

Modelling of Turbulent Flames with
Transported Probability Density Function and
Rate-Controlled Constrained Equilibrium Methods

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Abstract

In this study, turbulent diffusion flames have been modelled using the Transported Probability Density Function (PDF) method and chemistry reduction with the Rate-Controlled Constrained Equilibrium (RCCE). RCCE is a systematic method of chemistry reduction which is employed to simulate the evolution of the chemical composition with a reduced number of species. It is based on the principle of chemical time-scale separation and is formulated in a generalised and systematic manner that allows a reduced mechanism to be derived given a set of constraint species. The transported scalar PDF method was coupled with RANS turbulence modelling and this PDF-RANS methodology was exploited to simulate several turbulent diffusion flames with detailed and RCCE-reduced chemistry. The phenomena of extinction and reignition, soot formation and thermal radiation in these flames are explored.

Sandia Flames D, E and F have been simulated with both the detailed GRI-3.0 mechanism and RCCE reduced mechanisms. Scatter plots show that PDF methods with simple mixing models are able to reproduce different degrees of local extinction in Sandia piloted flames. The PDF-RCCE results are compared with PDF simulations with the detailed mechanism and with measurements of Sandia flames. The RCCE method predicted the three flames with the same level of accuracy of the detailed mechanism.

The methodology has also been applied to sooting flames with radiative heat transfer. Semi-empirical soot model and Optically-thin radiation model have been combined with the PDF-RCCE method to compute these flames. Methane flames measured by Brooks and Moss [26] have been predicted using several RCCE mechanisms with good agreement with measurements. The propane flame with preheated air [162] has also been simulated with the PDF-RCCE methodology. Gaseous species profiles of the propane flame compare reasonably with measurements but soot and temperature predictions in this flame were weak and improvements are still needed.

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Declaration of originality

I declare that the thesis presented herein is my own work and has been generated by me as a result of my research at the University of Manchester and Imperial College London. It has not been submitted in any form for any other degree or diploma. Information derived from published or unpublished work of others has been acknowledged and listed to the best of my ability.

Salem Elbahloul, September 2013

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Nomenclature

Roman Symbols

a_{lm}	non-dimensional anisotropy of the turbulent Reynolds stress $\widetilde{u_l'' u_m''}$	
A_{st}	total soot surface area per unit volume of gaseous mixture	$\text{m}^2(\text{soot})/\text{m}^3$
$a_{\alpha s}^c$	constraints matrix: contribution of species s into constraint α	
$a_{\beta s}^e$	number of atoms of element β in species s	
c_l	convection CFL number in the l^{th} direction	
c_p	specific heat at constant pressure	$\text{J}/(\text{kg K})$
$C_{p,s}$	molar specific heat at constant pressure of species s	$\text{J}/(\text{kmol K})$
$c_{p,s}$	specific heat at constant pressure of species s	$\text{J}/(\text{kg K})$
C_α	value or composition of constraint α	
C_ϕ	time scale ratio	
df_l	diffusion number in the l^{th} direction	
D	fuel nozzle diameter	m
D_θ	thermal diffusivity	m^2/s
D_s	mass diffusivity of species s	m^2/s
d_{st}	average diameter of spheroid soot particles	m
Da	Damköhler number	

D_{eff}	effective diffusivity $\left(\frac{\nu_t}{\sigma} + \frac{\nu}{Sc}\right)$	m^2/s
E_r	activation energy of the chemical reaction	
E_β	composition of element β	
g	specific Gibbs free energy	J/kg
g_m	gravitational acceleration in the m^{th} direction	m/s^2
$\Delta H_{f,s}^o$	standard-state molar enthalpy of formation for species s	J/kmol
$\Delta h_{f,s}^o$	standard-state specific enthalpy of formation for species s	J/kg
h	total specific enthalpy	(J/kg) or (m^2/s^2)
H_s^o	partial standard-state molar enthalpy of species s	J/kmol
h^*	sample space variable for enthalpy	
$J_{l,h}$	molecular flux of enthalpy in the l^{th} direction	W/m^2
$J_{l,s}$	molecular flux of species (s) in the (l^{th}) spatial direction	$\text{kg}/(\text{m}^2 \text{ s})$
k	turbulence kinetic energy	m^2/s^2
k_k^f, k_k^b	rate constant of the forward or backward reaction k	
l	length scale	m
l_m	mixing length	m
Le_s	Lewis number of species s	
M_s	chemical symbol of species s	
Ma	Mach number	
M_c	number of constraints	
M_e	number of chemical elements	
N_A	Avogadro number (6.022×10^{26})	$1/\text{kmol}$

N_R	number of chemical reactions	
N_r	number of realisations	
N_s	number of gas-phase species or composition variables	
n_s	specific mole number of species s	kmol/kg
n_t	total mole number per mass of mixture (reciprocal of W)	kmol/kg
N_{pc}	current number of particles per cell	
N_{pc}^o	initial number of particles per cell	
N_{pp}	number of particle pairs selected for mixing in Curl's model	
N_{sc}	number of transported scalar variables	
$N_{p_{st}}$	soot particle number density	1/kg
$\mathcal{P}$	probability density function	
p	pressure	kg/(m s ²)
P_k	production rate of turbulence kinetic energy due to shear	m ² /s ³
P_{lm}	production rate of the Reynolds stress due to shear	m ² /s ³
Pr	Prandtl number	
Pe	Peclet number ($Re.Sc$)	
$\tilde{Q}$	density-weighted or Favre average	
$\langle Q \eta \rangle$	conditional average of a quantity conditioned on mixture fraction	
$\overline{Q}$	Reynolds average or unweighted mean of a quantity	
Q	an arbitrary physical quantity	
$\dot{q}_{rad}$	heat loss rate by radiation (enthalpy source term)	W/m ³
R	universal gas constant = 8.3143×10^3	J/(kmol K)

Re	Reynolds number	
Re_t	turbulent Reynolds number	
Sc	Schmidt number	
Sc_s	Schmidt number of species s	
t	time	s
T or T^*	temperature	K
u_l	velocity component in the l^{th} direction	m/s
W	mean molecular weight of the gaseous mixture	kg/kmol
W_s	molecular weight of species s	kg/kmol
$\underline{x}$	vector for position in physical space	m
x_l	position in physical space in the l^{th} direction	m
X_s	mole fraction of species s	kmol (<i>species</i>)/kmol (<i>mixture</i>)
y	position in direction normal to the flow or distance from the wall	m
Y_s	mass fraction of species s	kg (<i>species</i>)/kg (<i>mixture</i>)
Y_{st}	soot mass fraction	
z	mixture fraction	

Greek Symbols

δ_{lm}	Kronecker delta (= 1 if $l = m$, = 0 if $l \neq m$)	
θ_s^{mix}	evolution of scalar s by micromixing	
ε	dissipation rate of turbulence kinetic energy	m ² /s ³
η	mixture fraction sample space	
κ	Von Karman constant = 0.41	

κ_B	Boltzmann constant (1.38065×10^{-23})	J/K
λ	thermal conductivity	W/(m K)
λ_α^c	constraint potential	
λ_β^e	element potential	
μ	dynamic viscosity	kg/m s
μ_t	turbulent viscosity	kg/m s
μ_s	chemical potential for species s	J/kmol
μ_s^o	chemical potential at the standard state for species s	J/kmol
ν	kinematic viscosity	m ² /s
ν_t	turbulent viscosity ($\nu_t = \mu_t/\rho$)	m ² /s
ν_{sk}	net molar stoichiometric coefficient of species s in reaction step k	
ν'_{sk}, ν''_{sk}	forward and backward molar stoichiometric coefficients of species s in reaction step k	
ρ	mass density	kg/m ³
ρ_{st}	soot density	kg(soot)/m ³
σ_k	apparent turbulent Prandtl number for k	
σ_z	turbulent Prandtl number for mixture fraction	
σ_ε	apparent turbulent Prandtl number for ε	
σ_s	turbulent Prandtl or Schmidt number of species or scalar s	
τ	time scale	s
τ_ϕ	scalar mixing time scale	s
τ_{lm}	component of the viscous stress tensor	kg/(m s ²)

τ_w	wall shear stress	kg/m s ²
$\underline{\phi}$	a set of scalar or composition variables	
ϕ_s	transported scalar or species s	
χ	scalar dissipation rate of mixture fraction	
χ_s	dissipation rate of species or scalar s	
χ_{st}	scalar dissipation rate at stoichiometry	
ψ_s	sample space variable for ϕ_s	
$\dot{\Omega}_s$	mass production rate of species s by chemical reaction	kg/(m ³ s)
$\dot{\omega}_s$	molar production rate of species s by chemical reaction	kmol/(m ³ s)
$\hat{\omega}_k$	molar rate of elementary chemical reaction	kmol/(m ³ s)
ω	turbulence frequency	1/s

Superscripts and Subscripts

$(p), (q)$	pair of notional particle
$*$	notional PDF particle
α	kinetic constraint
β	chemical element
$"$	fluctuation about density-weighted mean
$'$	fluctuation about unweighted mean
$cell$	finite volume cell
i	number of carbon atoms
k	chemical reaction index
l, m, n	indices of physical space directions

r realisation

s index of chemical species or scalar quantities

Abbreviations

TCI Turbulence Chemistry Interaction

TRI Turbulence Radiation Interaction

ANN Artificial Neural Network

ARM Augmented Reduced Mechanism

ASM Algebraic stress model

CFD Computational Fluid Dynamics

CMC Conditional Moment Closure

CSP Computational Singular Perturbation

DNS Direct Numerical Simulation

EMST Euclidean Minimum Spanning Tree model

FDF Filtered Density Function

HACA H-Abstraction-C₂H₂-Addition

IECM Interaction by Exchange with the Conditional Mean model

IEM Interaction by Exchange with the Mean model

ILDm Intrinsic Low Dimensional Manifolds

LES Large-Eddy Simulation

LMSE Linear Mean square Estimation model

LOI Level of Importance

MC Mapping Closures

CD Coalescence-Dispersion Model

MCD Modified Coalescence-Dispersion models

MEPDF Multi-Environment PDF

MMC Multiple Mapping Conditioning

NLEVM Non-Linear Eddy-Viscosity Models

ODE Ordinary Differential Equation

PAH Polycyclic Aromatic Hydrocarbon

PBE-PDF Population Balance Equation-Probability Density Function

PDE Partial Differential Equation

PDF Probability Density Function

QSSA Quasi-Steady-State Approximation

RANS Reynolds-averaged Navier-Stokes

RCCE Rate-Controlled Constrained Equilibrium

RCCE- M_c RCCE reduced mechanism with M_c constraints

RJC round jet correction

RNG Renormalisation Group

RSM Reynolds-stress model

SGS Subgrid scale

Chapter 1

Introduction

1.1 Background and Objectives

Combustion of hydrocarbon fuels occurs in most vehicle engines and in several industrial devices. In addition, it is a source for a major part of the power generated in the world. There have been some attempts to use alternative sources for power generation to decrease the consumption of hydrocarbon fuels. However, the world demand for this type of energy has kept rising and this has called for the need to conserve energy resources. Another issue is the environmental pollution produced by devices involving combustion of hydrocarbon fuels. It is accompanied by the emission of several pollutants such as nitric oxides NO_x , sulphur oxides (SO_x) and soot in addition to the release of heat and primary combustion products like CO_2 and CO . So combustion takes part in global warming because of the high level of greenhouse gases like CO_2 and acid rain. NO_x , particularly N_2O , contribute to the destruction of the ozone (O_3) layer [188] exposing earth to more ultraviolet radiation. Therefore, legislative limitations have been introduced to minimise the level of these emissions to help save the environment. In addition, soot formation is a complex phenomenon which needs to be optimised. It is being utilised to enhance radiative heat transfer in some practical systems such as furnaces and boilers. The design of more efficient combustion systems can play an important role in conserving the power resources and reduction of emission levels. The interest in improving the efficiency of combustion systems to meet the limits of emission levels has motivated

research on combustion flows.

Modelling methods have become an important tool for understanding combustion flows due to the difficulty, cost and hazard of experimental methods. Experimental measurements are, however, essential to aid the verification of the phenomena involved and for the validation of calculations. Combustion in most engineering applications occurs predominantly within turbulent flow conditions. Turbulent combustion flows involve several complicated and coupled processes, such as fluid flow, chemistry, heat transfer and radiation, which are interacting with each other. In addition, there is the fact that both flow and chemistry exhibit a wide range of scales. The complex nature of turbulent combustion has been an obstacle to accurate predictions and to a complete interpretation of the phenomena. Despite these difficulties, both experimental techniques and numerical computations have been exploited to develop understanding of this branch of science and substantial progress has been made in the theoretical and computational developments [119]. Since there are many difficulties in performing detailed measurements and computations of combustion flows at the practical prototype scale, the common approach has been to design laboratory-scale flames for which detailed experimental measurements are provided to validate the numerical calculations. Advanced numerical calculations, including LES computations, of these small-scale systems have become tractable with modern computational resources. The computations can be reliably compared with measurements with the ability to specify the boundary conditions more accurately and by minimising any uncertainties arising from sensitivity to configuration and scale of device.

Combustion flows are mostly categorised using two limiting ideal cases, the premixed and non-premixed flames. In the premixed flames, the fuel and oxidiser are initially fully premixed while in the non-premixed flames they are initially separated and combustion occurs as they mix. The non-premixed flames are also called the diffusion flames. They are the model problem for many practical systems like furnaces and other types of burners.

Despite the considerable advances in this field, full interpretation of turbulent premixed and non-premixed combustion has not been established. This is mainly due to the complex nature of turbulence, chemical kinetics and the coupling between several processes, particularly in practical systems such as engines, gas turbines and furnaces. The existence of complex chemistry with a wide range of scales and its interaction with turbulence result in a multiple number of combustion regimes which may occur in a single device. Coupling between chemical reaction and turbulent fluctuations hinders the computation of turbulent combustion using simple turbulence models because species formation rates and heat release are highly nonlinear functions of temperature and composition. The mathematical representation of complex chemistry and its interaction with turbulence in CFD computations forms a major difficulty in the calculation methods of turbulent flames.

The growing use of combustion for transportation and power generation as well as in other domestic and industrial energy systems, together with the parallel rise of hydrocarbon fuel prices and environmental issues have increased the importance of reliable computation of combustion flows. An accurate representation of the turbulence-chemistry interaction (TCI) is an important element of the turbulent combustion modelling or simulation. For this purpose, we use the transported PDF approach closed at the scalar level. Transported Probability Density Function (PDF) methods have proved to be excellent in reproducing complicated phenomena such as extinction and reignition which are of concern for safe and reliable operation of combustion devices.

Accurate chemistry models have to be employed so that effects of the chemical kinetics are correctly reproduced. This has motivated the employment of comprehensively detailed chemical mechanisms in turbulent combustion simulations which has been facilitated by the massive advances in computational resources. However, the computational cost with detailed chemical mechanisms are still prohibitively expensive particularly for practical applications and with complex real fuels. In addition, the progress in the validation of kinetic data for heavy hydrocarbons and multi-component fuels has been obstructed by the extremely large number of ele-

mentary reactions in their mechanisms and the multitude of uncertainties present in them. If these mechanisms are reduced, rate constants of key reactions can be validated and refined with less effort. These issues highlight the need for efficient and systematic methods of chemical mechanism reduction. One important feature of the reduction method is that it should preserve the important finite-rate effects in the original detailed mechanism. The Rate-Controlled Constrained Equilibrium (RCCE) is one of the systematic methods of mechanism reduction that has shown good performance with laminar flames and has also been applied to turbulent flames. The current study concentrates on detailed monitoring of the performance of RCCE by comparing it with the original comprehensive kinetic mechanism. The combined PDF-RCCE methodology is also extended to compute flames with soot formation and thermal radiation.

