Numerical Modelling of Natural Gas Combustion

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Abstract

Currently, with the rapid advancement of the computer power, computer models for simulating the combustion of hydrocarbon fuels are widely adopted among researchers and engineers to study combustion phenomena due to wide range of residential and industrial consuming of hydrocarbon fuels.

In this thesis, a numerical model with detailed reaction mechanism which is tailored for studying the behaviour of combustion of natural gas has been introduced and validated with available experimental data. The numerical model attempts to comprehensively simulate the physical conditions (temperature and pressure), equivalent ratio, and fuel dilution and strain rate effect in the laminar flames.

Studies on different kinds of reaction mechanism were also performed. Detailed mechanisms with hundreds of elementary reactions and species are available for the combustion of alkanes as a result of the consistent pursuit of mechanism development over several decades. The chemical reaction scheme presented in this work was developed by Smith et al. [61]. The mechanism consists 325 elementary chemical reactions and 53 species for natural gas combustion. The optimized conditions for the mechanism is 1000 to 2500 K and 10 Torr to 10 atm. The experimental data of laminar flame speed and species concentration profiles are used to validate this kinetic mechanism for natural gas combustion.
Numerical study on premixed burner models has been carried out. The general theory of its embedded thermo-physical behaviour is discussed. In addition, experimental literatures are reviewed; methods of experiments and their associated advantages and limitation were also presented. Experimental measurements of laminar flame speed of methane and ethane had been presented at standard and elevated pressure and temperature over wide range of fuel-air equivalence ratio. In general, premixed laminar flame model by CHEMKIN produced the best agreement with experimental data. The model is considered as a suitable candidate for considering

Finally numerical study of laminar diffusion flame is presented by non-premixed burner models. The model was applied to simulate the effects of fuel dilution and strain rate on the laminar flames. The computed results compared well with the measured data. Laminar diffusion flamelet approach is introduced to predict highly non-equilibrium flame. By using this approach, chemical kinetic effects can be incorporated into turbulent flames with significantly reducing the required computing time to solve the fire problems. The detailed kinetic mechanism and numerical models (premixed and non-premixed) have been introduced to simulate the oxidation of hydrocarbons up to C₂ species under various conditions. The computed laminar flame speed and structure are in a good agreement with experimental data.
Acknowledgments

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I wish to acknowledge the assistance given by Mr Anthony Chun Yin Yuen for his help on the numerical modelling. I also express my thanks to all my friends for their moral support.

I owe my family an expression of gratitude for their patience, understanding and encouragement.

Lastly, but not the least, I am thankful to all faculty, staff, colleagues and friends who made my stay at RMIT university a memorable experience.
List of Publications

Within the period of this research, some of the research works related to the topic of this thesis has been published or submitted for publication, in a number of international conference proceedings or journals, as follows:

Refereed International Conference Papers/Poster

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CHAPTER 1 Introduction

General Introduction

In the past decades, due to the growing of population, there has been an enormous increase of energy demand around the world. To meet the energy needs, combustion has played a major role in the conversion of energy, including heat generation, transport and electrical energy. Recently, as increasing the power of computer, complex burner systems could be simulated more accurately and efficiently. Therefore, models have become an important tool in the design process of modern combustion applications. The aim of this thesis is to obtain further understanding of fundamental of combustion for development and application of models.

This chapter provides an introduction of the characteristics behaviour of combustion process. Following that, it describes briefly Natural Gas as the research fuel. Finally, a brief description to background and research motivation of this thesis is presented.

1.1 Combustion: general principles

In this section, general theory and fire definition are firstly introduced. Combustion is the process of the exothermic chemical reactions between a fuel and
an oxidant. The quantitative treatment of combustion processes requires some understanding of fundamental concepts and definitions, which also are described in this section. In the following section, the equations of chemical kinetic are developed by Glassman [12].

1.1.1 Chemical Kinetic

1.1.1.1 The law of mass action

All chemical reactions take place at a definite rate, which depends on the conditions of the system, including the temperature, effects of radiation, reactants concentration and the presence of catalysts. The rate of the reaction may be expressed in terms of the concentration of any of reacting substances and of any reaction products [12]. For a one-step chemical reaction represented by

$$\sum_{i=1}^{N} v'_i M_i \leftrightarrow \sum_{i=1}^{N} v''_i M_i$$

(1.1)

where $v'_i$ and $v''_i$ are the coefficient of the reactants and products, $M$ is the arbitrary specification of all chemical species, and $N$ is the total number of species. The disappearance rate of a chemical species $RR_i$, is expressed as

$$RR_i = k \prod_{j=1}^{N} (M_j)^{v'_j}$$

(1.2)

where $k$ is the specific reaction rate coefficient. In a real reaction, the concentration change rate of a species $i$ is expressed as
\[
\frac{d(M_i)}{dt} = [v_i^* - v_i'] RR_i = [v_i^* - v_i'] k \prod_{j=1}^{n} (M_j)^{v_j'}
\] (1.3)

1.1.1.2 Rates of Reactions

For most chemical reactions, where two species have the capability to react, the collisions of these species dominate the rates of reaction. An arbitrary second order reaction could take the following form

\[a + b \rightarrow c + d\] (1.4)

For the arbitrary reaction (1.1), the rate reaction expression is expressed as:

\[-RR = \frac{d(a)}{dt} = -k(a)(b)\] (1.5)

For an elementary reaction the Arrhenius law states that

\[
\frac{d\ln k(T)}{dT} = \frac{E_a}{R^\alpha T^2}
\] (1.6)

where \(E_a\) is the activation energy of the reaction, if \(E_a\) is a constant with respect to temperature, integrating Eq. 1.6

\[k(T) = Ae^{-E_a/R^\alpha T}\] (1.7)

where \(A\) is the pre-exponential factor. Based on collision theory, the factor \(A\) is not strictly constant, but depends on temperature. Current practice form is expressed as:

\[k = AT^b \exp(-E/RT)\] (1.8)

According to Arrhenius, molecules will react, only if they have energy greater than a certain number. There exists the thermal condition, which induced the energy from
collision to unreacted molecules, and molecules lead to products by those great energy.

![Reaction coordinate diagram](image)

Figure 1-1 Energy as a function of a reaction coordinate for a reacting system

The state of the reacting species at this activated energy can be regarded as some intermediate complex that leads to the products. In Figure 1-1, symbol $E_A$ represents the activation energy of the reaction. $E_b$ represents the activation energy of the backward reaction, in which the product species can revert to reactants and is much larger than $E_A$ for the forward step.

1.1.2 Types of Flame

The most important classifications of fundamental combustion phenomena is different flame types - Premixed and Non-Premixed. Types of flame not only have the direct influence of mixing rate in reaction rate, but also affect the structures of flame. Normally, the combustion system consists two reactants; a fuel and an
oxidizer that must be mixed together to facilitate combustion process. Therefore, the mixing is an essential element in combustion, different mixing ratios could lead to different flame characteristics. In a premixed case, the reactants are already well mixed before reaction. On the other hand, a non-premixed flame, the reactants are separated initially and brought together through the process of diffusion, then mixed in a common region and reaction takes place. In the literature, non-premixed combustion is also called "diffusion combustion". Figure 1-2 shows the schematic Bunsen burner, which presents the both the premixed and non-premixed flames. Fresh air and fuel go through the intake ports, then mix together and travel along the burner tube. Combustion then takes place at the sublet of the tube, exhibiting a blue colour flame structure. When the mixture is fuel rich, excess fuel would pass through the premixed flame front and react with oxygen in the ambient air, which creates a non-premixed flame since the fuel and oxygen separated initially.

![Schematic of the Bunsen flame](image)

*Figure 1-2 Schematic of the Bunsen flame [137]*
1.1.2.1 Premixed Flames

Figure 1-3 shows a premixed flame structure, which divides the flame into two zones: the preheat zone and reaction zone. In preheat zone, reaction occurred slowly and releases small amount of heat. However, in reaction zone, fuel and oxidiser react fast, which releases bulk of the heat and creates intermediate species. The fast reaction zone is therefore relatively thin, usually less than a millimetre at ambient pressure. In this thin zone, species concentration and temperature gradients are very large, and heat diffusion travel back to the preheat zone, because of activation energy provided by these gradients, which causes the flame to be self-sustaining.

Figure 1-3 The Internal Structure of Premixed Flame [137]
1.1.2.2 Non-Premixed Flames

Unlike premixed flame’s very narrow reaction zone, diffusion flames have a wider reaction zone over which the composition changes and chemical reaction can take place, which are due to some inter diffusion of reactants and products. Hottel and Hawthorne [29] were the first to make detailed measurements of species distributions in a concentric laminar Hydrogen-air diffusion flame. Figure 1-4 shows the structure of the non-premixed flame.

Figure 1-4 Structure of the non-premixed flame: (a) physical configuration of a one-dimensional, purely diffusive system; (b) temperature and concentration profiles with finite flame thickness [136]
The structure of a non-premixed flame consists of three zones: fuel-rich zone, oxidizer-rich zone and reaction zone. In the fuel-rich and oxidizer-rich zones, fuel and oxidizer travel toward each other, through diffusion and convective motion in the system. Within the reaction zone, fuel and oxidizer are heated then meet and mix, and eventually react with each other rapidly. The combustion products and heat of combustion then travel away from the reaction zone to fuel-rich and oxidizer-rich zones. Unlike premixed flame, the reaction zone of non-premixed flame has finite thickness, because the reaction occurs at a finite rate and complete reaction cannot be accomplished.

### 1.2 Natural Gas

Investigation of combustion process needs to select a hydrocarbon as the reactant fuel; natural gas is a more reasonable and considerable fuel. Natural gas is a mixture of hydrocarbon gases that consists methane, ethane, propane, butane and other hydrocarbon compounds [5]. As an energy source, Natural gas is often used for cooking, heating, and generating electricity. Table 1-1 shows world primary energy consumptions, Nature gas as the one of the fossil fuel sources, which represents more than 21 per cent of total energy consumption. As the most affordable energy available to the residential costumer, natural gas has been used for house cooking, heating and electricity generation. The energy information administration (EIA) estimates that in the future, 80% increased electricity generation capacity is created by natural gas. Recently, with technological advancements, natural gas also has been used in the vehicles. According to the Worldwide NGV statistics, there are currently
more than 170 million Natural Gas Vehicles (NGVs) on the road around the world [6]. The types of vehicle include passenger cars, buses, vans and even trucks.

Table 1-1 World Primary Energy Consumption, 1998 [7]

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<th>Primary Energy (exajoules)</th>
<th>Primary energy</th>
<th>Percentage of total</th>
<th>Static reserve production ratio (years)</th>
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<tr>
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</tr>
<tr>
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<td>6.5</td>
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<tr>
<td>Total</td>
<td>402</td>
<td>9.58</td>
<td>100</td>
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Natural gas is often considered as the cleanest fossil fuel that produces less carbon dioxide than either coal or oil [5] and far fewer pollutants than other hydrocarbon fuels. Figure 1-5 shows air pollutant emissions by different kinds of hydrocarbon fuels. Natural gas also produce significantly lower emissions of pollutants such as unburnt hydrocarbons (UHC), carbon monoxide (CO), nitrogen oxides (NO\textsubscript{x}), smoke oxides (SO\textsubscript{x}) and particulate matter (PM), as compared to any other hydrocarbon fuel [7]. On the other hand, natural gas is widely used to be the fuel for residential heating and cooking around world. In the United States, approximately 23 per cent of the total natural gas consumed is used for residential purposes [5]. Therefore, better understanding of combustion of natural gas is valuable for the control of emission gas control and safety analysis of building fire.
The main composition of Natural gas is Methane, accounting for 90%. Therefore, Methane can be used as a kind of surrogate for Natural gas, because of Methane's simple molecular structure, which is made up one carbon atom and four hydrogen atoms, and is referred to as CH₄. Table 1-2 shows the composition of natural gases at different areas. We can see that composition of natural gas is quite different in different countries, e.g. in Russia 98% of natural gas is methane, but in Netherlands only 82%; natural gas also contains ethane, propane, nitrogen and carbon dioxide. In this thesis, methane and ethane therefore will be used as a surrogate for natural gas. There are two reasons to consider the combustion process of Methane and Ethane. The first reason, which is more speculative, is given by the fact that in literature there is much more information about the local chemical composition within the flame for methane-air and ethane-air mixtures than gasoline -
air mixture [8-10]. The other reason is that recently, as the most important factor in simulation, chemical mechanisms of methane and ethane are optimized and validated with experimental data. In the following chapters, methane-air and ethane-air mixtures are studied through experimental and numerical investigating.

<table>
<thead>
<tr>
<th></th>
<th>Frigg (North Sea)</th>
<th>Urengoi (Russia)</th>
<th>Pittsburgh (USA)</th>
<th>Groingue (Netherlands)</th>
<th>Abu Dhabi (UAE)</th>
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1.3 Background and Motivation

This section presents the objectives for the research. Firstly, from a historical view, it introduces the importance of combustion in our daily lives. Secondly, it briefly discusses the current combustion modelling.

1.3.1 Historical background

Fire has played a significantly important role in people’s lives. Since the early stage of civilization, fire was used for cooking, heating, and lighting and also as a weapon to fight off wild animals. As understanding of fire increased, people start to convert heat generated from fire into applications, for example; the propulsion of rockets, internal combustion engines, and gas turbines. Today, combustion of
hydrocarbon fuels has become a very important part of our daily life. With technology development, social production and human life require more energy. However, the increasing demand of energy also brings negative impacts to the earth. The emission of pollutant exhaust gases, such as carbon dioxide (CO$_2$), sulphur oxides (SO$_x$) and nitric oxides (NO$_x$), soot and unburnt hydrocarbons have had a serious impaction on the environment [1]. Therefore, fuel economy and emission control have become more intense and crucial to meet the tightening pollution regulations.

In contrast, the wide adoption of fire not only brings colour and benefit to our lives but also endangers our lives at the same time. Thousands of cases show evidence that fire can easily become out of our control and kill lives in minutes. These uncontrollable fires often referred to as “fire disasters” or “unwanted fires”. In fact, since the beginning of the history, our ancestors learnt to use fire and to prevent the “unwanted fire” simultaneously. Even after exhaustive efforts, “unwanted fire” still occurs frequently such as building fire; in developed countries like America, around 80% of all fire death was caused by building fires [94]. To minimize and prevent such losses, efforts should be made to investigate the physical and chemical phenomenon characterising the building fires.

In recent years, the increasing cost of fossil fuels and stringent regulations regarding limits for exhaust emission have increased interest in alternative fuels, such as solar, tide and wind energy. However, combustion is still expected to be very important in the energy conversion in the future, such as biomass, natural gas and hydrogen combustion. To increase the efficiency of the combustion process,
advanced combustion models play a key role in the design of new combustion processes to predict detailed information, such as flame stability, temperature profiles and pollutant exhaust gases or soot. On the other hand, accurate prediction of the consequence of fire is crucial for fire safety analysis and assessment of designs for fire protection measures.

1.3.2 Research Motivation

Combustion has been an important research subject for a long time. Early studies were focused on the understanding of the fundamentals of fires. Most studies were carried out through experimental analysis. At the same time, some numerical models were also developed, however, due to limitation of computer power; numerical studies were restricted to simplified models. With the development of computers, more complex models including detailed chemical kinetics and molecular transport have been introduced. The more sophisticated models have allowed a more in-depth study on the influence of chemistry and reaction conditions on the combustion processes, including the laminar flame speed that is a very important parameter for the propagation of a combustion mixture.

Exhaust gas recirculation (EGR) system has been developed to reduce the exhaust emissions and pollution such as nitrogen (NOx) produced by vehicles [13]. This system recirculates small amount of the exhaust gas back to combustors to lower the temperature of combustion process and reduces the NOx emission [14-16]. However, EGR system could also decrease the flame speed in the combustion, which causes an unstable combustion process to increase energy loss and decrease
efficiency. To overcome these problems, researchers proposed adding hydrogen in the EGR system to increase the flame speed of combustion [17]. Therefore numerical simulation of EGR gas (CO and CO$_2$) and hydrogen diluted in the fuel is required to help in the combustor design.

On the other hand, accurate prediction of the consequence of fire is crucial for fire safety analysis and assessment of designs for fire protection measures. Based on Cheung and Yeoh [18] study, a fully-coupled large Eddy simulation (LES) has been carried out to simulate the temporal combustion behaviour of a large-scale buoyant pool fire. Although the pulsation effect of fire was properly captured, a single chemical reaction was adopted which could pose inappropriate interpretation of instantaneous heat release rate and vorticity generation. Combustion of fire involves hundreds of chemical reactions where the embedded kinetics plays a predominant role of the resultant heat release rate and species concentrations. Due to its complexity and intensive computational requirement, combustion kinetics simulations were used to be limited for combustion in laboratory scale. Most the existing fire models (e.g. Fire Dynamics Simulator – FDS) therefore only consider one or just few chemical reactions in simulation. With advancement of computer technology, integrating kinetics in fire modelling has become feasible. To investigate the influence of chemical kinetics on the vortical structures of fire, a LES model coupled with detailed chemical kinetics should been developed based on laminar flamelet approach.

The laminar flamelet approach could be used to simplify the three dimensional detailed combustion models and maintain a reasonable level of accuracy
significantly. The flamelet can be considered to be an extension of the "flame sheet model which assumes infinitely fast chemical reaction such that the reaction zone is an infinitely thin interface [11]. Through simulating laminar flames to determine the thermo chemical properties completely, statistical probability density function methods are used to embed the laminar flamelet in a turbulent flame. The flamelet models have been very useful in combining turbulence and non-equilibrium chemistry [3-4]. The primary advantage of flamelet approach is that the detailed chemical kinetic effects can be incorporated into turbulent flames. The other advantage is that without using empirical coefficients, the chemical time scales and diffusion process occurring at small scales can be captured correctly [4].

