L \) here does not represent the Markstein length. Markstein length is obtained numerically as \( \frac{dS_b}{dK} \) as \( K \to 0 \).

3.4.4 Nonlinear Model II

Another nonlinear model is based on Ronney and Sivashinsky (1989) who derived an equation for outward propagating flame that allows arbitrary Lewis number. Therefore, it is expected to be more general than the linear model. The use of this model with improved performance has been demonstrated by (Kelley and Law, 2009; Chen, 2011; Halter et al.,
If the analysis is restricted to adiabatic, quasisteady flames, the model is expressed as given by Kelley and Law (2009).

\[
\left( \frac{S_b}{S_b^0} \right)^2 \ln \left( \frac{S_b}{S_b^0} \right) = -2 \frac{L_b K}{S_b^0}
\]

(3.17)

The integration of the above equation based on Kelley and Law (2009) gives

\[
t = A \left[ E_1(\ln \xi^2) - \frac{1}{\xi^2 \ln \xi} \right] + C
\]

(3.18)

Where

\[
A = \frac{2L_b}{S_b^0}, \quad r_f = -\frac{2L_b}{\xi \ln \xi}, \quad E_1(x) = \int_x^{\infty} \frac{e^{-z}}{z} \, dz
\]

A, L_b and C can be determined from regression and flame speed by \( S_b^0 = \frac{2L_b}{A} \). It was noted by Halter et al. (2010), the convergence on the integrated equation is tricky and highly dependent on initial values of \( S_b^0 \) and \( L_b \). The process recommend by Halter et al. (2010) involves minimization of

\[
\Sigma_{i=1}^{N} \left| \left( \frac{S_b}{S_b^0} \right)^2 \ln \left( \frac{S_b}{S_b^0} \right)^2 + 2 \frac{L_b K}{S_b^0} \right|
\]

(3.19)

and then the use of the obtained values as inputs for the integrated equation (3.18) proposed by Kelley and Law (2009). The same method is used here. It is also noted that the integrated equation does not consider compression correction and only the minimization method is used when compression correction is included. Since the minimization process (when
integrated equation is not used) involves \( \frac{dr_f}{dt} \), the numerical differentiation of the radius-time data can introduce uncertainties because the random uncertainties in radius data due to finite pixel resolution, flame aberration and image processing get amplified. Various models are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Linear Stretch</strong></td>
<td>( \frac{dr_f}{dt} \left( 1 + \frac{r_f}{3\gamma P \frac{dP}{dr_f}} \right) = S_b^0 - L_b K ) 3.12</td>
</tr>
<tr>
<td><strong>Linear Curvature</strong></td>
<td>( \frac{r_f^2}{2} + \frac{1}{3\gamma} \int \frac{r_f^2}{P \frac{dP}{dr_f}} dr_f = S_b^0 \int r_f dt - 2L_b \ln r_f + C ) 3.13</td>
</tr>
<tr>
<td><strong>Nonlinear Model II</strong></td>
<td>( t = A \left[ E_1(\ln \zeta^2) - \frac{1}{\zeta^2 \ln \zeta} \right] + C ) 3.14</td>
</tr>
</tbody>
</table>

\[
A = \frac{2L_b}{S_b^0}, \quad r_f = -\frac{2L_b}{\ln \zeta}, \quad E_1(x) = \int_x^\infty \frac{e^{-z}}{z} \, dz
\]
3.4.5 Comparison of Models

The time-pressure-radius data presented previously for CH\(_4\)/air, \(\phi = 1\) flame was analyzed using various models presented above with and without compression correction. The flame radius data in Fig. 3.16 has some random scatter. When the data is numerically differentiated to get \(\frac{dr_f}{dt}\) and plotted as \(S_b\) (without compression correction) vs \(K\), the scatter get greatly amplified as shown in Fig. 3.20(a). In Fig. 3.20(a), the data is shown by differentiating in 3 ways (a) taking adjacent points to evaluate \(\frac{dr_f}{dt}\), (b) fitting a local quadratic polynomial through 3 adjacent points and (c) fitting a local quadratic polynomial through 5 adjacent points and using that to evaluate \(\frac{dr_f}{dt}\). Clearly, the scatter in the radius data gets greatly amplified on differentiation.
Figure 3. 20 - Flame speed vs stretch. (a) Experimental data and (b) fitted curves for linear stretch model without compression correction. CH\textsubscript{4}/air, $\phi$=1, P=1atm, T=296K
The correlations based on regression of the equations 3.12 and 3.13 are also shown in Fig. 3.20(b) and the values for $S_b^0$ and $L_b$ along with standard errors and $R^2$ for regression are shown in Table 3.2. The important observation is high $R^2$ and small standard error when integrated equation is used. The integrated equation circumvents the need for finite differencing and $S_b^0$ and $L_b$ are obtained directly from the experimental data.

The validity of regression can be further assessed by looking at the residuals, which are defined as the difference between the experimentally measured radii and those predicted by the regression. The residuals are shown in Fig. 3.21 and are noted to be very small and randomly distributed. In fact, the largest residual values here correspond to less than half of a pixel and are due to finite camera resolution. Large $R^2$ and small and randomly distributed residuals demonstrate that the integrated equation describes the experimental data properly.

Table 3.2 - Flame speed and Markstein length values, standard errors and $R^2$ for Linear stretch model without compression correction. CH$_4$/air, $\phi$=1, P=1 atm, T= 296 K

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Standard Error</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adjacent difference</td>
<td>$S_b^0$ (cm/s)</td>
<td>270.48</td>
<td>8.45</td>
</tr>
<tr>
<td></td>
<td>L$_b$ (cm)</td>
<td>0.078</td>
<td>0.020</td>
</tr>
<tr>
<td>Quadratic fit - 3 points</td>
<td>$S_b^0$ (cm/s)</td>
<td>273.78</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td>L$_b$ (cm)</td>
<td>0.084</td>
<td>0.010</td>
</tr>
<tr>
<td>Quadratic fit - 5 points</td>
<td>$S_b^0$ (cm/s)</td>
<td>276.36</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>L$_b$ (cm)</td>
<td>0.092</td>
<td>0.005</td>
</tr>
<tr>
<td>Integrated equation</td>
<td>$S_b^0$ (cm/s)</td>
<td>278.99</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>L$_b$ (cm)</td>
<td>0.098</td>
<td>0.005</td>
</tr>
</tbody>
</table>

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Figure 3.21 - Residuals for flame radius from linear stretch model without compression correction. CH₄/air, φ= 1, P=1 atm, T=296 K

A comparison of the linear stretch model with and without compression correction is shown in Fig. 3.22. Experimental data shown for reference is based on evaluating $\frac{dr_f}{dt}$ by fitting a local quadratic polynomial through 5 adjacent points. Consistent with Fig. 3.19, compression correction increases with increasing radius or decreasing stretch. This leads to higher flame speed and Markstein length with compression correction.

A comparison of various models with and without compression correction is shown in Fig. 3.23 and 3.24. All models demonstrate excellent fit with $R^2$ close to 1 despite of differences in Markstein length and flame speed. The values for $S_u^o$ and $L_b$ from various
models are summarized in Table 3.3. Taking the linear curvature model as the base, the linear stretch and the Nonlinear Model II overpredict and underpredict the flame speed, respectively by around 2%. The differences in $L_b$ are more drastic.

Figure 3.22 - Linear stretch model with and without compression correction. CH$_4$/air, $\phi=1$, P=1 atm, T=296 K
Figure 3. 23 - Effect of different models without compression correction. CH₄/air, φ=1, P=1atm, T=296K
3. 24 - Effect of different models with compression correction, CH₄/air, φ=1, P= 1atm, 
T=296K

Table 3.3 - Comparison of predictions from various models. CC means that compression 
correction is included. CH₄/air, φ=1, P=1 atm, T=296 K

<table>
<thead>
<tr>
<th></th>
<th>Linear stretch</th>
<th>Linear Curvature</th>
<th>NM II</th>
<th>Linear stretch - CC</th>
<th>Linear Curvature - CC</th>
<th>NM II - CC</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₀ (cm/s)</td>
<td>36.88</td>
<td>36.15</td>
<td>35.53</td>
<td>39.03</td>
<td>38.35</td>
<td>37.60</td>
</tr>
<tr>
<td>% change</td>
<td>2.01</td>
<td>Base</td>
<td>-1.71</td>
<td>1.79</td>
<td>Base</td>
<td>-1.96</td>
</tr>
<tr>
<td>Lₜ (cm)</td>
<td>0.098</td>
<td>0.073</td>
<td>0.060</td>
<td>0.130</td>
<td>0.096</td>
<td>0.078</td>
</tr>
<tr>
<td>% change</td>
<td>33.80</td>
<td>Base</td>
<td>-18.00</td>
<td>35.11</td>
<td>Base</td>
<td>-19.03</td>
</tr>
</tbody>
</table>

This completes the description of the experimental facility procedures that were 
developed or implemented for data interpretation.
CHAPTER IV

LAMINAR FLAME SPEED MODELING

4.1. Packages for Flame Speed Modeling

Modeling of flame speed was done using Premix (Kee et al., 1985) and Agnisoft. Premix is a well-established and popular package for modeling adiabatic planar flames with detailed chemistry and transport. Agnisoft is a recent package for analysis of gas phase chemical kinetics and can be used for modeling homogeneous autoignition, laminar premixed flames and opposed jet diffusion flames. Both packages are essentially same as far as governing equations and solution method are concerned, and were used for determination of flame speeds for planar, 1-D, adiabatic, laminar premixed flames. The following governing equations and rate expressions are adapted from CHEMKIN (Kee et al., 1985 and Kee et al., 1995)

4.2. Governing Equations

The assumption that the pressure remains constant across the flame greatly reduces the complexity of the problem since the momentum equation no longer needs to be considered. The governing equations then reduce to the continuity equation, the species conservation equation, and the energy equation. The equations governing steady, isobaric, quasi-one-dimensional flame propagation may be written as follows
Continuity:

\[ \dot{M} = \rho u A \]  \hspace{1cm} (4.1)

Energy:

\[ \dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \lambda A \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^{K} \rho y_k V_k c_{pk} \frac{dT}{dx} + \frac{A}{c_p} \sum_{k=1}^{K} \omega_k h_k W_k = 0 \]  \hspace{1cm} (4.2)

Species:

\[ \dot{M} \frac{dY_k}{dx} + \frac{d}{dx} \left( \rho A Y_k V_k \right) - A \omega_k W_k = 0 \]  \hspace{1cm} (k = 1, 2, ..., K)  \hspace{1cm} (4.3)

Equation of state:

\[ \rho = \frac{p \bar{W}}{R_u T} \]  \hspace{1cm} (4.4)

In these equations \( x \) denotes the spatial coordinate; \( \dot{M} \) the mass flow rate; \( T \) the temperature; \( Y_k \) the mass fraction of the \( k^{th} \) species; \( \rho \) the pressure; \( u \) the velocity of the fluid mixture; \( \rho \) the mass density; \( W_k \) the molecular weight of the \( k^{th} \) species; \( \bar{W} \) the mean molecular weight of the mixture; \( R_u \) the universal gas constant, \( \lambda \) the thermal conductivity of the mixture; \( c_p \) the constant pressure heat capacity of the mixture; \( c_{pk} \) the constant pressure heat capacity of the \( k^{th} \) species; \( \omega_k \) the molar rate of production by chemical reaction of the \( k^{th} \) species per unit volume; \( h_k \) the specific enthalpy of the \( k^{th} \) species; \( V_k \) the diffusion velocity of the \( k^{th} \) species; and \( A \) the cross-sectional area of the stream tube encompassing the flame.
For freely propagating flames, boundary conditions are of given composition, pressure and temperature at inlet and zero gradients at the exit. Mass flow rate, $\dot{M}$, is an eigenvalue and must be determined as part of the solution. Therefore, an additional boundary condition is required, or alternatively one degree of freedom must be removed from the problem. The location of the flame is fixed by specifying the temperature at one point. This is sufficient to allow for the solution of the flame speed eigenvalue $\dot{M}$.