Chapter 2

Governing Equations and Turbulence Modelling

2.1 Introduction to turbulence

Turbulent flows are frequently observed in our everyday surroundings and broadly experienced in a variety of industrial and engineering applications. The study of turbulent flows is very important for practical applications in which it occurs. Whether the presence of turbulence is desirable or unwanted, insight and understanding of its behaviour as well as its effects on other phenomena is crucial for the improvement of these applications. This is because turbulence influences other processes like mixing, transport of momentum and heat transfer. The influence of turbulence is desirable and essential for the performance of some devices. In chemical reactors for example, turbulence enhances mixing of fuel and oxidiser streams or reactants with products. Turbulence has attracted a lot of research for well over a century and many different experimental and mathematical techniques have been developed to study this phenomenon.

It is widely agreed that turbulent flows can not be precisely defined but can be described as unsteady, three-dimensional and chaotic motion of fluids [210, 114]. This irregular and unpredictable type of flow is commonly viewed as eddies (whorls) with a range of scales which are sensitive to the flow initial and boundary conditions.

In high Reynolds number flows, the characteristics of these eddies are independent of the fluid's molecular properties [210, 186]. The evolution of turbulence is characterised by the energy cascade phenomena between these eddies: a portion of the mean kinetic energy is being transferred into the largest eddies by stretching and straining and other instabilities in the mean flow. The energy is then fed into the smaller ones and this energy cascade continues to the smallest scales. The smallest eddies dissipate its energy into heat by viscous stresses [25]. Since the large eddies do not dissipate energy into heat directly and all the energy is fed to the smaller ones, the turbulent energy transfer rate is controlled by the large scales.

An important feature is that turbulent flow experiments are usually regarded as unrepeatable because turbulent flow evolution is sensitive to the initial and boundary conditions. At least perturbations to the flow will inevitably exist. Any small perturbations in the initial and boundary conditions would affect the evolution of flow properties. Because of this complicated nature of turbulence and sensitivity to perturbations, the values of flow quantities can not be uniquely and exactly determined for every realisation of the flow since they evolve randomly. Thus, they should be treated as random variables and need statistical tools to estimate them.

2.2 Kolmogorov Similarity Hypotheses

Kolmogorov [109] introduced the theory of local isotropy of turbulence. It was stated that when a reference frame is appropriately chosen so that velocity differences within a domain are considered, the turbulence is locally isotropic within a domain if the statistical distribution of the resulting velocity differences is universal and invariant of coordinate reflection and rotation. The theory also states that the local isotropy applies to the small scales of high Reynolds number flows and away from flow singularities since within a sufficiently small domain, statistics of velocity fluctuations are approximately universal and independent of rotations of the coordinates. In other words the small scales of motion are statistically isotropic

since they are not distinguished by the physical coordinates. One implication is that these isotropic small scales are independent of the effect of the mean flow on the large eddies. It is known that the large eddies are anisotropic since they are controlled by the boundary conditions and mean flow. These effects, however, diminish as the energy is repeatedly transferred to smaller eddies in a random mechanism. At some small length scale, turbulent motions become universal and independent of these directional and geometrical effects. Based on this theory, Kolmogorov introduced two extra similarity hypotheses. The first of the two states that the statistics of the small-scale which are assumed to be in local isotropy are solely determined by the molecular viscosity and the dissipation rate. This range of scales is named the universal equilibrium range [186] and it is divided into two parts. The finer scales of this range which are largely influenced by viscous effects are referred to as the dissipation range [186, 9, 236]. The Kolmogorov length scale is the scale of the smallest eddy and is defined as:

$$\eta = \left(\frac{\nu^3}{\varepsilon} \right)^{1/4} \quad (2.1)$$

While the scale of the largest eddy is controlled by the size of the device and boundary conditions, the Kolmogorov length scale is determined only by the dissipation rate and the viscosity. In other words as the Reynolds number is increased, eddies with smaller length scale are formed before dissipation by viscosity occurs. It is deduced that the ratio between the largest and smallest scales of turbulence is approximately equal $(Re_t)^{3/4}$, where Re_t is the Reynolds number of turbulence.

The second part of the equilibrium range is the inertial subrange which has scales larger than the dissipative scales and hence viscosity effects on them are unimportant. Kolmogorov's second hypothesis refers to this intermediate range of turbulent scales showing that they are controlled by dissipation rates only. These hypotheses were refined by Kolmogorov in 1962 [110].

It has been noted [186, 81, 230] that the intermittent behaviour of the fine scales in space and time gives evidence of differences with Kolmogorov's hypothesis indi-

cating that it is not perfect for all flows and possibly explaining a reason for the observed deviation or departures from this hypotheses. Flandoli [57] presented a detailed review of the hypothesis and introduced some implications and conditions for it. For idealised cases with slight anisotropy, the intermittency of small scales and deviation from local isotropy can be confidently ignored in simplified turbulence modelling and in simple flow configurations.

2.3 The Conservation Governing Equation

Multicomponent turbulent reacting flows are governed by a set of nonlinear partial differential equations. In addition to the continuity and Navier-Stokes equations which are sufficient for the description of the flow of a fluid, transport equations for the composition and energy are required. These equations are usually derived from the conservation laws of mass (for the continuity and composition equations), momentum (Navier-Stokes equations) and energy (e.g. enthalpy equation). These equations can be formulated in a generalised form in the three spatial dimensions and constitute terms representing all aspects of the fluid flow and associated physical and chemical processes. Here, we write the equations which are applicable for a wide range and different classes of flows with combustion, both laminar and turbulent, premixed and non-premixed. However, it is important to point out that these equations are written assuming Newtonian fluid with constant viscosity and low Mach number ($Ma \ll 1$). Some terms in the energy conservation equation such as the kinetic energy and frictional heating are neglected. Similarly, terms associated with the effects of spatial variations of pressure on the energy are also neglected while retaining the transient pressure term $\left(\frac{\partial p}{\partial t}\right)$ which is important in some combustion flows such as IC reciprocating engines. Work done against body forces is also assumed to be negligible in comparison to thermal energy of combustion flows. A major simplification is that Fick's laws for binary mass diffusion is invoked for the multicomponent scalar field which does not preserve the sum of mass fractions to one, particularly in situations where molecular diffusion effects are dominant.

Fourier's law for thermal diffusion is also considered.

Continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_l}{\partial x_l} = 0 \quad (2.2)$$

Navier-Stokes (Momentum) equations

$$\frac{\partial \rho u_m}{\partial t} + \frac{\partial \rho u_l u_m}{\partial x_l} = \frac{\partial \tau_{lm}}{\partial x_l} - \frac{\partial p}{\partial x_m} + \rho g_m \quad (2.3)$$

The viscous stress tensor of a Newtonian fluid maybe expressed by the following relation:

$$\tau_{lm} = \mu \left(\frac{\partial u_m}{\partial x_l} + \frac{\partial u_l}{\partial x_m} \right) - \frac{2}{3} \mu \frac{\partial u_n}{\partial x_n} \delta_{lm} \quad (2.4)$$

Species conservation equation

Mass fraction

$$\frac{\partial \rho Y_s}{\partial t} + \frac{\partial \rho u_l Y_s}{\partial x_l} = - \frac{\partial J_{l,s}}{\partial x_l} + \dot{\Omega}_s \quad (2.5)$$

where $(J_{l,s})$ is the molecular flux of species (s) in the (l^{th}) spatial direction and is approximated by Fick's law, giving:

$$J_{l,s} = - \frac{\mu}{Sc_s} \frac{\partial Y_s}{\partial x_l} \quad (2.6)$$

where Schmidt number of the species is the ratio of the kinematic viscosity to the species mass diffusivity:

$$Sc_s = \frac{\nu}{D_s} = \frac{\mu}{\rho D_s} \quad (2.7)$$

Specific mole number

It might be more natural to express the composition of reacting mixture in mole number since chemical reactions are usually quantified with moles not mass fractions. The specific mole number (n_s) is related to the mass fraction (Y_s) and mole fraction (X_s) as follows:

$$n_s = \frac{Y_s}{W_s} = n_t X_s \quad (2.8)$$

where (n_t) is the total mole number (per unit mass) of the mixture which is the sum of specific mole numbers of all species present in the mixture:

$$n_t = \sum_{s=1}^{N_s} n_s = \frac{p}{\rho R T} = 1/W \quad (2.9)$$

The transport equation of the specific mole number of a reacting species has a similar form to its mass fractions equation. It can be written:

$$\frac{\partial \rho n_s}{\partial t} + \frac{\partial \rho u_l n_s}{\partial x_l} = - \frac{\partial}{\partial x_l} \left(\frac{\mu}{Sc_s} \frac{\partial n_s}{\partial x_l} \right) + \dot{\omega}_s \quad (2.10)$$

Similarly, the chemical source terms in the equations of the species specific mole number and mass fraction are also related by the molecular weight:

$$\dot{\omega}_s = \frac{\dot{\Omega}_s}{W_s} \quad (2.11)$$

Enthalpy equation

The total specific enthalpy (h) includes the sensible (thermal), the chemical and kinetic energy contributions. Assuming that the kinetic energy contribution is neglected for low Mach number flows, the specific enthalpy of the mixture can be defined with the following expression:

$$h = \int_{T_{ref}}^T c_p dT^* + \sum_{s=1}^{N_s} Y_s \Delta h_{f,s}^o = \int_{T_{ref}}^T c_p dT^* + \sum_{s=1}^{N_s} n_s \Delta H_{f,s}^o \quad (2.12)$$

where $(\Delta h_{f,s}^o)$ and $(\Delta H_{f,s}^o)$ are, respectively, the specific and molar standard-state ($p_0 = 1 \text{ bar}$) heats of formation for species s which is evaluated at the reference temperature ($T_{ref} = 298.15 \text{ K}$). They take negative values if formation of the species from its elements at the standard state pressure and reference temperature is exothermic. The specific constant-pressure heat capacity (c_p) of the mixture in ($\text{J}/(\text{kg K})$) can be estimated from the individual species heat capacities, either the mass-based ($c_{p,s}$) or the molar-based ($C_{p,s}$) as follows:

$$c_p = \sum_{s=1}^{N_s} Y_s c_{p,s} = \sum_{s=1}^{N_s} n_s C_{p,s} \quad (2.13)$$

The transport equation for the enthalpy of the mixture can be written:

$$\frac{\partial \rho h}{\partial t} + \frac{\partial \rho u_l h}{\partial x_l} = -\frac{\partial J_{l,h}}{\partial x_l} + \frac{\partial p}{\partial t} - \dot{q}_{rad} \quad (2.14)$$

The molecular flux of the enthalpy can be written in a diffusion form as well:

$$J_{l,h} = \frac{\mu}{Pr} \frac{\partial h}{\partial x_l} + \sum_{s=1}^{N_s} \left(\frac{\mu}{Sc_s} - \frac{\mu}{Pr} \right) h_s \frac{\partial Y_s}{\partial x_l} \quad (2.15)$$

and Prandtl number is the ratio of the kinematic viscosity to the thermal diffusivity $\left(D_\theta = \frac{\lambda}{\rho c_p} \right)$. Prandtl number is then given by:

$$Pr = \frac{\nu}{D_\theta} = \frac{\mu}{\lambda/c_p} = \frac{\mu}{\rho D_\theta} \quad (2.16)$$

Lewis number of the species is given by:

$$Le_s = \frac{Sc_s}{Pr} = \frac{\lambda}{\rho c_p D_s} \quad (2.17)$$

An additional approximation which is sometimes invoked for turbulent flows and will be considered in this study is that the diffusivities of all species are equal. A global Schmidt number Sc will appear in the species equations as well as the enthalpy equation. In addition, if Lewis number is given the value of unity, the term in the enthalpy flux equation (2.15) which contains the quantity $\left(\frac{\mu}{Sc_s} - \frac{\mu}{Pr} \right)$ will

disappear. The transient pressure term can be neglected $\left(\frac{\partial p}{\partial t} \approx 0\right)$ in open flames, turbine combustors and furnace burners but not in IC reciprocating engines.

2.4 Overview of Turbulence Simulations and Modelling

Despite the random behaviour of turbulent flows, they are accurately described by a set of deterministic PDEs. However, an exact theoretical solution of the equations for practical flows could not be achieved. Direct Numerical Simulations (DNS) has not become a tractable approach for every-day calculations of turbulent flows, mainly due to the huge amount of detail contained in these flows. This results from the presence of a wide range of scales of motion that need to be resolved making the simulation a quite infeasible task even with prescribed initial and boundary conditions.

In turbulent reacting flows, it is usually the case that a much wider range of scales need to be resolved. Fortunately, however, predictions of important flow quantities do not necessarily require resolution of all spatial and temporal scales. Closure for the unresolved terms in the averaged or filtered Navier-Stokes equations is provided by models of turbulence. Several of these models have been based on consideration of important scales only and have led to significant simplification of this highly nonlinear problem. The most common of these are the Large Eddy Simulation (LES) approach and the Reynolds Averaged Navier-Stokes (RANS) equations approach. Development of approaches based on probability function e.g. the transported Probability Density function PDF for turbulent flows has also been developed and investigated. In this chapter, a review and discussion of the status of DNS and LES approaches as well some RANS models is discussed in the first few sections. In this study, the transported PDF approach is only applied to the scalar field as a combustion model and therefore we will discuss it in the context of combustion models only.

In the context of turbulent combustion and other reactive flows, classical methods of modelling non-reacting turbulent flows alone fail to describe the system because they do not include information on the nature of the problem. Combustion is a multi-scale chemical process that interacts with the turbulent motion and the computation has to contain some way of representing this interaction between turbulence and chemistry. The most widely traditional way to solve this problem has been to retain the closure of the flow field part with classical turbulence models and extend them to reacting flows by coupling them with models that incorporate chemistry and a methodology for its interaction with turbulence.

2.5 Direct Numerical Simulations

In this approach the instantaneous governing transport equations (Navier-Stokes equations and any relevant scalar transport equations such as composition and enthalpy) are directly solved using numerical simulations with complete resolution of all the spatial and temporal scales of motion. These equations, themselves, are independent of the flow considered and the solution for a specific flow problem is specified by the initial and boundary conditions appropriate for the considered flow. The size of the solution domain is ideally taken to be the size of the device itself or part of it which could be more than one order of magnitude larger than the largest turbulence scale. At least it must be large enough to encompass the large energy containing scales. The smallest scales (i.e. the Kolmogorov length and time scale) must also be fully and explicitly resolved by the grid points. Since, the largest turbulent eddy is $(Re)^{3/4}$ larger than the Kolmogorov length scale, a range of scales which span several orders of magnitude needs to be resolved in every direction of the three spatial dimensions. It is clear from this how computationally expensive DNS is for high Reynolds-number flows. Roughly, the computation requirement for DNS varies as Reynolds number to the cube, especially if the time step is sensitive to the Reynolds number through the CFL criterion. DNS also involves codes generating huge amount of data and with memory-intensive loops which current computer memories fail to handle. Simulation monitoring, management and optimisation of

the large amount of data and processing of the results also require advanced knowledge of computer science and technology. Up to the end of last century, DNS simulations were limited to ideal cases with simple configurations and up to moderate Reynolds number turbulent flows because of the limitation of the computational resources.