Modern combustion systems are designed with high efficiency, low air pollution emissions and to be safe. However, theoretical investigation of these systems is difficult to solve the nonlinear or high degrees of freedom questions. On the other hand, experimental investigation could cost amount of money and time, and sometimes data could be inaccessible. Therefore, numerical prediction is a feasible and economic way to establish the criteria for designing the combustors under these detriments. The objective of the present research is to develop two numerical models, (i) laminar premixed flame model and (ii) laminar diffusion flame model, which are tailored for simulating natural gas combustion for different pressure, stoichiometry and temperature. Moreover, the performance of premixed flame model in simulation of natural gas combustion would be used to investigate the effects of CO, CO$_2$ and H$_2$ diluted in natural gas for the EGR system study. Performance of the diffusion flame model would be also demonstrated and used to study the stretched diffusion flame in building fire. Moreover, the chemical mechanism should also be developed
to give the model ability to simulate the chemical reaction, because chemical mechanism presents the collection of the elementary reactions necessary to describe an overall reaction. This chemical mechanism should also be tested by various benchmark tests and validated with experimental data.

1.4 Thesis Outline

The thesis consists of seven chapters. This chapter introduces some background and phenomena of fires. A brief view of fundament of combustion process is also presented. The important of the natural gas as investigation fuel is also discussed. The motivation of this research is also included in the previous section.

In CHAPTER 2, a literature review of calculation of laminar flame speed is presented. The thermo-physical behaviour of laminar flame speed is also discussed. In addition, experimental literatures are reviewed; methods of experiments and their associated advantages and limitation are also presented. Experimental measurements of laminar flame speed of methane and ethane have been presented at standard and elevated pressure and temperature over wide range of fuel-air equivalence ratio. Finally experimental measurements of laminar flame structure of premixed and non-premixed flames are presented.

In CHAPTER 3, a number of chemical mechanisms (single step, reduced and detailed mechanisms) is introduced and compared to simulate the combustion of
methane. The advantage and limitation of each kind of the mechanism is also discussed. Finally, four detailed mechanisms are introduced and compared with each other to find the most suitable mechanism that is used in the numerical model to simulate the laminar flame of methane-air mixture.

In CHAPTER 4, the equations that are used to model combustion processes are presented. Thermodynamic, chemical rate, species transport properties and chemical equilibrium is described. The equations governing steady, isobaric, and quasi one dimensional premixed laminar flame propagation and conservation equations that govern the behaviour of opposed flow are discussed.

In CHAPTER 5, numerical model of combustion process and chemical mechanism is validated through comparing experimental data of laminar premixed flame speed with numerical results for flames of methane, ethane and their mixtures. Comparison of laminar flame speed of methane – air mixture is also made at elevated pressures and temperatures. Finally, numerical model is used to calculate the laminar flame speed of methane – air mixture, when it is diluted with exhaust gas (CO₂ and CO) and hydrogen, which helps to increases the reaction rate.

In CHAPTER 6, Numerical model of combustion process and chemical mechanism are validated through comparing experimental data of diffusion flame structure with numerical results for methane – air mixtures. Validated model and chemical mechanism are used to simulate the effects of strain rate on the various properties of diffusion flame such as flame structure, soot formation and extinction.
Finally, laminar diffusion flamelet approach is introduced. It is used to investigate the influence of chemical kinetics on the vortical structures of fire.

In closing, CHAPTER 7 concludes and discusses the finding of this research work. Suggestions of further research works are also listed.
CHAPTER 2 Literature Review

Laminar flame speed is one of the fundamental properties characterizing the global combustion rate of a fuel-oxidizer mixture [95]. To study the premixed flame phenomena, it often serves as the reference capacity. This chapter provides a brief overview of laminar flame speed and structure. In section 2.1, the theoretical properties of laminar flame speed and dependence on physical conditions such as pressure and temperature are presented. In section 2.3, methods of experiments and their associated advantages and limitation in the literature are also discussed. In section 2.4, experimental data of laminar flame speed and structure of methane and ethane are presented.

2.1 Theoretical Analysis

2.1.1 The Laminar Flame Speed

The laminar flame speed is an important parameter in the determination of the propagation and stabilization of premixed flames. It is the velocity of unburned gases, which travel through the combustion flow normal to the flow surface. Thermal theories of Mallard and Le Chatelier [19] present the earliest theoretical analysis of laminar flame speed; they proposed that in the flame propagation, the governing
mechanism is the transmission of heat back to through gas layer. The weakness of this theory is that the determination of ignition temperature does not exist. Later, Zeldovich and Frank-Kamenetskii [20] proposed an improved thermal theory. In their theory, diffusion of molecules and heat are included firstly, but the diffusion of free radicals is not considered. In 1934, Lewis and von Elbe [21] advanced the theory of particle diffusion to deal with the ozone reaction; Lewis and von Elbe’s theories were further studied by Tanford and Pease [22], they proposed a diffusion theory and postulate that the diffusion of radicals is more important than the temperature gradient. However, in this diffusion theory, the govern equations for mass diffusion are the same as thermo diffusion. Hischfelder et al. [23] concluded that thermal effects pre dominated in the chemical reaction and the analysis for flame speed should follow the thermal theory. More recently, there are new approaches that use asymptotic analyses to provide more accurate formula and further clarification of the flow structure [24-26].

2.1.1.1 Mallard and Le Chatelier Theory

In the complex reaction, it is very difficult to interpret important parameters. The thermal theory developed by Mallard-Le Chatelier [19] provides a simple way to establish these in laminar flame propagation. Figure 2-1 shows the schematic of the flame structure developed by Mallard and Le Chatelier (Temperature T versus Mixing fraction X) [19], it can be seen that there are two zones (preheat zone I and reaction zone II) separated at ignition points.
In this theory, heat conducted from zone II is assumed to raise the temperature of unburned gases $T_o$ to the ignition temperature $T_i$. If the temperature gradient is linear, then enthalpy equation becomes

$$\dot{m}c_p(T_i - T_0) = \lambda \frac{(T_f - T_0)}{\delta} A \quad (2.1)$$

where $C_p$ is specific heat capacity for constant pressure, $T_f$ is the flame temperature, $A$ is area, $\delta$ is reaction zone thickness for steady flows and $\lambda$ is thermal conductivity. Since it is a one dimensional problem,

$$\dot{m} = \rho Au = \rho S_L A \quad (2.2)$$

then the flame speed $S_L$ can be expressed as

$$S_L = \left[ \frac{\lambda(T_f - T_i)}{\rho c_p(T_i - T_0) \delta} \right]^{-1} \quad (2.3)$$
If the total rates of mass entering and consumption in the reaction zone are equal, then the flame velocity becomes

$$\delta = S_L \tau = S_L \frac{1}{\frac{d\delta}{dt}}$$

(2.4)

$$S_L = \left[ \frac{\lambda(T_f - T_i)}{\rho c_p(T_f - T_0) \rho} \right]^{1/2} \sim \left( \frac{\alpha \omega}{\rho} \right)^{1/2}$$

(2.5)

where $\rho$ is the unburned gas density, $\alpha$ is the thermal diffusivity, and $\omega$ specifies the reaction rate. This theory demonstrates the general trends of laminar flame speed.

2.1.1.2 Effects of pressure on the laminar flame speed

As discussed, the laminar flame speed could be affected by physical parameter changes. Firstly, the change of flame speed respected to a variation of pressure will be discussed. The general statement of the pressure dependence in the rate term is $\dot{\omega} \sim P^n$. Thus Eq.2.4 becomes

$$S_L \sim (P^{n-2})^{1/2}$$

(2.6)

where $n$ is the overall order of the reaction e.g. for a second-order hydrocarbon oxidation, $n$ equals two and flame speed is independent of pressure [12]. However, experimental results show that laminar flame speeds of hydrocarbon decrease as the pressure increases [42-44]. Because third-order reaction $H + O_2 + M \rightarrow HO_2 + M$ (M is the three-body) has played an important role in the chain branching: the heat release rate is slowed by this reaction [12].
2.1.1.3 Effects of temperature on the laminar flame speed

As expected, temperature is another important physical parameter that affects the flame speed, because the high activation energy Arrhenius kinetic controls the reaction process. The flame speed expression shows that the rate expression $\dot{\omega}$ is related to the temperature, thus, it assumes that

$$S_L \sim \left[\exp\left(-\frac{E}{RT_f}\right)\right]^{1/2}$$  \hspace{1cm} (2.7)

where the flame temperature $T_f$ has a dominant influence on the laminar flame speed, On the other hand, the effect of the unburned gases temperature on the laminar flame speed could be explained using flame temperature term. The flame temperature can be expressed as

$$T_f = T_o + \left(\frac{q_c}{c_p}\right)Y_u$$  \hspace{1cm} (2.8)

where $q_c$ is the chemical heat release, $Y_u$ is the mass fraction of unburned gases, and $T_o$ is the unburned gases temperature that is showed in the degree to alter the flame temperature. Therefore, the increasing of unburned gases temperature will raise the flame temperature $T_f$, and then increase the laminar flame speed.

2.1.1.4 Effects of equivalence ratio on the laminar flame speed

One should notice that the laminar flame speed is affected by the flame temperature; therefore the variations between flame temperature and equivalence ratios could be used to explain the effects of the equivalence ratio on the laminar flame speed. Figure 2-2 shows the flame temperature versus equivalence ratio and the temperature peak at the stoichiometric mixture ratio. In case the reaction is over
oxidized, which means that the oxygen fraction is more than stoichiometric fraction, the flame temperature is absorbed for heating the excess oxygen. The flame temperature is therefore dropped from the stoichiometric value. If the fuel fraction is more than stoichiometric fraction, the reaction will be under-oxidized; in this case all the carbon and hydrogen will not be burned completely by oxygen, resulting in less energy release and temperature decrease.

![Figure 2-2 Flame temperatures versus equivalence ratio](image)

The highest flame temperature appears at the stoichiometric ratio; however an interesting phenomenon in the experimental data is that the maximum flame temperature of hydrocarbon mixed with air occurs slightly on the fuel rich side of the fuel equivalence ratio. One reason is that on the fuel rich side, there is a higher concentration of intermediates in the products of mixture (e.g. CO and H₂), which are diatomic molecules. On the lean side, the products contain more concentration of triatomic molecules such as CO₂ and H₂O. As the specific heats of triatomic molecules are larger than the diatomic molecules, the maximum flame temperatures should shift slightly to the rich side [27]. A more detailed analysis has been
conducted by Law [28] who identified the cause of this rich shifting. He concluded that the phenomenon of fuel rich shifting is a consequence of reduced heat release in the presence of product dissociation. The shifting direction is determined by the highest heat release and depends on the specific heat per unit mass of the mixture product at the stoichiometric ratio. It demonstrates that there is more dissociation on the lean side, therefore heat release peaks on the rich side in the combustion of hydrocarbon-air.

2.2 Experimental Analysis

2.2.1 Experimental Methods

The Mallard-Le Chatelier provides a theoretical determination of the general trends for the laminar flame speed with pressure and temperature. In this section, experimental analysis will be discussed to measure the laminar flame speed of fuels (methane and ethane), and verify the Mallard-Le Chatelier theory. For experimental studies, the main task is to create a perfectly flat adiabatic flame in a homogeneous flow, which is sensitive to perturbations. Recently, adiabatic flames have been achieved to measure the adiabatic flame speed in several experiments such as stagnation flow [31], combustion vessel [32] or burner [33]. However, the laminar flame speed was not measured accurately in these experiments, because of heat loss or stretched and distorted flame by curvature.
2.2.1.1 Counterflow Method

Be aware of the importance of stretch, Law [34] developed the counterflow flame technique to study the laminar flame speeds from stretched flames. In this experiment, the counterflow is generated to creating a closely planar and adiabatic flame between the two nozzles, and the axial flame speed profile is measured by the Laser Doppler Velocimetry (LDV) along the centreline of the counterflow. Fig 2-3 and 2-4 show that the flame speed is measured as a function the stretch rate $a$ for the given mixture. After that, then linearly extrapolating flame speed is lineally extrapolated to the zero stretch rates, and then the unstretched laminar flame speed could be nearly approximated.

Figure 2-3 Typical axial velocity profile a stagnation flame (reproduced from [34])

Figure 2-4 Dependence of the flame speed $S_L$ on the strain rate (reproduced from [34])
There are several advantages of the counterflow technique, firstly, two nozzles generate the inlet flows, and because of the symmetry heat losses are minimized upstream and downstream. Secondly, LDV measured local flame speed experienced by specific flame segments; therefore the flow field influences would include the buoyancy effects automatically [35]. Finally, because of the positively stretched nature of the flame, flame front diffusion thermal instabilities are not favoured [35]. Through this technique, Law had measured nearly unstretched laminar flame speed of mixtures of small hydrocarbon and hydrogen with various stoichiometric ratios and pressures.

2.2.1.2 Heat Flux Method

Botha and Spalding [33] measured the heat loss by determining temperature change of the cooling water flowing through a burner to investigate flame stabilisation. However, this temperature change was too small to be measured accurately. The other problem was that near the adiabatic flame speed, the flame becomes unstable. Therefore adiabatic flame speed could not be measured in this situation. In order to address these problems, heat flux method was introduced by de Goey and co-workers to stabilize adiabatic flat flames and measure adiabatic flame speed [36]. In the heat flux method, the flat flame is stabilized by a perforated plate burner on a brass 2 mm thick plate with a hexagonal pattern of small holes [37].
Fig 2-5 shows the front and top views of the burner. The thin burner plate makes the distribution of temperature, which presents how well the flame is stabilized on the burner, to only depend on the heat loss from flame to burner. This method measures the heat loss more accurate comparing with Botha and Spalding measurement. More researches have used this method to analyse the perfect one dimensional adiabatic flame [37-38]. The method has been further improved by the adaption of the burner [39]. Now unstretched flat adiabatic flames have been created as the reference flames.

### 2.2.2 Experimental Results – Laminar Flame Speed

Table 2-1 shows measurements of laminar flame speed of methane and air mixture at stoichiometric ratio, ambient temperature and pressure as found in several literatures. The results of these experiments appear to be quite different (from 40.5 to 35.7 cm/s). With carefully correcting the stretch effects, recent experiments represent more accurate measurements of adiabatic flame speed, which is around 36±1 cm/s for a stoichiometric mixture.
### 2.2.2.1 Equivalence Ratio

Figure 2-6 shows the comparison of recent experimental data. Vagelopoulos et al. [40] developed an ultralow strain rate flame; by changing the strain rate from positive to negative, the flame speed is measured effectively comparing with the traditional counterflow techniques. The classical counterflow technique performed by Vagelopoulos [31] provided a high laminar flame speed of methane-air mixture. Van Maaren [38] corrected the Law’s measurements with stretch model and measured the flame speed, which is close to the recent results using heat flux method [39].

![Graph showing laminar flame speed as function of equivalence ratio](image)

Figure 2-6 Laminar flame speed of methane as function of equivalence ratio at 1 atm and 298 K
For the other important species in the natural gas, ethane, there is not as numerous measurements of laminar flame speed as for methane in literatures. Warnatz [87] firstly measured those values, and then more data were provided by the Vaglelopolouos et al. [40] and Egolofopoulos et al. [88]. Recently, Konnov et al. [89] and de Goey [39] performed measurements for ethane by using the heat flux methods. Figure 2-7 shows the measurements of flame speed of ethane – air mixture. The early Warnatz’s measurement had a quite large value for the flame speed, compared to the other results. Compared to heat flux method’s result, it appears that measurements of Egolofopoulos [88] are slightly higher, and Vaglelopolouos’ results [89] are seemed to shift a little to right. However, the two measurements are quite close to each other for flux methods, which are expected to represent a more accurate values for the unstretched laminar flame speed that other methods.
2.2.2.2 Initial Pressure

Figure 2-8 shows that Rozenchan [43] experimental measurements of laminar flame speed of methane-air as a function of the both equivalence ratio and pressure. Laminar flame speed is peak at the equivalence ratio of between 1 and 1.1, and decreases as the mixture getting to lean or rich. When the pressure increases, the overall reaction ratio will drop. Therefore the flame speed will decrease as pressure increasing, and the decrease rate of laminar flame speed is peak at the stoichiometric ratio.

Figure 2-8 Laminar flame speed versus equivalence ratio at various pressure and 298 K [43]
Figure 2-9 shows the laminar flame speed as the function of initial pressure at stoichiometric ratio. Measurements include the data of Egolfopoulos et al. [41] at pressures 0.5-2 atm, Hassan et al. [42] at pressures 0.5-4 atm, and results at pressures 1-10 atm from literatures of Rozenchan et al. [43], Lowry et al. [44] and Gu et al. [32]. The experimental measurements follow the theoretical expectation that it is trend of decreasing laminar flame speed with increasing pressure, because heat release rate is slowed by the third-order reaction in chain branching.

![Laminar Flame Speed versus initial pressure](image)

Figure 2-9 Laminar Flame Speed versus initial pressure at 298 K and stoichiometry
2.2.2.3 Initial Temperature

The dependence of flame speed on the unburned gas temperature of the methane and air mixture was determined in wide range of equivalence ratios. Figure 2-10 shows that NASA [45] experimental measurements of laminar flame speed of methane-air mixture as a function of the both equivalence ratio and temperature. Laminar flame speed is peak at the equivalence ratio of between 1 and 1.1, and decreases as the mixture getting to lean or rich. When the temperature increases, the overall reaction ratio will increase, therefore the flame speed will increase.

Figure 2-10 Flame speed as function of equivalence ratio at various temperature and 1 atm [45]
In Figure 2-11, a comparison of several experimental results for a stoichiometry mixture at different temperature under atmosphere pressure. As depicted, the trends of the different methods roughly coincide, and the data obtained by Gu et al. [32] and NASA [45] agree well with the heat flux measurements [46]. The experimental data follow the theoretical expectation: as the unburned gas temperature rise, the laminar flame speed will increase, because the flame temperature has a large effect on the reaction ratio in the Arrhenius kinetic.