The modeling of planar, laminar premixed flames based on above governing equations requires chemical kinetic mechanism along with thermodynamic and transport data for all the species.

4.3. Reaction Rate Expressions

The chemical kinetic mechanism includes all the elements, species and reactions from which rates of reactions are computed. An example of a truncated mechanism is given in Fig. 4.1

```
ELEMENTS
O  H  C  N  AR
END
SPECIES
H2      H       O       O2      OH      H2O     HO2     H2O2
C       CH      CH2     CH2(S)  CH3     CH4     CO      CO2
HCO     CH2O    CH2OH   CH3O    CH3OH   C2H     C2H2    C2H3
…………………………
END
REACTIONS
2O+M<=>O2+M     1.200E+17  -1.000  .00
H2/2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/3.60/ C2H6/3.00/ AR/.83/
………………
END
```

Figure 4.1 - Example of a chemical kinetic mechanism
The rates for the elementary reactions in the kinetic mechanism depend on composition, temperature and pressure. These rates are expressed in different ways, which is briefly described here.

An elementary reaction $i$ involving $K$ species can be expressed in general form as

$$\sum_{k=1}^{K} v'_{kl} M_k \leftrightarrow \sum_{k=1}^{K} v''_{kl} M_k \quad i = 1, 2, 3, ..., l \quad (4.5)$$

Where $v'_{kl}$ and $v''_{kl}$ are stoichiometric coefficients and $M_k$ is the chemical symbol for species $k$. The production rate of $k^{th}$ species, which is required in equations (4.2) and (4.3), can be written as

$$\dot{\omega}_k = \sum_{i=1}^{l} v_{kl} q_i \quad (4.6)$$

where $v_{kl} = v''_{kl} - v'_{kl}$ and $q_i$ is the progress variable for the $i^{th}$ reaction given by

$$q_i = k_{fi} \prod_{k=1}^{K} [M_k]^{v'_{kl}} - k_{ri} \prod_{k=1}^{K} [M_k]^{v''_{kl}} \quad (4.7)$$

where $[M_k]$ is the molar concentration for species $k$ and $k_{fi}$ and $k_{ri}$ are the forward and reverse specific reaction rate constants for the $i^{th}$ reaction.

For most of the reactions an Arrhenius expression is used as follows

$$k_{fi} = A_i T^{\beta_i} \exp \left( - \frac{E_i}{RT} \right) \quad (4.8)$$

For which the pre-exponential factor $A_i$, temperature exponent $\beta_i$ and the activation energy $E_i$ are specified in the mechanism and $R$ is the universal gas constant. The reverse
rate constant, $k_{ri}$ can be evaluated by using the equilibrium constant $K_{ci}$ as $k_{ri} = \frac{k_{fi}}{K_{ci}}$. The calculation of the equilibrium constant requires thermodynamic data.

$$K_{ci} = \exp \left( -\frac{\Delta G^0_i}{R_u T} \sum_{k=1}^{K} \nu_{ki} \right)$$

(4.9)

where $\Delta G^0_i$ is the change in Gibbs energy at standard state for reaction $i$.

$$\Delta G^0_i = \Delta H^0_i - T \Delta S^0_i = \sum_{k=1}^{K} \nu_{ki} H^0_k - T \sum_{k=1}^{K} \nu_{ki} S^0_k$$

(4.10)

where $H^0_k$ and $S^0_k$ are the standard state (1atm) enthalpy and entropy for the $k^{th}$ species.

In some reactions, such as in dissociation or recombination reactions, a third body is required for the reaction to occur. When a third body is required, the progress variable is modified to account for the effective third body concentration as follows

$$q_i = \left( \sum_{k=1}^{K} a_{ki} [M_k] \right) \left( k_{fi} \prod_{k=1}^{K} [M_k]^{\nu_{ki}'} - k_{ri} \prod_{k=1}^{K} [M_k]^{\nu_{ki}''} \right)$$

(4.11)

where $a_{ki}$ is the third body efficiency of species $k$ in the $i^{th}$ reaction. The first term on the right hand side becomes the total concentration $[M]$ if all species have same third body efficiency of one. For the example reactions shown below, the third body efficiencies for various species are specified along with the Arrhenius parameters.
The Arrhenius reaction rate expression, described previously, depends only on temperature. However, under certain conditions, some reaction rate expressions depend on both pressure and temperature. As an example, consider methyl recombination. In the high pressure limit, the appropriate description of the reaction is $CH_3 + CH_3 \leftrightarrow C_2H_6$, whereas in the low pressure limit a third body is required to provide the energy for the reaction and the appropriate description is $CH_3 + CH_3 + M \leftrightarrow C_2H_6 + M$. At low or high pressure limits, the reaction rate is only temperature dependent. However, the rate expression is more complicated between the limits. Such reactions are described as $CH_3 + CH_3 (+M) \leftrightarrow C_2H_6 (+M)$. Note $M$ inside the parentheses. There are several ways to represent the rate expression for such reactions in between the low and high pressure limits. The Lindemann method is the simplest and Troe (Gilbert et al., 1983) and Stewart (Stewart et al., 1989) are more accurate.

Arrhenius expressions are used for both low and high pressure limits

$$k_0 = A_0 T^{\beta_0} \exp \left( -\frac{E_0}{RT} \right)$$  \hspace{1cm} (4.12)
\[ k_\infty = A_0 T^{\beta_\infty} \exp \left( -\frac{E_\infty}{RT} \right) \]

where subscript 0 and \( \infty \) represent the low and high pressure limits. The rate constant at any pressure is expressed as

\[ k = k_\infty \left( \frac{P_r}{1 + P_r} \right) F \]

(4.13)

\[ P_r = \frac{k_0 [M]}{k_\infty} \]

(4.14)

\( F \) is unity in the Lindemann formulation. In the Troe formulation, \( F \) is given by

\[ \log F = \left[ 1 + \left[ \frac{\log P_r + c}{n - d(\log P_r + c)} \right]^2 \right]^{-1} \log F_{\text{cent}} \]

\[ c = -0.4 - 0.67 \log F_{\text{cent}} \]

\[ n = 0.75 - 1.27 \log F_{\text{cent}} \]

(4.15)

\[ d = 0.14 \]

\[ F_{\text{cent}} = (1 - \alpha) \exp \left( -\frac{T}{T^*} \right) + \alpha \exp \left( -\frac{T}{T^{**}} \right) + \exp \left( -\frac{T}{T^{***}} \right) \]

The parameters \( \alpha, T^*, T^{**}, T^{***} \) are specified with the reaction. For the pressure dependent reaction shown below, Arrhenius parameters for low and high pressure limit are shown. Also included are the Troe parameters and third body efficiencies of species.
Another method for describing pressure dependent reactions is based on the direct interpolation of reaction rates specified at individual pressures. Different rate parameters are given for discrete pressures within the pressure range of interest and the actual reaction rate at the current pressure is computed through logarithmic interpolation of the specified rate constants. For a given reaction, the rate parameters are provided for a set of pressures $P_j$. For pressure $P$ between $P_i$ and $P_{i+1}$, the rate is obtained as

$$
\log k = \log k_i + (\log k_{i+1} - \log k_i) \frac{\log P - \log P_i}{\log P_{i+1} - \log P_i}
$$

For the reaction shown below, rate parameters for discrete pressures are given and the actual rate is calculated from logarithmic interpolation.

\[
\text{CH}_3 + \text{OH} \leftrightarrow \text{CH}_2\text{O} + \text{H}_2 \quad 3.502\times10^5 \quad 1.441 \quad -3244.0 \\
PLOG/ 0.0100 \quad 3.502E+005 \quad 1.441 \quad -3244.0/ \\
PLOG/ 0.1000 \quad 8.854E+005 \quad 1.327 \quad -2975.0/ \\
PLOG/ 1.0000 \quad 1.650E+007 \quad 0.973 \quad -2010.0/ \\
PLOG/ 10.0000 \quad 5.374E+009 \quad 0.287 \quad 280.0/ \\
PLOG/ 100.0000 \quad 9.494E+018 \quad 0.287 \quad 280.0/ 
\]
4.4. Thermodynamic Expressions

The thermodynamic data is provided in the form used in the NASA chemical equilibrium code by Gordon and Mcbride (1971). An example of thermodynamic data for H$_2$ species is shown below.

```
H2    TPIS78H  2  0  0 0G  200.000  6000.00  1000.00  1
  2.93286575E+00  8.26608026E-04  1.46402364E-07  1.54100414E-11-6.88804800E-16  2
  -8.13065581E+02-1.02432865E+00  2.34433112E+00  7.98052075E-03-1.94781510E-05  3
  2.01572094E-08-7.37611761E-12-9.17935173E+02  6.83010238E-01  0.00000000E+00  4
```

Figure 4.5 - Example of thermodynamic data

There are 14 coefficients in lines 2 to 4 for two temperature ranges. These are typically denoted as $a_1, a_2, \ldots, a_7$ for the high temperature range followed by the coefficients for the low temperature range. The first line includes the low, high and intermediate temperature value that is used to split the entire temperature range.