In combustion, the CPU requirement for DNS is usually much higher than for inert flows. The chemical reaction usually occurs at scales much smaller than the smallest scales of motion implying that grids finer than for inert flows are needed to secure resolution of the inner structure of thin reaction layers. As for temporal integration, the ratio between the integral time scale of the flow and the time scale of fastest reaction in hydrocarbon combustion leads to a number of time steps in the order of a million steps or more [52]. Further, a large number of transport equations for important representative scalars (e.g. chemical species) need to be solved in the simulation. The challenge of direct simulations of turbulent combustion is quite severe when one thinks of employing a comprehensive chemical mechanism on a three-dimensional DNS grid in which all the flow and flame length scales have to be resolved. Inclusion of a complex chemical scheme is essential at least when there is an interest in accurate predictions of pollutant formation or phenomena related to finite-rate kinetics such as ignition mechanism.

However, it should be highlighted that DNS has become a useful learning tool, not for the prediction and design of practical applications, but as a validation for turbulence models. Its unequalled level of accuracy and resolution provide us with insight information about the details of the flow. This is specifically useful where experimental data are not available or not accessible. While experimental data are needed for validation of DNS computations, DNS covers the lack of measurements. DNS contributes along with experiments to revealing more knowledge of the flow physics and chemistry as well as guiding and calibrating new closure models of turbulent flows.

A common practice that has been adopted for long time to accelerate DNS calculations is to simulate with some idealisation or decoupling between ingredients of the problem. The researcher would concentrate on some of the phenomena of the flow by targeting the relevant processes with exact simulation while introducing simplified approximations for other processes in order to capture the mechanisms of the phenomena under consideration. In the simulation by Lee and Pope [121], DNS was performed to analyse the processes responsible for extinction in non-premixed flames and to assess the validity of combustion models for capturing this phenomenon. The simulation involved assumption of constant-density flow with isotropic turbulence and one-step chemistry. The grid size was enough to resolve scales which are 5 times smaller than the Kolmogorov length scale of the flow considered. This grid resolution guarantees that any flame scales thinner than the smallest eddy are fully resolved. Recently, some DNS studies of turbulent combustion are either reduced to two-dimensional flow field so that detailed chemistry can be incorporated or that three-dimensional DNS with simplified chemistry is adopted [33].

By this and similar practises, DNS is currently contributing to the understanding of the fundamentals of turbulent combustion such as the interaction between turbulent eddies and chemical reaction. This is mainly due to the advances in hardware and software technologies of computers. It is only quite recently that advances in computer resources and new numerical schemes have made it possible to perform three-dimensional direct simulations for some real flow cases including flows with turbulent combustion [37]. It is still, however, computationally prohibitive for near-wall flows and high Re even for laboratory-scale problems. It becomes computationally impossible when applied to flows in practical applications. There are expectations, though for a change in the position of DNS as the computer capability is showing exponential growth. Overall, scientists estimate that even with an optimistic forecast of computer developments, the computational cost of DNS methods will most likely hold to be prohibitive and limited to a certain range of turbulent flows of practical interest.

2.6 Large-Eddy Simulations approach

As implied in its name, the mathematical concept of the large eddy simulation [LES] approach is to resolve explicitly the large spatial and temporal scales of motion while smaller scales which can not be resolved by the discretized system are modelled. The large scales of motion carry most of the energy and anisotropy of the flow and they are greatly affected by the flow geometry while small scales tend to be more isotropic and less affected by the flow geometry [176]. The basis of LES is consistent with Kolmogorov's hypothesis [109] which assumes that the fine scales of turbulence are locally isotropic and independent of the large scales.

Spatial filtering is explicitly applied so that the transport equations of the filtered velocity are derived from the Navier-stokes equations. Temporal filter is automatically and implicitly introduced since time and length scales of turbulence are directly related. The sub-grid scale (SGS) stress tensor which appears in the filtered equations is modelled using the so-called sub-grid scale (SGS) model, whose role is mainly to provide a mechanism for the dissipation. Thus by this approach, much of the computational cost inherited by exhaustive DNS would be avoided.

Initially, LES received wide attention and interest for the study of non-reacting flows. It has been widely argued that, in high-Reynolds-number inert flows and away from the walls, the resolved energy-containing large scales dominate most of the important flow processes. The latter can, therefore, be described independently from the universal fine scales [59] with some loose coupling by a model determining the SGS stress tensor. One of the simplest sub-grid scale (SGS) models is the model introduced by Smagorinsky [198]. As the grid resolution is increased, the unresolved scales become more universal and contain less energy than simple models such as those based on the eddy-viscosity approximation may become sufficient if numerical instabilities are eliminated. Thus, grid refining has another effect to make the sub-grid contribution less important which is different from the effect of reducing the error of discretization scheme. However, grid refinement is restricted by the computational cost. Advanced sub-grid models are more capable in producing the fine structures of complex flows more accurately with moderately resolved length

scales (i.e. very fine grids are not required) [63, 194].

One of the merits of LES, which justifies the extra cost of its use, is the better and more detailed description of complex flow structures that it can provide compared to RANS models. LES is capable of predicting unsteady flows and capturing flows with instabilities or complex phenomena such as vortex shedding, rotation and recirculation. In addition, when applying LES to turbulent combustion flows, the detailed structure produced allows for more accurate distinction between small-scale zones of unburned and burned mixtures. This should facilitate for more accurate understanding of the turbulence-chemistry interaction [176].

Application of LES to reactive flows and particularly to turbulent combustion has received growing attention recently mainly due to the continuous rise in the computing power that is making LES less computationally prohibitive. In flows involving turbulent combustion, some relevant processes such as molecular mixing and reaction occur predominantly within the unresolved sub-grid scales. This roughly indicates that the closure problem in LES for reacting flows is similar to that in the RANS approach. In LES, since the reaction source term is a highly nonlinear function of the composition and temperature and it occurs within the unresolved scales, some statistical approach describing the fluctuations of the scalar sub-grid scales is required. Through this approach, the effect of the reaction on the large-scale scalar field (the filtered source term) can be calculated. The combustion models used in conjunction with LES are analogues to those used in the RANS context. The combustion models that will be discussed in the next chapter in the context of RANS simulations have also been applied with LES such as the flamelet and CMC models. Recently, there has been some focus on solving the filtered probability density function in conjunction with LES and developing methods for its implementation such as the stochastic field methods [158, 84, 96]

The cost of the LES lies between the DNS and the RANS and, in contrast with DNS, the cost usually increases weakly, if not independent, with Re , as in free shear

flows or when near-wall modelling is applied. However, there is still a strong interest in RANS modelling particularly for steady flows and simple geometries or when concentrating on processes such as ignition, scalar mixing or particulate formation. In combustion systems where unsteady and complex flow processes are dominant and influence the reaction, LES is indeed favoured to RANS models such as in gas turbine combustors and reciprocating engines. In some cases, the computational time with LES is reported to be quite comparable to that of unsteady three-dimensional RANS second moment closure if the two grids are comparable. This would support the view that LES is advantageous in the unsteady three-dimensional non-stationary flows such as in the IC reciprocating engines. For the latter, this may be justified further by the fact that the range of scales which are dominant and need to be resolved is moderate in IC engines due to the relatively low Re and the reasonable size of the solution domain [194]. The major obstacle would be shifted to the computational cost of the chemical source term since inclusion of finite rate chemistry is required. The predictions of parameters like flame ignition probability and other important phenomena in spark ignition combustors are quite expensive with detailed chemistry [97, 161, 206, 54]. This is actually one of the reasons pressing for the employment of reduction methods of chemical kinetics with LES.

2.7 Reynolds-Averaged Navier-Stokes equations (RANS) Approach

The RANS approach is based on decomposing the flow quantities into mean values and turbulent fluctuations. By considering the Reynolds averaging process, the instantaneous conservation equations are solved for the mean flow field while all time and length scales of turbulence are decoupled from the mean flow and do not require direct resolution. This process leads to the loss of some details of the turbulent flow and the appearance of unclosed turbulent terms representing the effect of turbulent eddies on the mean flow field. These unclosed terms are dealt with using turbulence modelling. This approach which was initially formulated for turbulent inert flows has been extended to turbulent reactive flows by averaging all

scalar transport equations and supplementing them with a model for the unclosed correlations of scalar fluctuations.

2.7.1 Averaging Process

The averaging process is based on applying the famous proposition of Reynolds in 1884. The instantaneous flow quantities are decomposed into averages and fluctuating components. If the Reynolds unweighted average of a quantity Q is denoted by $\overline{Q}$, we express the Reynolds' proposition:

$$Q(\underline{x}, t) = \overline{Q}(\underline{x}, t) + Q'(\underline{x}, t) \quad (2.18)$$

Ensemble averaging is usually the most applicable way to estimate the mean of a random quantity. In flow measurements, the ensemble mean of any quantity can be approximated by taking the average over a sufficiently large number of independent and equivalent experiments or many realisations of the same experiment. The ensemble Reynolds averaging can be defined as follows:

$$\overline{Q}(\underline{x}, t) = \lim_{N_r \rightarrow \infty} \frac{1}{N_r} \sum_{r=1}^{N_r} \{Q(\underline{x}, t)\}^{(r)} \quad (2.19)$$

This definition implies that as the number of realisations N_r is increased, the average becomes independent of this number. In other words the statistical error is reduced and vanishes in the limit of an infinite number of realisations. For specific kinds of flows, simpler modes of averaging can be adopted to approximate the mean. For example, in statistically stationary flows, time averaging of a large time series of measurements or predictions would give a valid estimate for the ensemble mean. The time averaging can be mathematically expressed with the following integral:

$$\overline{Q}(\underline{x}) = \frac{1}{(t_2 - t_1)} \int_{t_1}^{t_2} Q(\underline{x}, t) dt \quad (2.20)$$

where $(t_2 - t_1)$ is the time interval for averaging which should be long enough relative to any flow time of interest so that the average of the stationary flow is independent of time. Another example of types of averaging which is applicable to

specific flows is the spatial averaging which can be applied to flows with statistical homogeneity in space.

Averaging process (e.g. Reynolds time averaging) is then performed on all the terms of the instantaneous transport equations to obtain equations in terms of averaged quantities. For constant-density flows, the Reynolds unweighted averaging results in a set of averaged transport equations which have a form similar to the instantaneous set of equations. In variable-density flows such as in combustion, density fluctuations are induced by strong variations in composition and heat release. Then unweighted averaging produces extra terms involving correlations of density fluctuations and the closure problem would be complicated further. Favre (density-weighted) averaging has the advantage of eliminating these terms. If the decomposition is expressed in the weighted form:

$$Q(\underline{x}, t) = \tilde{Q}(\underline{x}, t) + Q''(\underline{x}, t) \quad (2.21)$$

and the density-weighted ensemble average is defined as:

$$\tilde{Q} = \frac{\overline{\rho Q}}{\bar{\rho}} = \frac{1}{\bar{\rho}} \left[\lim_{N_r \rightarrow \infty} \frac{1}{N_r} \sum_{r=1}^{N_r} \{\rho Q\}^{(r)} \right] \quad (2.22)$$

where the dependence on space and time were left out in this relation for simplicity.

It can be deduced that:

$$\overline{\rho Q''} = 0 \quad (2.23)$$

and the relation between the un-weighted and weighted average is:

$$\bar{Q} - \tilde{Q} = \overline{Q''} \neq 0 \quad (2.24)$$

As an example, we apply it to the following term (note that density is not

decomposed):

$$\begin{aligned}
\overline{\rho u h} &= \overline{\rho (\tilde{u} + u'') + (\tilde{h} + h'')} \\
&= \overline{\rho \tilde{u} \tilde{h}} + \overline{\rho u'' \tilde{h}} + \overline{\rho h'' \tilde{u}} + \overline{\rho u'' h''} \\
&= \overline{\rho \tilde{u} \tilde{h}} + \overline{\rho u'' h''}
\end{aligned} \tag{2.25}$$

It is seen that correlations with density fluctuations do not appear in the Favre averaged equations. Favre averaging, therefore, produces correlations similar to those obtained when conventional unweighted averaging is applied to constant density flows. The moment closure problem is then reduced to the same level as in constant density flows.

2.7.2 Favre Averaged Transport Equations

The following averaged equations are derived from equations (2.2),(2.3),(2.10) and (2.14). Flow Reynolds number (Re) is assumed to be high that molecular diffusion fluxes are negligible compared to turbulent fluxes and by dropping the transient pressure term for open flames, we arrive at the following averaged equations:

Continuity equation

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_l}{\partial x_l} = 0 \tag{2.26}$$

Navier-Stokes (Momentum) equations

$$\frac{\partial \bar{\rho} \tilde{u}_m}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_l \tilde{u}_m}{\partial x_l} = -\frac{\partial \bar{p}}{\partial x_m} - \frac{\partial \bar{\rho} \widetilde{u_l'' u_m''}}{\partial x_l} + \bar{\rho} g_m \tag{2.27}$$

Mole number

$$\frac{\partial \bar{\rho} \tilde{n}_s}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_l \tilde{n}_s}{\partial x_l} = -\frac{\partial \bar{\rho} \widetilde{u_l'' n_s''}}{\partial x_l} + \bar{\omega}_s \tag{2.28}$$

Enthalpy equation

$$\frac{\partial \bar{\rho} \tilde{h}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_l \tilde{h}}{\partial x_l} = -\frac{\partial \bar{\rho} \widetilde{u_l'' h''}}{\partial x_l} - \dot{\bar{q}}_{rad} \tag{2.29}$$

In the above averaged equations, the first type of unclosed terms are the second-moment quantities which are conventionally approximated by turbulence modelling. These are the turbulent stresses (also called Reynolds stresses $\widetilde{\bar{\rho}u_l''u_m''}$) and the turbulent scalar fluxes. The latter include the turbulent diffusional transport of enthalpy ($\widetilde{\bar{\rho}u_l''h''}$) and the turbulent diffusional transport of chemical species concentration ($\widetilde{\bar{\rho}u_l''n_s''}$). The mean source terms such as the species formation rate ($\overline{\dot{\omega}_s}$) and mean heat loss by radiation ($\overline{\dot{q}_{rad}}$) require different approaches usually because they are non-linear functions of dependent random variables and modelling is needed for the mechanism of their interaction with turbulence. The latter poses the main problem in modelling of turbulent reactive flows. In the next few sections we describe the two main classes of RANS turbulence modelling; the eddy-viscosity models and the second-moment closure.