![Figure 2-11 Flame speed versus initial temperature at 1 atm and stoichiometry](image)

**2.2.3 Experimental Results – Flame Structure**

2.2.3.1 Structure of Premixed Flame

There are several investigations on the structure of premixed flame; one study on standard natural gas is invested by EI-Sherif [47] to see the effects of minor alkanes on the combustion, and paper concluded that an increase of ethane concentration in natural gas leads to an increase in flame speed, CO and NOx at very lean flames. Tan et al. [48] measured and developed the specie concentration profiles for the oxidation of methane, ethane, propane and their mixtures under a wide range
of conditions. Bakali et al. [49] further studied methane-high alkane mixture in jet-stirred reactor, and introduced new experimental data for the oxidation of methane–ethane mixture at atmospheric pressure. Recently Tran et al. [50] present the study of the structure of laminar premixed stoichiometric flames at low pressure, investigating fuel includes pure methane, ethanol and methane-ethanol mixtures. Figure 2-12 and Figure 2-13 show the temperature and mole fraction of main species of methane-air premixed flame at room temperature and atmosphere pressure.

![Figure 2-12 Temperature profiles of premixed flame of methane-air mixture at 1 atm and 298 K](chart1.png)

**Figure 2-12 Temperature profiles of premixed flame of methane-air mixture at 1 atm and 298 K [50]**

![Figure 2-13 Mole fraction profiles of premixed flame of methane-air mixture at 298 K and 1 atm](chart2.png)

**Figure 2-13 Mole fraction profiles of premixed flame of methane-air mixture at 298 K and 1 atm [50]**
2.2.3.2 Structure of Non-premixed Flame

Strained laminar diffusion flames were studied to develop a fundamental understanding of flame structure, extinction limits, soot and NOx emission, and for application in the flamelet model of turbulent combustion [52]. The combustion of the diffusion flame occurred at the fuel and oxidant gas interface is often studied in counter flow burners and depends more on the diffusion rate of reactants. Compare to laminar premixed flames, the flame stabilization of non-premixed flame is not understood well, due to the lack of a global parameter reflecting the reaction rates. Therefore, numbers of experiments focus on the investigation of the effects of aerodynamic stretch on diffusion flame. The measurements of global parameters such as flame location, temperature and heat releasing have been studied by Smooke et al. [52] and Du et al. [53].

Sung et al. [54] developed the stretch rate effect on the structure of diffusion flame. Experimental results show that as the strain rate increases, the structure of diffusion flame becomes thinner, where the thermal thickness approximately proportional to one over square root strain rate. Recently, Cheng et al. [55] study the oxygen concentration effect on the structure of methane diffusion flames. When oxidizer is changed from air to oxygen enriched mixture, the portion of nitrogen in the oxidizer mixture drops, which will cause a significant increase in the diffusion flame temperature. Flame temperature depends on the oxygen concentration of the oxidizer significantly, when oxygen concentration varies from 23% to 100%, the flame temperature rises about 800 K.
2.3 Concluding Remarks

In this chapter, a detailed discussion has been made of the theoretical calculation of laminar flame speed and its experimental measurements. Methods of experiments and their associated advantages and limitation were also presented.
Older experiments measured the laminar flame speed inaccurately, because flame is stretched and distorted by curvature or heat loss. Recent heat flux method introduced by de Goey and co-workers [36] creates the adiabatic flat flames and improves the measurements of laminar flame speed.

Experimental measurements of laminar flame speed of methane and ethane had been presented at standard and elevated pressure and temperature over wide range of fuel-air equivalence ratio. Finally experimental measurements of laminar flame structure of premixed and non-premixed flames are also presented. The measurements are therefore used to validate the numerical premixed and diffusion flames model in CHAPTER 5 and CHAPTER 6.
CHAPTER 3 Reaction Mechanism

In the previous chapter, theoretical and experimental analysis of laminar flame speed and structure are introduced. To simulate a chemical reaction, reaction mechanism is one of the essential elements, because it presents the important fundamental reaction paths in overall reaction. The chemical mechanism is the collection of the elementary reactions necessary to describe an overall reaction [96]. To describe a particular global reaction, it may involve a few or hundreds of steps.

A complete mechanism developed for all reaction used should describe the all products, stereochemistry and function of a catalyst. Relative rates of the steps and overall reactions should also be described [97]. The intermediates of reaction are temporary products and reactants in the reaction steps, and these chemical species often unstable and ephemeral. Therefore the precise reaction mechanism is an important part of accurate predictive modelling. In this chapter, three kinds of mechanism (single step, reduced and detailed mechanisms) for modelling chemical reaction are presented.

3.1 Single Step Mechanism

Historically simplicity combustion chemistry was first described as a global one-step reaction in which fuel and oxidizer react to form products. Although
detailed reaction mechanisms have become available, empirical single-step reaction mechanism is still need in order to make problems responsive to theoretical analysis. In laminar combustion, the reaction rate is defined as disappearing rate of the reactants to form products or the forming rate of products. The single-step reaction mechanism is expressed as

\[ \text{Fuel} + \text{Oxidant} \rightarrow \text{Products} \]  \hspace{1cm} (3.1)

For the methane, the stoichiometric reaction is given by

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  \hspace{1cm} (3.2)

The reaction rate can be expressed in terms of the Boltzmann factor \( \exp(-E_a/RT) \), specifying the fraction of collisions that have an energy greater than the activation energy \( E_a \), as suggested by Arrhenius [140]. The rate expression of the single reaction is

\[ k = A_o \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (3.3)

where, \( A_o \) is the pre-exponential factor, which represents the collision frequency and usually expressed as a function of temperature \((AT^n)\). For given chemical changes, the appropriate values of \( A \), \( n \) and \( E_a \) are based on the nature of the elementary reaction, and not affected by the species’ concentrations or temperature [141].
Table 3-1 Flame Temperature (K) in methane–air mixtures at various chemical mechanisms [97]

<table>
<thead>
<tr>
<th>Equivalence ratio</th>
<th>Single-step</th>
<th>Reduced</th>
<th>Detailed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>2017</td>
<td>2005</td>
<td>1999</td>
</tr>
<tr>
<td>1</td>
<td>2320</td>
<td>2250</td>
<td>2228</td>
</tr>
<tr>
<td>1.2</td>
<td>2260</td>
<td>2200</td>
<td>2135</td>
</tr>
</tbody>
</table>

The laminar flame speed is predicted well over wide ranges of conditions by using the single-step mechanism, but there are some important uncertainties. In the combustion of methane-air mixture, the reaction products not only contain the CO₂ and H₂O, but also involve small amount of important intermediates such as CO and H₂ and free radical species including H, O and OH in equilibrium. Therefore the flame temperature should be lower than the single-step predicted result, because the intermediate species reduce the total heat releasing of reaction [98]. Table 3-1 shows the magnitude of this effect in the case of methane-air mixtures; adiabatic flame temperatures of the reaction are overestimated by the single step mechanism. The overestimation of adiabatic flame temperatures grows with increasing equivalence ratio and is directly related to the amounts of CO and H₂ in the reaction products.

3.2 Reduced Mechanism

As discussed, the incompletely oxidized species existed at the burned gas. These intermediates such as CO and H₂ are not completely consumed until the entire hydrocarbon species have reacted [63]. To accurately simulate oxidation of hydrocarbons up to propane, it generally believed that hundred reactions and more than 30 species are needed. However, it is not necessary to determine all the
reactions rate and species accurately in order to obtain the global properties such as laminar flame speed or extinction strain rate. Limitation of computer power in the twenty century could also not be sufficient to solve the problem in such a complex mechanism. Therefore, it is good option to reduce the detailed chemical mechanism to a few steps with reactants, products and fewer intermediates according to computer time requirements [141]. In the mid-1980s, the reduced mechanisms were derived and published for premixed methane flames [56-57] and diffusion flames [58], and they serve as the example to develop methods to reduce kinetic mechanism.

Eq. 3.4-3.7 shows an example of the four steps reaction mechanism for methane, which is proposed by Jones and Lindstedt [59],

\[ CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \]  \hspace{1cm} (3.4)
\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]  \hspace{1cm} (3.5)
\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]  \hspace{1cm} (3.6)
\[ CO + H_2O \rightarrow CO_2 + H_2 \]  \hspace{1cm} (3.7)

This scheme only considers 6 species, compares to the detailed reaction mechanism; the predictions of major species agree well with the measurements for premixed and diffusion flames, and the computer time is further reduced. To simulate the methane combustion of a spatially developing transitional free jet flame at moderate Reynolds number, Liu [61] proposed a different four-step reaction mechanism, which is
\begin{align*}
CH_4 + 2H + H_2O & \rightarrow CO + 4H_2 & \text{(3.8)} \\
CO + H_2O & \rightarrow CO_2 + H_2 & \text{(3.9)} \\
H + H + M & \rightarrow H_2 + M & \text{(3.10)} \\
O_2 + 3H_2 & \rightarrow 2H + 2H_2O & \text{(3.11)}
\end{align*}

The reactions of the H2-H2O and CO-CO2 equilibrums are the other schemes that can be added in the burned gas region. Edelman and Fortune [64] combine a single-step reaction to form CO and H2, together with a detailed reaction mechanism for CO and H2 oxidation. This quasi-global reaction mechanism is used to study the induction delays in shock tubes and stability limes. Duterque et al. [99] further evaluated the CO, CO2 and H2 species during the combustion of methane-air mixture. In their studies, a quasi-global mechanism was developed and validated with experimental data to predict the performance of burners and combustors. This approach includes the important species and elementary reactions, and can provide more accurate adiabatic flame temperature and equilibrium species concentration.

Table 3-2 shows the quasi global mechanism for CO-H2-O2 system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>$E_a,(J.mol^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + O₂ = O + OH</td>
<td>$2.2 \times 10^{14}$</td>
<td>0.0</td>
<td>16.8</td>
</tr>
<tr>
<td>H₂ + O = H + OH</td>
<td>$1.8 \times 10^{10}$</td>
<td>1.0</td>
<td>8.9</td>
</tr>
<tr>
<td>O + H₂O = OH + OH</td>
<td>$6.8 \times 10^{13}$</td>
<td>0.0</td>
<td>18.4</td>
</tr>
<tr>
<td>OH + H₂ = H + H₂O</td>
<td>$2.2 \times 10^{13}$</td>
<td>0.0</td>
<td>5.1</td>
</tr>
<tr>
<td>H + O₂ + M = HO₂ + M</td>
<td>$1.5 \times 10^{15}$</td>
<td>0.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>O + HO₂ = O₂ + OH</td>
<td>$5.0 \times 10^{13}$</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H + HO₂ = OH + OH</td>
<td>$2.5 \times 10^{14}$</td>
<td>0.0</td>
<td>1.9</td>
</tr>
<tr>
<td>H + HO₂ = H₂ + O₂</td>
<td>$2.5 \times 10^{13}$</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>OH + HO₂ = H₂O + O₂</td>
<td>$5.0 \times 10^{13}$</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Reaction | $A$ | $n$ | $E_a (J.mol^{-1})$
--- | --- | --- | ---
$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$ | $1.0 \times 10^{13}$ | 0.0 | 1.0
$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$ | $1.2 \times 10^{17}$ | 0.0 | 45.5
$\text{HO}_2 + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$ | $7.3 \times 10^{11}$ | 0.0 | 18.7
$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$ | $1.0 \times 10^{13}$ | 0.0 | 1.8
$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ | $1.5 \times 10^7$ | 1.3 | -0.8
$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$ | $3.1 \times 10^{11}$ | 0.0 | 37.6
$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{O}$ | $5.9 \times 10^{15}$ | 0.0 | 4.1
$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{M}$ | $1.5 \times 10^{14}$ | 0.0 | 23.7
$\text{OH} + \text{M} = \text{O} + \text{H} + \text{M}$ | $8.0 \times 10^{19}$ | -1.0 | 103.7
$\text{O}_2 + \text{M} = \text{O} + \text{O} + \text{M}$ | $5.1 \times 10^{15}$ | 0.0 | 115.0
$\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$ | $2.2 \times 10^{14}$ | 0.0 | 96.0
$\text{H}_2\text{O} + \text{M} = \text{H} + \text{OH} + \text{M}$ | $2.2 \times 10^{16}$ | 0.0 | 105.0

### 3.3 Detailed Mechanism

Although quasi-global mechanism further improves the simulation of composition and temperature in the burned gas, it cannot predict well the flame structure and species concentrations in the flame zone. The detailed mechanism involves hundreds of chemical species and thousands of reaction steps based on measurements of elementary reaction rate coefficients. Westbrook and Dryer [65] developed a chemical mechanism modelling of hydrocarbon combustion that has been used by many researchers. Miller and Kee [66] provided a selective view of chemical kinetics and combustion modelling. Barbe *et al.* [73] developed a more comprehensive mechanism that has been validated with the experimental data of methane oxidation between 773 and 1573 K at atmospheric pressure. Frenklach [74-75] recommended the creation of optimal performance reaction mechanisms by
fitting the parameters of some reaction steps to bulk experimental data. The oxidation of natural gas is studied by GRI-Mech 3.0 mechanism [67]. This mechanism is based on elementary reactions and rate parameters, which is given by experimental and theoretical determination [68]. Based on the GRI-Mech mechanism, Appel [68] introduced a mechanism to compute the soot formation for small hydrocarbon-air mixture. Recently, Konnov [69] and EI Bakali et al. [70] separately developed the detailed combustion mechanisms, which were optimised to study the various combustion characteristic behaviours: oxidation of simple hydrocarbon-air mixture, NO emission, flame speed and flame structure etc.

### 3.3.1 Gas Research Institute's Mechanism (GRI-Mech 3.0)

GRI-Mech 3.0 is an optimized detailed chemical reaction mechanism carried out by the American universities including UC Berkeley, Stanford, Texas and SRI international. It is designed to calculate the natural gas chemical reaction process [67]. GRI-Mech 3.0 consists of 325 elementary chemical reactions with associated rate coefficient expressions and thermo chemical parameters for 53 species to perform the ranges of 0.1–5 in equivalence ratio, 1000–2500 K in temperature, and 10 torr–10 atm in pressure. To simulate and interpret the effect of different composition of natural gas–air chemical reactions, the chemical kinetics mechanism used in the calculation must be capable of the calculation of the pure methane and methane–ethane fuel blends.
3.3.2 Appel, Bockhorn and Frenklach’s Mechanism (Appel)

Appel is a detailed chemical kinetic model for soot formation developed by Joerg Appel, Henning Bockhorn and Michael Frenklach [68]. It is updated from the Wang-Frenklach [71] mechanism with development of a new model for soot surface growth, and gas-phase reactions, soot particle coagulation, aromatic chemistry, soot particle aggregation. The model was tested against experimental profiles of chemical species, aromatics, soot volume fractions, and soot particle diameters for laminar premixed flames of methane, ethane, ethylene, and acetylene.

3.3.3 Konnov's Mechanism (Konnov)

The Konnov Mechanism created by Konnov [69] contains 1200 reactions amongst 127 species, which can be used to calculate the hydrogen, carbon monoxide, formaldehyde, methanol, methane, methanol, ethane, propane and some of their mixtures. The Konnov mechanism deals with C_1-C_3 hydrocarbons and their derivatives, n-H-O chemistry and NO_x formation in flames. The mechanism has been validated with experimental data available for flame speed and flame structure, ignition, and oxidation of C_1-C_3 hydrocarbons.

3.3.4 GDF-Kin chemical Mechanism

GDF-Kin is a detailed kinetic mechanism specific to natural gas (C1-C6) combustion developed in collaboration with PC2A and ICARE Laboratories [70]. It
CHAPTER 3 Reaction Mechanism

is consist of 874 reactions amongst 121 species and validated between temperature 400 and 2200 K, pressure 0.04 and 10 atm and equivalence ratio between 0.2 and 5. GDF-kin is a detailed mechanism. Recently, GDF-Kin 3.0 is carried out with NOx and prompts NO modules and mainly focuses impact of pollutant emissions and gas quality.

<table>
<thead>
<tr>
<th>Mechanisms</th>
<th>Species No.</th>
<th>Reaction No.</th>
<th>Hydrocarbon</th>
<th>Soot</th>
<th>Prompt-NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRI 3.0[67]</td>
<td>53</td>
<td>325</td>
<td>C1-C3</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Appel[68]</td>
<td>102</td>
<td>551</td>
<td>C1-C3</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Konnov 0.6[69]</td>
<td>127</td>
<td>1200</td>
<td>C1-C3</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>GDFkin 3.0[70]</td>
<td>121</td>
<td>874</td>
<td>C1-C6</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 3-3 shows the reaction mechanisms, GRI-Mech 3.0 is a very comprehensive mechanism that has been used to simulate the combustion of methane, ethane and their mixtures in number of literatures [32,39,42]. However some aspects of natural gas combustion chemistry such as soot formation are not described by GRI-Mech 3.0. In this mechanism, species such as propane, methanol and acetylene are also not validated with experimental data. The GRI-Mech 3.0 mechanism cannot be used to model these pure fuels (e.g. describing the burning of pure propane). The description of the small hydrocarbon reaction such as methane and ethane in Appel mechanism is based on the GRI-Mech 1.2 [100] (early version of GRI-Mech 3.0), and it also provides the detailed mechanism for soot formation. Although Konnov and EI Bakali et al. [70] developed the more accurate mechanisms for C2 and high order hydrocarbons, most recent studies using those mechanisms are
analysing emission of NO\textsubscript{x}. Therefore, in the following study GRI-Mech 3.0 is used to model the combustion process of methane, ethane and their mixtures in two reasons: one is that GRI-Mech 3.0 has been validated well with the many experiments [32,39,42] for methane and ethane. The other reason is that by using GRI-Mech 3.0, the computing time could be largely reduced due to less chemical reactions and species in comparison of other detailed mechanisms.