Using these coefficients, the specific heat at standard state is given by

$$\frac{c_{pk}^o}{R} = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4$$ (4.17)

The enthalpy, by integrating the specific heat, as

$$\frac{H_k^o}{RT_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{6k}$$ (4.18)

and the entropy as

90
\[
\frac{S_k^0}{R} = a_{1k} \ln T_k + a_{2k} T_k + \frac{a_{3k}}{2} T_k^2 + \frac{a_{4k}}{3} T_k^3 + \frac{a_{5k}}{54} T_k^4 + a_{7k}
\] (4.19)

4.5. Transport Properties

Transport properties, particularly thermal conductivity and mass diffusivity, are required for solving the laminar flame structure. The evaluation of pure species properties follows from the standard kinetic theory of gases, but a range of possibilities exist for evaluating mixture properties. Computation of multi-component diffusion coefficients is accurate but computationally expensive. Mixture averaged transport properties along with thermal diffusion are often used satisfactorily. The mixture averaged formulation is used here.

Pure species viscosity is given by the standard kinetic theory as (Hirschfelder et al., 1954)

\[
\mu_k = \frac{5}{16} \frac{(\pi m_k k_B T)^{\frac{1}{2}}}{\pi \sigma_k^2 \Omega^{(2,2)*}}
\] (4.20)

Where \( \sigma_k \) is the Lennard-Jones collision diameter, \( m_k \) is the molecular mass, \( k_B \) is the Boltzmann constant. The collision integral \( \Omega^{(2,2)*} \) depends on the reduced temperature and reduced dipole moment.

The binary diffusion coefficients are given in terms of pressure and temperature as
\[ D_{kj} = \frac{3}{16} \frac{(2\pi k_B T^3 / m_{jk})^{\frac{1}{2}}}{P\pi \sigma_{jk}^2 \Omega^{(1,1)*}} \]  \hspace{1cm} (4.21)

where \( m_{jk} \) is the reduced molecular mass for \((j,k)\) species pair, and \( \sigma_{jk} \) is the reduced collision diameter. The collision integral \( \Omega^{(1,1)*} \) is based on Stockmayer potential.

The pure species thermal conductivities are computed for evaluating mixture-averaged thermal conductivities. The individual species conductivities are assumed to be composed of translation, rotational and vibrational contributions (Warnatz, 1982)

\[
\lambda_k = \frac{\mu_k}{W_k} (f_{trans}C_{v,trans} + f_{rot}C_{v,rot} + f_{vib}C_{v,vib})
\]  \hspace{1cm} (4.22)

The transport properties, namely individual component viscosity, thermal conductivity and binary diffusivity, are pre-calculated and fitted in a polynomial fashion where the logarithm of property is fitted against logarithm of temperature. A third order polynomial is used and fitting errors are generally less than 1%.

For viscosity

\[
\ln \mu_k = \sum_{n=1}^{N} a_{n,k} (lnT)^{n-1}
\]  \hspace{1cm} (4.23)

For thermal conductivity

\[
\ln \lambda_k = \sum_{n=1}^{N} b_{n,k} (lnT)^{n-1}
\]  \hspace{1cm} (4.24)

The fits are done for each pair of binary diffusion coefficients as

\[
\ln D_{kj} = \sum_{n=1}^{N} d_{n,jk} (lnT)^{n-1}
\]  \hspace{1cm} (4.25)
Mixture averaged diffusion coefficient for species $k$ is then evaluated as (Bird et al., 1960)

$$D_{km} = \frac{1 - Y_k}{\sum_{j \neq k}^K (X_j/D_{kj})} \quad (4.26)$$

and the mixture averaged thermal conductivity by (Mathur et al., 1967)

$$\lambda = \frac{1}{2} \left( \sum_{k=1}^K X_k \lambda_k + \frac{1}{\sum_{k=1}^K (X_k/\lambda_k)} \right) \quad (4.27)$$

4.6. Diffusion velocity

For the mixture-averaged formula, the diffusion velocity $V_k$ for equations 4.2 and 4.3 is taken to be composed of three parts

$$V_k = v_k + w_k + V_c \quad (4.28)$$

$v_k$ is the ordinary diffusion velocity and is given in the Curtiss-Hirschfelder approximation (1949) by

$$v_k = -D_{km} \frac{1}{X_k} \frac{dX_k}{dx} \quad (4.29)$$

A non-zero thermal diffusion velocity $w_k$ is included only for the low molecular weight species H, H$_2$, and He.

$$w_k = -\frac{D_{km}\Theta_k}{X_k} \frac{1}{T} \frac{dT}{dx} \quad (4.30)$$
where $\Theta_k$ is the thermal diffusion ratio. The sign of $\Theta_k$ makes the lower molecular weight species diffuse from low to high temperature regions.

The correction velocity $V_c$ (independent of species but a function of the distance $x$) is included to insure that the mass fractions sum to unity (or equivalently $\Sigma_{k=1}^{K} y_k v_k = 0$)

4.7. Solution Method

The numerical solution procedure begins by making finite difference approximations to reduce the boundary value problem to a system of algebraic equations. The initial approximations are usually on a very coarse mesh that may have as few as five or six points. After obtaining a solution on the coarse mesh, new mesh points are added in regions where the solution or its gradient changes rapidly. An initial guess for the solution on the finer mesh is obtained by interpolating the coarse mesh solution. This procedure continues until no new mesh points are needed to resolve the solution to the degree specified. This continuation from coarse to fine meshes has several important benefits. The system of algebraic equations is solved by the damped modified Newton algorithm. However, if the Newton algorithm fails to converge, the solution estimate is conditioned by integration in time. This provides a new starting point for the Newton algorithm that is closer to the solution, and thus more likely to be in the domain of convergence for Newton’s method.

The number of grid points can be adaptively refined by using appropriate values for GRAD and CURV. GRAD and CURV control the number of grid points inserted in the regions of high gradient and high curvature, respectively. In the current computations, grid independence was checked by decreasing the value of GRAD to 0.002.
Figure 4.6 - Effect of GRAD on grid points and flame speed. CURV = 0.2.

Stoichiometric Methane/Air flame at 298 K, 1 atm with GRI Mech 3.0

Figure 4.7 - Methane/Air flame structure at 298 K, 1 atm, φ=1.0 with GRI Mech 3.0
The number of grid points and flame speed for stoichiometric Methane/Air flame using GRI Mech 3.0 are shown in Fig. 4.6. Change in GRAD from 0.1 to 0.002 changes flame speed by 2.5%. As an example, converged flame structure is also shown in Fig. 4.7. The flame thickness is less than a millimeter.
CHAPTER V
CHARACTERIZATION OF DCF AND RESULTS ON LAMINAR FLAME SPEED

5.1. Introduction

In order to establish the suitability of the designed DCF for flame propagation studies, CFD simulations for characterization of the temperature field inside the DCF and validation experiments were conducted. The CFD simulations provided important information about the thermodynamic state of the gas at the end of compression and delineated the physical conditions that can be accessed in the DCF for experiments. Further the validation experiments in static as well as dynamic mode confirmed that the data obtained from the new facility is comparable to data from other facilities. Following the characterization and validation, flame speed data for DME is presented and compared with kinetic models.

5.2. Validation in the Static Mode

In the static mode, the piston remains stationary and the facility is simply a spherical bomb. Flame speeds were determined for methane/air flames at atmospheric pressure. The data from the present measurements along with the experimental results of Vagelopoulos and Egolfopoulos (1998), Hassan et al. (1998), Gu et al. (2000), Rozenchan et al. (2002) and Qin and Ju (2005) are shown in Fig. 5.1. Predictions from GRI-Mech. 3.0 are also
shown for reference. The present data matches very well with the literature data, demonstrating the reliability of the new facility in the static mode.

![Graph showing comparison of flame speed data with literature data.]

**Figure 5.1 - Comparison of the present flame speed data with literature data.**

CH₄/Air, P=1 atm, T = 298 K

5.3. **Validation in the Dynamic Mode**

In the dynamic mode, the compression stroke of the piston is used to achieve elevated pressure and temperature before the initiation of flame. The most important requirement is the ability to have a homogeneous and quiescent core at elevated pressure and temperature after compression. The compression stroke in DCF is similar to
compression in RCMs; the only difference is that RCMs entail much faster compression (20 - 60 ms typically) than DCF. Various studies in RCMs (e.g. Daneshyar et al., 1973; Griffiths et al., 1993; Lee and Hochgreb, 1998; Clarkson et al., 2001; Mittal and Sung, 2005; Würmel and Simmie, 2005) have shown the existence of a roll-up vortex due to piston motion, which leads to the mixing of pockets of cold gases from the wall boundary layer with the hot gases in the core region. Similar phenomenon is also expected in DCF. However, the roll-up vortex can be minimized by using a crevice on the periphery of the piston. The importance of incorporating an optimized crevice on the periphery of the compression piston for achieving a homogeneous temperature field in the core of the reaction chamber for RCMs is now widely recognized (Griffiths et al., 1992; Clarkson et al., 2001; Mittal and Sung, 2006 and 2007). In order to systematically examine the effect of the compression stroke on the thermodynamic state at the end of compression in DCF, Fluent CFD package was used as discussed next.

5.3.1 CFD Based Characterization of the DCF

Due to the cylindrical geometry of the combustion chamber, the simulations were conducted for an axisymmetric configuration using the Fluent CFD package. The computations were performed from the beginning of the compression stroke for compression of air. All calculations were for laminar flow since the piston velocity is small (< 3 cm/s) and any turbulence would anyway yield the facility unusable for laminar flame studies. Initially, the gas mixture at rest was specified with uniform temperature and pressure. For all cases investigated, the initial mixture temperature was kept constant at 300 K. A fixed temperature of 300 K and no-slip conditions were specified at the wall
Simulations used implicit solver with the Pressure-Implicit Split-Operator (PISO) algorithm for pressure-velocity coupling, and second order upwind discretization for density and momentum.

In the simulations, the piston starts from rest and its velocity profile was deduced based on the measured pressure trace. The procedure to deduce the velocity of the piston during the compression process is described as follows. Since compression process can be approximated as polytropic in nature, the relation of \( \frac{P_C}{P_0} = (CR)^n \) is employed to determine the index of polytropic compression, \( n \), which is taken as a constant. Here, \( P_C \) is the measured pressure at the end of compression, \( P_0 \) is the initial pressure, and \( CR \) is the geometric compression ratio. Once the index of polytropic compression is calculated, the volume of the combustion chamber during compression, \( V(t) \), can be expressed as \( V(t) = V_0\left[\frac{P_0}{P(t)}\right]^{1/n} \), where \( V_0 \) is the initial volume before compression begins and \( P(t) \) is the experimental pressure trace. Subsequently, the velocity of the piston during compression, \( Vel(t) \), can be obtained by \( Vel(t) = \left[\frac{dV(t)}{dt}\right]/(\pi D^2/4) \), where \( D \) is the diameter of the reaction chamber and \( dV(t)/dt \) is the time rate of change of the chamber volume. Based on this approach, it was noted that the piston accelerates rapidly after the start of compression and reaches a peak velocity which remains almost constant until the piston reaches close to the end of the compression stroke. Near the end of the compression stroke, the piston decelerates rapidly due to the hydraulic damping provided by the built in cushion in the cylinder and maintains a lower constant velocity for a short duration, followed by a second rapid deceleration that brings it to rest. Consequently, the velocity profile, as shown in Fig. 5.2 was used in simulations. It was also noted that the average velocity of the piston was
around 2.54 cm/s, regardless of stroke. This feature was preserved in simulations as the stroke was varied.