2.7.3 Eddy-viscosity models

The turbulent eddy-viscosity models are based on the stress-strain approximation introduced by Boussinesq in 1877 [186, 114]. It drew an analogy between the Newtonian viscous stresses and the turbulent Reynolds stresses. The generalised formulation of this approximation states that the anisotropic parts of the Reynolds stresses ($\widetilde{u_l''u_m''} - \frac{2}{3}\delta_{lm}\tilde{k}$) are proportional to the mean strain field by introducing a turbulent quantity called the effective eddy viscosity ($\mu_t = \bar{\rho}\nu_t$). The generalised form of the linear eddy-viscosity formulation is given by the following relation:

$$\begin{aligned}\widetilde{\bar{\rho}u_l''u_m''} &= -\mu_t \left(\frac{\partial \tilde{u}_l}{\partial x_m} + \frac{\partial \tilde{u}_m}{\partial x_l} \right) + \frac{1}{3}\delta_{lm}\widetilde{\bar{\rho}u_n''u_n''} \\ &= -\mu_t \left(\frac{\partial \tilde{u}_l}{\partial x_m} + \frac{\partial \tilde{u}_m}{\partial x_l} \right) + \frac{2}{3}\delta_{lm}\tilde{\rho k}\end{aligned}\tag{2.30}$$

where the Kronecker delta ($\delta_{lm} = 1$ if $l = m$, $=0$ if $l \neq m$). Similarly, the eddy-viscosity approximation may be applied to the scalar turbulent flux:

$$\widetilde{\bar{\rho}u_l''\phi_s''} = \frac{\mu_t}{\sigma_s} \frac{\partial \tilde{\phi}_s}{\partial x_l}\tag{2.31}$$

σ_s is the turbulent Prandtl or Schmidt number of the scalar ϕ_s . Now a model is needed for the specification of the turbulent (eddy) viscosity (ν_t) which is equivalent to $(\mu_t/\bar{\rho})$. This is achieved by employing the mixing-length hypothesis and/or solving one or more transport equation(s) for turbulent quantities. These are outlined in the following sub-sections.

2.7.3.1 Mixing-length (Zero-equation) model

This model does not solve a transport equation for any turbulent quantity. The mixing length is approximated by some algebraic expression e.g. as a function of position. The earliest form of this model is the mixing-length theory that is attributed to Prandtl in 1925. For the so-called two-dimensional thin shear flow in which there is only one non-zero velocity gradient ($\frac{\partial \tilde{u}_1}{\partial x_2}$), the eddy viscosity was prescribed algebraically by the following relation:

$$\nu_t = l_m^2 \left| \frac{\partial \tilde{u}_1}{\partial x_2} \right| \quad (2.32)$$

A more general form can be taken as:

$$\nu_t = l_m^2 \sqrt{\left(\frac{\partial \tilde{u}_l}{\partial x_m} + \frac{\partial \tilde{u}_m}{\partial x_l} \right)^2} \quad (2.33)$$

In near wall flows, the mixing length (l_m) is usually specified to be proportional to the distance from the wall (y) such that ($l_m = \kappa y$) in the log-law region. Many damping functions have been proposed to extend this formula throughout the near-wall region. The major limitation of the mixing length model is the need to specify the mixing length which is dependent on the geometry of the flow and the wall distance might be difficult to define. Another limitation is that the turbulent viscosity vanishes whenever the strain rate vanishes leading to under-predictions of turbulence close to separation and reattachment.

2.7.3.2 One-equation models

Eddy-viscosity models are usually classified by the number of equations solved for turbulent quantities. One-equation models avoid the second limitation of the zero-equation models mentioned above by eliminating the use of the strain rate to define the turbulent viscosity and thus it will not vanish when the strain rate vanishes. A common one-equation model solves the transport equation of the turbulent kinetic energy k . The use of k in this model is attributed to both Prandtl and Kolmogorov. Mixing length scale is still required and the eddy viscosity is modelled with the relation:

$$\nu_t = C_\mu^{1/4} \tilde{k}^{1/2} l_m \quad (2.34)$$

The dissipation rate needed for the equation of k is modelled in terms of k and l_m , usually with a relation like:

$$\tilde{\varepsilon} = C_\mu^{3/4} \frac{\tilde{k}^{3/2}}{l_m} \quad (2.35)$$

Despite the advantage in accuracy achieved by this model over the zero-equation models, the drawback of incompleteness remains as the length scale still has to be specified. To remove this incompleteness, Spalart and Allmaras [200, 201] developed another one-equation model that solves a transport equation for the eddy viscosity itself. This model was initially developed for applications in aerodynamic flows such as boundary-layer separation over an aerofoil. The model has, subsequently, been modified to improve its performance and to make it applicable to different types of flows such as flows with rotation and curvature effects [67].

2.7.3.3 The $k - \varepsilon$ (two-equation) model

Two equation models solve the transport equation of k and another turbulent quantity. There are many choices for the second variable. The most widely known two-equation models are the $(k - \varepsilon)$ model and the $(k - \omega)$ model. (ω) is the turbulent frequency which is the reciprocal of the turbulent integral time scale τ . Other

two-equation models have also been developed like $(k - l)$, $(k - \tau)$ and $(k - k\tau)$ models.

The $(k - \varepsilon)$ model is the most widely used eddy-viscosity model and is incorporated in most commercial and several academic CFD codes. The model has shown encouraging applicability to modelling simple flows in a variety of applications such as heat transfer, multi-phase flows and combustion. It is a complete turbulence model which provides sufficient information like the length and time scale that are needed for the modelling of additional processes such as those in turbulent reactive flows. The formulation of the model in the standard form was originally proposed by Jones and Launder [94, 95]. Since $\tilde{\varepsilon}$ is obtained from its transport equation, a new relation for ν_t is used:

$$\nu_t = C_\mu \frac{\tilde{k}^2}{\tilde{\varepsilon}} \quad (2.36)$$

One can arrive at this equation by eliminating the mixing length from equations (2.34) and (2.35). Alternatively, it can be readily deduced from the stress-strain relation for two-dimensional simple shear flow with local equilibrium which is given as:

$$\widetilde{u_1''u_2''} = -C_\mu \frac{\tilde{k}^2}{\tilde{\varepsilon}} \frac{\partial \tilde{u}_1}{\partial x_2} = \nu_t \frac{\partial \tilde{u}_1}{\partial x_2} \quad (2.37)$$

The transport equations for the mean turbulent kinetic energy k and its dissipation rate ε in the Favre-averaged form can be written:

$$\frac{D\tilde{k}}{Dt} = \frac{\partial}{\partial x_m} \left[\left(\frac{\nu_t}{\sigma_k} + \nu \right) \frac{\partial \tilde{k}}{\partial x_m} \right] + \tilde{P}_k - \tilde{\varepsilon} \quad (2.38)$$

$$\frac{D\tilde{\varepsilon}}{Dt} = \frac{\partial}{\partial x_m} \left[\left(\frac{\nu_t}{\sigma_\varepsilon} + \nu \right) \frac{\partial \tilde{\varepsilon}}{\partial x_m} \right] + c_{\varepsilon 1} \frac{\tilde{\varepsilon}}{\tilde{k}} \tilde{P}_k - c_{\varepsilon 2} \frac{\tilde{\varepsilon}^2}{\tilde{k}} \quad (2.39)$$

The diffusion term in the two transport equations is written by analogy to the eddy-diffusivity approximation using the eddy viscosity ν_t and turbulent Prandtl numbers σ_k and σ_ε . An effective total viscosity is employed, though the molecular

viscosity's contribution is negligible when Re is high and can be dropped. Consideration of additional terms for variable-density flows can be found in [99]. $\widetilde{P}_k$ is the production rate of k which is defined by the relation:

$$\widetilde{P}_k = -\widetilde{u_l'' u_m''} \frac{\partial \widetilde{u}_l}{\partial x_m} \quad (2.40)$$

By introducing the eddy-viscosity relation to the Reynolds stress tensor in the previous equation, an alternative formula maybe written for $\widetilde{P}_k$:

$$\widetilde{P}_k = \nu_t \frac{\partial \widetilde{u}_l}{\partial x_m} \left(\frac{\partial \widetilde{u}_l}{\partial x_m} + \frac{\partial \widetilde{u}_m}{\partial x_l} \right) \quad (2.41)$$

The values of the constant coefficients of the model in the standard form are given in the following table:

C_μ	$c_{\varepsilon 1}$	$c_{\varepsilon 2}$	σ_k	σ_ε
0.09	1.44	1.92	1	1.3

The above form and coefficient values are fixed empirically for some simple flows see e.g. [115, 67]. In general, the weaknesses of the model are linked to the eddy-viscosity approximation and/or to the modelled (ε) equation. The linear diffusivity fails in flows with weak streamline curvature, in swirling flows and in wakes. Further, in near wall flows and adverse pressure gradient, the model predicts too-high viscosity (skin friction) which explains the preference of the $(k - \omega)$ model for flows over aerofoils [115]. In buoyancy-affected flows, additional source terms and other modifications have been considered but these flows pose a real challenge to linear eddy viscosity models.

The model has been subject to several modifications [including changing coefficient values] to avoid weaknesses and disappointing predictions in certain flows. However, there is no version of the model that provides a unique and universal improvement. For example, the spread rate of the round jet is commonly improved in the $k - \varepsilon$ computations by reducing ($c_{\varepsilon 2}$) to a value like 1.8. Jones and Kakhi used a value of 1.85 for this coefficient and set C_μ to 0.065 instead of 0.09. Merci, Roekaerts

and coworkers [144, 193] performed calculations of turbulent diffusion jet flames using the three versions of this model. The first two were with the linear eddy form but differed in the $c_{\varepsilon 2}$ value (1.92 or 1.8) while the third was with the non-linear eddy form of the model. The modified coefficient ($c_{\varepsilon 2} = 1.8$) linear eddy calculation and the non-linear eddy model showed a considerable advantage over the standard ($c_{\varepsilon 2} = 1.92$) linear eddy model in the predictions of the round jet spreading rate. A different modification which is sometimes referred to as the round jet correction (RJC) is to use an additional source term in the ε equation such as the version proposed by Pope [177] and others. The ε equation in the version derived using the Renormalisation Group (RNG) theory of small scales [165] was also modified with an additional term.

2.7.3.4 Near-Wall RANS modelling

When there is a solid surface (wall), a very thin viscous sublayer is formed adjacent to the wall in which flow variables vary steeply. Modified low-Reynolds-number forms of the $k-\varepsilon$ model were developed to account for viscous and other near-wall effects. They usually employ a modified ε transport equation and additional near-wall tuning coefficients [116]. However, a very fine grid is required to resolve this layer which results in a quite expensive modelling. Alternatively, the near-wall sublayer is commonly treated using wall functions like those based on the Log-Law of the wall. The non-dimensionalizing wall-friction velocity $\sqrt{\tilde{\tau}_w/\bar{\rho}}$ can be replaced by $\sqrt{\tilde{k}}$ [117]. The computational cost reduces significantly with the use of wall functions. Craft et al. [42] developed an analytical wall-function approach. Turbulent viscosity is set to zero within the viscous sublayer. Some schemes employ a simplified model for ε in the near wall node such as assuming a prescribed dissipation length scale for the fully developed near-wall region. Wall-function approaches are also applicable to advanced RANS modelling such as non-linear eddy-viscosity models and second moment closures (Reynolds stresses models).

2.7.3.5 Non-linear eddy-viscosity models

The linear eddy-viscosity models have been widely used for industrial applications and have proven to be a valuable tool for predictions of a wide range of turbulent flows. However, there are some deficiencies inherent in them that do not exist in the Reynolds stress models. Consequently, linear eddy viscosity models fail in flows with complex strain fields, non-equilibrium flows and turbulent secondary flows in ducts. To remedy this problem, many suggestions have been made to extend the strain rate effects on the stress field. One option is to propose a more general non-linear formulation in which the linear relation is retained as the leading term. The non-linear formulation of the stress-strain relation may include quadratic and even cubic combinations of the strain rate and vorticity. This approach is called the non-linear eddy-viscosity model (NLEVM). It does provide some level of anisotropy of the stresses allowing for some improvements over the linear model. In flows with stronger anisotropy, the NLEVM approach alone does not encompass adequate representation of such a feature of the turbulent field. This has been remedied by solving a transport equation for one of the invariants of the non-dimensional stress anisotropy ($a_{lm} = \widetilde{u_l'' u_m''} / \tilde{k} - \frac{2}{3} \delta_{lm}$) such as the double product $a_{lm} a_{lm}$ or possibly using a higher anisotropy product [43]. The NLEVM is usually found to introduce some numerical complications which limit the motivations to use them except for flows where the linear eddy viscosity models fail.

2.7.4 Second-moment closure

This class of models is based on the solution of transport equations for second-moment quantities such as the differential Reynolds-stress model (RSM) which solves transport equations for the six components of the Reynolds stress tensor ($\widetilde{u_l'' u_m''}$). It is a more complex closure level which provides more details on the characteristics of the flow and the turbulent processes that accompany it. If scalar calculations are involved, transport equations for the turbulent scalar fluxes ($\widetilde{u_l'' \phi_s''}$) and possibly equations for cross-correlations of scalar fluctuations ($\widetilde{\phi_{s_1}'' \phi_{s_2}''}$) are also solved. Clearly in multicomponent flows such as a reacting mixture with a large number of species, a full second moment closure of the scalar field would involve a large number

of transport equations. The practical choice in flows with multi-species composition is to describe the composition with a reduced set of variables. By doing so, solution of transport equations for a few representative scalars (e.g. fuel mixture fraction, reaction progress variable and/or enthalpy) is sufficient. Important individual chemical species such as the fuel mass fraction may still need to be transported even with the reduced composition description. Therefore, only second moment correlations involving the fluctuations of these scalars need to be included in the second moment closure.

Essentially, an equation for the dissipation of turbulent kinetic energy $\tilde{\varepsilon}$ is solved when solving the $\widetilde{u_l'' u_m''}$ equations while the turbulent kinetic energy is obtained by summing the three normal Reynolds stresses ($k = \frac{1}{2} \widetilde{u_n'' u_n''}$). Similarly, an equation for the scalar variance $\widetilde{\phi_s''^2}$ is involved when solving $\widetilde{u_l'' \phi_s''}$. The transport equations of Reynolds stresses and turbulent scalar fluxes and variance can be derived from the equations of the instantaneous and mean flow variables.