3.4 Concluding Remarks

In this chapter, a number of chemical mechanisms (single-step, reduced, and detailed mechanisms) have been introduced. The advantage and limitation of each kind of mechanism are discussed. The single-step mechanism predicts well the flame speeds over wide ranges of conditions, but overestimates the adiabatic flame temperature without calculating CO and H\textsubscript{2} in the combustion products, which could lower the total heat of reaction. Reduced mechanism combined the single equation of CH\textsubscript{4}-O\textsubscript{2} with detailed chemistry of CO-H\textsubscript{2}-O\textsubscript{2} in equilibrium in improvement of measuring adiabatic flame temperature. Although it could not accurately simulate specie profiles of the oxidation of hydrocarbons, it works as the intermediate between the single-step mechanism and the detailed mechanism according to computer time requirements.

Four detailed mechanisms are introduced and compared with each other to find the most suitable mechanism that is used in the numerical model to simulate the laminar flame of methane-air mixture. GRI-Mech 3.0 requires less computational time as it has fewer number of chemical reactions and species. Therefore, GRI-Mech
3.0 mechanism will be used in numerical study of laminar premixed and non-premixed flames in CHAPTER 6 and CHAPTER 7 due to the limitation of computer power.
CHAPTER 4 Mathematical Modelling

4.1 General

In the previous chapter, different kinds of reaction mechanism for hydrocarbon fuels were introduced. To perform the flame calculations, the modelling approach, which is based on one-dimensional flame using CHEMKIN [101], will be presented in this chapter. Firstly, the historical development and basic structure of CHEMKIN are introduced, and then computational methodology based the theory adopted in CHEMKIN is introduced in following sections. Computational Methodology presented in section 4.2 is based on the CHEMKIN Theory Manual [134].

CHEMKIN is very popular software that is designed to facilitate simulations of elementary chemical reaction and analyse chemical kinetic and molecular transport, especially in processes involving chemically reacting flow and heterogeneous reactions at surfaces. CHEMKIN evolved from its origin as a Sandia National Laboratory combustion kinetic code (CHEMKIN II) into commercial quality software. Recent, it is maintained and enhanced by Reaction Design, Inc. [102]. Fig 3-1 shows the general structure of the CHEMKIN collection, there two major elements (Gas-phase package and Transport package). The CHEMKIN library contains reaction mechanisms and thermodynamic information (specific heat,
enthelpy and entropy). The transport information (viscosity and conductivity) are included in the transport library.

Figure 4-1 Structure of the CHEMKIN collection [101]
CHAPTER 4 Mathematical Modelling

4.2 Computational Methodology

4.2.1 Thermodynamic

4.2.1.1 Gas Equation of State

The equation of state used is based on an ideal gas law of multi-fluid gas. The multi-fluid gas formulation allows the temperature to be specified for each species, \( T_k \). This formulation collapses to the more usual thermal-equilibrium relation in the case where all species temperatures \( T_k \) are equal to the gas temperature. The general equation of state is given by

\[
P = \sum_{k=1}^{K} [X_k]RT_k
\]

(4.1)

Where \( X_k \) is the mass fraction, while the mean mass density is defined by

\[
\rho = \sum_{k=1}^{K} [X_k]W_k
\]

(4.2)

The mean molecular weight may be defined variously as

\[
\bar{W} = \frac{1}{\sum_{k=1}^{K} Y_k/W_k}
\]

(4.3)

4.2.1.2 Standard-state Thermodynamic Properties

Using arbitrary-order polynomial fits, the molar heat capacities at constant pressure are defined as

\[
\frac{c_{pk}^0}{k} = \sum_{m=1}^{M} a_{mk} T^{(m-1)}
\]

(4.4)
The superscript $^0$ prefers to the standard-state, which is an ideal gas at 1 atmosphere for gas-phase species. For perfect gases, the heat capacities are independent of pressure, and the standard-state values become the actual values. The standard-state molar enthalpy is given by

$$\frac{H_k^0}{R T_k} = \sum_{m=1}^{M} \frac{a_{mk}T_k^{(m-1)}}{m} + \frac{a_{M+1,k}}{T_k} \tag{4.5}$$

where $a_{mk}$ is the coefficients of the polynomial that fits the thermodynamic properties $M$ is the total number of coefficients of the polynomial, and $a_{M+1,k}R$, is the standard heat of formation at 0 K. Since the polynomial representations are usually not valid at this temperature, $a_{M+1,k}R$ is evaluated from knowledge of the standard heat of formation at 298 K. The standard-state molar entropy is written as

$$\frac{S_k^0}{R} = a_{1,k}\ln T_k + \sum_{m=2}^{M} \frac{a_{mk}T_k^{(m-1)}}{(m-1)} + a_{M+2,k} \tag{4.6}$$

where $a_{M+2,k}R$ is evaluated from knowledge of the standard-state entropy at 298 K.

### 4.2.2 Species Transport

In solving chemically reacting flow problems, transport is often used to balance the chemical production and destruction due to convection, diffusion, or conduction. In some cases, such as laminar premixed and diffusion flames, transport properties play an important role to determine the gas state, because transport of species and energy can become rate limiting. For most applications, mixture
averaged approach based on the work of Warnatz [77] and Kee et al [78] is used to address the gas mixture properties from pure species properties.

4.2.2.1 Pure Species Viscosity and Binary Diffusion Coefficients

The single component viscosity is given by the standard kinetic theory expression [79],

$$\eta_k = \frac{5}{16} \sqrt{\frac{\pi m_k k_B T}{\sigma_k^2 \Omega^{(2,2)^*}}}$$  \hspace{1cm} (4.7)

where $\sigma_k$ is the Lennard-Jones collision diameter, $m_k$ is the molecular mass, $k_B$ is the Bolzmann constant, and $T$ is the temperature. The collision integral $\Omega^{(2,2)^*}$ depends on the reduced temperature, given by

$$T_k^* = \frac{k_B T}{\varepsilon_k}$$  \hspace{1cm} (4.8)

and the reduced dipole moment, given by

$$\delta_k^* = \frac{1}{2} \frac{\mu_k^2}{\varepsilon_k \sigma_k^3}$$  \hspace{1cm} (4.9)

The binary diffusion coefficients [79] are given in terms of pressure and temperature as

$$D_{kj} = \frac{3}{16} \sqrt{\frac{2\pi k_B T^3 / m_{jk}}{p \pi \sigma_{jk}^2 \Omega^{(1,1)^*}}}$$  \hspace{1cm} (4.10)

Where $m_{jk}$ is the reduced molecular mass for the $(j, k)$ species pair.
4.2.2.2 Pure Species Thermal Conductivities

The individual species are assumed to conductivit

to be composed of translational, rotational, and vibrational contributions as given by Warnatz [77].

\[ \lambda_k = \frac{\eta_k}{W_k} (f_{\text{trans}}.C_{v,\text{trans}} + f_{\text{rot}}.C_{v,\text{rot}} + f_{\text{vib}}.C_{v,\text{vib}}) \]  

(4.11)

where

\[ f_{\text{trans}} = \frac{5}{2} \left( 1 - \frac{2}{\pi} C_{v,\text{trans}} \frac{A}{B} \right) \]  

(4.12)

\[ f_{\text{rot}} = \frac{\rho D_{kk}}{\eta_k} \left( 1 + \frac{2A}{\pi B} \right) \]  

(4.13)

\[ f_{\text{vib}} = \frac{\rho D_{kk}}{\eta_k} \]  

(4.14)

\[ A = \frac{5}{2} \frac{\rho D_{kk}}{\eta_k} \]  

(4.15)

\[ B = Z_{\text{rot}} + \frac{2}{\pi} \left( \frac{5}{3} C_{v,\text{rot}} + \frac{\rho D_{kk}}{\eta_k} \right) \]  

(4.16)

4.2.2.3 The Mass, Momentum, and Energy Fluxes

The momentum flux is related to the gas mixture viscosity and velocities by

\[ \tau = -\eta (\nabla v + (\nabla v)^T) + \left( \frac{2}{3} \eta - K \right) (\nabla \cdot v) \hat{\delta} \]  

(4.17)

Where \( v \) is the velocity vector, \( \nabla v \) is the dyadic product, \( (\nabla v)^T \) is the transpose of the dyadic product, and \( \hat{\delta} \) is the unit tensor [80], \( \eta \) is the average values for the mixture viscosity, and \( K \) is the bulk viscosity. The energy flux is given in terms of the thermal conductivity \( \lambda_0 \) by


\[ q = \sum_{k=1}^{K} j_k h_k - \lambda_0 \nabla T - \sum_{k=1}^{K} \frac{RT}{W_k x_k} D^T_k d_k \] \hspace{1cm} (4.18)

### 4.2.3 Premixed Laminar Flames

The chemical mechanism is usually studied by the burner-stabilized laminar premixed flames in the combustion. One-dimensional flames can be effectively made by steady detailed experimental data of temperature and species profiles. Miller [81-82] use the flame model to interpret experimental observations and to verify combustion chemistry and pollution formation.

#### 4.2.3.1 1-D Flame Equations

For these equations, assume one-dimensional flow with uniform inlet conditions. The governing conservation equations reduce to:

**Continuity**

\[ \dot{M} = \rho u A \] \hspace{1cm} (4.19)

**Energy**

\[ \dot{M} \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \frac{\lambda A}{c_p} \frac{dT}{dx} \right) + \frac{A}{c_p} \sum_{k=1}^{K} \rho Y_k V_k c_{pk} \frac{dV_k}{dx} + \frac{A}{c_p} \sum_{k=1}^{K} \omega_k h_k W_k = 0 \] \hspace{1cm} (4.20)

**Species**

\[ \dot{M} \frac{dY_k}{dx} + \frac{d}{dx} (\rho A Y_k V_k) - A \dot{\omega}_k W_k = 0 \] \hspace{1cm} (4.21)

**Equation of State**

\[ \rho = \frac{\rho \bar{W}}{RT} \quad (4.22) \]

Giving the law of mass action and the forward rate coefficients, reaction proceeds are assumed in the modified Arrhenius form,

\[ k_f = AT^\beta \exp \left( \frac{-E_A}{RT} \right) \quad (4.23) \]

4.2.3.2 Mixture-averaged Transport Properties

For the mixture averaged formula, it assumes the diffusion velocity \( V_k \) to be composed of three parts,

\[ V_k = \nu_k + \omega_k + V_c \quad (4.24) \]

where \( \nu_k \) is the ordinary diffusion velocity and is given in the Curtiss-Hirschfelder [79]

\[ \nu_k = -D_{km} \frac{1}{X_k} \frac{dX_k}{dx} \quad (4.25) \]

where \( X_k \) is the mole fraction, and the mixture averaged diffusion coefficient \( D_{km} \) is given in terms of the binary diffusion coefficients \( D_{kj} \)

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

A non-zero thermal diffusion velocity is included only for the low molecular weight species \( H, H_2, \) and \( He. \)
4.2.3.3 Boundary Conditions

In the burner-stabilized flames, the appropriate boundary conditions could be assumed from the work of Curtiss and Hirschfelder [79]. The temperature and mass flux fractions \( \varepsilon_k = Y_k + \rho Y_k V_k A / \dot{M} \) are specified at the cold boundary, and vanishing gradients at the hot boundary. At the cold boundary, the mass flux fractions and the temperature is given by:

\[
\varepsilon_{k,1} - Y_{k,1} - \left( \frac{\rho Y_k V_k A}{M} \right) \left. \right|_{j=\frac{z}{2}} = 0 \tag{4.27}
\]
\[
T_1 - T_b = 0 \tag{4.28}
\]

where \( \varepsilon_{k,1} \) is the inlet reactant fraction of the \( k \)th species and \( T_b \) is the specified burner temperature. At the hot boundary it specifies that all gradients vanish:

\[
n_{k,1} - N_{k,1} - \left( \frac{\rho Y_k V_k A}{M} \right) \left. \right|_{j=\frac{z}{2}} = 0 \tag{4.29}
\]
\[
T_{j} - T_{j-1} = 0 \tag{4.30}
\]

4.2.4 Opposed-flow

For the Opposed-flow Flame, a steady-state solution is computed for axisymmetric diffusion flames between two opposing nozzles. The radial speed is assumed to vary linearly in the radial direction; the dimension of flow is reduced from three to one mathematically. Therefore the fluid properties are simplified to be functions of the axial distance only. Then the temperature, species and velocity profiles are predicted by the one-dimensional model. Kee et al. [84] initially developed the one-dimensional model to derive the Opposed-flow Flame Simulator.
for opposed-flow flames. Von Karman [85] studied the incompressible flows and developed the similarity solutions, which are used to reduce the three-dimensional stagnation flow. Finally, the study of Schlichting [86] makes the reduction more easily.

4.2.4.1 Planar Diffusion

Figure 4-2 shows that two nozzles are concentric linear directed towards each other in the planar geometry. Between the two nozzle, a two dimensional flow is produced by this structure with a stagnation line. When the fuel exists in one stream and oxidizer in the other stream, a diffusion flame is established. Usually the stagnation plane of the diffusion flame sit on sits on the oxidizer side, because the large air requirement for most fuels.

![Diagram of the planar opposed-flow diffusion flame](image.png)

Figure 4-2 The planar opposed-flow diffusion flame

At steady-state, conservation of mass in planar coordinates is given by
\[
\frac{\partial (\rho u)}{\partial x} + \frac{1}{\xi^{n-2}} \frac{\partial (\rho v \xi^{n-2})}{\partial \xi} = 0
\]  
(4.31)

Where \( u \) is the axial velocity, \( v \xi \) is the radial velocity and \( \rho \) is the mass density. von Karman [85] recognized that variables should be in the function of \( x \) only, it defines

\[
G(x) = \frac{-(\rho v \xi)}{\xi}
\]  
(4.32)

\[
F(x) = \frac{\rho u}{(n-1)}
\]  
(4.33)

where the continuity equation reduces to

\[
G(x) = \frac{dF(x)}{dx}
\]  
(4.34)

The perpendicular momentum equation is satisfied by the eigenvalue

\[
H = \frac{1}{\xi^{n-2}} \frac{\partial p}{\partial \xi} = \text{constant}
\]  
(4.35)

The perpendicular momentum equation is

\[
H - (n - 1) \frac{d}{dx} \left( \frac{FG}{\rho} \right) + \frac{nG^2}{\rho} + \frac{d}{dx} \left[ \mu \frac{d}{dx} \left( \frac{\xi}{\rho} \right) \right] = 0
\]  
(4.36)

Energy and species conservation are

\[
\rho u \frac{dT}{dx} - \frac{1}{c_p} \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \frac{\rho}{c_p} \sum_k c_{pk} V_k \frac{dT}{dx} + \frac{1}{c_p} \sum_k h_k \dot{\omega}_k + \frac{1}{c_p} \dot{Q}_{rad} = 0
\]  
(4.37)

where \( \dot{Q}_{rad} \) is the heat loss due to gas and particle radiation.
\[ \rho u \frac{dY_k}{dx} + \frac{d}{dx} (\rho Y_k V_k) - \dot{\omega}_k W_k = 0 \quad k = 1, \ldots, K \]  

where the diffusion velocities are given by the mixture averaged formulation

\[ V_k = -D_{km} \frac{dX_k}{dx} - \frac{U_k}{\rho Y_k T} \frac{d\rho}{dx} \]  

### 4.2.4.2 Emission Index

The total fuel-mass flow rate coming into the system can be obtained from fuel inlet properties as

\[ \dot{m}_{\text{fuel}} = \rho_F (u_F + V_{\text{fuel,F}}) Y_{\text{fuel,F}} = (\rho u Y_{\text{fuel}})_F \]  

where subscript \( F \) and \( \text{fuel} \) denote fuel boundary and all fuel species of the system, respectively. The fraction of fuel consumed at a given location \( x \) can be computed by the ratio of accumulated fuel consumption and total fuel mass flow rate as

\[ I_f(x) = -\frac{\int_0^x \dot{\omega}_{\text{fuel}}(l) W_{\text{fuel,l}} dl}{\dot{m}_{\text{fuel}}} \]  

and the fraction of unburned fuel is \( 1 - I_f(x) \). The emission index of a pollutant, for example NO, can be calculated as

\[ EI_{\text{NO}}(x) = \frac{\int_0^x \dot{\omega}_{\text{NO}}(l) W_{\text{NO,l}} dl}{I_f(x)} \times 1000 \quad [\text{gm} - \text{NO/kg} - \text{fuel}] \]  

The total NO emission index from the flame is

\[ EI_{\text{NO}}(L) = \frac{\int_0^L \dot{\omega}_{\text{NO}}(l) W_{\text{NO,l}} dl}{I_f(L)} \times 1000 \quad [\text{gm} - \text{NO/kg} - \text{fuel}] \]
4.2.5 Numerical Solution Methods

4.2.5.1 Starting Estimates

To begin the iteration, a starting estimation of the solution is required in one-dimensional steady-state reactor models. Figure 4-3 shows the general form of this estimate, which assumes that a reaction zone exist in the combustion. The reactants are specified at one end of this zone and the reactants vary from their unreacted states to the products that are found on the far-end of the flow domain. Short lived Intermediate species can be also identified and assumed to have a Gaussian profile. In this profile, that peak height is specified in the centre of the reaction zone and the width is assumed to be 1/10 of the peak value at the reaction zone edges.

![Diagram](image_url)

Figure 4-3 The general form of the starting estimate

4.2.5.2 Modified Damped Newton’s Method

Newton’s method determines a sequence of iterations or approximate solutions that approach the true solution. For the sake of notational ease, these approximate is call solution vectors. The objective is to find a vector that satisfies
\[ F(\phi) = 0 \] (4.44)

In our case the vector \( \phi \) is composed as follows

\[ \phi = (T_1, Y_{1,1}, ..., Y_{K,1}, \ldots, T_j, \ldots, Y_{k,j}, \ldots, \dot{M}_j, \ldots, T_j, Y_{1,j}, \ldots, Y_{K,j}, \dot{M}_j)^T \] (4.45)

Newton’s method produces a sequence \( \{\phi^{(n)}\} \) that converges to the solution of the nonlinear equations \( F(\phi) \). The purest form of the algorithm

\[ \phi^{(n+1)} = \phi^{(n)} - \left( \frac{\partial F}{\partial \phi} \right)^{-1} \phi^{(n)} \] (4.46)

### 4.3 Concluding Remark

In this chapter, it provides a broad overview of the relationships and formulations used in calculations of chemical property and source terms. It also provides brief derivations and explanations of the governing equations solved by premixed and diffusion models, as well as discussion of numerical solution techniques.