At the end of compression, the piston comes to rest and remains there for the subsequent time steps. A time step of 2.77 ms was taken during both the compression stroke and the post-compression period. Independence with respect to the size of the time-step and grid distribution was ascertained by using time step smaller by a factor of 10 as well as a grid with 4 times the number of cells in the base grid. Figure 5.3 shows the computational grid at the end of the compression stroke. Fine grids can be seen near all the walls. The maximum grid size, near the axis, was 1 mm.

![Piston velocity profile for simulations. Stroke = 20.32 cm.](image)

Figure 5.2 - Piston velocity profile for simulations. Stroke = 20.32 cm.
The pressure trace for a simulation with stroke = 20.32 cm, $P_0 = 2.33$ bar, and $T_0=300$ K is shown in Figure 5.4 (a). The compression duration is 8 s. $P_c$ is 10.7 bar and the sudden inflection in the pressure profile is due to deceleration near the end of compression.

The temperature profiles, including the maximum instantaneous temperature, mass averaged temperature of the chamber (excluding crevice) and the mass averaged temperature of the entire chamber are shown in Fig. 5.4 (b). The difference between the mass averaged temperature and maximum temperature indicates enormous non-uniformity in the chamber temperature.
Figure 5.4 - Simulated result from compression of air. Stroke = 20.32 cm, $P_0 = 2.33$ bar.

(a) Pressure trace (b) maximum temperature (solid line), mass averaged temperature excluding crevice (dashed line), and mass averaged temperature (dash-dotted line)

However, our primary concern is the temperature in the core region where flame is to be initiated. The velocity and temperature fields at the end of compression are shown in
Fig. 5.5. In the main combustion chamber, the peak velocity is less than 1 cm/s. Even though a roll-up vortex is evident that also entrains the cold boundary layer inside, the thermodynamic state in the center region seems to be uniform. More insight is provided by Fig. 5.6 in which the maximum instantaneous velocity and temperature difference in the center 2.5 cm radius region is plotted. This region is the zone of interest (ZOI), in which flame propagation is observed. The temperature difference, $\Delta T$, here is the difference between the maximum and minimum temperature in the ZOI. In the ZOI, the peak velocity increases during compression and decreases rapidly near the end of compression and is less than 0.5 cm/s at the end of compression. In addition, $\Delta T$ at the end of compression is less than 0.5 K. Therefore, the ZOI is practically quiescent and has uniform temperature for flame propagation studies.

Furthermore, the temperature in the ZOI is accurately predicted by the adiabatic core hypothesis which is often used in RCMs (Tanaka et al., 2003; Mittal and Sung, 2006; Healy et al., 2008). This hypothesis assumes no mixing between the cold boundary layer and the hot ZOI, and the only way the effect of near-wall heat loss penetrates the ZOI is through the expansion of the ZOI caused by the cooling of the boundary layer.

Therefore, the compressed gas temperature, $T(t)$ in the ZOI at any time, based on the assumption of an adiabatic core, can be calculated by measured pressure as:

$$\int_{T_0}^{T(t)} \frac{\gamma}{\gamma - 1} \frac{dT}{T} = \ln \left( \frac{P(t)}{P_0} \right)$$
Figure 5.5 - Velocity (cm/s) and temperature fields (K) at the end of compression.

Stroke = 20.32 cm, $P_0 = 2.33$ bar, $P_c = 10.7$ bar

The temperature evaluated based on this hypothesis matched exactly with the maximum instantaneous temperature in Fig. 5.4(b). This demonstrates that, at least from
CFD simulations, the facility is capable of providing uniform and well characterized thermodynamic state in the ZOI.

![Graph of ΔT vs Time]

Figure 5.6 - Maximum instantaneous velocity (solid line) and ΔT (dashed line) in the ZOI. Stroke = 20.32 cm, P₀ = 2.33 bar, P_c = 10.7 bar

It was shown by Mittal et al. (2012) that compressed pressure and stroke length play a vital role in altering vortex formation. They showed that as the compressed gas pressure is reduced, the temperature homogeneity deteriorates due to the combined effect of thicker boundary layer and increased flow velocities. Therefore, it is imperative to characterize the thermodynamic state of ZOI over a wide range of operating conditions spanning variation in pressure and stroke.
Figure 5.7 - Velocity (cm/s) and temperature fields (K) at the end of compression. Stroke $= 20.32$ cm, $P_0 = 0.25$ bar, $P_c = 1$ bar
Figure 5.8 - Velocity (cm/s) and temperature fields (K) at the end of compression. Stroke

\[ = 20.32 \text{ cm}, P_0 = 0.97 \text{ bar}, P_c = 4.23 \text{ bar} \]

Such a characterization was conducted. Simulated temperature and velocity fields for DCF for lower \( P_0 \) and \( P_c \) while keeping the stroke same are shown in Figs. 5.7 to 5.9, clearly demonstrating the effect of compressed pressure. In all figures same scale is used for
depicting velocity and temperature fields. These results are summarized in Figs. 5.10 and 5.11. The peak chamber temperature decreases with decrease in pressure due to an increase in the thermal diffusivity which increases heat loss, and also due to the mixing of the core region with the cold boundary layer at low pressures. Maximum ZOI velocity and $\Delta T$ increase with decrease in pressure as shown in Fig. 5.11. The rapid increase in $\Delta T$ at lower pressures is due to the effect of vortex.

Figure 5. 9 - Velocity (cm/s) and temperature fields (K) at the end of compression. Stroke = 20.32 cm, $P_0 = 1.64$ bar, $P_c = 7.4$ bar
Figure 5.10 - Simulated pressures and maximum instantaneous temperatures. Stroke = 20.32 cm, $P_0$ = 0.25, 0.97, 1.64, 2.33 bar
Figure 5. 11 - Maximum instantaneous ΔT and velocity in the ZOI. Stroke = 20.32 cm, $P_0=0.25, 0.97, 1.64, 2.33$ bar. Pressure increases from the top curve to the bottom curve.
A number of simulations were conducted over a variation of stroke length and initial pressure. In these simulations, \( \Delta T < 3 \) K at the end of compression was used as the criterion for taking a case as acceptable. The results from these simulations are summarized in Figs. 5.12 and 5.13. In Fig. 5.12, for a given stroke and \( P_0 \), the points below the curve manifested \( \Delta T > 3 \) K and those above had \( \Delta T < 3 \) K. The experiments in DCF should be conducted in the region above this boundary in Fig. 5.12 to get reliable data. A plot of \( T_c \) vs stroke for the boundary of Fig. 5.12 is shown in Fig. 5.13(a) and the \( P_c \) vs \( T_c \) boundary is shown in Fig. 5.13(b). The region to the right of this boundary yields \( \Delta T < 3 \) K. These simulations were crucial and established the region accessible to DCF based on the requirement of uniform ZOI conditions.

It is also noted that the compression time for longer stroke is quite long. For instance, it takes 20 s for a stroke of 50.8 cm. Such a long compression time yields thick boundary layer. It is possible that the curve in Fig. 5.13(b) could be shifted to the left by optimizing piston speed and resorting to faster compression. Too fast compression, however, is undesirable as it can induce turbulence in the chamber. Furthermore, these simulations were conducted for air and the actual conditions after compression will depend on the thermal conductivity and specific heat ratio of the gas. However, for a given stroke, \( P_c \) is the most important parameter and we can take the boundary shown in Fig. 5.12(b) as the guideline for gas mixtures with different specific heat ratios.
Figure 5. 12 - Accessible pressure vs stroke in DCF based on CFD simulations
Figure 5.13 - Accessible pressure and temperature in DCF based on CFD simulations
5.3.2 Validation and Experimental Results in the Dynamic Mode

Focus of the following work is on the dynamic mode; so obtained data from the dynamic mode will be presented and compared with the data in the literature. In dynamic mode, the piston compresses the mixture to elevated pressure and temperature before the initiation of flame. The comparison of flame speed data in the static mode has been previously presented in Fig. 5.1. This validation clearly showed the reliability of current measurements in the static mode.

Validation of the measurements from the newly innovated facility was conducted using a methane-air mixture and compared to the existing flame speed data from literature. The measurements were compared because of the availability of methane-air flame speed data over a range of temperatures and pressures. There is some data for elevated pressure but only few investigators have acquired data at elevated temperatures. So, our motivation was to obtain the data for atmospheric to elevated pressures (1 to 20 bar) and temperatures from 298 K to 500 K.

Sample pressure traces for nonreactive and reactive $CH_4/air$ mixture are shown in Fig. 5.14. The nonreactive experiment is conducted using $CH_4/N_2$ mixture of same heat capacity as the reactive mixture to ensure same heat release. The two pressure traces obtained at the time of compression match closely. Before combustion, the mixture is first compressed. There is an inflection point in the pressure trace during compression due to deceleration of the piston assembly towards the end of compression. Peak pressure on the data scale signifies the moment at which the piston stops. Spark is initiated at the end of
compression at elevated pressure and temperature. Experiments over a range of pressures and temperatures can be conducted by varying initial pressure and stroke length.

Figure 5.14 - Sample pressure traces for nonreactive and reactive mixtures at compressed pressure of 10 bar. CH₄/air, ϕ=1

The obtained methane-air laminar flame speed data at 1 bar and elevated temperatures are compared with experimental data by Gu et al. (2000), Rozenchan et al. (2002) and Velloo et al. (2010) in Fig. 5.15. Experimental flame speed data presented by these authors is in the temperature range of 300 K to 400K only. Only single experimental data from counter flow flame measurement was obtained by Veloo et al. (2010) at temperature of 343K. For reference, predictions by using the mechanisms of GRI-Mech
GRI-Mech 3.0 and San Diego-Mechanism are also presented in Fig. 5.15. GRI-Mech 3.0 is an optimized mechanism to model natural gas combustion with 325 reactions and 53 species. The mechanism is used extensively for predictions over a wide range of temperatures and pressures. Another comparison consists of San Diego Mechanism developed by Williams and co-worker at the University of California at San Diego with 235 reactions and 43 species, which allows combustion of C₁-C₃ fuels.

![Figure 5.15 – Comparison of present laminar flame speed with literature, CH₄/air, φ=1, Pressure =1bar, T=298K – 443K.](image-url)
To obtain higher temperature and pressure, initial pressure and stroke was adjusted. The present data is noted to agree well with other experiments as well as with the San Diego Mechanism.