The terms that appear in the transport equations of the Reynolds stresses for simple flows are mentioned here. On the right-hand side, we have the total derivative term which includes the temporal evolution and convection by mean flow field. On the left hand side, we have the production tensor ($\tilde{P}_{lm}$), the dissipation tensor ($\tilde{\varepsilon}_{lm}$), the pressure-strain or (pressure-scrambling) tensor ($\tilde{R}_{lm}$) and the diffusion tensor ($\tilde{D}_{lm}$) of the Reynolds stress. The transport equations of the Reynolds stresses, turbulent scalar flux and scalar variance are now written:

Reynolds stresses tensor

$$\frac{D\widetilde{u_l'' u_m''}}{Dt} = \tilde{P}_{lm} - \tilde{\varepsilon}_{lm} + \tilde{R}_{lm} + \tilde{D}_{lm} \quad (2.42)$$

$$\tilde{P}_{lm} = - \left(\widetilde{u_l'' u_n''} \frac{\partial \tilde{u}_m}{\partial x_n} + \widetilde{u_m'' u_n''} \frac{\partial \tilde{u}_l}{\partial x_n} \right) ,$$

$$\tilde{\varepsilon}_{lm} = 2\nu \frac{\partial \widetilde{u_l''}}{\partial x_n} \frac{\partial \widetilde{u_m''}}{\partial x_n} , \quad \tilde{R}_{lm} = \frac{p}{\rho} \overline{\left(\frac{\partial u_l''}{\partial x_m} + \frac{\partial u_m''}{\partial x_l} \right)} \quad and$$

$$\tilde{D}_{lm} = \frac{\partial}{\partial x_n} \left(\nu \frac{\partial \widetilde{u_l'' u_m''}}{\partial x_n} - \widetilde{u_l'' u_m'' u_n''} - \frac{\overline{p u_l''}}{\rho} \delta_{ln} - \frac{\overline{p u_m''}}{\rho} \delta_{mn} \right)$$

Turbulent scalar flux equation

$$\frac{D \widetilde{u_l'' \phi_s''}}{Dt} = \tilde{P}_{l,s}^{u''\phi''} - \tilde{\varepsilon}_{l,s}^{u''\phi''} + \tilde{R}_{l,s}^{u''\phi''} + \tilde{D}_{l,s}^{u''\phi''} + \tilde{S}_{l,s}^{u''\phi''} \quad (2.43)$$

$$\tilde{P}_{l,s}^{u''\phi''} = - \left(\widetilde{u_l'' u_n''} \frac{\partial \tilde{\phi}_s}{\partial x_n} + \widetilde{\phi_s'' u_n''} \frac{\partial \tilde{u}_l}{\partial x_n} \right) ,$$

$$\tilde{\varepsilon}_{l,s}^{u''\phi''} = (\nu + D_s) \frac{\partial \widetilde{u_l''}}{\partial x_n} \frac{\partial \phi_s''}{\partial x_n} , \quad \tilde{R}_{l,s}^{u''\phi''} = \frac{\overline{p \partial \phi_s''}}{\rho \partial x_l} ,$$

$$\tilde{D}_{l,s}^{u''\phi''} = \frac{\partial}{\partial x_n} \left(- \widetilde{u_l'' u_n'' \phi_s''} - \frac{\overline{p \phi_s''}}{\rho} \delta_{ln} \right) \quad \text{and} \quad \tilde{S}_{l,s}^{u''\phi''} = \frac{\overline{u_l'' \dot{\omega}_s''}}{\bar{\rho}}$$

Scalar variance equation

$$\frac{D \phi_s''^2}{Dt} = \tilde{P}_s^{\phi''} - \tilde{\chi}_s + \tilde{D}_s^{\phi''} + \tilde{S}_s^{\phi''} \quad (2.44)$$

$$\tilde{P}_s^{\phi''} = -2 \widetilde{\phi_s'' u_n''} \frac{\partial \phi_s}{\partial x_n} , \quad \tilde{\chi}_s = 2 D_s \frac{\partial \widetilde{\phi_s''}}{\partial x_n} \frac{\partial \phi_s''}{\partial x_n}$$

$$\tilde{D}_s^{\phi''} = \frac{\partial}{\partial x_n} \left(D_s \frac{\partial \phi_s''^2}{\partial x_n} - \widetilde{u_n'' \phi_s''^2} \right) \quad \text{and} \quad \tilde{S}_s^{\phi''} = 2 \frac{\overline{\phi_s'' \dot{\omega}_s''}}{\bar{\rho}}$$

One of the main attractive features of the second moment closure is that the production terms due to shear and mean scalar gradients ($\tilde{P}_{lm}$, $\tilde{P}_{l,s}^{u''\phi''}$, $\tilde{P}_s^{\phi''}$) do not contain unknown higher moments and are thus readily closed. Buoyancy terms were not inserted in these equations. However, when buoyancy forces are present, they generate more turbulence which would be represented by additional production terms appearing in every equation. Production by buoyancy is usually in closed form as well. Modelling of the other terms in the transport equations, though is required. The pressure-strain tensors ($\tilde{R}_{lm}$, $\tilde{R}_{l,s}^{u''\phi''}$) represent an important element of the second moment closure and they have received much modelling efforts due to the different physical processes associated with its sub-terms. The scalar variance equation does not contain a pressure-strain correlation.

The molecular diffusion contribution in the turbulent scalar flux $\widetilde{u_l'' \phi_s''}$ was omit-

ted for clarity. Diffusion by turbulence (represented by the triple moments) can be conveniently modelled by analogy of the eddy-diffusivity or perhaps more appropriately by the generalized gradient-diffusion hypothesis (GGDH) of Daly and Harlow [46]. The dissipation term in the Reynolds stresses is usually modelled by the assumption of isotropy ($\tilde{\varepsilon}_{lm} = \frac{2}{3}\delta_{lm}\tilde{\varepsilon}$). Dissipation rate of the scalar variance is modelled by assuming proportionality between the dynamic and scalar time scales and the time scale ratio may be assumed as a constant C_ϕ , thus mathematically expressing:

$$\tilde{\chi}_s = \frac{C_\phi}{2} \frac{\varepsilon}{k} \tilde{\phi}_s'^2 \quad (2.45)$$

The turbulent flux and variance of reactive scalars are also generated by fluctuations in chemical reaction ($\tilde{S}_{l,s}^{u''\phi''}$, $\tilde{S}_s^{\phi''}$) which disappear only if the scalar is inert (conserved).

There is a broad range of models for the unclosed terms. These models have been developed and improved over the years to make the performance at this closure level more accurate. Both the most basic form of the differential RSM and the algebraic version (Algebraic stress model ASM) have similar limitations that neither of the two capture the strong anisotropy observed in some complex flows and in regions with strong velocity-pressure interactions such as near-wall regions. For instance, Launder [115] noted that the pressure reflection from solid surfaces influences the transfer of kinetic energy to the wall-normal stress. This influence makes the turbulent energy redistribution process in these regions different from that in free flows. The overall effect of the wall is the reduction of the return to isotropy since wall reflections cause damping of the velocity fluctuations normal to the surface. This process could only be correctly predicted by second moment closure if advanced and more satisfactory submodels were employed. In this regard, Craft and coworkers (see e.g. [44] and references cited there) developed the two-component-limit Reynolds Stress (TCL-RSM) model. The TCL-RSM model is based on enforcing constraints that maintain realizable stresses in the two-component turbulence i.e. when one of the components of velocity fluctuations drops to zero. They have found that the TCL-RSM version is superior and has more general applicability than simpler ver-

sions for a wide range of complex flows in addition to avoiding the need for specific corrections.

There is a vast literature on the developments and applications Reynolds-stress models but we do not intend to discuss them in detail here. RSM has been applied to turbulent flames such as the work by Lindstedt and Vaos who performed second moment calculation of turbulent flames [132].

In general, the second moment closure is more difficult and more costly than with eddy-viscosity models (e.g. $k - \varepsilon$ model). In the RSM, there are seven equations that need to be solved. These equations are coupled and more complicated than the equation of k . Hence they need more user expertise and greater coding efforts. Further, the solution of the $k - \varepsilon$ model is usually smoother and numerically more stable probably due to the diffusive nature of turbulence in these equations [170]. The extra effort needed in the RSM is usually weighed against the advantage of accuracy. Although this is not very convincing in simple flows, the RSM is applicable to complex flows where the eddy viscosity models fail such as flows with secondary motions. It is also worth noting that the advantage they provide for complex flows, although, inevitably, accompanied with some modelling complexity, is now well recognised and their cost is not considered to be excessive.

Chapter 3

Turbulent Combustion and Modelling of Non-premixed Combustion

3.1 Introduction

As it has been shown in the previous chapter, the Favre averaging of the conservation equations limits the closure problem to a few terms. In non-reacting flows the unclosed quantities are the Reynolds stresses $\widetilde{(u''_l u''_m)}$. If scalar mixing is involved, then closure is also needed for second-moment scalar quantities such as the turbulent scalar fluxes $\widetilde{(u''_l \phi''_s)}$ and scalar variances $\widetilde{(\phi''_s{}^2)}$. In turbulent combustion flows, the chemical reaction process as well as other relevant processes like thermal radiation and particulate formation appear as new source terms (e.g. $\overline{\dot{\omega}_s}$, $\overline{\dot{q}_{rad}}$) in the transport equations of mean scalar variables. These averaged terms are unclosed since they can not be obtained from mean quantities only. Due to their nature, the interaction between these processes and turbulence occurs in a complicated manner introducing additional closure problems which are different from that of the turbulent transport. This problem is mainly caused by the presence of a large number of scalar components and the wide range of flow and chemical scales. That is why combustion is considered to be a complicated combination of physical and chemical processes interacting strongly with each other.

Mass density (ρ) is an important quantity which always needs to be determined in calculations of combustion flows. The influence of combustion on the flow field (such as the effects of heat release and evolution of composition) is usually implied in the variation of mean density.

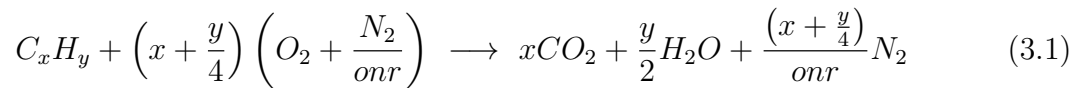
In this chapter, we will introduce the theory of combustion chemistry and its kinetics to see how closure and computational problems are introduced by the reaction source term. The chapter would then continue to discuss how this problem is approached in the case of turbulent non-premixed combustion through the introduction of several models for the latter.

3.2 Combustion chemistry

3.2.1 Global gas-phase chemistry

The simplest and most ideal case for combustion chemistry is to assume complete reaction between fuel and oxidiser at stoichiometric ratios. The fuel and oxidiser are assumed to be completely and instantly consumed and the burned mixture will constitute combustion products only. In such a case, the products of the combustion of hydrocarbon fuels would be CO_2 and H_2O only.

If the oxidiser is air, then Nitrogen is usually assumed to be an inert species which does not affect the reaction or amount of heat release but reduces the temperature of the burned mixture since it forms most of the air. This can be described by the following stoichiometric reaction:



This case assumes a single global reaction at the stoichiometric condition. This reaction is instantaneous and the reaction zone would be a layer or sheet with infinitely small thickness. Reactants and products do not coexist. In the case of non-premixed combustion, reactants (fuel and oxidiser) are always separated by the reaction zone

as they are converted to products instantly as they mix. However, the combustion reactions in practical combustors can occur at conditions where the air-fuel ratio is different from the stoichiometric ratio. An event may occur, such that the mixture does not have enough residence time to get fully mixed or when reactions can not be considered instantaneous compared to other processes. This leads to the so-called "incomplete combustion" in which there will be some excess fuel and/or oxidiser as well as other products of incomplete combustion such as CO, H₂, unburned hydrocarbons and other species. Nitrogen may also participate in the reactions and nitric oxides NO_x are formed at high temperatures in addition to other species containing the nitrogen atom.

Like other chemically reacting flows, the studies of combustion chemistry show that there is a large series of chemical reaction steps which are even reversible, unlike the above irreversible one-step reaction. Products dissociate at high temperatures and form back other products. The reaction steps are called elementary reactions which occur at different rates, constituting a complex chemical mechanism of combustion which involves large number of species including radical species. These chemical mechanisms are governed by chemical kinetics which along with diffusive transport processes represent a dominant feature of combustion and govern important phenomena like ignition and extinction. The theory of chemical kinetics is described in the next section.

It is appropriate at this stage to point out that chemical equilibrium state is indeed more reasonably justifiable than irreversible one-step chemistry. If, for example, the mixture resides for enough time in the reaction zone, it is more reasonable to assume that it reaches chemical equilibrium state than to assume global full reaction due to the significant dissociation rates occurring at such high temperatures. The assumption that equilibrium dominates finite-rate chemistry though, is only justified when chemistry is not kinetically controlled, such as when chemical reactions occur at a more rapid rates than other physical processes. Computation of combustion with the full chemical equilibrium assumption is known to be sufficient

for estimates of heat release and major species concentrations. Although a large number of species can be included in the calculations, the results for the composition will be compromised particularly for the minor species and when there is a concern for other parameters controlled by rates of elementary reactions. Chemical equilibrium can be coupled with the conserved-scalar presumed-PDF approach to solve turbulent combustion and this will be explored later in this chapter. The methodology of determining the equilibrium composition using thermodynamic laws is a starting point for the formulation of the rate-controlled constrained equilibrium (RCCE) state. In the RCCE, combustion is assumed to reach partial equilibrium states which are controlled by the most important and most relevant finite-rate chemical kinetics.

3.2.2 Detailed gas-phase chemical kinetics

As stated above, a realistic chemistry of combustion usually involves a large set of elementary reactions which are reversible, and each of these elementary reactions proceeds at its own rate. The chemical kinetic mechanism refers to the list of these elementary reactions and related information such as the rate-constant coefficients and the thermodynamic data.

A chemical mechanism involving N_R elementary reaction steps and N_s species can be written in the following generalised form:

$$\sum_{s=1}^{N_s} \nu'_{sk} M_s \rightleftharpoons \sum_{s=1}^{N_s} \nu''_{sk} M_s \quad (k = 1, \dots, N_R) \quad (3.2)$$

The net formation rate of individual species is obtained from the chemical mechanism using its net molar stoichiometric coefficients ($\nu_{sk} = \nu''_{sk} - \nu'_{sk}$) and the rates of all individual elementary reactions ($\hat{\omega}_k$). The chemical source term in the specific mole number equation ($\dot{\omega}_s$) in kmol/(m³.s) can be formulated as follows:

$$\dot{\omega}_s = \sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k) \quad (s = 1, \dots, N_s) \quad (3.3)$$

and the chemical source term in the species mass fraction conservation equation ($\dot{\Omega}_s$ in $kg/(m^3.s)$) is given by:

$$\dot{\Omega}_s = W_s \sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k) \quad (s = 1, \dots, N_s) \quad (3.4)$$

Chemical kinetics of elementary reactions are obtained according to the law of mass action which relates the elementary reaction rates to their rate constants and the molar concentrations of reactants. In this law, which is derived from the collision theory of ideal gases [228], concentration of reactants are raised to exponents that are equal to their respective stoichiometric coefficients. In other words ν'_{sk} is associated with the forward rate-constant k_k^f and ν''_{sk} is associated with the backward rate-constant k_k^b . Therefore, the net reaction rate of an elementary reaction step with both forward and backward rates can be expressed by the following equation:

$$\hat{\omega}_k = k_k^f \prod_{s=1}^N [\rho n_s]^{\nu'_{sk}} - k_k^b \prod_{s=1}^N [\rho n_s]^{\nu''_{sk}} \quad (3.5)$$

where $[\rho n_s]$ represents the species molar concentration per unit volume e.g. $kmole/m^3$. The rate constants of the elementary reactions (k_k^f, k_k^b) are governed by the Arrhenius law which expresses the dependence on temperature.

$$k_k(T) = BT^a \exp(-E_r/RT) \quad (3.6)$$

where B and a are constants. The pre-exponential factor BT^a which is a function of temperature is also called the frequency factor. E_r is the activation energy of the reaction.