The governing differential equations are solved by the Premixed Flame Model based on the burner-stabilized flame and uses implicit finite difference and steady-state methods to define the flame dynamics. The steady and adiabatic one dimensional premixed laminar flame is studied by this model in CHAPTER 5. For the Opposed-flow Flame Model, a steady-state solution is computed for
axisymmetric diffusion flames between two opposing nozzles. The radial speed is assumed to vary linearly in the radial direction; the dimension of flow is reduced from three to one mathematically. Therefore the fluid properties are simplified to be functions of the axial distance only. This model is used to simulate laminar diffusion flame in CHAPTER 6.
CHAPTER 5 Numerical Study on the Premixed Laminar Flame

5.1 General

Previous chapter has presented details of the numerical method for calculation of laminar flame speed and flame structure of hydrocarbon – air mixtures. In this chapter, numerical study on the premixed laminar flame will be presented. Firstly, through comparing the calculation and literature measurement of laminar flame speed, numerical model and reaction mechanism are validated. In next section, the validated numerical model will be used in prediction of the effects of fuel dilution on the laminar flame.

5.2 Premixed Laminar Flame Model

In this chapter, predictions are performed by the Premixed Flame Model (CHEM KIN). As discussed in CHAPTER 4, the Premixed Flame Model based on the burner-stabilized flame is used to solve the governing equations using the steady-state methods. Flame temperature, which strongly affects the chemistry, is needed to be accurately measured to conclude the chemical kinetics. Temperature
profile is unknown in numerical simulation study; therefore model usually uses the energy conservation to determine the temperature profile with ignition of heat losses to the external environment, and then solves species transport equations.

5.2.1 Model Setup

The flame speeds of methane-air mixtures are calculated for the following conditions to study the impact of varying inputs of operating conditions such as pressure and temperature, stream properties such as concentrations:

1. Equivalence ratios are 0.6-1.5.
2. Unburned Gas Temperature is 298-615 K
3. Pressure is 1-10 atm
4. Flow rate is 40 cm/s
5. Fuel Fractions of Total Fuel Species are 100%-25% methane and 0%-75% ethane.

A total of 14 parameter-study cases were conducted to cover the range of operating conditions. The automatic estimation of the starting temperature profile was used to calculate the temperature profiles. It also used a mixture averaged formulation in determining the species ordinary diffusion coefficients and fluxes. Initial grid is based on the temperature profile estimate. The domain of 10 mm is specified for the grid. The relative gradient and curvature parameters for the grid are set to 0.1 and 0.5, and maximum number of grid points is set to 200. Absolute Tolerance and Relative Tolerance for the solver are set to 1.0E-9 and 0.0001. GRI-Mech 3.0 detailed mechanism for the combustion of small hydrocarbons is used.
for modelling premixed laminar flame. Full detail of this reaction mechanism, thermo chemical data and transport data, see the Appendix A.

5.3 Experimental Validation of the Numerical Model for the Laminar Flame Speed

The laminar flame speed of a perfectly one dimensional adiabatic flame is an important quantity to validate and optimize chemical reaction mechanisms. Therefore numerical model and reaction mechanism should be validated with laminar flame speed in the literature firstly, and then they can be used to simulate the one-dimensional adiabatic flame problems.

5.3.1 Laminar Flame Speed at Ambient Conditions

In the experimental work by de Gory [39] and Dirrenberger et al. [90], the adiabatic laminar flame speed of methane, ethane and propane as well as their mixtures were studied and measured in different of equivalence ratios, initial temperature and pressure. Among these data, one of the test results is satisfactory for the laminar flame model simulation. This particular set of data is therefore employed for comparison in the present study.
5.3.1.1 Experimental Arrangement

The stabilizing flat adiabatic flames are created using heat flux method to measure adiabatic flame speed. In the heat flux burner, certain parts of the burner was controlled by thermostat at constant temperature: cooling jacket at 20°C and heating jacket at 85°C, while temperature distribution is measured by thermocouples in the burner plate. The burner plate is 30 mm diameter. Mass Flow Controllers (MFCs) supplies a gas mixture flow, which becomes homogeneous before getting the reaction layer. If the flame speed remains lesser than about 50 cm/s, then the laser Doppler velocimetry (LDV) will investigate the velocity profiles above the burner [103].

Table 5-1 shows the summary of the fuel and oxidiser profiles studied at standard physical conditions. Cases measure the laminar flame speed of two hydrocarbons (methane and ethane) and their mixtures. Experiments were performed at room temperature, atmospheric pressure and using synthetic air (79% N₂ and 21% O₂).

Table 5-1 Summary of experimental cases studied at standard physical conditions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fuel (vol)</th>
<th>Oxidizer (vol)</th>
<th>T (K)</th>
<th>P (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 2</td>
<td>0</td>
<td>100%</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 3</td>
<td>75%</td>
<td>25%</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 4</td>
<td>50%</td>
<td>50%</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 5</td>
<td>25%</td>
<td>75%</td>
<td>21%</td>
<td>79%</td>
</tr>
</tbody>
</table>
5.3.1.2 Result and Discussion

In this section, the results of experiments, which were performed by de Goey [39], are used as the reference data to compare with the results of modelling. In the literatures, experiments use the heat flux method, which has been discussed as the prefer method to measure the flame speed accurately in Chapter 2.

Figure 5-1 presents the experimental and numerical laminar flame speed of methane–air mixture in function of the equivalence ratio at room temperature and atmospheric pressure. The laminar flame of methane-air mixture has a maximum flame speed of 37 cm/s for an equivalence ratio of 1.1, and would decrease as the mixture becoming rich or lean. The results obtained by the numerical method agree well with the experimental measurements from the literature, but here is a slight difference between measurements and prediction, when the mixture is lean or rich. This could be caused by that the real equivalent ratio may be affected by the entrainment of the ambient air in flat flames [104].

![Figure 5-1 Comparison between experimental (symbol) and predicted (solid line) laminar flame speed of methane-air mixture at 298 k and 1 atm [39]]
Comparing to methane, the laminar flame of ethane-air mixture has a higher maximum flame speed of 42 cm/s for an equivalence ratio of 1.1. The flame speed of ethane is higher than methane, because ethane has more C-H bonds and could release more heat, when it is burning. The flame of ethane is stabilized much easier than methane [90]. The results of experimental and numerical laminar flame speed of ethane-air mixture at room temperature and atmospheric pressure are plotted in the Figure 5-2. The predicted results are in good agreement with experimental measurements.

Figure 5-2 Comparison between experimental (symbol) and predicted (solid line) laminar flame speed of ethane-air mixture at 298 k and 1 atm [39]

As discussed in CHAPTER 1, the main composition of natural gas is methane with smaller amounts of heavier compounds such as ethane. Although, the study of pure composites has provided useful results, it is also needed to validate the methane–ethane mixtures, which are investigated and experiments performed by Dirrenbergeret al. [90], were performed at room temperature and atmospheric pressure. Figure 5-3 presents the laminar flame speed of methane (mole fraction 25%
to 75%-ethane mixture in range of the equivalence ratios from 0.7 to 1.5. Numerical results slightly over-predicted the laminar flame speed, compared with experimental data. These over-predictions are also seen in the validation of pure methane and ethane fuels, because GRI-Mech 3.0 mechanism was validated with the old measurements, which had higher values of laminar flame speed than the recent data. The agreement between the recent experimental data for methane and ethane and predicted results from GRI-Mech 3.0 mechanism indicates that this mechanism is able to predict accurate results for the laminar flame speed of methane-air and ethane-air.

Figure 5-3 Comparison between experimental (symbol) and predicted (lines) laminar flame velocity of methane with varies mole fraction of ethane at 1 atm and 298 K [90]
5.3.2 Laminar Flame Speed at Variable Temperature and Pressure

In the previous section, numerical model and reaction mechanism has been validated with laminar flame speed of methane and ethane at room temperature and atmospheric pressure. However combustion process is not only occurred at standard environment. In some cases the unburned gas preheated to reduce exhaust gas emission, or combustion performed at higher pressures to increase efficiency in the gas turbine. Therefore numerical model and mechanism should be validated in the elevated temperature and pressure.

5.3.2.1 Experimental Arrangement

A brief description of numerical modelling of the effects of temperature and pressure on laminar flame is described herein. More detailed information regarding the experimental setup can be referred in NASA [45] and Rozenchan [43]. NASA measured laminar flame speed with preheated reactants. The fuel and the air were metered, mixed, electrically preheated, and burned above a vertical brass tube. For methane, a 120-centimeter length of 15.7-millimetre-inside-diameter tubing was used. Temperatures were measured with iron-constantan thermocouples. The gas temperature at the burner port was periodically checked by locating an aspirating thermocouple over the centre of the port. The gas temperatures at the burner-tube inlet and at the port were maintained within 308 K of each other. Flame speeds were determined from the shadowgraphs by the total-area method, wherein the average normal flame speed is equal to the volume rate of flow of the unburned mixture divided by the surface area of the cone formed by the combustion.
Rozenchan [43] designed double–chamber to allow a demand of amount increase in the reasonable experimental pressure over single chamber. In this design, an inert mixture is filled into the outer chamber for two reasons. One reason is that during flame propagation, the pressure accumulation could be absorbed. The other one is that before the pressure accumulation becomes significant, the flame propagation could be determined. For the double-chamber, the dimension of inner vessel is 82.55 mm diameter × 127 mm length and outer chamber has 273.05 mm diameter × 304.8 mm length. In the experiment, the unburned gas temperature is 298 K and initial flame acceleration is minimized by using minimum ignition energy.

Table 5-2 shows the summary of the fuel and oxidiser profiles studied at elevated pressure and temperature. Cases measured the laminar flame speed of methane at that were performed at pressure 1 to 10 atm and temperature 298 to 615 K using synthetic air (79% N₂ and 21% O₂).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fuel (vol)</th>
<th>Oxidizer (vol)</th>
<th>T (K)</th>
<th>P (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₄</td>
<td>C₂H₆</td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>Case 6</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 7</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 8</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 9</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 10</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 11</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 12</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 13</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>Case 14</td>
<td>100%</td>
<td>0</td>
<td>21%</td>
<td>79%</td>
</tr>
</tbody>
</table>
5.3.1.1 Results and Discussion

Measured and predicted unstretched laminar flame speeds are plotted as function of fuel equivalence ratio, with pressure and temperature as parameters, in Figure 5-4 and Figure 5-5.

There is a good agreement between the measurements and predictions of unstretched laminar flame speed. Trend of laminar flame speed agrees well with the measurements; it decreases as the pressure rises, but increases as the temperature rises. However, predictions using the GRI-Mech 3.0 scheme seem to slightly overestimate laminar flame speed. The reason has been discussed in last section: GRI-Mech 3.0 mechanism was validated with old measurements, which has higher values of laminar flame speed. The errors of predicted results are about 5% to 10% and remain nevertheless acceptable. All these points confirm GRI-Mech scheme as a good compromise to predict laminar flame speeds at varies pressure and temperature despite a lack of experimental data to validate the scheme over a wider range of pressure and initial gas temperature.
Figure 5-4 Comparison between experimental (symbol) and predicted (solid line) Laminar Flame speed versus initial temperature at equivalence ratio =1 and atmospheric pressure [45]

Figure 5-5 Comparison between experimental (symbol) and predicted (Solid line) Laminar Flame speed versus initial pressure at equivalence ratio =1 and 298 K [43]
5.4 Sensitivity Analysis

In the previous section, the numerical model and reaction mechanism are validated with experimental laminar flame speed of methane and ethane flames at various initial temperatures and pressures. Predicted results agree well with the experimental measurements. In addition to continuation of numerical modelling, the sensitivity analysis, which are able to determine the effect of the chemical parameters, is needed in understanding a complex mechanism, since it indicates which parts of the mechanism are important for a given problem [105].

The number of chemical parameters to introduce in a flame computation with complex detailed chemistry (e.g. GRI-Mech 3.0) can be counted in hundreds. Therefore, for a given flame property, it is essential to know which of these parameters are really important. Figure 5-6 and Figure 5-7 show the most sensitive reactions for methane-air flame at various equivalence ratios and pressures. It sees that the two most important reactions in the combustion process are

\[ H + O_2 \rightarrow O + OH \]  \hspace{1cm} (5.1)
\[ CO + OH \rightarrow CO_2 + H \]  \hspace{1cm} (5.2)

Reaction paths analyses indicated the initial conditions (pressure and equivalence ratio) influence the main oxidation routes. Figure 5-6 shows that methane is mainly consumed by metathesis with \( OH \) at rich lean side

\[ CH_4 + OH = CH_3 + H_2O \]  \hspace{1cm} (5.3)
When the equivalence ratio increases, methane reaction with $H$ is becoming more important

$$CH_4 + H = CH_3 + H_2$$

(5.4)

The formation of $CH_3O$ in mixtures at high pressure via $CH_3 + HO_2$ is favoured. The concentration of $CH_4$ is sensitive to the kinetics of this reaction, particularly under high pressure conditions.

$$CH_3 + HO_2 = CH_3O + OH$$

(5.5)

The relative important of the above reactions depends strongly on the equivalence ratio. The comprehensive chemical mechanism for the oxidation of methane was studied by Hughes et al. [93]. Compared literature’s data with the results of the present simulations, it shows good agreement between the data and modelling results.
Figure 5-6 Normalized sensitivity on the flame speed of methane–air flame, (a) at 1 atm and equivalence ratio = 0.7, (b) at 1 atm and equivalence ratio = 1.3
Figure 5-7 Normalized sensitivity on the flame speed of methane–air flame, (a) at 1 atm and equivalence ratio = 1, (b) at 5 atm and equivalence ratio = 1.
5.5 Numerical simulation of Fuel Dilution in the Premixed Laminar Flame

5.5.1 Effects of Carbon Dioxide on the Oxidation of Methane

Yossefi et al. [108] studied the effects of carbon dioxide dilution on oxidation of methane and ethane, particularly on the production of OH and concluded that the chemical effect is important in the dilution process. Hainsworth et al. [109] studied the effect of replacing nitrogen by carbon dioxide in methane-air diffusion flames experimentally and computationally. They showed that as the carbon dioxide increase in the mixture, the concentration of OH and flame temperature both decrease. Konnov et al. [110], Liu et al. [111] and Han et al. [112] reported that the carbon dioxide dilution also decreases laminar flame speed.

To study effect of carbon dioxide dilution, a methane-air premixed flame with 0.29%, 0.3115% and 0.35% diluents (18.5% CO\textsubscript{2} and 81.5% N\textsubscript{2}) are simulated to predict the laminar flame speed, and compare results with experimental data [110, 112]. Figure 5-8 and Figure 5-9 clearly show that laminar flame speed decreases as the increasing carbon dioxide; although results show that model over predicts the laminar flame speed over all equivalence ratios and dilutions, error is quite small about $\pm 1 \text{ cm/s}$. 
5.5.2 Effects of Carbon Monoxide on the Oxidation of Methane

Scholte and Vaags [115] firstly studied the effects of carbon monoxide dilution on laminar flame speed of methane–air mixtures. They used “flame cone”
method, measure maximum flame speed as a function of carbon dioxide mole fraction in the fuel. This study concluded that the laminar flame speed gradually increases with the CO amount increasing. In the 1990s, it has been realized that “flame cone” method has its weak point, because flames were strained. Vaglelopolous [116] performed new experiment to study the flame speed using counterflow method. This method introduced more accurate and better measurements for laminar flame speed of CH₄– CO – Air mixtures. Ren et al. [117] studied the effect of carbon monoxide dilution on the NOₓ emission of Methane–air in strained laminar flames. Measurements showed that enrichment by carbon monoxide leads to small increase in the NOₓ formation. Recently, Konnov [118] uses heat flux method to study effects of carbon monoxide dilution on laminar flame speed and NOₓ formation in unstretched methane–air flames. In this method, an overall accuracy of the flame speed is estimated to be better than ±1 cm/s in the whole range of enrichment by carbon monoxide.

![Graph](image)

Figure 5-10 Predicted (solid lines) and experimental (symbol) laminar flame speed of CH₄-Air-CO flames versus equivalence ratio at 1 atm and 298 K [118]
Figure 5-10 shows the laminar flame speed of \( \text{CH}_4 - \text{CO} \) – air flames at room temperature and atmospheric pressure with different mole fraction of carbon monoxide in the fuel. The predicted results agree well with the Konnov measurements. Model slightly over-predicted the flame speed; it could because of the Konnov experiments correct the stretch effect to measure the laminar flame speed. Figure 5-11 shows the flame speed of methane-air as a function of carbon monoxide mole fraction. As increasing the mole fraction of carbon monoxide, flame propagation is accelerated in mixtures; according to the predicted results, it is more effective in fuel lean flames.

![Graph showing laminar flame speed vs % CO for CH4-air-CO flames](image)

Figure 5-11 Predicted (solid lines) and experimental (symbol) laminar flame speed of \( \text{CH}_4 \)-air-CO flames versus % CO diluted at stoichiometry, 1 atm and 298 K [118]

### 5.5.3 Effects of Hydrogen on the Oxidation Methane

As discussing in last section, Scholte and Vaafs [115] firstly performed the experiment to study the effects of hydrogen dilution on laminar flame speed of methane-air mixtures. Later Liu et al. [119] and Huang et al. [120] further studied
these effects in the CH$_4$-H$_2$-air flames and concluded that as the hydrogen fractions increase in the mixture, there is an increase in the flame speed. The potential of hydrogen diluted by hydrocarbon is studied by Law and kwon [121] to defeat explosion hazards. Experimental data shows that as adding a small amount of methane into hydrogen, the laminar flame speed could be reduced largely. Recently, Hu et al. [122] studies the combustion of CH$_4$-H$_2$-air flames at elevated temperature and pressures. Results show that the unstretched laminar flame speed increases, as the hydrogen fraction and unburned gas temperature rise, and decrease as the pressure increases.