The above presented data were for atmospheric pressure and higher temperatures. The experiments were conducted at a higher pressure of 5 bar and the data is presented in Figure 5.16 – Comparison of present laminar flame speed with literature, CH₄/air, φ=1, Pressure =5 bar, T=298K – 463K.
Fig. 5.16. At 5 bar, the study was able to obtain flame speed up to temperature of 463 K, which is beyond the maximum temperature available from the only prior study by Gu et al. Predictions by the San Diego Mechanism match very well at temperatures below 350K and less than 5% under prediction is noted at the maximum temperature data point.

Figure 5.17 – Comparison of present laminar flame speed with literature, CH$_4$/air, $\phi=1$,
Pressure =10 bar, T=298K – 495K.

In Fig. 5.17, the data is presented for a further elevated pressure of 10 bar at temperatures up to 495 K. The present data matches well with the data of Gu et al. at temperatures below 360 K. However, the data of Gu et al. shows a decrease in flame speed
increment rate as temperature increases, which is certainly an anomaly. The data matches reasonable well with GRI-Mech 3.0, however a discrepancy of up to 10% is noted with the San Diego Mechanism.

![Graph showing comparison of laminar flame speed with mechanisms](image)

Figure 5.18 – Comparison of present laminar flame speed with mechanisms, CH₄/air, φ=1, Pressure = 20 bar, T=298K – 410K.

Only 2 data points were accumulated from current work for 20 bar as shown in figure 5.18. Because of difficulty in experiments at higher pressures, only 1 data has been
produced by Rozenchan et al. (2002) which exactly agrees with the present data. Further, the San Diego mechanism matches very well with the present data.

In summary, the results for all the above cases for methane/air agree well with the literature data. Even though the literature data is extremely scarce, the comparison presented above serves as a validation of the new facility in the dynamic mode. Moreover, extension of data range to elevated pressures and elevated temperatures makes DCF a reliable experimental setup. Experimental data for DME/air mixtures is presented in the following.

5.3.3 Experimental Results Using DME

Figure 5.19 shows a comparison of the laminar flame speed for DME/O\textsubscript{2}/N\textsubscript{2} (DME/air) obtained in the present study against experimental work by Daly et al. (2001), Qin et al. (2005), Zhao et al. (2004), Chen et al. (2012) and Jomaas et al. (2005). There are few other important works by various authors, but due to problem of clarity they have not been included in the graph. Except Zhao et al. (2004), in which the flame study was obtained using stagnation technique, all the reported data in the Fig. 5.19 is using spherical flame technique. These data do not match with each other and shows a lot of disagreement. The difference in equivalence ratio at peak laminar flame speed are observed between the data of Huang et al. (2007) and Zhao et al. (2004) with a difference value of $\Delta \phi = 0.2$, while the difference of laminar flame speed between two obtained data has a value of $\Delta S_0 = 9$cm/sec.
Figure 5.19 - Laminar flame speed of the mixture and its comparison with literature data.

DME/O$_2$/N$_2$ (air), $\phi=0.8$-1.6, Pressure=1 atm, T=298K.

These discrepancies are much larger than for methane/air mixtures, and remain unexplained. Probably the most important reason is due to the size of the combustion chamber and data interpretation. Experiments by Huang et al (2007) were done in a cuboidal type of combustion chamber of size (4.25 X 4.25 X 5.31) inch, while, stagnation
flame technique was implemented by Zhao et al. (2004). Burke et al. (2009) concluded that flame radii can be measured up to 30% of the chamber radius with marginal wall effects and showed the effect of cylindrical chamber geometry on shapes of flames. Present work also does not match with any other experimental work, but among the pool of data it is smooth throughout range of equivalence ratio and shows an average agreement. At lean condition it is near to Quin et al. (2005) while at rich condition it is closer to Zhao et al. (2004).

As discussed in chapter 3, the effect of compression on the flame speed is shown in Fig. 5.20 (a) for DME/air mixtures. Solid lines represent current data, where the upper line is the laminar flame speed in which compression correction was implemented. Laminar flame speed, given by other solid lines, in which compression has been considered but not density, is similar to above, stating that there is minimal effect of considering density.

There is a moderate difference in laminar flame speed when comparing without considering compression and density effect. The difference for equivalence ratio at 1.2 is about $\Delta S_o = 2.53\text{cm/sec}$, which is about 5% of the peak value.
Figure 5.20 (a) - Effect of compression and density correction on laminar flame speed of the mixture DME/O₂/N₂ (air) compared with few literature data, Φ= 0.8-1.6, Pressure=1atm, T= 298K

\[ ΔS_o = 2.53\text{cm/sec} \]
Figure 5.20(b) shows a comparison between three models; Linear, Linear curvature and Non-linear Model II, which were discussed in section 3.4. The comparison shown is with and without compression correction.
Figure 5.22 - Comparison of unburned Markstein length with current literature data, DME/O$_2$/N$_2$ (air), $\phi=0.8 – 1.6$, Pressure=1bar, T=298K.

It is observed that there is a significant difference towards lean mixture and no effect of these three models on the rich side. The difference in maximum laminar flame speed with and without compression correction is 3.65 cm/s.

Markstein length characterizes the sensitivity of propagation of flame to stretch rate and influences flame stability. Figure 5.21 shows unburned Markstein length of DME/air mixture at a pressure 1bar and various equivalence ratios from 0.8 to 1.6. In the figure, the
burned Markstein length presented by Chen et al (2012) and Huang et al. (2007) were corrected to unburned using density ratio.

The obtained plot shows a descending trend with ascending equivalence ratio which agrees well with the literature trend. This decrement of Markstein length with equivalence ratio implies that the flame propagation speed is more sensitive to the stretch rate for lean mixtures. Obtained data is somewhat higher in comparison to the literature data.

![Graph](image)

**Figure 5.23 - Laminar flame speed data of the major work by various authors**

DME/O₂/N₂ (air), φ=1.0, Pressure = 1 bar, T=298 K – 427K
Figure 5.22 illustrates the effect of unburned temperature on flame speed at atmospheric pressure and equivalence ratio of 1.0. As shown in Fig. 5.22, the data from various studies are concentrated at temperature of 298 K at an equivalence ratio of 1.0, and no data is available at elevated temperatures. The laminar flame speed from various researches is in a wide window of 37 cm/sec to 46 cm/sec at 298 K. The present study extends the data for the temperature of 298 K to 427 K at an equivalence ratio of 1.0 for DME/air mixture and gives an average laminar flame speed of 43.38 cm/sec at 298 K in comparison to other experimental data.

![Graph showing comparison of laminar flame speed with mechanisms.](image)

Figure 5.24 – Comparison of present laminar flame speed with mechanism.

**DME/O\textsubscript{2}/N\textsubscript{2} (air), \phi=1.0, Pressure=1bar, T=298K – 426K**
Figure 5.23 shows the laminar flame speed obtained from current work using DCF compared with the existing mechanism from San Diego Laboratory, University of California at San Diego (Prince and William, 2015). In total, there are 55 species and 261 reactions. The mechanism is in good agreement with the obtained experimental laminar flame speed. Another mechanism by Burke et al. (2016) has also been compared. Burke’s mechanism predicts much higher flame speed than the current experimental results.

![Diagram showing comparison of laminar flame speed with different mechanisms.](image)

**Figure 5.25** – Comparison of present laminar flame speed with mechanism.

DME/O$_2$/N$_2$ (air), $\phi=1.0$, Pressure = 5bar, $T = 298K – 471K$
At 5 bar, the San Diego mechanism agrees exactly with the current experimental data as shown in Fig. 5.24 over the entire temperature range. Present data shows a strong positive dependence of laminar flame speed on temperature which is also perfectly predicted by the model. But, mechanism by Burke et al. predicts higher flame speed values.

Similar, agreement is shown for the measurement of laminar flame speed at 10 bar as shown in the Fig. 5.25 with the San Diego mechanism. Again, an excellent agreement with the San Diego mechanism is noted. But Burke et al. mechanism predicts much higher and the difference increases with an increase in temperature.

![Graph showing comparison of laminar flame speed with mechanism.](image)

Figure 5.26 – Comparison of present laminar flame speed with mechanism.

DME/O₂/N₂ (air), φ=1.0, Pressure =10bar, T=298K – 470K
Figure 5.26 shows the laminar flame speed of DME/air at 20 bar for two temperature points. Mechanism prediction by San Diego mechanism is in good agreement with the two laminar flame speed obtained at temperature 295K and 405K. Similar to previous pressures, Burke et al. mechanism is not able to predict laminar flame speed at 20 bar. Due to difficulty in experiments, less data was obtained at this pressure.

![Graph showing laminar flame speed comparison](image)

Figure 5.27 - Laminar flame speed of mixture DME/air, $\phi = 1.0$, Pressure=20 bar, $T=298K$ and 405K
5.4. Flame morphology

Sample images of flame obtained from the special single-mirror schlieren technique implemented in this facility are shown in Fig. 5.27. The images are for DME/air mixture at 10 bar of initial pressure at the temperature of 376 K and equivalence ratio of 1.0. Similarly, Fig. 5.28 shows sample flame images for DME/air mixture at pressures of 1 bar and 20 bar at temperature of 298K and equivalence ratio of 1.0. At lower pressure the flame front is smooth throughout. Minimum spark energy was supplied for the mixture to minimize the effect of spark on initiation of flame. But the effect of spark persists and causes rapid rise or irregular flame kernel at small radius though it pacifies as the flame propagates. In Fig. 5.27, for CH₄/air mixture at 10 bar, radius up to 5 millisecond was not considered for analysis.