3.3 Other important processes in diffusion flames

In non-premixed flames, diffusion is an essential process for combustion to occur and has been viewed as a rate-limiting and controlling process. The outcome of a chemical reaction depends on the rate of diffusion of reactants into the reaction zone and how rapidly they mix by molecular diffusion [176]. If chemistry is much faster

than the flow processes, molecular diffusion will be a rate-limiting process in laminar flames. In turbulent non-premixed flames however, mixing of the fluid elements are strongly influenced by the turbulent stretching of the flow, and mixing first occurs at larger scales. This is called macromixing. Scalar concentration gradients are then steepened at smaller scales, generating new smaller scalar fluctuations [170]. This effect of mixing enhancement by turbulence is progressively transferred to the smallest scales where molecular diffusion is effective. Pope [187] pointed out that since it is observed that the flame height does not vary with the jet velocity and Reynolds number, molecular diffusion is not the rate-limiting process in turbulent jet diffusion flames. This phenomenon actually demonstrates a central role for turbulent mixing since the increase in flame velocity is accompanied by an equivalent parallel decrease in the turbulent mixing time scale. However, Damköhler number which is the ratio between the flow time scale and the chemical time scale $Da = \tau_m/\tau_c$, is also decreased. Turbulent jet flames with low Da undergo complicated phenomena like extinction or extinction followed by reignition which indicate strong interaction between turbulent mixing and chemical reaction and in some situations neither of the two is the only rate-limiting process.

3.4 Unclosed averaged source terms

3.4.1 Chemical reaction closure

In the ideal case, chemical kinetics should be used to evaluate the reaction rate term. But, chemical mechanisms (if known) usually involve a large number of species and a large number of elementary reactions. In addition there are large variations between the scales of these reactions such that an efficient inclusion of detailed mechanisms into conventional models of turbulent flows poses a formidable challenge. Furthermore, it has been shown that the reaction source term is a highly non-linear function of temperature and species concentrations. Therefore, when averaging or filtering is applied, there is no straightforward way of expanding this term without getting unclosed multidimensional moment correlations. The chemical source term, therefore, presents a highly unresolved closure problem in models like moments methods

due to the non-linearity of the reactions rate equations and the existence of many reaction steps. Mean quantities of the composition, temperature and density do not produce the correct chemical reaction rate due to the complicated coupling between these scalars and the appearance of correlated fluctuations. From one view, turbulent fluctuations have a strong effect on the chemistry through the generation of multi-dimensional scalar fluctuations. Therefore, knowledge of covariances and even (if possible) some higher moment correlations along with mean quantities is theoretically insufficient to evaluate the mean of the combustion reaction rate. It has been widely recognised for decades (as has been shown by Libby and Williams [124]) that, even for the most simple case of one-step irreversible reaction and with Favre averaging, several complications are encountered when the averaging process is applied to the instantaneous reaction source term. In the case of unweighted averaging, the problem is even more complicated due to the appearance of extra terms involving density fluctuations. Libby and Williams [124] and others put forward an interpretation for this complexity such that the effective chemical reaction rate is influenced by the multitude of heterogeneities in composition and temperature which are generated and modified by turbulent fluctuations. On the other hand, heat released by reaction and density variations have an effect on the turbulent structure [19]. In addition, combustion reactions occur in a wide range of time scales and hence every elementary reaction interacts differently with turbulent scales [170]. The coupling between the turbulent flow field and the combustion chemical reaction rate is thus a complicated mechanism which is usually referred to as the turbulence-chemistry interaction (TCI) phenomenon.

3.4.2 Thermal radiation closure

In addition to chemical reaction, combustion is also accompanied by a loss of heat through thermal radiation. Radiation in turbulent flows poses a problem that is similar to the problem of chemistry. Radiative heat flux is governed by non-linear functions of temperature and species concentrations as well and is also affected by turbulent fluctuations. Thus, like the chemical source term, inclusion of heat radiation in calculations of turbulent flows is not straightforward and requires the consid-

eration of a phenomenon which is called the turbulence-radiation interaction (TRI) [148]. However, chemical kinetics has received much more attention and there have been many more advances in chemical mechanisms than is the case with radiation mechanisms. The most probable reasons for this are the mathematical complexity of radiation mechanisms and the fact that some flames are non-luminous and exhibit a low amount of radiation. These flames are either computed without any consideration for radiation (adiabatic flow assumption) or with traditional simplified models for the turbulence-radiation interaction (TRI). Non-luminous flames are considered to be close to the optically-thin limit [148] which have little self-absorption, and radiation emission is dominant. However, in optically thick luminous flames, the amount of radiative loss constitutes a considerable amount relative to the total heat release by combustion. The amount of radiation is strongly affected by TRI which causes temperature to be considerably lower than when all turbulent fluctuations are ignored (i.e non-TRI model). Thus, a calculation of radiative heat flux and a representation of turbulence radiation interaction (TRI) need to be properly encompassed when calculating these flames.

TCI models such as the presumed and transported PDF models can also provide a mechanism for TRI representation since both phenomena are manifested by scalar fluctuations. The Transported PDF approach has the advantage that it does not impose any limitation on the details of the chemical kinetics or the thermal radiation model, and both chemical and radiation source terms therefore appear in closed and exact forms. Several simple and advanced models for TCI which have been developed to compute turbulent combustion flows are now reviewed.

3.5 Models based on the conserved scalar theory

In the early stages of combustion modelling, one widely invoked assumption to predict global properties of turbulent non-premixed flames was that chemistry is much faster than mechanical transport so that the Damköhler number Da is much greater than unity.

The theory of infinitely fast chemistry in diffusion flames led to the deduction that, under certain assumptions, instantaneous values of the species concentrations, temperature and density are uniquely related to a single conserved scalar which is the mixture fraction. The assumptions required are that the flow Mach number is low and the pressure is thermodynamically constant. The multi-component diffusion is replaced by Ficks law, species have equal diffusivities and unity Lewis number. The mixture fraction, which is an important quantity for diffusion flames, is defined as the fraction by mass of the mixture that originated from the fuel inlet stream. It usually takes the value of one in the fuel inlet stream and zero in the oxidant inlet stream. The modelled transport equations for the mean and variance (first and second moment) of mixture fraction can be written in the Favre-averaged form:

$$\frac{\partial \bar{\rho} \tilde{z}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_l \tilde{z}}{\partial x_l} = \frac{\partial}{\partial x_l} \left(\frac{\mu_t}{\sigma_z} \frac{\partial \tilde{z}}{\partial x_l} \right) \quad (3.7)$$

$$\frac{\partial \bar{\rho} \tilde{z}''^2}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_l \tilde{z}''^2}{\partial x_l} = \frac{\partial}{\partial x_l} \left(\frac{\mu_t}{\sigma_z} \frac{\partial \tilde{z}''^2}{\partial x_l} \right) + 2 \frac{\mu_t}{\sigma_z} \left(\frac{\partial \tilde{z}}{\partial x_l} \right)^2 - \bar{\rho} \tilde{\chi} \quad (3.8)$$

In the above equations, equal diffusivities and unity Lewis number assumptions have been applied. Molecular diffusion is neglected compared to turbulent transport. All turbulent transport terms have been modelled with gradient diffusion. For turbulent flux in the equation of (z) , this is shown by equation (3.9) while equations (3.10) and (3.11) show how turbulent flux and production terms appearing in (z''^2) equation have been modelled.

$$-\frac{\partial}{\partial x_l} \left(\bar{\rho} \tilde{u}_l'' \tilde{z}'' \right) = \frac{\partial}{\partial x_l} \left(\frac{\mu_t}{\sigma_z} \frac{\partial \tilde{z}}{\partial x_l} \right) \quad (3.9)$$

$$-\frac{\partial}{\partial x_l} \left(\bar{\rho} \tilde{u}_l'' \tilde{z}''^2 \right) = \frac{\partial}{\partial x_l} \left(\frac{\mu_t}{\sigma_z} \frac{\partial \tilde{z}''^2}{\partial x_l} \right) \quad (3.10)$$

$$-2 \bar{\rho} \tilde{u}_l'' \tilde{z}'' \left(\frac{\partial \tilde{z}}{\partial x_l} \right) = 2 \frac{\mu_t}{\sigma_z} \left(\frac{\partial \tilde{z}}{\partial x_l} \right)^2 \quad (3.11)$$

The two equations are commonly included in a RANS solution or the filtered form of these equations are solved with LES. The most important quantity in the above equations for combustion modelling is the scalar dissipation rate $\tilde{\chi}$ appearing in the $\widetilde{z''^2}$ equation. The exact form and modelling of this quantity is similar to $\tilde{\chi}_s$ in Eq. (2.44) and (2.45). It is perhaps beneficial to state here the specific exact and modelled expressions for the dissipation rate of the mixture fraction variance:

$$\tilde{\chi} = 2D \left(\widetilde{\frac{\partial z''}{\partial x_n} \frac{\partial z''}{\partial x_n}} \right) = \frac{C_\phi}{2} \frac{\varepsilon}{k} \widetilde{z''^2} \quad (3.12)$$

The PDF of the mixture fraction can be constructed (approximately) from the statistics of the first and second moments of mixture fraction if its shape is presumed. This requires solution of the transport equations of the mean and variance of mixture fraction. If density-weighted averaging is employed, then the PDF will be the density-weighted PDF which can be defined as:

$$\tilde{\mathcal{P}}(z; x, t) = \frac{1}{\bar{\rho}} \int_{\rho_{min}}^{\rho_{max}} \rho \mathcal{P}(\rho, z; x, t) d\rho \quad (3.13)$$

Once the presumed-shape PDF of the mixture fraction is determined from the statistics of its moments, the mean value of a scalar can be computed from:

$$\tilde{\phi}_s(x, t) = \int_0^1 \phi_s(z) \tilde{\mathcal{P}}(z; x, t) dz \quad (3.14)$$

The mean density can be obtained from the equation (dependence on space and time are dropped for clarity):

$$\frac{1}{\bar{\rho}} = \int_0^1 \rho^{-1}(z) \tilde{\mathcal{P}}(z) dz \quad (3.15)$$

The most commonly used PDF shape is the beta-function PDF. Chan [34] argued that this PDF type exhibits both the Dirac shape which is suitable for representing the flow regions with strong intermittency and the Gaussian shape for the well-mixed regions. The mathematical form of the beta PDF is stated in [82]. Jones and

Whitelaw [98] performed equilibrium calculations with several PDF shapes (double delta, clipped Gaussian and the beta PDF). Their calculations with double delta function were unsatisfactory, while the results with the clipped Gaussian and the beta PDF were successful. However, they emphasized that the calculations showed relatively low sensitivity to the precise shape of the PDF provided it was constructed from a continuous function.

3.5.1 One-step irreversible reaction model

The simplest of models where the theory of the conserved scalar can be applied is the infinitely fast chemistry model with a single-step irreversible reaction. Here, the reaction zone is an infinitely thin layer with products of the stoichiometric reaction [170]. The mixture around the reaction zone will be either fuel and product or oxidant and product. The instantaneous species concentrations and temperature are linearly related to the instantaneous mixture fraction but for the mean quantities the relation is non-linear due to the random fluctuations [18]. Knowledge of the mixture fraction PDF enables the computation of the mean composition, temperature and density. The presumed-shape PDF approach is commonly employed for this purpose. The simplicity of the one-step irreversible reaction model is inevitably accompanied with inaccurate predictions of the flow as it neglects dissociation of combustion products thereby not allowing any intermediate products such as CO to be formed. Temperatures considerably higher than the equilibrium value have been observed.

3.5.2 Chemical Equilibrium Model

At high temperatures, dissociation of products occurs allowing for intermediate species and radicals such as [CO, H₂, H, OH and O] to be formed. The assumption that the chemical reaction is reversible but fast enough to reach chemical equilibrium leads to considerable simplification of the modelling since the evaluation of the mean reaction rate is avoided and consequently no kinetic mechanism is required. The thermo-chemical state depends only on the mixture fraction but with a non-linear relation. The equilibrium model, therefore, applies the infinitely fast chemistry assumption and the conserved scalar theory so that temperature, com-

position and density can be obtained from knowledge of the mixture fraction using thermodynamic laws and data. Because of turbulence, both mixture fraction and other scalars have fluctuations. Like the one-step reaction model, the mean scalar field can be evaluated from the instantaneous values using the presumed PDF of the mixture fraction by minimizing the free energy of the mixture [98]. The chemical equilibrium model can alternatively be coupled with the transported PDF approach, which is equivalent to solving the PDF of the mixture fraction.

This model offers a considerable improvement over the one-step irreversible reaction, particularly for temperature and major species prediction, but it has significant limitations [19]. The main deficiency of the model is the failure to reproduce the strong interaction between chemistry and turbulence and the inaccurate estimation of CO, H₂ levels in fuel-rich regions and of species involving slow chemistry such as NO_x and soot. The equilibrium CO levels increase progressively with the equivalence ratio and the model produces unreasonably high CO concentration in fuel rich regions [82]. Further, if turbulent mixing is intensified, then non-equilibrium effects will be important and the chemical equilibrium will be unable to predict the compositional properties.

However the equilibrium model acts as one of the simplest models that is capable of producing the overall structure of flames which do not experience extinction, complicated ignition mechanism or other strong turbulence-chemistry interaction phenomena. It also provides good estimates of heat release and power output using a significantly cheaper approach.

3.5.3 Flamelet models

The laminar flamelet approach assumes that the turbulent diffusion flame comprises an ensemble of laminar diffusion flamelets. Reaction occurs in thin layers embedded within the structure of turbulent eddies. This is based on the idea that chemical time scales of combustion are usually shorter than the turbulent time scale. In the previous section, we have stated that if chemistry is infinitely fast so that $[Da \gg 1$

], then chemical equilibrium may be invoked. However, as turbulence is intensified or in the presence of finite-rate chemical processes, the mixture becomes unable to reach the full equilibrium state, despite the fact that reaction may still be faster than the dynamics of the flow. Effectively, when turbulent mixing is enhanced, turbulent time scale and Da are decreased and consequently chemical reaction rates have to be considered. Turbulence leads to the stretching and straining of the thin reaction layers resulting in a challenge between mixing and finite-rate chemistry. One simplified way of accounting for these effects is by the introduction of the flamelet model which has some capability of capturing moderate kinetic effects since finite rate chemistry can be incorporated in flamelet calculations. However, the flamelet concept does not apply for slow chemistry (like NOx) or phenomena affected by deep non-equilibrium effects such as ignition and extinction because it assumes that the flame responds immediately to aerodynamic straining.

The idea of using laminar flamelets in a turbulent flame was introduced conceptually by Williams [227]. Liew, Bray and Moss [e.g. [125]] showed that the data of a measured laminar flame can be utilised to construct an ensemble of laminar flamelets inside the turbulent diffusion flame. This led to significant improvements in predictions of CO and H₂ concentrations over the equilibrium model. Later, the same authors [126] modelled turbulent non-premixed methane-air flames using flamelets parametrised by scalar dissipation rate at peak temperature to incorporate the effect of stretching on the flamelet. Peters [169] provided an early review of the laminar flamelet model and presented its formulation for turbulent non-premixed flames. He pointed out that by using the mixture fraction as an independent variable the application of a general coordinate transformation at the flame surface leads to a one dimensional quasi-steady structure of all scalar profiles in terms of the mixture fraction. This transformation can be achieved by simply assuming that one of the spatial coordinates is locally normal to the flame surface. The dependence on this direction is then replaced by the dependence on mixture fraction. Further, the derivatives in the tangential directions of the physical space are neglected in comparison to those in the mixture fraction space. The scalar dissipation rate at stoichiometric mixture

fraction (χ_{st}) is taken as an external parameter and can be taken as an additional dimensionality of the flamelet acting like a diffusion coefficient [170].