Model based on the experiment performed by Coppens et al. [113], which studies the adiabatic flame speed and NO formation in CH$_4$– H$_2$– air flames, is used to predict dilution of H$_2$ in the methane-air flames. Figure 5-12 and Figure 5-13 shows the unstretched laminar flame speed versus and equivalence ratio and different mole fraction of hydrogen. Laminar flame speed is increased with the increase of mole fraction of Hydrogen, and increasing trend becomes more apparently at more fraction of hydrogen. As discussed, the increase of hydrogen fraction raises the concentration of radicals from the activation reaction region [123]. Hydrogen also has small specific heat and high fuel-air ratio. Thus, as increasing the hydrogen fraction, the mixture specific heat decreases with causing in the increase of reaction rate and adiabatic temperature and the reaction rate.
CHAPTER 5 Numerical Study on the Premixed Laminar Flame Model

Figure 5-12 Predicted (solid lines) and experimental (symbol) laminar flame speed of CH₄-Air-H₂ flames versus equivalence ratio at 1 atm and 298 K [113]

Figure 5-13 Predicted (solid lines) and experimental (symbol) laminar flame speed of CH₄-air-H₂ flames versus % H₂ diluted at stoichiometry, 1 atm and 298 K [113]
5.6 Concluding Remarks

A numerical study concerning Premixed Laminar Flame Model and GRI-Mech 3.0 mechanism for simulation of fuel dilution in the premixed laminar flame of methane-air flame were carried out and compared with experimental data.

Firstly, numerical model of combustion process and chemical mechanism are validated with experimental data of laminar premixed flame speed for methane, ethane and their mixtures at room temperature and atmospheric pressure. Comparison of laminar flame speed of methane – air mixture is also made at elevated pressures and temperatures. Although, numerical model slightly over predict the laminar flame speeds: about 5% errors, predicted results agree well with the experimental measurements.

Finally, numerical model is used to calculate the laminar flame speed of methane–air mixture, when it is diluted with exhaust gas (CO₂ and CO) and hydrogen, which helps to increases the reaction rate. Predicted results shows that the laminar flame speed increases as the portions of CO and H₂ diluted in the fuel rise, however it decreases as the portions of CO₂ diluted in the fuel rise; CO₂ would decrease the total chemical reaction rate. As a result, it can be concluded that the premixed flame model and GRI-Mech 3.0 scheme is optimum approximation order for simulating the effects of fuel dilution on the small hydrocarbon flames such as methane-air flame.
CHAPTER 6 Numerical Study on the Laminar Diffusion Flame Model

6.1 General

Previous chapter has presented details of validation of numerical model and GRI-Mech 3.0 mechanism with experimental laminar flame speeds, and prediction of the effects of fuel dilution on the laminar flame. In this chapter, numerical study on the diffusion laminar flame will be presented. Firstly, through comparing the prediction and measurements of laminar flame structure in the literature, numerical model and reaction mechanism are validated. In next section, the validated numerical model will be used in prediction of the effects of strain rate on the diffusion laminar flame. Finally, the laminar flamelets approach, which can be embedded in a turbulent flame, is discussed to model the complex turbulent combustion.

Turbulent combustion (building fire or internal combustion engine) includes unsteady and multidimensional flow fields, complex chemical and physical processes, and number of reacting species [131]. To ease the complex problem, researches have classified the turbulent combustion laminar flamelet system based on the chemical reaction and spatial and temporal scales of turbulence [131]. By considering the transient response and the chemical kinetics, an amount of studies have been focused on understanding diffusion flame behaviour exposed to the strain
rate [132]. The strained laminar flamelet approach is predicted by using detailed chemical mechanism for non-premixed combustion, and then can be embedded in a turbulent flame using statistical Probability Density Function (PDF) methods. The strained laminar flamelet approach has the advantage to merge the chemical mechanism into turbulent flames, and the pre-process the chemistry pre-processed to offer significant computational savings.

6.2 Laminar Diffusion Flame Model

In this chapter, predictions are performed by the Diffusion Flame Model. As discussed in CHAPTER 4. The geometry of planar counterflow is used by Diffusion Flame Model to produce a two-dimensional planar flow field is shown in Figure 6-1. The diffusion Flame Model is based on a finite field including the eigenvalue in the equation solutions. The distance $L$ between the two nozzles is needed to be specified to determine the strain rate from the speed profile $u$. The global strain rate given by:

$$\text{Strain Rate} = 2 \times \frac{\text{Velocity}}{\text{Separation distance}} = 2 \times \frac{u}{L}$$
6.2.1 **Diffusion Flame Model Setup**

The flame structure of methane-air mixtures are calculated for the following conditions to validate the diffusion flame model and reaction mechanism.

1. Equivalence ratio is 1
2. Unburned Gas Temperature is 298 K
3. Pressure is 1 atm
4. Strain rate is 42 s⁻¹

The model solves the gas energy equation and uses plateau profile for initial guess to calculate the temperature profiles. It also uses a mixture averaged formulation in determining the species ordinary diffusion coefficients and fluxes. Initial grid is based on the temperature profile estimate. The model uses adaptive gridding; the spacing of the 14 initial grid points has been specified. The ending
axial position and estimated centre position are set to 13 mm and 6.5 mm according to the study case. The relative gradient and curvature parameters for the grid are set to 0.5 and 0.5, and maximum number of grid points is set to 100. The gas inlet velocities (25.5 cm/s) are set for both fuel and oxidizer. Absolute Tolerance and Relative Tolerance for the solver are set to 1.0E-6 and 0.001.

GRI-Mech 3.0 detailed mechanism for the combustion of small hydrocarbons is used for modelling laminar diffusion flame. One should be known is the Appel mechanism is used to numerical study the strain rate effect on the soot formation, because the GRI-Mech 3.0 does not describe the soot of natural gas combustion chemistry. In the Appel mechanism, the description of the small hydrocarbon (methane and ethane) reaction is founded on the GRI-Mech 1.2 [100], which is also the used in the GRI-Mech 3.0 for the description of C₁ combustion chemistry.

6.3 Experimental Validation of the Numerical Model for the Diffusion Flame structure

6.3.1 Experimental Arrangement

Experimental data measured by Sung et al. [53] is used to validate the numerical model. In this experiment, the counterflow is developed between the two convergent nozzles burners, which has 14 mm exit diameters and distance between these nozzles is 13 mm. The fuel and oxidizer flows consist of 23% methane / 77%
nitrogen and 23% oxygen / 77% nitrogen by volume. The experimental inlet velocity of fuel and oxidizer flows are 25.5 cm/s. Species concentrations and flame temperature are measured by Spontaneous Raman spectroscopy (SRS). Table 5-1 shows the summary of the fuel and oxidiser profiles studied at standard physical conditions. Case1 measures the diffusion flame structure of methane, and experiments were performed at 298 K, at atmospheric pressure.

Table 6-1 Summary of experimental cases studied at standard physical conditions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fuel (vol)</th>
<th>Oxidizer (vol)</th>
<th>T (K)</th>
<th>P (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₄</td>
<td>N₂</td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>Case 1</td>
<td>23%</td>
<td>77%</td>
<td>23%</td>
<td>77%</td>
</tr>
</tbody>
</table>

6.3.2 Results and Discussion

Figure 6-2 shows the experimental [53] and predicted temperature profile for heat losses [92]. There profiles are used in the numerical prediction of the species concentration profiles to estimate the influence of the uncertainties on chemical species profiles. The predicted mole fraction of the major species at stoichiometric ratio, atmosphere pressure and room temperature are shown in Figure 6-3. One can see that the predicted concentration profiles of reactants and products (methane, oxygen, carbon dioxide and water) are in good agreement with the experimental data.
Figure 6-2 Experimental (symbols) and computed (solid lines) temperature profiles in the diffusion methane – air flame at stoichiometric ratio, 1 atm and 298 K [53]

Figure 6-3 Experimental (symbols) and computed (solid lines) concentration profiles of CO₂, CH₄, O₂, H₂O and CO in the diffusion methane–air flame at stoichiometric ratio, 1 atm and 298 K [53]

Figure 6-4 shows the experimental and predicted concentration profiles of intermediate species (H, OH and CH₂O). Comparing to experimental results, mole fractions of H, OH and CH₂O in the burnt gases are under-computed. However the errors on mole fraction of these species are still reasonable and acceptable;
experimental data are well predicted by the numerical model. As discussed in last chapter, sensitivity analysis shows that methane is mainly consumed with H and OH.

Figure 6-4 Experimental (symbols) and computed (solid lines) concentration profiles of H, OH and CH$_2$O in the diffusion methane–air flame at stoichiometric ratio, 1 atm and 298 K [53]

### 6.4 Numerical Simulation of the Stretched Diffusion Flame

#### 6.4.1 Strain Rate Effect on the Diffusion Flame Structure

Strain rate could affect the diffusion flame structure significantly. Sung et al. [54] studied the diffusion flame structure response to strain rates $a = 42, 56$ and 90 s$^{-1}$; results showed that as the strain rate increase, the diffusion flame structure becomes thinner and its thermal thickness approximately proportional to one over square root $a$. Later, Cheng et al. [114] performed the studies of the oxygen-enhanced methane diffusion flames at higher strain rates $a = 60, 130$ and 168
Because increasing strain rate, the reactant residence time is shorter than the chemical reaction time and incomplete reaction will cause the flame to extinguish. Therefore, for higher strain rate, oxygen-enhanced flame is developed to find the effects on the diffusion flame structure. Figure 6-5 shows the species profiles for methane-air diffusion flame at different strain rates (42, 56 and 90 s\(^{-1}\)). Numerical model is based on the study performed by Sung et al. [48]; fuel consisted of 23% methane in nitrogen and oxidizer consisted of 23% oxygen in nitrogen too. The simulation results of major species agree well with the experimental data.

Figure 6-5 Experimental (solid lines) and predicted (symbols) major species profiles in the coordinates, at various strain rate \(a\). (a) \(a = 42\) s\(^{-1}\), (b) \(a = 56\) s\(^{-1}\), and (c) \(a = 90\) s\(^{-1}\) [54]
Figure 6-6 shows the temperature profiles for different strain rates, there is a good agreement between experimental data and predictions. As we can see, with the strain rate increasing, the peak temperature slightly drops from 1684 K to 1592 K, and the flame zone becomes narrower; flame thickness decreases about 2 mm. Another thing should be mentioned is that in the non-premixed flame, the rate of diffusion of the fuel into the oxidizer controls the rate of combustion, therefore the specific reaction mechanism should not be very important except very near extinction [114].

![Temperature profiles](image)

Figure 6-6 Experimental (lines) and predicted (symbols) Temperature profiles in the coordinates, at various strain rate \( a \). (a) \( a = 42 \) s\(^{-1}\), (b) \( a = 56 \) s\(^{-1}\), and (c) \( a = 90 \) s\(^{-1}\) [54].

### 6.4.2 Strain Rate Effect on the Soot Formation

In laminar diffusion flames, soot formation is a more fundamental study, especially for the case of building fire, where fuel-air mixture reacts in non-homogeneous conditions. Grosschmidt et al. [124] concluded that the strain rate
is an important parameter, which affects the soot formation in the diffusion flame. Kent and Bastin [125] performed early study on the simple turbulent jet flame and concluded that as the characteristic strain rate increases, the average soot volume fraction decreases, and the decreasing rate is lower at high strain rate. Later, Qamar et al. [126] concluded that there is a negative relationship between global strain rate and total volume fraction of soot. Experimental studies of steady counter flow diffusion flame performed by Decroix and Roberts [127] confirm that as increasing the strain rate, soot volume fraction and the thickness of soot zone decrease. Recently, Yamamoto [128] studies the effect of strain rate on soot formation in acetylene diffusion flames. Results show that strain rate does not significantly affect the major species concentration profiles in flames, but soot is very strongly influenced by strain rate.

![Graph](image)

Figure 6-7 Maximum mole fraction of soot in a function of the strain rate for ethylene flame
Figure 6-7 and Figure 6-8 show maximum volume and mole fraction profiles of total soot computed for different strain rates. The numerical results confirm a global sensitivity of the total amount of soot to the strain rate; as the strain rate increase, both the maximum volume and mass fraction of soot formation decrease and decreasing rate become significant after higher strain rate 70 s\(^{-1}\).

### 6.4.3 Strain Rate Effect on the NO Formation

In laminar diffusion flames, NO formation is another more fundamental studies to control and reduce pollutant emissions from transportation source. Sanders et al. [129] developed the laminar flamelet model for predictions of NO\(_x\) emissions from the turbulent hydrogen jet diffusion flames. The study concluded that there was a clear negative relationship between the strain rate and NO emission, because thermal NO is formed by oxidation of nitrogen in air and requires sufficient temperature and time to produce NO [128].
Figure 6-9 shows mass fraction profiles of NO emission predicted for different strain rates. In the reaction zone, the residence time of species is affected by the strain rate, specify for the slow reactions such as the ones associated with the thermal NO production mechanism, which have a much greater sensitivity to this parameter [130]. As the increasing the strain rate, the residence time become shorter and there is an increasing transport of fuel and oxidizer into the flame, which provides more fuel and oxidizer in the flame and results in an initial increase in the mass fractions of NO. When the strain rate keeps increasing, the transport of fuel and oxidizer becomes more important and begins to lower the NO formation.

Figure 6-9 Mass fraction profiles of predicted NO emission versus strain rate
6.5 The Strained Laminar Flamelet Approach

Recently, the concept of Large Eddy Simulation (LES) in turbulence modelling emerged in computational fluid dynamics. Certainly, researchers in fire modelling also started to employ the concept in their field models such as building fire simulation. In the LES, statistical ensemble of laminar diffusion flamelets approach is assumed to exist to solve the flame problem [134].

In order to predict non-equilibrium flame, the state relationships need to be modified by the consideration of the strain rate and the strained laminar flamelet approach. The approach is based on sub grid modelling for turbulent reacting flows developed by Cook and Riley [135] for non-premixed turbulent flames. This method accounts for finite-rate chemistry by invoking the laminar flamelet approximation and applies the Large Eddy Probability Density Function of a mixture fraction. By assuming that mixing and reaction occur in local thin regions of steady, one-dimensional, laminar counterflow flames, the instantaneous mixture fraction value can be represented by a probability density function. Due to its turbulence nature, the mixture fraction fluctuates around the mean value with respect to time.

The mean mass fraction of fuel, oxidant, products and intermediate chemical species are calculated by an assumed form of Beta function PDF and two additional scalar variables: mixture fraction $Z$ and its variance $Z'$. The Beta function PDF is calculated by the following equations which are in terms of $Z$ and $Z'$:

$$P(f) = \frac{Z^{a-1}(1-Z)^{b-1}}{\int_0^1 Z^{a-1}(1-Z)^{b-1}dz}$$  \hspace{1cm} (6.1)
where

\[ \alpha = Z \left[ \frac{Z(1-Z)}{Z'} - 1 \right] \] (6.2)

\[ \beta = (1 - Z) \left[ \frac{Z(1-Z)}{Z'} - 1 \right] \] (6.3)

By calculating the mean and variance of the mixture fraction (i.e. \( Z \) and \( Z' \)), the shape of the Beta function PDF can be obtained. With the shape of the PDF, the mean mass fraction of the chemical species (i.e. the expected value of the chemical species) which participate in the combustion processes can be calculated by the PDF convolution integral over the instantaneous mass fraction value of the chemical species in the mixture fraction space:

\[ \bar{Y}_i = \int_0^1 Y_i(f) P(f) \, df \] (6.4)

where \( Y_i(f) \) is the instantaneous mass fraction of the chemical species \( i \) in the mixture fraction space.

Based on the mechanism, a flamelet library with a range of scalar dissipation is construction using the commercial chemistry simulation package - CHEMKIN. The main role of a SGS reaction model for turbulent non-premixed combustion is designed to incorporate the effect of subgrid fluctuations in the thermo-chemical variables on the filtered chemical source term. On the basis of the mixture fraction-based approach, all the species mass fractions can be taken to be functions of only the mixture fraction. Using this assumption, Bilger [142] derived the expression for the rate of reaction for the \( i \)th species, which can also be found in Kuo
The instantaneous heat release rate is determined for $N$ species from Eq. (6.6).

\[
\omega_i = -\frac{1}{2} \rho \chi \frac{d^2 Y_i}{dz^2} \quad (6.5)
\]

where $\chi$ is the instantaneous scalar dissipation

\[
\omega_T = -\sum_{i=1}^{N} h_{f_i}^{o} \omega_i \quad (6.6)
\]

where $h_{f_i}^{o}$ is the $i$th species standard heat of formation

where $\rho$, $Y_i$ and $Z$ are the density of air, mass fraction of $i$th species and mixture fraction respectively. In LES, the flame is typically not spatially resolved by the computational grid. It is assumed that at the subgrid level there exists a statistical ensemble of laminar diffusion flamelets each satisfying universal state relationships. Under near-equilibrium conditions, the state relationships could be represented such as those of equilibrium chemistry assumption or experimental state relationships established by Sivathanu and Faeth [144]. In order to predict highly non-equilibrium flame events such as lift-off or extinction, the state relationships need to be modified by the consideration of the scalar dissipation and to distinguish between burning and extinguished flamelets – the strained laminar flamelet approach. More details regarding the SGS reaction model can be found in Cheung and Yeoh [18].