Formation of large-scale folds in the flame is observed at all pressure from 1bar to 20 bar. Large-scale wrinkle in the flame is basically an effect of uneven initiation of spark and interesting factor to detect. Once the flame was initiated, the wrinkle in CH₄/air mixture at 10 bar at stationary condition was formed after 25 milliseconds, while in case of DME/air mixture at 13.6 ms. The wrinkle further develops into cracking of cells which is a consequence of thermal diffusive instability. When mass diffusivity of the deficient reactant becomes sufficiently greater than the thermal diffusivity of the mixture, a smooth flame is turned into unstable resulting in cracking of cells (Bechtold & Metalon, 1987). It has been observed that increment in temperature decreases the time of formation of cells in flame surface. For CH₄/air mixture, at 10 bar, cracking was observed after 25 ms at 298 K, while the time reduced to 12 ms at the temperature of 493K. Furthermore, for DME/air mixture, at 10bar, cracking was observed after 13.6 ms and it significantly decreased to 7
ms of time at 20 bar concluding cells formation time decreases with increase in pressure. Uniformly cracked cell formation time of 13.6 ms is in good agreement with the reported data by Qin and Ju (2004) of 12.5 ms using DME/air mixture at 10 bar in stationary condition. At 20 bar, for CH₄/air mixture, at the 298 K cracking in cells was observed after 13.6 ms while in DME/air mixture after 7 ms.
Figure 5.28 - Sequence of sample flame images for DME/air mixture at 5 millisecond apart, Pressure=10 bar, Temperature= 376 K and Equivalence ratio= 1
Figure 5.29 - Sample flame images for DME/air mixture at Pressure = 1 bar and 20 bar, Temperature = 298 K, Equivalence ratio (ϕ) = 1.0
The difference of cracking of CH\textsubscript{4}/air after 12 ms at 493 K and 25 ms at 298 K clearly states that the stability of flames decreases as temperature increases. The cells cracking time of DME/air mixture was observed 13.6 ms, which is less and approximately half in comparison to CH\textsubscript{4}/air mixture. Within the initiation of cracking limit, relation between stretch and flame speed holds and are meaningful for the calculation of flame speed (Bradley et al. 1994). Figure 5.29 shows the difference between large scale wrinkle and cracking of cells within the flame surface. Observation of cracking of cells may also depend on the sensitivity of the schlieren imaging system.

![Sample schlieren flame images](image)

(a) (b)

Figure 5.30 - Sample schlieren flame images (a) With wrinkle only for CH\textsubscript{4}/air, at 298 K, 10 bar (b) With cracked cells for DME/air, at 298 K, 20 bar
5.5. Uncertainty Analysis

Various sources contribute to uncertainty in the obtained results of flame speed measurements. Moffat (1985) indicated uncertainty analysis as a powerful tool to locate the sources of trouble in experiments. An uncertainty analysis has been done for methane/air and DME/air mixture, at pressures of 1, 5, 10 and 20 bar and temperature from 298 K to 495 K at equivalence ratio of 1.0. There were maximum of 6 sets of experiments done for the verification of repeatability of the experiments. Systematic or bias error has a limitation that its value may not be obtained easily. If we consider from the very beginning process of gas-mixing inside the mixing tank, it has been shown that small changes in the room temperature can cause variation in mixture which are prepared by the partial pressure methods, leading to an uncertainty in the flame speed data.

Table 5.1 shows major sources, Bios error (Systematic) $U_s$ and Precision error (Random) $U_r$, that contribute to uncertainties in experiments. The combustible mixture is prepared in a chamber for sufficient time which has a stirrer bar attached to assure proper gas mixing. Pressure transducer of 0-20 PSI and 0-500 PSI were used to make a mixture, while piezo-electric pressure sensor was used to obtain the pressure data inside the combustible chamber. K-type thermocouple was used to record the initial room temperature.

Schlieren imaging system involves high speed camera resolution error, optical distortion and distance per pixel calibration. High speed camera has a resolution error under precision error though it is very less in comparison to other sources.
Table 5.1 - Various contributing sources for elemental uncertainties for the facility

<table>
<thead>
<tr>
<th>#</th>
<th>Source</th>
<th>Measurement</th>
<th>Bios error</th>
<th>Precision error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>Pressure</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>Pressure Transducer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Accuracy (linearity,</td>
<td>0 - 20PSI</td>
<td>0.25%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hysteresis, repeatability)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) Display resolution</td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>Pressure Transducer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Accuracy (linearity,</td>
<td>0 - 500PSIG</td>
<td>0.25%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>hysteresis, repeatability)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) Display resolution</td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>Pressure sensor</td>
<td>PSI</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Linearity</td>
<td></td>
<td>0.10%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><strong>Temperature</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>K type thermocouple</td>
<td>K</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Accuracy (K)</td>
<td></td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) Display resolution</td>
<td></td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td><strong>Imaging</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>Hi speed camera</td>
<td>cm</td>
<td>0.0016</td>
<td></td>
</tr>
<tr>
<td></td>
<td>resolution (cm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>Optical distortion (cm)</td>
<td>cm/sec</td>
<td>0.0139</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>Schlieren imaging in cm/pixel</td>
<td>cm/pixel</td>
<td>0.0139</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>Image calibration</td>
<td>cm</td>
<td>0.0139</td>
<td></td>
</tr>
<tr>
<td></td>
<td>resolution</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Image calibration using Matlab program to calculate the radius of the flame also has an error and has been assigned equivalent to 1 pixel of the image. For repeatability...
error, which is associated with random error, value of repeatability, \( R=6 \), has been used under confidence level of 95%. Obtained values in the table are based on the manufacturer specification or experimental value calculation. Uncertainty for the calculation of flame speed has been determined as explained by Moffat (1988), where, total experimental uncertainty of the system is estimated by root-sum-of-squares (RSS) method.

\[
\text{Total uncertainty} = \sqrt{U_s^2 + U_r^2}
\] (5.1)

Where, \( U_s \)

\[
= \pm \sqrt{\left( \frac{\partial S_l(x_1)}{\partial x_1} \right)^2 + \left( \frac{\partial S_l(x_2)}{\partial x_2} \right)^2 + \ldots + \left( \frac{\partial S_l(x_n)}{\partial x_n} \right)^2}
\] (5.2)

\[
U_s = \pm \sqrt{\sum_{i=1}^{n} \left( \frac{\partial S_l(x_i)}{\partial x_i} \right)^2}
\] (5.3)

Measurement uncertainty, including random (precision) error \( U_r \) and Systematic (bias) error \( U_s \), with 95% of confidence is given by,

\[
U_{total} = \sqrt{U_s^2 + \left( \frac{U_r}{R} \right)^2} \quad 95\%
\] (5.4)
Equation 5.3 clearly gives an idea that the uncertainty $U_s$ is a functional relation between unburned reference laminar flame speed, initial pressure, initial temperature, equivalence ratio of the mixture, flame speed, schlieren imaging limits and optical distortion and other elemental sources which are given in Table 5.1. Functional relationship must be known in order to calculate uncertainty. Laminar flame speed depends on the equivalence ratio, pressure and temperature of the system. Various correlations have been proposed for the prediction of burning speed at variable pressure and temperature with respect to equivalence ratio. In the current study, correlations have been developed and proposed for higher temperature and pressure of methane/air mixture and DME/air mixture based on the experimental obtained data.

Due to different fuel type, separate correlations were developed for methane/air and DME/air mixtures. Since the experiments were conducted for a constant equivalence ratio, $\Phi=1$; effect of equivalence ratio has been neglected. As suggested by Metghalchi and Keck (1980), a power law equation holds true to correlate the sensitivity of laminar flame speed as shown in equation 5.5.

$$Su(\Phi, P, Tu) = Su_o \left( \frac{Tu(\Phi)}{Tu_0(\Phi)} \right)^\alpha \left( \frac{P(\Phi)}{P_0(\Phi)} \right)^\beta$$

(5.5)

Where, $Su_o$ is the unburnt flame speed at reference pressure of $P_0=1$ bar, $Tu_0=298$K, $\alpha$ and $\beta$ are fitted constants. Value of $\alpha$ was found 1.55 for both methane/air and DME/air mixtures, while value of $\beta$ for these two mixtures were calculated different, -0.35 and -0.28, respectively. This signifies that unburnt flame speed responds similarly at higher
temperature for both types of mixtures. But in case of pressure, methane/air is more sensitive than DME/air.

Equation 5.6 represents the correlation for methane/air mixture and equation 5.7 for DME/air. Least square methods were used to fit the correlation to experimental pressure of 1 bar, 5 bar, 10 bar and 20 bar, and temperatures from 298 K to 493 K.

\[
Su(P, Tu) = Su_0 \left( \frac{T_u}{298} \right)^{1.55} \left( \frac{P}{1 \text{ bar}} \right)^{-0.35} \tag{5.6}
\]

\[
Su(P, Tu) = Su_0 \left( \frac{T_u}{298} \right)^{1.55} \left( \frac{P}{1 \text{ bar}} \right)^{-0.28} \tag{5.7}
\]

A comparison of correlations with experimental data is shown in Figs. 5.29, 5.30. The developed correlation has excellent agreement, particularly for DME.

On the basis of obtained correlation equations, uncertainty in laminar flame speed has been calculated separately for both mixtures. Partial derivative of the correlation was taken with respect to temperature and pressure. A simplified equation 5.8 has been presented, which gives an uncertainty in measured flame speed due to temperature and pressure.

\[
\frac{U_s}{S_u} = \sqrt{\left( \frac{U_T}{T} \right)^2 + \left( \frac{U_P}{P} \right)^2} \tag{5.8}
\]

Where, \( U_s \) = Uncertainty in laminar flame speed
$U_T$, $U_P =$ Uncertainty in temperature and pressure

$S_u =$ Laminar flame speed at temperature $T$, and pressure $P$

Figure 5.31 – A comparison of correlation with experimental data for CH$_4$/air mixture, equivalence ratio = 1
Figure 5.32 - A comparison of correlation with experimental data for DME/air mixture, equivalence ratio = 1

Uncertainty in flame speed for few cases of both mixtures has been calculated and presented in table 5.2. For two given mixtures of CH₄/air and DME/air, random and systematic errors were calculated using the RSS method. For CH₄/air and DME/air mixtures at 298K and 1bar, repetition of experiments were done for 6 times. Due to experimental difficulties, only 3 experiments were conducted for 20 bar, which gives higher percentage of uncertainty for both mixtures. Highest percentage of 6% has been calculated for methane/air mixture at 477 K, 10 bar.
Table 5.2 - Sample flame speed uncertainty for two mixtures at an equivalence ratio = 1

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$\phi$</th>
<th>Pressure (bar)</th>
<th>Temperature (K)</th>
<th>Repeated measurements (R)</th>
<th>Flame speed (cm/sec)</th>
<th>Std deviation $\sigma_{\text{Laminar Flame Speed}}$ (cm/sec)</th>
<th>$U_{\text{Total}}$ (cm/sec)</th>
<th>Overall uncertainty %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4/air</td>
<td>1</td>
<td>1</td>
<td>298</td>
<td>6</td>
<td>36</td>
<td>$\pm$ 0.8</td>
<td>1.55</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5</td>
<td>387</td>
<td>4</td>
<td>30.41</td>
<td>$\pm$ 0.86</td>
<td>1.84</td>
<td>6.05</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>10</td>
<td>477</td>
<td>4</td>
<td>32.83</td>
<td>$\pm$ 0.475</td>
<td>1.05</td>
<td>3.09</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>20</td>
<td>410</td>
<td>3</td>
<td>18.95</td>
<td>$\pm$ 0.39</td>
<td>0.9</td>
<td>4.74</td>
</tr>
<tr>
<td>DME/air</td>
<td>1</td>
<td>1</td>
<td>393</td>
<td>6</td>
<td>66.86</td>
<td>$\pm$ 0.72</td>
<td>1.56</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5</td>
<td>448</td>
<td>4</td>
<td>52.05</td>
<td>$\pm$ 0.615</td>
<td>1.65</td>
<td>3.17</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>10</td>
<td>386</td>
<td>4</td>
<td>33.92</td>
<td>$\pm$ 0.205</td>
<td>0.5</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>20</td>
<td>294</td>
<td>3</td>
<td>18.23</td>
<td>$\pm$ 0.28</td>
<td>0.6</td>
<td>3.29</td>
</tr>
</tbody>
</table>
5.6. Sensitivity Analysis of DME-air mixture