The viewing of turbulent flames as a brush of thin laminar flamelets parametrised by the scalar dissipation rate as a measure of stretching characterizes how the effect of turbulence on chemistry is incorporated in this approach. This view was supported by the observation that the composition and temperature of flamelets are universally related to the mixture fraction and that a parametric dependence on a measure of the flow strain rate can be asymptotically invoked in turbulent flames. Laminar flamelet properties were initially extracted from experimental results but later computations like those of the steady counterflow laminar diffusion flame were commonly used [82]. The approach thus allows integration of chemistry to be performed separately from turbulent field calculations. The pre-computed chemistry is used to construct flamelet libraries (e.g. lookup tables) from which composition evolution in the turbulent flame can be interpolated. The thickness of the flame zone should be less than the Kolmogorov length scale. The chemical reactions occur at more rapid rates than mixing processes so that separation of chemistry from flow calculations can be justified [170].

In the flamelet model, the scalar field is obtained by assuming that scalar quantities are uniquely related to the mixture fraction. This relationship can be constructed by applying a universal coordinate transformation of the equations into the mixture fraction space. The flamelet equations can be written:

$$\rho \frac{\partial \phi_s}{\partial t} = \rho \frac{\chi}{2} \frac{\partial^2 \phi_s}{\partial z^2} + \dot{\omega}_s \quad (3.16)$$

Reynolds number is assumed to be sufficiently high for molecular diffusivity to be neglected with confidence. The unsteady term is usually dropped to give the steady flamelet equation:

$$\rho \frac{\chi}{2} \frac{\partial^2 \phi_s}{\partial z^2} + \dot{\omega}_s = 0 \quad (3.17)$$

The model effectively computes the statistical moments of temperature and composition of turbulent diffusion flame from those of the mixture fraction. This can be done by combining the flamelet equations with the presumed-shape PDF model. The presumed PDF of the mixture fraction alone (Eq. 3.14) can be employed to obtain the flamelets at a specific value of strain. Alternatively, the dimensions of the statistical distribution can be increased to include the statistics of the scalar dissipation rate at stoichiometry. The joint PDF of the mixture fraction and χ_{st} is therefore determined in order to solve the equations of the Stretched Laminar Flamelet model;

$$\tilde{\phi}_s(x, t) = \int_0^\infty \int_0^1 \phi_s(z, \chi_{st}) \tilde{\mathcal{P}}(z, \chi_{st}; x, t) dz d\chi_{st} \quad (3.18)$$

Traditional flamelet formulations assume that combustion occurs in a single regime and are based on either fully premixed or fully non-premixed combustion modes. In addition the reaction zone is assumed to be very thin compared to turbulent scales. However, as turbulence is intensified, small eddies can penetrate and destroy the thin flamelet reaction layer. Flamelets undergo straining and broadening leading to occurrence of non-flamelet regimes or extinction of the flame. The applicability of the flamelet model in these situations is questionable. In addition when slow processes like NO formation and soot are considered, transient (unsteady) effects have to be incorporated. These complexities imply that chemistry can not respond instantaneously to rapid variations in the scalar dissipation rate which represents a main weakness of the steady flamelets. The unsteady flamelet were proposed to remedy this problem [172]. The unsteady flamelet is described by Eq. (3.16). A Lagrangian flamelet time t_{fl} which is correlated to the stream-wise distance is introduced in the unsteady flamelet model:

$$t_{fl} = \int_0^x \frac{1}{u(x' | \tilde{z} = z_{st})} dx \quad (3.19)$$

Flamelet formulations have been improved to account for differential diffusion effects in turbulent non-premixed flames [173]. Pitsch and Peters derived modified

flamelet equations with the non-unity variable Lewis numbers. The mixture fraction is solely determined from the solution of a transport equation which uses the thermal diffusivity as the mixture fraction diffusivity. In this study, the model was tested using constant values for Lewis numbers of all chemical species which were adjusted with ad hoc analysis to give best flame predictions.

Kolla and Swaminathan [107] performed strained flamelet calculations of turbulent premixed flames. The strained flamelet model they constructed is parametrised by a modelled scalar dissipation rate of the reaction progress variable as a measure of turbulence effect on the laminar flamelet.

3.5.4 Conditional Moment Closures

This approach was introduced to provide a simple closure for the chemical source term by deriving the transport equations of the conditionally averaged reactive scalars and assuming that fluctuations around the latter are negligible. Conditional moments of flow quantities are the means, variances, covariances and higher moments extracted only from the realisations which satisfy a specified condition. The conditional mean of species concentration conditioned on mixture fraction is $\langle \phi_s | \eta \rangle = \langle \phi_s(x, t) | z = \eta \rangle$. The conditional averaging is better performed with Favre (density-weighted) form to avoid the appearance of conditional density fluctuations. The approach was initiated independently by Klimenko [105] and Bilger [20]. The modelled transport equations governing the conditional mean of scalars were derived from their joint PDF equation by Klimenko [105]. Bilger [20], on the other hand, started from the transport equations of reactive scalars using the decomposition method. The same set of equations for the conditional means are obtained by the two different derivations. In non-premixed combustion, conditioning is usually made on the mixture fraction. It is based on the observed strong correlation in turbulent diffusion flames between reactive scalars and mixture fraction so that the latter may be utilised as an independent variable in a similar manner to the flamelet models. In other words the mixture fraction is exploited as a primary conditioning variable by which fluctuations around the conditional averages of the reactive scalars are minimised since their unconditional fluctuations are assumed to be dominantly pro-

duced by fluctuations in mixture fraction [113]. The CMC equation for the scalar conditional mean can be written as follows:

$$\begin{aligned} \langle \rho | \eta \rangle \frac{\partial \langle \phi_s | \eta \rangle}{\partial t} = & - \langle \rho u_l | \eta \rangle \frac{\partial \langle \phi_s | \eta \rangle}{\partial x_l} + \langle \rho \chi_s | \eta \rangle \frac{\partial^2 \langle \phi_s | \eta \rangle}{\partial \eta^2} + \langle \dot{\omega}_s | \eta \rangle \\ & + \frac{1}{\tilde{\mathcal{P}}(\eta)} \frac{\partial}{\partial x_l} \left[\langle \rho u_l'' \phi_s'' | \eta \rangle \tilde{\mathcal{P}}(\eta) \right] + e_q \end{aligned} \quad (3.20)$$

All terms on the right-hand side are unclosed and require modelling. The variables that require modelling are the conditional velocity, the conditional scalar dissipation rate, the conditional reaction source term and the conditional scalar flux. The last term e_q which represents the molecular diffusion contribution on the conditional mean and the effects of differential diffusion also requires modelling but may be neglected if Re is high and differential diffusion is not important.

The conditional mean source term does not introduce the same problem as the unconditional mean source term, as closure of the latter can not be achieved using unconditional means or even by including second moments (section 3.4). On the contrary, scalar conditional averages are sometimes sufficient to estimate the conditional mean source term (first order closure) by inserting conditional means in the conventional instantaneous form for the source term. The reasoning behind this is that the source term dependence on the fluctuations is eliminated with conditional averaging since conditional fluctuations are relatively insignificant compared to the conditional means. First order closure of the chemical source term can be expressed as:

$$\langle \dot{\omega}_s(\rho, \phi) | \eta \rangle = \dot{\omega}_s(\langle \rho | \eta \rangle, \langle \phi | \eta \rangle) \quad (3.21)$$

Once the conditional averages are computed from the solution of their modelled transport equations, the unconditional averages of the density and reactive species are obtained by weighting their conditional averages using the PDF of the conditioning variable.

$$\tilde{\phi}_s = \int_0^1 \langle \phi_s | \eta \rangle \tilde{\mathcal{P}}(\eta) d\eta \quad (3.22)$$

The PDF of the conditioning variable can be determined using the presumed PDF approach. Reduced and detailed chemical kinetics can be incorporated in CMC modelling to simulate a variety of phenomena and in a wide range of practical problems within realistic computational cost.

The first-order conditional moment closure is only adequate when second and higher conditional moments are negligible. Strong turbulence-chemistry interaction such as in flames with extinction or regimes of premixing prior to ignition in a non-premixed flame result in significant fluctuations around the conditional mean. This is caused by the weakened correlations between the conditioned scalars and the conditioning variables (e.g. mixture fraction). In these instances, the CMC equations remain valid but a more complicated closure is required to account for the presence of significant fluctuations which are not produced or associated with mixture fraction fluctuations. The first alternative strategy to treat these strong fluctuations is through higher-order conditional moment closures. Second-order conditional moment closures have been developed and widely applied to non-premixed flames including flames with soot formation e.g. [56, 233, 229]

The other strategy for improved closures of the source term is the multiple conditioning, such as the double-conditioning closure. Increasing the number of the conditioning variables has been found to strengthen the CMC methodology because conditional averages and their fluctuations are found to be correlated to several quantities rather than to mixture fraction only. Cha et al. [31] exploited the scalar dissipation rate as a second conditioning variable. Their study tries to improve the efficiency of CMC in predicting the influence of turbulent fluctuations on the reaction rates in order to capture the extinction and re-ignition in turbulent flames more accurately. Although statistical independence of conditioning variables from each other is not required it allows for simpler determination of their joint PDF from the product of their marginal PDFs. The sensible enthalpy has also been used along with mixture fraction for double-conditioning CMC [112].

The CMC approach has been applied recently with success to premixed combustion using the reaction progress variable as a conditioning variable. Recently, Amzin

et al. [7] developed a CMC model for turbulent premixed flames with a modelled algebraic expression for the conditional scalar dissipation rate of the reaction progress variable.

3.6 Transported PDF Models

The transported PDF method is the approach which solves the transport equation of the single-point single-time Eulerian joint probability density function (PDF) of a set of flow properties such as the velocity components and/or the chemical scalars. Thus, the method does not require a presumed shape for the PDF. It has been regarded as one of the most powerful tools for modelling of turbulent reactive flows because of its satisfactory coupling between turbulence and chemical reaction and its ability to reduce the number of terms that require modelling [75]. A main advantage of this approach is that the closure problem of the chemical reaction is eliminated. In PDF methods, the chemical reaction rate can be computed from local quantities without mathematical complications. These merits support the broad applicability of the transported PDF methods, particularly for different modes of turbulent reactive flows. Here some details will be given on PDF methods in the context of RANS simulations although some aspects of its analogue in LES, the Filtered Density Function (FDF), will be pointed to.

The development of this approach began with the work of Lundgren [136, 137] who proposed a method for the derivation and solution of the joint PDF equation of the velocity field. The derivation of the joint PDF transport equation using the fine-grained method, which was employed by Lundgren, invokes the concept that the PDF is the expectation of delta function. The same method has been adopted by O'Brien [164] for the joint PDF of the scalar field. Application of the transported PDF approach to reactive flows incorporated solutions of the PDF of the scalar field, which describes the thermo-chemical state of a reacting flow as in the early work by Dopazo and OBrien [49] and Pope [183].

The interest in adopting PDF methods in reacting flows was motivated further when some non-flamelet composition realisations were spotted experimentally. The measurement of compositions which are not predictable by conventional flamelets gave indication that different combustion regimes exist in turbulent flames [21]. This encouraged the development of a method of general applicability to different combustion modes and regimes which also offers a realistic coupling between turbulence and other processes such as multi-scale finite-rate chemistry and radiation. Since the presumed PDF approach becomes intractable when the dimensionality of the thermo-chemical state is increased by inclusion of detailed chemistry, the transported PDF model was a good candidate to handle this type of problem.

Conventional grid-based numerical techniques like the finite-difference and finite-volume are inappropriate for the solution of the multi-dimensional joint PDF equation. The reason is that every dependent variable whose statistics are included in the PDF becomes a dimension of the space of independent variables. This causes the computational cost [memory requirement and CPU time] to increase roughly exponentially with the dimensionality of the PDF resulting in excessively expensive and prohibitive computations [184]. Alternatively, Monte Carlo methods devised by Pope [178, 184] were employed since the computational cost rises only linearly with the dimensionality, and thereby making solution of PDF methods a tractable approach for turbulent reactive flows. The attractiveness of Monte Carlo methods and their capacity to handle detailed chemical kinetics were reasons for the wide interest in PDF methods. The huge development of computer resources also contributed to the development and progress of PDF methods [82]. It has emerged from being limited to laboratory-scale and simple flows to being a compelling technique for modelling reactive flows with large number of species. It is a general alternative approach which can replace other conventional models for computing flows in practical applications. The approach can be readily extended to account for other flow processes associated with reactive flows. In particular, the one-point processes do not introduce any closure difficulties as they can be obtained from local quantities. The PDF approach has indeed been extended to treat processes like radiation and

particulate formation, and has been applied to multiphase flows [128, 41, 142].

The development of transported PDF methods evolved mainly in two types of PDF equations dependent on whether velocity is included in the joint PDF or not. These two classes of PDF are therefore usually named the Joint Velocity-Composition PDF and the Composition PDF. The latter is the PDF which does not include any velocity or turbulence statistics. It is also named the Scalar PDF since an energy quantity is usually included with the composition.

3.6.1 Types of the Joint PDF method

3.6.1.1 The joint scalar PDF method

The joint scalar PDF is one of the classes of transported PDF methods that has received wide attention and development. It is also referred to as the joint composition PDF, but the first name may be preferred as the scalar field comprises, in addition to chemical composition, other related variables such as enthalpy and non-compositional particulate formation parameters. It contains all the one-point statistics of the scalar field so that the Favre-averaged mean of a scalar quantity $\tilde{\phi}_s$ and its variance $\widetilde{\phi_s'^2}$ are obtained using the density-weighted scalar PDF $\tilde{\mathcal{P}}(\underline{\psi})$:

$$\tilde{\phi}_s = \int \psi_s \tilde{\mathcal{P}}(\underline{\psi}) d\underline{\psi} \quad (3.23)$$

$$\widetilde{\phi_s'^2} = \int \left(\psi_s - \tilde{\phi}_s \right)^2 \tilde{\mathcal{P}}(\underline{\psi}) d\underline{\psi} \quad (3.24)$$

A general form of the modelled scalar PDF equation, its closure and solution strategy are presented in the next chapter. No velocity statistics or any turbulent quantities are included in this class of PDF. As a consequence, turbulent transport which appears as a term with conditional velocity fluctuation in the joint scalar PDF equation Eq. (4.1) is unclosed and requires modelling. The scalar PDF method has therefore, to be coupled with either a RANS turbulence model (such as the $k - \varepsilon$ eddy-diffusivity model as in [93], or RSM model as in [93, 131, 129]) , or large eddy simulations (LES) [158]. These CFD calculations supplement the PDF with

the mean velocity and the required turbulent quantities. The turbulent diffusion process is commonly approximated with a model consistent with the flow field closure which depends on what turbulent quantities can be extracted from the CFD calculation. Gradient diffusion model can consistently be used when the PDF is coupled with an eddy-diffusivity model. The main difficulty in all transported PDF approaches with multi-scalar transport is the modelling of the micromixing process which arises from molecular diffusion terms in the species conservation equations.