### 6.5.1 Experimental Arrangement

Experimental measurements are based on study of Cheung and Yeoh [18], the finite volume method is employed to discrete the above filtered governing equations on a collocated gird. Second-order central differencing is adopted for all
spatial derivatives approximations. The advancement of the solution in time is achieved numerically by using the predictor-corrector approach. Numerical simulation was conducted of a 1-m diameter methane pool fire experiment of Tieszen et al. [145]. A cubic computational domain of 3 m length was employed for the simulation. A methane fuelled burner with 1m diameter was centrally placed on the floor level of the domain. A methane inlet velocity of 9.7 cm/s was specified at the burner corresponding to a fire of 2.07 MW heat release rate measured in the experiment. For the heat release considered in this investigation, the characteristic length of the pool fire is approximately of the order of 1.3m and thus a non-uniform Cartesian mesh of 96$^3$ control volumes was generated within the domain. Finer grid cells with the minimum spacing of 1.4 cm were generated above the burner to better capture all the finer-scale features of the vortical flame structure. The traction-free boundary condition was employed for all lateral boundaries. For the top boundary, a zero gradient condition was imposed for all the transport variables. To prevent flow entering the domain from its top, which might incur numerical instabilities; velocities with negative values were forced to zero.

6.5.2 Results and Discussion

6.5.2.1 Flamelet library

Firstly, flame extinction should be considered, because it is critical combustion performance factor in low emissions combustor, burners, rockets and many other combustion devices. Determination of strain rate at extinction is also a critical point in the strained laminar flamelet approach. Extinction limits of diffusion flame are affected by many factors, such as of unburned gas temperature, fuel and
oxygen dilution in the mixture, and pressure. According to Puri and Seshadri [133], for a methane diffusion flame with mass fraction of fuel equals to one and mass fraction of oxygen equals 0.23 (Stoichiometric mixture fraction $Z_{st} = 0.0544$) at 300 K and 1 atm, the strain rate at extinction equals 271 s$^{-1}$.

By using laminar diffusion model and GRI-Mech 3.0 Mechanism, the concentration profiles for the chemical species are predicted, and then mean mass fractions of these species are calculated by an assumed form of Beta function PDF. The ranges of mixture fraction $Z$ and its variance $Z$ are 0-1 and 0-0.25. Figure 6-10 to 6-13 show the calculated instantaneous mass fraction of the main chemical species (CH$_4$, O$_2$, CO$_2$, and H$_2$O) in the function of mean and variance of the mixture fraction for the various strain rate $a$ (0, 100, 200, 280 s$^{-1}$).
Figure 6-10 Calculated instantaneous mass fraction of CH₄ in the function of mean and mean and variance of the mixture fraction for the various strain rate $a$. (a) $a = 0$, (b) $a = 100 \text{ s}^{-1}$, (c) $a = 200 \text{ s}^{-1}$ and (d) $a = 280 \text{ s}^{-1}$ (near extinction)
Figure 6-11 Calculated instantaneous mass fraction of O$_2$ in the function of mean and mean and variance of the mixture fraction for the various strain rate $a$. (a) $a = 0$, (b) $a = 100$ s$^{-1}$, (c) $a = 200$ s$^{-1}$ and (d) $a = 280$ s$^{-1}$ (near extinction)
Figure 6-12 Calculated instantaneous mass fraction of CO$_2$ in the function of mean and mean and variance of the mixture fraction for the various strain rate $a$. (a) $a = 0$, (b) $a = 100$ $\text{s}^{-1}$, (c) $a = 200$ $\text{s}^{-1}$ and (d) $a = 280$ $\text{s}^{-1}$ (near extinction)
Figure 6-13 Calculated instantaneous mass fraction of $\text{H}_2\text{O}$ in the function of mean and mean and variance of the mixture fraction for the various strain rate $a$. (a) $a = 0$, (b) $a = 100 \text{ s}^{-1}$, (c) $a = 200 \text{ s}^{-1}$ and (d) $a = 280 \text{ s}^{-1}$ (near extinction)
6.5.2.2 Velocity distribution

Based on the laminar flamelet approach, a LES model of a large-scale buoyant pool fire coupled with detailed chemical kinetics has been developed. A quasi-steady state solution was obtained when the physical time arrived at 30s. Time-averaged field quantities were then extracted by performing time-weighted averaging calculation over 8s of instantaneous solutions. Figure 6-14, where time-averaged horizontal and vertical velocity contour plots were compared with measured results. In general, the predicted time-averaged velocity contours are in good agreement with the measurements. As depicted, due to air entrainment, horizontal velocities in both directions meet at the centre fire bed; forming two high velocity regions at the lower level. In between these two regions the horizontal velocity component is nearly zero; appearing as a gap in the figure.

In comparison to the measurement, the predicted gap between two velocity regions has been slightly over-predicted. Such error could be attributed to the insufficient grid resolution for LES models to resolve the microscopic baroclinic vorticity generation near the burner surface. On the other hand, compared to our previous study (Cheung and Yeoh [18]), noticeable improvements were found in the exiting numerical result. As single step chemistry and same numerical mesh were adopted in previous study, this shows that the inclusion of detailed chemistry resulted in considerable improvement in capturing the non-equilibrium combustion processes; especially near the fire bed where fuel rich conditions were likely.
Figure 6-14 Comparison of time-averaged velocity component contours captured from PIV measurement of Tieszen et al. [145] (left) and present LES model (right) at the centre-plane of the fire: (a) U velocity (horizontal) and (b) V velocity (vertical)
6.5.2.3 Instantaneous temperature and velocity distribution

Figure 6-15 shows the instantaneous velocity field at the centre plane of the fire plume captured by the PIV measurement of Tieszen et al. [145] and the present LES model with detailed chemical kinetics. The three sequential PIV results on the left column clearly illustrate the relationship between large vortical structures (as pointed in the figure) and the puffing cycle. At the start of the cycle, turbulent eddies were firstly stemmed from the base of the fire which has been caused by baroclinic vorticity generation. Owing to the amalgamation of eddies and buoyancy forces, the size of vortical structures continuously increased and accelerated in vertical direction until it has been advected out of the image. A broad overview of the figure suggested that the predicted instantaneous velocity fields were in excellent agreement with the PIV measurements.

Velocity vectors of predicted results also exhibited similar behaviour distribution to the experimental data. Special attention was paid to the simulated vortical structures at both sides of the fire. As depicted in the figure, the vortical structures were successfully captured by the present model. From the start to the end of puffing cycle, the simulated vortical structures were created at the fire base and continuously developed in size and convected upward away through the top of plot. The above development of the vortices was clearly aligned with the observations of PIV measurements. Vortex locations of the numerical results were also comparable to the measurement.
Figure 6-15 Three instantaneous temperature and velocity field at the centre plane of the fire plume captured by PIV measurement of Tieszen et al. [145] (left) and the present LES model (right): (top) start; (middle) 1/4 and (bottom) 2/4 of puffing cycle.
6.6 Concluding Remarks

A numerical study concerning Laminar Diffusion Flame Model and GRI-Mech 3.0 mechanism for simulation of fuel dilution in the counterflow laminar flame of methane-air flame were carried out and compared with experimental data.

Firstly, numerical model of combustion process and chemical mechanism are validated through comparing experimental data of diffusion flame structure with numerical results for methane–air mixtures. Comparison of experimental and predicted results focuses on the concentration profiles of main species (CH$_4$, O$_2$, CO$_2$, H$_2$O and CO) in the diffusion methane – air flame at stoichiometric ratio, atmosphere pressure and room temperature. Comparison of the predicted intermediate species (H and OH), which affect the reaction rate mostly, and the experimental data is also performed; there is a good agreement between predicted results and experimental measurements.

Validated model and chemical mechanism are used to simulate the effects of strain rate on the various properties of diffusion flame such as flame structure, soot, and NO formation. Results show that as the strain rate increasing, the diffusion flame structure becomes thinner and thickness is proportional to one over square root strain rate and the total soot volume fraction decreases. However NO formation would increase firstly due to more fuel and oxidizer transport. As the strain rate increasing continually, residence time is decreased and there is then a decrease in mass fraction of NO. Finally, laminar diffusion flamelet approach is introduced to predict non-equilibrium flame, and the state relationships are modified by the consideration
of the strain rate. Results are applied by the Large Eddy Probability Density Function of and used to investigate the influence of chemical kinetics on the vortical structures of fire.
CHAPTER 7 Conclusions and Recommendations

7.1 Conclusions

At Present, combustion as the oldest technology of mankind has provided about 90% of worldwide energy support. To better understand its complex embedded chemo-physical behaviour, numerical models and reaction mechanism for solving its chemo-physical behaviour has been introduced to simulate several combustion problems.

In CHAPTER 2, laminar flame speed and structure as the important parameters in the determination of the propagation and stabilization of premixed and diffusion flames are reviewed by theoretical and experimental literatures. Experimental measurements of laminar flame speed of methane and ethane had been presented at standard and elevated pressure and temperature over wide range of fuel-air equivalence ratio, and laminar flame structure of premixed and diffusion flames are also presented.

In CHAPTER 3, a number of chemical mechanisms (single step, reduced and detailed mechanisms) is introduced and compared to simulate the combustion model of methane. The advantage and limitation of each kind of the mechanism is also
discussed. Finally, four detailed mechanism are introduced and compared with each other to, and GRI-Mech3.0 developed by the Smith et al. [67], is chosen in the numerical model to simulate the laminar flame of methane-air mixture. In modelling of the hydrocarbon kinetics, analyses of reaction mechanisms also help us to understand the importance of the reactions.

In CHAPTER 4, CHEMKIN software is introduced to perform the simulation of complex chemical reactions. Methods of the calculations of thermodynamic, chemical rate, species transport properties and chemical equilibrium are described in detailed mathematical equations, which are used to model combustion processes.

In CHAPTER 5, premixed flame model of combustion process and GRI-Mech 3.0 mechanism are validated through comparing experimental data of laminar premixed flame speed with numerical results for methane, ethane and their mixtures. Comparison of laminar flame speed of methane – air mixture is also made at elevated pressures and temperatures. Finally, numerical model is used to calculate the laminar flame speed of methane – air mixture, when it is diluted with exhaust gas (CO₂ and CO) and hydrogen, which helps to increases the reaction rate. Predicted results shows that the laminar flame speed increases as the portions of CO and H₂ diluted in the fuel rise, however it decreases as the portions of CO₂ diluted in the fuel rise; CO₂ would decrease the total chemical reaction rate.

In CHAPTER 6, opposed flow model of combustion process and chemical mechanism are validated through comparing experimental data of diffusion flame structure with numerical results for methane – air mixtures. Validated model and
chemical mechanism are used to simulate the effects of strain rate on the various properties of diffusion flame such as flame structure, soot formation and extinction. Results show that as the strain rate increasing, the diffusion flame structure becomes thinner and thermal thickness is proportional to one over square root strain rate and the total soot volume fraction decreases. However NO formation would increase firstly due to more fuel and oxidizer transport. As the strain rate increasing continually, residence time is decreased and there is then a decrease in mass fraction of NO. Finally, laminar diffusion flamelet approach is introduced. It is used to investigate the influence of chemical kinetics on the vortical structures of flame.

7.2 Limitations of the Developed Numerical Model

While modelling the natural gas combustion for the present study, a number of assumptions and limitation had been incorporated. This section lists out the limitations the numerical model and reaction mechanism.

First, as mentioned in the previous section, both premixed and opposed flow laminar flame models solve the gas energy equation to calculate the temperature profiles and use a mixture averaged formulation in determining the species ordinary diffusion coefficients and fluxes. Although by using mixture averaged formulation for determining species ordinary diffusion coefficients and fluxes, the simulation could be usually running faster and often easier to converge, it is less accurate to predict the results such as laminar flame speed and structure.
Second, GRI-Mech 3.0 mechanism had been used in the present study, the predicted results agree well with experimental measurements before 2000. However, recent experimental method such heat flux methods measure more accurate heat loss, and then get lower laminar flame speed comparing with older methods. Readers attempting to use the GRI-Mech 3.0 mechanism in simulating laminar flame problems should beware that the results of laminar flame speed are higher than recent experimental data.

### 7.3 Suggestion for Further Works

This research incorporated all the considerations of which are involved in natural gas combustion in the calculation. Although comprehensive considerations have been taken into account, various approaches could be followed to extend and enhance the content of this research work.

#### 7.3.1 Detailed Reaction Mechanism Consideration

In the last few years, reaction mechanism for elementary reactions was developed from the experimental results and validated with old experiments. Because of development of new experimental methods with considering heat loss, measurements have become more accurate and are slightly different from old experimental data. This indicates that the chemistry of oxidation of small
hydrocarbon fuel such as methane and ethane has not yet been studied well, and more work is needed to experimentally and theoretically investigate the elementary reactions. Computed results with optimized detailed mechanisms should be compared with new reliable bulk experimental data to achieve an advanced predictable description of the oxidation of small hydrocarbon fuels.

7.3.2 Applying Multicomponent Technique in Adiabatic Temperature Modelling

The multicomponent transport technique using the method developed by Dixon-Lewis [84] could be applied in both premixed and diffusion flame models, instead of the mixture-averaged technique. The multicomponent technique solves the equations of the species concentration, binary diffusion coefficients, molecular and thermodynamic properties to compute the coefficients of diffusion and thermal conductivities. By applying the multicomponent technique, the accuracy of computed results could be improved in the numerical model. However the computation time will also increase significantly.

7.3.3 Extending the Modelling to Three-Dimension

Although CHEMKIN is extremely useful to solve the chemical reacting problem, it has one limitation that is inability to extend analyses beyond the idealized
one-dimensional problems. One solution to this limitation would be to adapt the acknowledged chemistry solution methodology to a CFD code coupled with convection and diffusive process, buoyancy and entrainment induced fluid motion, turbulence mixing of scalar, soot formation and radiation heat transfer [135]. First step of this process has been discussed in CHAPTER 6, which is laminar diffusion flamelet approach. It could be used to investigate the influence of chemical kinetics on the vortical structures of fire.
REFERENCES


REFERENCES


REFERENCES


Appendix I

! GRI-Mech Version 3.0 7/30/99 CHEMKIN-II format
! See README30 file at anonymous FTP site unix.sri.com, directory gri;
! Worldwide Web home page http://www.me.berkeley.edu/gri_mech/ or
! Through http://www.gri.org, under ‘Basic Research’,
! For additional information, contacts, and disclaimer

ELEMENTS
O H C N AR
END

SPECIES
H2   H   0   02   OH   H2O   H2O2  H2O2
C    CH  CH2  CH2(S) CH3  CH4  CO  CO2
HCN  CH20 CH2OH CH30  CH3OH C2H  C2H2  C2H3
C2H4 C2H5 C2H6 HCO  CH2O  CH2OH HCOH  N   NH
NH2  NH3  NNH  NO  N2O  N2  N2

END

! THERMO

! Insert GRI-Mech thermodynamics here or use in default file

REACTI0NS
20+M<=>02+M  1.200E+17  -1.000  .00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ C0/ 1.75/ C02/ 3.60/ C2H6/ 3.00/ AR/ .83/
O+H+M<=>OH+M  5.000E+17  -1.000  .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ C02/2.00/ C2H6/3.00/ AR/ .70/
O+H2<=>H+OH  3.870E+04  2.700  6260.00
O+H2O<=>OH+O2  2.000E+13  .000  .00
O+H2O2<=>OH+H2O  9.630E+06  2.000  4000.00
O+CH<=>H+CO  5.700E+13  .000  .00
O+CH2<=>H+HCO  8.000E+13  .000  .00
O+CH2(S)<=>H2+CO  1.500E+13  .000  .00
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponential Factor</th>
<th>Temperature (K)</th>
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<tr>
<td>( O + CH_2(S) \leftrightarrow H + HCO )</td>
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<tr>
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<td>K</td>
<td>TROE</td>
<td>TROE Low/</td>
</tr>
<tr>
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<td>$H + OH + M &lt;=&gt; H_2O + M$</td>
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<td>Pre-exponential Factor</td>
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<tr>
<td>--------------------------------------------------------------</td>
<td>---------------</td>
<td>------------------------</td>
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<tr>
<td>$H + CH_2OH \leftrightarrow CH_2(S) + H_2O$</td>
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<tr>
<td>$H + CH_3O(\text{M}) \leftrightarrow CH_3OH(\text{M})$</td>
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<td>$H + CH_3O \leftrightarrow OH + CH_3$</td>
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<tr>
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<tr>
<td>$H + CH_3O \leftrightarrow CH_2(S) + H_2O$</td>
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<td>Reaction</td>
<td>Rate Constant</td>
<td>Preexponential Factor</td>
<td>Temperature</td>
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<tr>
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<tr>
<td>$H + \text{HCCOH} \rightarrow H + \text{CH}_2\text{CO}$</td>
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<td>$H_2/2.00 / H_2O/6.00 / CH_4/2.00 / CO/1.50 / CO_2/2.00 / C_2H_6/3.00 / AR/ 0.70$</td>
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<td>$\text{OH} + H_2 \rightarrow H + \text{H}_2\text{O}$</td>
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<td>$2OH (+M) \rightarrow \text{H}_2\text{O}_2 (+M)$</td>
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<td>$\text{TROE} / 0.7346$</td>
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<td>$OH + CH_3 \rightarrow CH_2 + \text{H}_2\text{O}$</td>
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<td>$OH + CH_3 \rightarrow CH_2(S) + \text{H}_2\text{O}$</td>
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<td>$OH + CH_2O \rightarrow HCO + \text{H}_2\text{O}$</td>
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<td>$OH + CH_3O \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{O}$</td>
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**Appendix**
<table>
<thead>
<tr>
<th>Reaction</th>
<th>K</th>
<th>T (K)</th>
<th>ΔH (kJ/mol)</th>
</tr>
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**LOW / 2.690E+28 -3.740 1936.00 /**