To understand the influence of individual reaction rate on burning of DME/air, sensitivity analysis was performed for four pressures of 1, 5, 10 and 20 bar and equivalence ratio 1, using San Diego mechanism which is presented in Fig. 5.32. Sensitivity scale of DME/air is similar to other various studies done by Daly et al. (2001) and Zhao et al. (2004). The following reactions have high positive sensitivity.

\[ H + O_2 = OH + O \quad \text{(R1)} \]

\[ CO + OH = CO_2 + H \quad \text{…… (R2)} \]

\[ CO + O_2 = CO_2 + O \quad \text{…… (R3)} \]

The first reaction, R1, has maximum sensitivity at 5 bar and continues to dominate for all the pressures. The reaction involving DME contribute to negative sensitivity, where, methoxymethyl radical (CH3OCH2) is formed by H-atom abstraction from DME.

\[ CH_3OCH_3 + H = CH_3OCH_2 + H_2 \quad \text{…… (R4)} \]

The consumption of methyl radical in reactions R5 and R6, with higher positive sensitivity, also plays a role in oxidation of DME.

\[ CH_3 + HO_2 = CH_3O + OH \quad \text{…… (R5)} \]

\[ CH_3 + OH = S-CH_2 + H_2O \quad \text{…… (R6)} \]
It was concluded by Qin and Ju (2004) and Daly et al. (2004) that destruction of formyl radicle (HCO) is important for all hydrocarbons including methane. Moreover, Daly et al. also proposed rate constants for 3 reactions which involve formyl radical. In the San Diego mechanism, sensitivity of formyl radicle is found to be very less and is not presented.
in the Fig. 5.32. It may also be concluded that reactions involving formyl radical may not have high sensitivity for stoichiometric mixture. A sensitivity analysis for ignition delay measurements is presented later in Fig. 6.5. A contrast of Figs. 5.32 and 6.5 reveals that the sensitive reactions for ignition delay are completely different from flame speed. This is due to the difference in controlling chemistry between the two experiments.
CHAPTER VI
DME AUTOIGNITION IN AN RCM

6.1. Introduction

DME is considered a potential diesel substitute, as it has a cetane number in excess of 55, is sulphur free and is cost competitive with traditional diesel (Olah et al., 2011). DME is readily derived from a number of resources that include biomass, coal, and natural gas. Furthermore, DME stores as a liquid at low pressures, thereby overcoming the safety issues associated with other variants of NG derived fuels, i.e., CNG and LNG. Du Pont & others have shown DME to be both non-toxic to humans and environmentally benign. Clearly, DME is a clean chemical that will not harm our environment.

DME with a chemical structure, CH3-O-CH3, is devoid of a C-C bond and further contains an oxygen atom. As a result, DME combustion does not constitute a readily available pathway for soot formation (Fleisch et al., 1995). This in turn facilitates use of very high levels of Exhaust Gas Recirculation (EGR) to result in NOx emissions well below the regulated emission levels (Brusstar et al., 2007). The prospect of emissions compliance without having to use expensive after treatment devices, such as urea SCR, makes use of DME very attractive. However, engine tests have shown that DME combustion, although sootless, is accompanied by high CO and HC emissions and may lead to lower efficiencies (Yoon et al., 2009).
Several detailed and skeletal chemical kinetic models for oxidation of DME at low and high temperature (Dagaut et al., 1996; Curran et al., 1998 and 2000; Fischer et al., 2000; Zheng et al., 2005; Zhao et al., 2008) have been reported in the literature. The ability of the mechanism to accurately predict autoignition characteristics at conditions relevant to engines is particularly important. Due to the low temperature reactions involving hydrocarbon radicals and molecular oxygen, DME manifests two-stage ignition and negative temperature coefficient (ntc) behavior. A kinetic model for engine applications should correctly predict such low temperature autoignition characteristics.

Autoignition of DME has been studied in shock tubes as well as in rapid compression machines (Burke et al., 2015; Mittal et al., 2008; Pfahl et al., 1996; Cook et al., 2009; Tang et al., 2012). The emphasis of the present study is on fuel rich and diluted conditions. Based on the conceptual picture of combustion in conventional compression ignition engines, (Dec, 1997) the partially premixed fuel, leading to autoignition after the start of injection, is overall fuel rich ($\phi \approx 2 - 4$), and therefore, autoignition characteristics at fuel rich conditions are important. Further, for low temperature combustion strategies that utilize higher exhaust gas dilution, for instance early-injection PPCI (Partially Premixed Compression Ignition), the cylinder gases are cooler than conventional diesel combustion conditions at the time of injection. Consequently, the pressure profile shows qualitatively different heat release characteristics wherein the first and second stage ignition is separated in time (Musculus et al., 2013). The low temperature kinetics at diluted conditions is, therefore, particularly relevant to advanced engine concepts. In this work, emphasis is placed on fuel rich and diluted conditions.
In the following, experimental facility and test conditions are first described, followed by the presentation of the data and comparison with kinetic models.

6.2. Experimental Facility

Experiments were conducted in a pneumatically driven and hydraulically damped RCM. In this facility, homogeneous fuel, oxidizer mixture is rapidly compressed to high pressure and temperature in 20-30 ms. It has a compression cylinder of 5.08 cm bore and an optimized crevice design to suppress the roll-up vortex. The end combustion chamber of 4.67 cm bore is connected to the compression cylinder through a gradually converging section. This design allows ‘crevice containment’, where the crevice is isolated from the main reaction chamber at the end of compression, which prevents additional mass flow into the crevice when chemical heat release takes place in the main chamber. The specifications of the RCM and the details of the CFD analysis to arrive at the optimized combustion chamber configuration were presented in (Mittal and Bhari, 2013; Mittal and Gupta, 2012; Mittal and Chomier, 2014). The compression stroke can be varied between 20.32 and 30.48 cm and the clearance volume is also adjustable allowing for a range of compression ratios up to 16. The dynamic pressure during the experiment is measured using a piezoelectric sensor (Kistler 6052C) and a charge amplifier (Kistler 5010B). The test mixtures are first prepared manometrically inside a 19 L stainless steel tank equipped with a magnetic stirrer and allowed to homogenize before feeding to the combustion chamber.

Autoignition investigations for DME/O₂/CO₂/N₂/Ar mixtures were conducted over the temperature range of 630–785 K, the pressure range of 8–38 bar, and for φ from 1 to
The mixture compositions and the ranges of compressed gas pressures and temperatures at the end of compression, $P_C$ and $T_C$, are given in Table 6.1. Note that the mixtures are highly diluted and $\phi$ is varied through a variation in the DME mole fraction while keeping $O_2$ mole fraction same. All compositions have similar specific heat and yield almost identical end of compression pressure and temperature ($\pm 2K$) under same conditions. The experiments for mixtures 1 and 2 were conducted for a constant end of compression pressure, $P_C$, of 36 bar and temperature was varied through compression ratio. Whereas for mixtures 3 through 6, initial pressure $P_0$ was kept fixed and a change in the compression ratio provided a simultaneous variation in $P_C$ and $T_C$.

Table 6.1 - Molar composition of test mixtures

<table>
<thead>
<tr>
<th>Mix</th>
<th>$\phi$</th>
<th>DME</th>
<th>$O_2$</th>
<th>$CO_2$</th>
<th>$N_2$</th>
<th>Ar</th>
<th>$P_0$ (bar)</th>
<th>$P_C$ (bar)</th>
<th>$T_C$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>4.5</td>
<td>91.5</td>
<td>0</td>
<td>36</td>
<td>640-780</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>17</td>
<td>59.2</td>
<td>19.8</td>
<td>36</td>
<td>640-780</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>2.5</td>
<td>3</td>
<td>0</td>
<td>90</td>
<td>4.5</td>
<td>0.5</td>
<td>8-19</td>
<td>630-785</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td>12-28</td>
<td>630-785</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>16-38</td>
<td>630-785</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>79</td>
<td>14</td>
<td>0.5</td>
<td>10-19</td>
<td>660-780</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td>15-28</td>
<td>660-780</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>20-35</td>
<td>660-760</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>17</td>
<td>35</td>
<td>41</td>
<td>0.75</td>
<td>15-28</td>
<td>660-780</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td>62.6</td>
<td>28.4</td>
<td>0.5</td>
<td>8-19</td>
<td>630-782</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.75</td>
<td>12-26</td>
<td>630-766</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>16-35</td>
<td>630-770</td>
</tr>
</tbody>
</table>
6.3. Kinetic Models

Experimental data are compared with kinetic models from literature (Zhao et al., 2008; Beeckmann et al., 2010; Burke et al., 2015). The model of Zhao et al. (2008) consists of 55 species and 290 reversible reactions, and has been validated for a wide range of physical conditions, including flow reactor species-time history profiles at pressures up to 18 atm, jet-stirred reactor species profiles up to 10 atm over the temperature range of 550 K – 1100 K, pyrolysis in a flow reactor up to 10 atm, shock tube ignition delay measurements at low and high pressures, species profiles in low pressure and atmospheric burner stabilized flames, and laminar flame speeds up to 10 atm.

The recent model from Burke et al. (2015) has been validated against ignition delay time data covering a wide range of conditions (T = 600–1600 K, P = 7–41 atm, φ = 0.3, 0.5, 1.0, and 2.0 in ‘air’ mixtures). This mechanism also applies pressure-dependent treatment to the low-temperature reactions of DME and has been validated using literature data including flow reactor, jet-stirred reactor, shock-tube ignition delay times, shock-tube speciation, flame speed, and flame speciation data. In contrast, the mechanism from Beeckmann et al (2010) is a skeletal mechanism based on the model from (Fischer et al., 2000) and consists of 31 species and 49 reactions.

Numerical modeling of experiments is performed using the Sandia SENKIN code (Lutz et al., 1988) in conjunction with CHEMKIN. The modeling begins from the start of the compression stroke, and includes the effect of heat loss after the end of compression. For each reactive experiment, a non-reactive experiment with a mixture of the same heat capacity was first conducted. The non-reactive pressure history is used to deduce the
effective volume based on adiabatic volume expansion. Separate polynomials are fitted to the effective volume during compression and post compression period. These fitted volume polynomials are subsequently used to simulate the experiment using SENKIN. Details of the heat transfer modeling approach are similar to Mittal and Sung (2007).

6.4. Results and Discussion

Results obtained from the RCM experiments has been discussed below focusing DME as a potential alternative fuel.

6.4.1 Sample Pressure Traces

Sample pressure traces for mixture 5 are shown in Fig. 6.1 for a fixed $P_0$ of 0.75 bar. It is noted that as compression ratio is varied, a simultaneous increase in $P_C$ and $T_C$ is manifested. Towards higher temperatures, the first stage ignition merges with the compression stroke and cannot be distinguished readily. Clearly, the chemical activity during compression can be significant and can’t be neglected.
In order to consistently report experimental data, the end of compression $P_C$ and $T_C$ for a corresponding nonreactive experiment are used as reference conditions. This is illustrated in Fig. 6.2 where reactive and nonreactive experimental pressure traces are shown. In the following, the end of compression conditions for nonreactive runs are used to report the experimental as well as simulated data. Nonetheless, for each experiment the entire compression stroke is simulated and there is one-to-one correspondence between the experiments and modeling. The ignition delay is defined as the duration from the end of compression to the inflection point in the pressure history during first and second stage ignition. Therefore, first stage ignitions during compression yield negative first stage ignition delay.
Figure 6.2 - End of compression conditions based on nonreactive experiments

6.4.2 Experimental Ignition Delays and Comparison with existing Kinetic Models

The experimental data for the first stage and total ignition delays along with model predictions are shown in Fig. 6.3, wherein the effect of pressure for various mixtures is presented. The predictions from Zhao et al. (2008) and Beeckmann et al. (2010) are quite close to each other. All mechanisms show same features, however the mechanism from Burke et al. (2015) yields higher ignition delays at lower temperatures than the experimental data.

The effect of equivalence ratio is presented in Fig. 6.4. The data for $\phi = 2.5$ shows inflection in the ignition delay profile. Here also all mechanisms capture the effect of
equivalence ratio; however the mechanism from Burke et al. (2015) overpredicts ignition delays at lower temperatures.

The data for $\phi = 1$ and $P_c = 36$ bar is shown in Fig. 6.5. In this case, a pseudo-ntc behavior is evident. However, the temperature of the present experiments is too low to manifest ntc behavior. This behavior is probably due to the reactivity during compression stroke. Even though the first stage delays are accurately predicted by all mechanisms, some discrepancy exists for the total delays.

Further, a comparison of the data (not shown here) for mixtures 1,2 and 4,5 revealed no noticeable influence of CO₂. This is consistent with the predictions from mechanisms.

In summary, the predictions from the mechanism of Beeckmann et al. and Zhao et al. are quite close to each other and agree reasonably well with the present experimental data.
Figure 6. 3 - Experimental (points) and computed (lines) ignition delays showing the effect of pressure. P_0= 0.5 bar (circles), 0.75 bar (triangles) and 1 bar (squares). Left panels – First stage ignition delays. Right panels- total ignition delays. Predictions from Burke et al (solid lines), Zhao et al. (dashed lines) and Beeckmann et al. (dotted lines).
Figure 6.4 - Experimental (points) and computed (lines) ignition delays showing the effect of $\phi$. $\phi = 2.5$ (triangles), 4 (circles), and 6 (squares). Left panels – First stage ignition delays. Right panels – total ignition delays. Predictions from Burke et al (solid lines), Zhao et al. (dashed lines) and Beeckmann et al. (dotted lines).

(a) $P_0 = 0.75 \text{ bar}$

(a) $P_0 = 1.0 \text{ bar}$
Figure 6.5 - Experimental (points) and computed (lines) ignition delays. Mix 2, $\phi = 1.0$, $P_C = 36$ bar. Left panel – First stage ignition delays. Right panels – total ignition delays. Predictions from Burke et al (solid lines), Zhao et al. (dashed lines) and Beeckmann et al. (dotted lines).

6.4.3 Flux and Sensitivity Analysis

A brute-force sensitivity is included in Fig. 6.6 in order to highlight the important reactions at conditions of present experiments. This analysis involves increasing and decreasing each reaction rate expression by a factor of two and calculating the effect on the predicted ignition delay time. The sensitivity coefficient $\sigma$ is defined as $\sigma = \log(\tau'/\tau'')/\log(2.0/0.5)$ where $\tau'$ is the ignition delay time calculated with the increased rate coefficient and $\tau''$ is the ignition delay time calculated using the decreased rate expression. This definition results in negative sensitivity coefficients for reactions promoting reactivity and positive coefficients for those inhibiting reactivity.

An integrated flux-analysis was conducted prior to ignition in order to give an indication of the dominant reactions taking place before ignition at 19 bar, 711 K and $\phi = 2.5$, shown in Fig. 6.6. The reaction primarily proceeds through oxygen addition to
CH₂OCH₂, followed by subsequent isomerization forming hydroperoxy-methoxymethyl radical CH₂OCH₂O₂H. CH₂OCH₂O₂H may undergo two routes: 1) β-scission releasing two formaldehyde molecules and a hydroxyl radical (i.e. CH₂OCH₂O₂H = 2CH₂O + OH); 2) reaction with molecular oxygen to form the O₂CH₂OCH₂O₂H radical, which consequently isomerizes and decomposes releasing two OH radicals. Of the two, β-scission dominates at the present conditions.

Looking at the sensitivity analysis, the first stage ignition is most sensitive to only three reactions involving (1) second O₂ addition to hydroperoxy-methoxymethyl radical, (2) isomerization of the methoxymethyl-peroxy radical, CH₃OCH₂O₂ and (3) β-scission of hydroperoxy-methoxymethyl radical. The first and second of these promote chain branching whereas the third opposes it since only one reactive OH radical is released through this path. The second stage ignition, in contrast, is sensitive to several other reactions which don’t have sensitivity to the first-stage ignition. The second-stage ignition is based on formation and decomposition of H₂O₂ and several reactions influence the build-up and decomposition of H₂O₂ pool.
Figure 6.6 - Sensitivity coefficients for DME autoignition using the mechanism of Zhao et al. Molar composition - DME/O2/N2/Ar = 2.5/3/90/4.5; Temperature = 711 K; Pressure = 19 bar

In summary, ignition delay data for DME is acquired using an RCM at diluted conditions over a range of equivalence ratios on the rich side. The agreement from the skeletal mechanism of Beeckmann et al. and the detailed mechanism of Zhao et al. is very good and the discrepancy is generally less than 30%, except when ignition delays are long. Work is underway to refine the detailed mechanism based on the important reactions identified above and reduce the mechanism to a reasonable size for engine simulations.
However, since the agreement from the mechanism of Beeckmann et al. is noted to be pretty good, the mechanism ‘as is’ is also deemed adequate.

Figure 6.7 - Integrated flux analysis (up to 900 K temperature due to pre-ignition heat release) for DME autoignition using the mechanism of Zhao et al. Molar composition - DME/O2/N2/Ar = 2.5/3/90/4.5; Temperature = 711 K; Pressure = 19 bar
CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1. Summary and Conclusions

DME is considered a potential diesel substitute, due to high cetane number. In addition, it offers the advantage of soot-free combustion. This in turn facilitates use of very high levels of EGR, resulting low NOx emissions. It is also a potential fuel for stationary gas turbines. The design of various types of engines that use DME as a fuel is greatly dependent on computational simulations which require validated chemical kinetic mechanisms that can reliably mimic the combustion and pollutant formation behavior of DME at physical conditions that are relevant to engines. In the present work, experimental data for autoignition and laminar flame propagation of DME is obtained to contribute to a better understanding and validation of chemical kinetics of DME, particularly at elevated pressures.

In order to obtain experimental data for validation of chemical kinetics, well characterized experimental facilities are required. The first objective of this work was to design a novel experimental facility, called DCF (Dynamic Combustion Facility) for studying laminar flame propagation at elevated pressures and temperatures. DCF was successfully designed and fabricated for studying outward propagating spherical flames at elevated pressures and temperatures. This included the computational fluid dynamics
(CFD) based optimization of the geometry of the combustion chamber, determination of the pneumatic and hydraulic arrangements for controlled compression, stress analysis of the components, preparation of the 3-D drawings for fabrication, working out the details of the optical imaging set-up, ignition system, synchronization, image processing and models for data interpretation.

In order to establish the suitability of the designed DCF for flame propagation studies, CFD simulations for characterization of the temperature field inside the DCF and validation experiments were conducted. The CFD simulations provided important information about the thermodynamic state of the gas at the end of compression and delineated the physical conditions that can be accessed in the DCF for experiments. Further, the validation experiments in static as well as dynamic mode confirmed that the data obtained from the new facility is comparable to the data from other facilities. Following the characterization and validation, flame speed data for DME was obtained over a range of pressures and compared with kinetic models.

Thereafter, autoignition of DME was investigated using a Rapid Compression Machine (RCM). Experiments were conducted over a range of compressed pressures (8-38 bar), compressed temperatures (630-785 K) and equivalence ratios (1-6). In addition, the effect of CO$_2$ addition on ignition was also investigated to gauge the effect of exhaust gas recirculation. Ignition delays were deduced from experimental pressure traces. Results showed that DME is very reactive and there is significant kinetic activity during the compression stroke. Experiments using CO$_2$ showed that there is no kinetic effect of CO$_2$ on ignition delay. The experimental data was compared with simulations from available detailed and skeletal chemical kinetic models. In general, there was good overall agreement.
and discrepancies were noted at low temperatures. The key reactions were identified through flux and sensitivity analysis and refinements made.

In summary, DCF by itself is a substantial contribution to the existing arsenal of experimental facilities and can extend the range of experimental studies to conditions beyond those attainable in existing facilities. The data obtained from DCF and RCM for flame speed and autoignition of DME constitute important dataset for mechanism refinement.

7.2. Recommendations for Future Work

The following recommendations for future work are made.

(1) The compression speed of the DCF can be optimized, which can potentially enlarge the pressure-temperature region accessible for experiments.

(2) With sufficient safety features incorporated, experiments for the DME flame speeds can be done at higher pressures and temperatures in the DCF.

(3) Capability of heating the reactants can be included in the DCF for experimentation with heavy liquid fuels.

(4) Liquid fuels can be explored in DCF, which are difficult to test in conventional facilities at elevated pressures and temperatures. Such experiments will bring out the advantages of DCF clearly.

(5) Autoignition of DME with water addition can be studied to mimic EGR environment.

(6) Autoignition and flame propagation of blends of DME with other relevant fuels can be studied.
(7) Further refinements to the kinetics of DME can be pursued in collaboration with chemical kinetic experts.


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