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**Appendix**

LOW / 2.690E+33 -5.110 7095.00 /

TROE/ .5907 275.00 1226.00 5185.00 /

H2/2.00/ H20/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

LOW / 1.880E+38 -6.360 5040.00 /

TROE/ .6027 208.00 3922.00 10180.0 /

H2/2.00/ H20/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

LOW / 3.400E+41 -7.030 2762.00 /

TROE/ .6190 73.20 1180.00 9999.00 /

H2/2.00/ H20/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

LOW / 13.45E+12 .000 400.00
Appendix

CH2OH + O2 ⇌ HO2 + CH2O  \[1.800 \times 10^{13}\]  0.0  900.00
CH3O + O2 ⇌ HO2 + CH2O  \[4.280 \times 10^{-13}\]  7.600  -3530.00
C2H + H2 ⇌ C2H2 + CO  \[1.000 \times 10^{13}\]  0.0  -755.00
C2H + H2 ⇌ C2H2 + CO  \[5.680 \times 10^{10}\]  1.390  1993.00
C2H + O2 ⇌ HCO + CO  \[1.000 \times 10^{13}\]  0.0  -755.00
C2H3 + O2 ⇌ HCO + CH2O  \[4.580 \times 10^{16}\]  1.390  1015.00
C2H4(+M) ⇌ H2 + C2H2(+M)  \[8.000 \times 10^{12}\]  0.440  86770.00

LOW / 1.580E+51  -9.300  97800.00/
TROE/ 0.7345  180.00  1035.00  5417.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ 0.70/
C2H5 + O2 ⇌ H2 + C2H4  \[8.400 \times 10^{11}\]  0.0  3875.00
HCCO + O2 ⇌ O + CO  \[3.200 \times 10^{12}\]  0.0  854.00
2HCCO ⇌ 2CO + C2H2  \[1.000 \times 10^{13}\]  0.0  0.0
N + NO ⇌ N2 + O  \[2.700 \times 10^{13}\]  0.0  0.0
N + O2 ⇌ NO + O  \[3.600 \times 10^{13}\]  1.000  10810.00
N + OH ⇌ NO + H  \[8.400 \times 10^{12}\]  0.0  3875.00
N2O + O2 ⇌ N2 + O2  \[3.870 \times 10^{14}\]  0.0  18880.00
N2O + H ⇌ N2 + OH  \[3.650 \times 10^{14}\]  0.0  21060.00
N2O(+M) ⇌ N2 + O(+M)  \[7.910 \times 10^{10}\]  0.0  56020.00

LOW / 6.370E+14  0.00  56640.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ 0.625/
H2 + NO ⇌ NO + O2  \[2.110 \times 10^{12}\]  0.0  -480.00
N + O + M ⇌ N + O  \[1.060 \times 10^{20}\]  -1.410  0.0
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ 0.70/
N2 + O + M ⇌ N2 + O2  \[3.900 \times 10^{12}\]  0.0  -240.00
N2 + O + H ⇌ NO + O  \[1.320 \times 10^{14}\]  0.0  360.00
NH + O ⇌ NO + H  \[4.000 \times 10^{13}\]  0.0  360.00
NH + H ⇌ NH2  \[3.200 \times 10^{13}\]  0.0  330.00
NH + OH ⇌ NO + H2  \[2.000 \times 10^{13}\]  0.0  0.0
NH + OH ⇌ NO + H2  \[2.000 \times 10^{13}\]  1.200  0.0
NH + O2 ⇌ NO + O  \[4.610 \times 10^{8}\]  2.000  6500.00
NH + O2 ⇌ NO + OH  \[1.280 \times 10^{14}\]  1.500  100.00
NH + N ⇌ N2 + H  \[1.500 \times 10^{13}\]  0.0  0.0
NH + H20 ⇌ NO + H2  \[2.000 \times 10^{13}\]  0.0  13850.00
NH + NO ⇌ N2 + OH  \[2.160 \times 10^{13}\]  -2.30  0.0
NH + NO ⇌ N2 + OH  \[3.650 \times 10^{14}\]  -4.50  0.0
NH2 + O ⇌ OH + NH  \[3.000 \times 10^{12}\]  0.0  0.0
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<td>2.000E+13</td>
<td>0.000</td>
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<tr>
<td>NNH + CH₃ ⇌ CH₄ + N₂</td>
<td>2.500E+13</td>
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<tr>
<td>H/N₀ + M ≈ HNO + M</td>
<td>4.480E+19</td>
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<tr>
<td>H₂ / 2.00 / H₂O / 6.00 / CH₄ / 2.00 / C₀ / 1.50 / C₀₂ / 2.00 / C₂H₆ / 3.00 / AR / 70 /</td>
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<tr>
<td>HNO + O ⇌ NO + OH</td>
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<tr>
<td>HNO + H ≈ H₂ + N₀</td>
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<td>CN + H₂O ≈ HCN + OH</td>
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<td>CN + O₂ ≈ NCO + O</td>
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<td>CN + H₂ ≈ HCN + H</td>
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<td>NCO + H ≈ NH + CO</td>
<td>5.400E+13</td>
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<td>NCO + OH ≈ NO + H⁺ + CO</td>
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<td>NCO + N ≈ N₂ + CO</td>
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<tr>
<td>NCO + O₂ ≈ NO + CO₂</td>
<td>2.000E+12</td>
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<td>NCO + M ≈ N+C+O+M</td>
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<td>H₂ / 2.00 / H₂O / 6.00 / CH₄ / 2.00 / C₀ / 1.50 / C₀₂ / 2.00 / C₂H₆ / 3.00 / AR / 70 /</td>
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<td>NCO + NO ≈ N₂O + CO</td>
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<td>H₂ / 2.00 / H₂O / 6.00 / CH₄ / 2.00 / C₀ / 1.50 / C₀₂ / 2.00 / C₂H₆ / 3.00 / AR / 70 /</td>
<td></td>
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<tr>
<td>HCN + O ≈ NCO + H</td>
<td>2.030E+04</td>
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<tr>
<td>HCN + O ≈ NH + CO</td>
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<tr>
<td>HCN + O ≈ CN + OH</td>
<td>3.910E+09</td>
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<tr>
<td>HCN + OH ≈ HOCN + H</td>
<td>1.100E+06</td>
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<tr>
<td>Reaction</td>
<td>K ( \times 10^3 )</td>
<td>( a )</td>
<td>( T ) (K)</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
<td>-------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>HCN + OH &lt;=&gt; HNCO + H</td>
<td>4.400E+03</td>
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<tr>
<td>HCN + OH &lt;=&gt; NH2 + CO</td>
<td>1.600E+02</td>
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<td>9000.00</td>
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<tr>
<td>H+HCN (+M) &lt;=&gt; H2CN (+M)</td>
<td>3.300E+13</td>
<td>0.000</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

LOW / 1.400E+26 -3.400 1900.00/

H2CN+N <=> N2 + CH2 | 6.000E+13 | 0.000 | 400.00 |
| C+N2 <=> CN + N | 6.300E+13 | 0.000 | 46020.00 |
| CH+N2 <=> HCN+N | 3.120E+09 | 0.880 | 20130.00 |
| CH+N2 (+M) <=> HCNN (+M) | 3.100E+12 | 0.150 | 0.00 |

LOW / 1.300E+25 -3.160 740.00/

TROE/ 0.6670 235.00 2117.00 4536.00 /

CH2+N2 <=> HCN+NH | 1.000E+13 | 0.000 | 74000.00 |
| CH2 (S) + N2 <=> NH + HCN | 1.000E+11 | 0.000 | 65000.00 |
| C+NO <=> CN + O | 1.900E+13 | 0.000 | 0.00 |
| C+NO <=> CO + N | 2.900E+13 | 0.000 | 0.00 |
| CH+NO <=> HCN+O | 4.100E+13 | 0.000 | 0.00 |
| CH+NO <=> H+NCO | 1.620E+13 | 0.000 | 0.00 |
| CH+NO <=> N+HCN | 2.460E+13 | 0.000 | 0.00 |
| CH2+NO <=> H+HNCN | 3.100E+17 | -1.380 | 1270.00 |
| CH2+N0 <=> O+H+HCN | 2.900E+14 | -0.690 | 760.00 |
| CH2+NO <=> H+HCN0 | 3.800E+13 | -0.360 | 580.00 |
| CH2 (S) +NO <=> H+HNC0 | 3.100E+17 | -1.380 | 1270.00 |
| CH2 (S) +NO <=> O+H+HCN | 2.900E+14 | -0.690 | 760.00 |
| CH2 (S) +NO <=> H+HNC0 | 3.800E+13 | -0.360 | 580.00 |
| CH3+NO <=> H2CN+H2O | 9.600E+13 | 0.000 | 28800.00 |
| CH3+NO <=> H2CN+OH | 1.000E+12 | 0.000 | 21750.00 |
| HCN+N0 <=> CO+H+N2 | 2.200E+13 | 0.000 | 0.00 |
| HCN+N0 <=> HCN+N0 | 2.000E+12 | 0.000 | 0.00 |
| HCN+O2 <=> O+HCO+N2 | 1.200E+13 | 0.000 | 0.00 |
| HCN+OH <=> H+HCO+N2 | 1.200E+13 | 0.000 | 0.00 |
| HCN+N <=> CH2+N2 | 1.000E+14 | 0.000 | 0.00 |
| HNCO+O <=> NH+CO2 | 9.800E+07 | 1.410 | 8500.00 |
| HNCO+O <=> HNO+CO | 1.500E+08 | 1.570 | 44000.00 |
| HNCO+O <=> NCO+OH | 2.200E+06 | 2.110 | 11400.00 |
| HNCO+H <=> NH2+CO | 2.250E+07 | 1.700 | 3800.00 |
| HNCO+H <=> H2+NC0 | 1.050E+05 | 2.500 | 13300.00 |
| HNCO+OH <=> NC0+H2O | 3.300E+07 | 1.500 | 3600.00 |
Appendix

HNCO + OH <=> NH2 + CO2  
\[ 3.300 \times 10^6 \quad 1.500 \quad 3600.00 \]

HNCO + M <=> NH + CO + M  
\[ 1.180 \times 10^{16} \quad .000 \quad 84720.00 \]

H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/

HN++H <-+ HNC (OH + HCN  
\[ 2.100 \times 10^{15} \quad -690 \quad 2850.00 \]

HCNO + H <=> NH2 + CO  
\[ 1.700 \times 10^{14} \quad -750 \quad 2890.00 \]

HCNO + H <=+ NH + CO2  
\[ 2.000 \times 10^0 \quad 2.000 \quad 2000.00 \]

HCNO + M <=+ NH + CO2  
\[ 1.180 \times 10^{16} \quad .000 \quad 84720.00 \]

HCNO + H <=+ OH + HCN  
\[ 2.700 \times 10^{11} \quad .180 \quad 2120.00 \]

HCNO + H <=+ NH2 + CO  
\[ 1.700 \times 10^{14} \quad -750 \quad 2890.00 \]

HOCN + H <=+ H + HNCO  
\[ 2.000 \times 10^0 \quad 2.000 \quad 2000.00 \]

HCCO + NO <=+ HCN + CO  
\[ 0.900 \times 10^0 \quad 0.000 \quad 1000.00 \]

CH3 + N <=+ CH2CN + H  
\[ 6.100 \times 10^{14} \quad -310 \quad 290.00 \]

CH3 + N <=+ HCN + H2  
\[ 3.700 \times 10^0 \quad 3.700 \quad 90.00 \]

NH3 + H <=+ NH2 + H2  
\[ 5.400 \times 10^0 \quad 2.400 \quad 9915.00 \]

NH3 + OH <=+ NH2 + H2O  
\[ 5.000 \times 10^7 \quad 1.600 \quad 955.00 \]

NH3 + O <=+ NH2 + O2  
\[ 9.400 \times 10^6 \quad 1.940 \quad 6460.00 \]

NH + CO2 <=+ HNO + CO  
\[ 1.000 \times 10^0 \quad 1.000 \quad 14350.00 \]

CN + NO2 <=+ NCO + N0  
\[ 6.160 \times 10^0 \quad -0.752 \quad 345.00 \]

NCO + NO2 <=+ N2O + CO2  
\[ 3.250 \times 10^1 \quad 3.250 \quad 705.00 \]

N + C <=+ H2 + CO  
\[ 3.000 \times 10^0 \quad 3.000 \quad 11300.00 \]

O + CH3 => H2 + CO2  
\[ 5.800 \times 10^{12} \quad .000 \quad 1500.00 \]

CH2 + O2 <=+ CH2O  
\[ 2.400 \times 10^0 \quad 2.400 \quad 1500.00 \]

CH2 + CH2 <=+ H2 + C2H2  
\[ 2.000 \times 10^1 \quad 2.000 \quad 10989.00 \]

OH + H2O <=+ H + CH2O  
\[ 6.820 \times 10^0 \quad 6.820 \quad 935.00 \]

C2H3 + O2 <=+ HO2 + C2H2  
\[ 3.030 \times 10^6 \quad 3.030 \quad 11.00 \]

O + CH3OO <=+ O + CH3 + CO  
\[ 2.920 \times 10^0 \quad 2.920 \quad 1808.00 \]

O2 + CH3OO <=+ H2O + CH3 + CO  
\[ 3.010 \times 10^0 \quad 3.010 \quad 39150.00 \]

H + CH3OO <=+ CH2 + CH3  
\[ 2.050 \times 10^0 \quad 2.050 \quad 2405.00 \]

H + CH3OO <=+ CH3 + H2  
\[ 2.050 \times 10^0 \quad 2.050 \quad 2405.00 \]

H2 + CH3 <=+ CH2 + CH4  
\[ 5.800 \times 10^2 \quad .000 \quad 1500.00 \]

CH2 + O2 <=+ H2 + CO2  
\[ 2.400 \times 10^0 \quad 2.400 \quad 1500.00 \]

CH2 + OH <=+ CH2 + H2  
\[ 2.000 \times 10^0 \quad 2.000 \quad 10989.00 \]

CH2 (S) + H2O <=+ CH2 + H2O  
\[ 6.820 \times 10^1 \quad 6.820 \quad 935.00 \]

C2H3 + O2 <=+ H20 + CH2  
\[ 3.030 \times 10^1 \quad 3.030 \quad 11.00 \]

C2H3 + O2 <=+ HO2 + C2H2  
\[ 1.337 \times 10^6 \quad 1.337 \quad 11.00 \]

O + CH3OO <=+ OH + CH2  
\[ 2.920 \times 10^2 \quad .000 \quad 1808.00 \]

O + CH3OO <=+ OH + CH3 + CO  
\[ 2.920 \times 10^2 \quad .000 \quad 1808.00 \]

O2 + CH3OO <=+ H2O + CH3 + CO  
\[ 3.010 \times 10^2 \quad .000 \quad 39150.00 \]

H + CH3OO <=+ CH2 + CH3  
\[ 2.050 \times 10^2 \quad 2.050 \quad 2405.00 \]

H + CH3OO <=+ CH3 + H2  
\[ 2.050 \times 10^2 \quad 2.050 \quad 2405.00 \]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature</th>
<th>Endothermicity</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + CH₃CHO → CH₃ + H₂O + CO</td>
<td>2.343E+10</td>
<td>0.730</td>
<td>-1113.00</td>
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<tr>
<td>H₂O + CH₃CHO → CH₃ + H₂O₂ + CO</td>
<td>3.010E+12</td>
<td>0.000</td>
<td>11923.00</td>
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<tr>
<td>CH₃ + CH₃CHO → CH₃ + CH₄ + CO</td>
<td>2.720E+06</td>
<td>1.770</td>
<td>5920.00</td>
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<tr>
<td>H + CH₂CO (+M) → CH₂CHO (+M)</td>
<td>4.865E+11</td>
<td>0.422</td>
<td>-1755.00</td>
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<tr>
<td>HO₂ + CH₃CHO → CH₃ + H₂O₂ + CO</td>
<td>3.010E+12</td>
<td>0.000</td>
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<tr>
<td>CH₃ + CH₃CHO → CH₃ + CH₄ + CO</td>
<td>2.720E+06</td>
<td>1.770</td>
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<tr>
<td>H + CH₂CO (+M) → CH₂CHO (+M)</td>
<td>4.865E+11</td>
<td>0.422</td>
<td>-1755.00</td>
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<tr>
<td>O + CH₂CHO → H + CH₂ + CO₂</td>
<td>1.500E+14</td>
<td>0.000</td>
<td>0.00</td>
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<tr>
<td>O₂ + CH₂CHO → OH + CO₂ + CH₂O</td>
<td>2.350E+10</td>
<td>0.000</td>
<td>1500.00</td>
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<tr>
<td>H + CH₂CO (&lt;) → CH₃ + HCO</td>
<td>2.200E+13</td>
<td>0.000</td>
<td>0.00</td>
<td></td>
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<tr>
<td>CH₃ + CH₂CO (&lt;) → CH₂CO + H₂</td>
<td>1.100E+13</td>
<td>0.000</td>
<td>0.00</td>
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<tr>
<td>OH + CH₂CO (&lt;) → H₂O + CH₂O₂</td>
<td>1.200E+13</td>
<td>0.000</td>
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<tr>
<td>OH + CH₂CO (&lt;) → HCO + CH₂OH</td>
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<td>CH₃ + CH₂H₅ (+M) → CH₄ + CH₂H₅ (+M)</td>
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<tr>
<td>O + CH₃H₇ → OH + CH₃H₇</td>
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<td>H + CH₃H₇ → CH₃H₇ + H₂</td>
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<tr>
<td>CH₃H₇ + H₂O₂ → HO₂ + CH₃H₇</td>
<td>3.780E+02</td>
<td>2.720</td>
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<td>CH₃ + CH₃H₇ → CH₃H₇ + CH₄</td>
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<tr>
<td>CH₃ + CH₄H₂ (+M) → CH₃H₇ (+M)</td>
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<tr>
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<tr>
<td>OH + CH₃H₇ → CH₂H₅ + CH₂O</td>
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<tr>
<td>H₂O + CH₃H₇ → O₂ + CH₂H₅ + CH₂O</td>
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<td>0.255</td>
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<tr>
<td>H₂ + CH₃H₇ + CH₂H₅ + CH₂O</td>
<td>2.410E+13</td>
<td>0.000</td>
<td>0.00</td>
<td></td>
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<tr>
<td>CH₃ + CH₃H₇ → 2CH₂H₅</td>
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<td>-0.320</td>
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