The number of submodels that need to be devised and number of unknown coefficients in the scalar PDF method are less than those in other classes of PDF closure. The solution of the scalar PDF equation in the context of RANS or LES computations implies that the advantage of the well established numerical CFD implementations of RANS or LES are retained.

3.6.1.2 The joint velocity-scalar PDF method

The other stream in considering PDF methods has been to include flow field variables such as the velocity components in the joint PDF so that mean convection and turbulent diffusion terms appear in closed forms. This approach has been explored and developed extensively, motivated initially by the fact that the PDF can provide closure for the mean and fluctuating velocity, and that gradient diffusion modelling of the turbulent transport is eliminated. The micromixing closure problem appears in this PDF as well and the micromixing modelling is identical to the scalar PDF method.

This class of PDF has been investigated through different ways and levels of dealing with the closure of turbulence. In some early developments of this methodology, quantities such as the turbulence time scale had to be supplied externally by a finite-volume RANS setting. Some implementations solved a modelled transport equation for turbulent dissipation rate ε or turbulent frequency ω . In the desire to develop self-contained PDF solutions the common practice has been to include

one of these quantities as a random variable in the joint PDF equation. Thus, joint velocity-dissipation-composition PDF [163, 182] and joint velocity-frequency-composition PDF [8, 209, 232] equations provide fuller mathematical closures. They contain estimates for all required flow field quantities and time scales by which standalone PDF solutions can be explored.

The joint velocity-frequency-composition PDF approach [8] has received more attention and has been widely developed and applied. However, several new terms which require numerical modelling are introduced in the implementation of this PDF such as the stochastic model for turbulent frequency. Optimal values for parameters in such models needed extensive effort and experimentation. A considerable amount of research which has been published on this approach deals with developing and improving the implementations of its submodels e.g. [80, 231, 235, 156, 157]. In addition, studies of the assessment and control of the numerical errors have been carried out e.g. [231]. One of the main issues that has been analysed is that conventional Monte Carlo solutions need correction algorithms to enforce consistency of the particle representation with the turbulent flow field [157, 80, 235].

In terms of assessing the numerical errors, Xu and Pope [231] and others explored the sources of numerical errors in the solution of the joint PDF equation of velocity, turbulent frequency and composition. The source of bias error, which is a deterministic error originating in the stochastic particle models, was tracked in [231]. The main issue with bias was that this error would increase with grid refinement despite the fact that it would decrease with larger number of particles. The source of bias was attributed to the original formulation of the stochastic differential equations whose coefficients were affected by numerical fluctuations. These numerical fluctuations were carried by the estimates of mean variables which are needed as inputs for these equations. Some of the terms which are considered as the main source of this error appear only in this type of PDF and are not observed in scalar PDF methods. As an example of this, they pointed out that some stochastic models for the turbulent frequency were found to induce most of this issue with bias. Modified

stochastic models for ω were proposed to decrease the dependence of bias on grid refinement.

3.6.2 Stochastic solution strategies in transported PDF methods

The transported PDF equation has been solved with Monte Carlo techniques in either the Eulerian or Lagrangian framework. The unclosed terms still need modelling even in these frameworks. However, the Eulerian or Lagrangian representation provides an alternative viewpoint which enables the configuration of physical models for these unclosed processes. In this section we introduce the common techniques which are used in the field of turbulent combustion.

3.6.2.1 Lagrangian-particle method

In the Lagrangian-particle method, the PDF equation which is derived in an Eulerian form is transformed into Lagrangian form by representing it with an ensemble of notional particles distributed in the spatial domain. These particles are moved in space and the new location and the properties of the particles are determined from the solution of stochastic and deterministic differential equations. These equations are constructed in a way that the particle evolution corresponds to the single-point single-time PDF of the reactive turbulent flow being considered. This correspondence between the notional particles and the PDF of the real flow is a main condition for validity and consistency of the solution. Similar consistency conditions are also required for other stochastic methods.

The Lagrangian particle method has been a main technique for solving the PDF equation both in the standalone particle methods and in the context of RANS simulations, as in this study. Joint PDF methods which include statistics of velocity components and turbulent quantities can be solved using standalone particle methods. However, it has been widely observed that hybrid FV-particle algorithms offer several numerical advantages over standalone particle methods even when the latter are considered self-sufficient and can provide a complete description of the flow.

These advantages include the reduction of numerical errors as well as improving the computational efficiency and convergence rates. In the hybrid FV-particle approach implemented by Jenny et al. [80], it is shown that the bias and statistical errors are dramatically reduced compared to standalone particle methods. They show that the source for large bias in standalone particle methods comes from the evolution of the mean velocity of the particles. Based on this finding, the bias was extensively diminished in the hybrid scheme by including the fluctuating velocity in the PDF instead of the mean velocity. This is because fluctuating velocity relaxes towards zero whereas mean velocity relaxes towards the mean.

It has been argued that a consistency between the mean particle density and the mean finite-volume (FV) fluid density should be preserved when both are estimated at the finite-volume cell level. This ensures that the particle field continues to be a valid representation of the modelled PDF transport equation. Initialising the particle field mass exactly the same as the FV fluid mass is essential but not enough to preserve the consistency of mass and density [235]. Another element of the consistency is that the mean of fluctuating velocity should be zero [157, 80, 156]. The consistency can only be maintained if the particles evolve precisely according to continuity equation and hence remain consistent to FV mass distribution. Even with very large number of particles and advanced particle advection schemes, mass inconsistency between the two fields will develop and grow. The inconsistency is thought to result from the growing of non-uniform particle distributions [235] and accumulation of numerical errors [157].

3.6.2.2 Eulerian-particle method

In some early formulations, the PDF was represented by stochastic particles that are treated with an Eulerian description, which is different from that in pure Lagrangian-particle methods. This is usually classified as the Eulerian-particle or the semi-Eulerian method which was initially proposed by Pope [178]. The method has later been applied to turbulent jet flames e.g. [91, 92, 93]. In this method, every cell has a number of particles which are located on spatial grid nodes without assigning

velocity components to them. Instead, transport in physical space is simulated by exchanging particles between neighbouring cells and the ensemble of a cell is updated accordingly.

Mobus et al. [147] carried out an analysis of the numerical performance of two Monte Carlo settings for the transported PDF approach. One of the settings used the Eulerian-particle formulation and the second used the Lagrangian-particle formulation. The numerical efficiency of the two settings was investigated and compared by applying them to a supersonic hydrogen-air diffusion flame. The numerical issues related to sources of numerical diffusion, spatial accuracy and computational cost in both implementations were explored. The improved spatial accuracy of the Lagrangian implementation showed some effect on the prediction of ignition of the flame. However, their Lagrangian particle exchange scheme seems to be time consuming causing the Lagrangian calculations to be numerically more expensive.

3.6.2.3 Eulerian stochastic-field Method

More recently, alternative Eulerian formulations, using either the notional stochastic or deterministic fields, have been devised. Valino [211] proposed the smooth stochastic field method and tested it for the PDF of a single scalar. Mixing was computed with the IEM mixing model and turbulent transport was modelled with the gradient-diffusion hypothesis which is usually adopted in scalar PDF methods. Subsequently, the method has been explored and applied to multi-scalar reactive flows in the RANS setting by Hauke and Valiño [74]. It has become quite popular in advanced LES of turbulent combustion e.g. [158, 96, 97].

In the stochastic field method, the PDF is represented by a number of notional Eulerian stochastic fields. The governing equations of these fields are partial differential equations which contain a stochastic term. The method gains its attractiveness from the type and characteristic of the field equations, such that conventional numerical techniques which are already established for CFD can be readily employed

to integrate them. This is because the PDEs of the stochastic fields are purely Eulerian, time-dependent, continuous and differentiable in space and of conservation-type. The method has been viewed as a promising candidate for coupling with LES to solve the subgrid PDF. Mustata et al. [158] argued that there is no risk of SGS fluctuations being introduced into the field equations. Moreover, he found that reducing these fluctuations with a well-resolved LES grid ensures that a reliable solution of the scalar field can be achieved with a moderately low number of fields. This method was thus shown to be advantageous from the computational cost perspective even in LES methods. A different version of Eulerian stochastic field methods has been formulated by Sabelnikov and Soulad for both for the joint velocity-scalar PDF [199] and the joint scalar PDF [195].

3.6.2.4 Multi-environment PDF method

Another method that has been applied to solve the PDF equation is the multi-environment PDF method (MEPDF) [208] in which the closure is performed with a method called the direct-quadrature-method-of-moments. This method has been implemented successfully using two environments and applied to turbulent flames with multi-scalar finite-rate chemistry [208]. A higher number of environments can be employed, though it has been reported that this would cause problems in the construction of the equations and difficulty in specification of the boundary conditions [208, 78]. The method has been recommended to transport the particle number density function in flows with particulate formation. It is argued that the method shares some of the properties of the Eulerian field method in the way that environments notion is applied here instead of fields. They differ, though in the fact that the MEPDF method is a deterministic formulation in which the system of PDEs being solved are deterministic and do not contain stochastic terms.

3.7 Reduction of detailed chemistry

3.7.1 Motivation for detailed chemistry reduction

In turbulent combustion, the gas-phase chemistry is evaluated by coupling a chemical mechanism of combustion with a turbulent CFD model using one of the statistical models for the thermo-chemical state. Inclusion of realistic chemistry requires that the chemical source term is dynamically updated with CFD calculations. PDF methods have the advantage of providing a strong and realistic representation of the interaction between turbulence and chemistry.

Detailed chemical mechanisms for several hydrocarbon fuels are now available with good accuracy and these mechanisms can be coupled directly with PDF methods without closure problems. However, there are a large number of species that participate in hundreds or thousands of elementary reactions occurring in these chemical mechanisms. The rates of elementary reactions are accounted for by Ordinary Differential Equations (ODE) representing the evolution of the chemical species. Direct calculations of the chemical source term from the detailed mechanism involve a coupled integration of all these ODE equations. Chemical reactions exhibit a wide range of time scales that then vary from infinitely fast rates to slow chemistry which might proceed at time scales larger than the flow field time scales. The presence of this large variation in reaction rates makes the integration of the differential equations computationally very stiff. Both the large size of detailed mechanisms and the computational stiffness are the main reasons why calculations of the chemical source term become a limiting factor in most simulations of combustion and other reactive flows.

Despite the fact that the increasing advancement of computational capacity has enabled researchers to incorporate detailed mechanisms in advanced models of turbulent reactive flows, such as the RANS-PDF and LES-PDF simulations of simple hydrocarbon flames, they are still computationally quite expensive. Thus, there is a strong interest, in general, in reducing the tediously heavy load from the compu-

tation of chemical kinetics in CFD calculations of turbulent reactive flows. In the transported PDF methods, since a large number of particles is needed for an efficient solution, the chemical reaction computation is performed repetitively for all or a major portion of these particles every time step. As a consequence, incorporation of a comprehensively detailed mechanism in PDF methods becomes an extremely burdensome procedure even with powerful parallel computing. This task would be even more computationally expensive for higher hydrocarbon fuels whose chemistry is more complex, and for practical applications with large-scale solution domains. The computational cost of detailed chemistry is still prohibitive in LES-PDF methods even for simple fuels. Reduction methods are also of interest to facilitate the analysis and improvement of comprehensive chemical kinetics of complex fuels. Reduced mechanisms allow for the refinement and validation of key reaction rates in the mechanisms of heavy hydrocarbons and multi-component fuels [223]

Another problem of direct integration of detailed chemical mechanisms is the large dimensionality of the combustion model. This dimensionality will be very high due to the large number of species involved in these mechanisms. Calculations of reactive flows with moments methods and the presumed PDF method become intractable if transport of a large number of species is involved. It might be argued, though that Monte Carlo methods have made the computational cost of single-point PDF modelling increase weakly with the dimensionality of chemical composition when we exclude the cost of chemical reaction. This is because the transported species or scalar becomes only a parameter, or say an independent variable, of the joint PDF equation. However, lower dimensionality of the chemical composition is generally desirable. It has an important advantage even in Monte Carlo simulations, as it eliminates unmanageable memory requirements experienced in LES and DNS, as well as when tabulation techniques are employed.

The problems arising from the large size of combustion chemical kinetic mechanisms are usually overcome by chemical mechanism reduction methods since they aim to reduce the computation time and provide a representation with lower di-

mensionality of the composition space. Moderate chemistry reduction of complex mechanisms, in which enough details of finite-rate chemistry are retained, represents a worthy compromise between the complexity of full mechanisms and the inaccuracy of globally reduced ones. Most methods of mechanism reduction are based on either eliminating the unimportant chemical reactions and species, as in skeletal reduction, or on time-scale separation [119]. The methods adopting the principle of time-scale separation are discussed in the following section.

3.7.2 Chemistry reduction with time-scale separation

Some species are governed by fast reactions and their concentrations are relatively quite small as they are produced and consumed at rapid rates [118]. As a consequence, they require much shorter times to reach steady state than other slow and rate-limiting species. The species with short time scales are usually called the steady-state species and are assumed to have little influence on the dynamical evolution of the chemical system. The slower species are usually governed by chemical reactions which have significant effects on the combustion process and hence the chemical kinetics of these species are important and predominant. This observation has motivated the need to decouple the fast reactions from the slower chemical kinetics to eliminate some of the stiffness of the calculations and to arrive at a simplified and reduced chemical system from the comprehensive mechanism.

This idea of chemistry reduction with time-scale separation is invoked in many methods such as the quasi-steady-state approximation (QSSA) partial equilibrium assumptions and the intrinsic low dimensional manifolds (ILDM) method [139, 138]. Derivation of reduced mechanisms for some of these methods such as the QSSA involves detailed investigations of the mechanism to identify the quasi-steady-state (QSS) species. Also, it requires specific assumptions and tuning of individual relations every time a reduced system is derived. The computational singular perturbation (CSP) method [71], and methods based on lifetime analysis such as the level of importance (LOI) method [134], establish criteria that provide automatic identification of major (non-steady state) and QSS species.

Tabulation methods are also utilised to reduce the computational burden of chemistry calculations. They involve the storage of precomputed chemistry integrations in libraries of data sets or some kind of tabular array. In early tabulation methods, low-dimensional lookup tables which are commonly computed using global chemical mechanisms were used for turbulent flame calculations. The evolution of composition is then obtained by interpolation from the lookup tables which are generated in advance of the CFD calculations. Consequently, repetitive interactive integration of chemical reaction in every time step is avoided in turbulent flame calculations. The limitation of the dimensionality of lookup tables to a small number of species is caused by interpolation difficulty and the excessive size of memory required by tables with higher dimensionality. This limitation implies that detailed mechanisms can not be tabulated unless globally reduced. It has been a common approach to facilitate the chemistry tabulation by reducing the dimensionality of detailed mechanisms. For example, the development of the intrinsic low dimensional manifolds (ILDM) method [139, 138] was mainly motivated by the need for low-dimensional chemistry tabulation. The ILDM method provides a transformation of the chemical system into a simplified system which is parametrised by a small number of manifolds (i.e. a reduced system). Subsequently the generated low-dimensional chemistry can be tabulated to replace the real-time integration of full mechanisms in PDF calculations of turbulent combustion.

An alternative and attractive tabulation approach is the Artificial Neural Network (ANN) technique. This method has been utilized for chemistry tabulation in turbulent combustion, such as the applications by [38] and [35]. The ANN has shown the ability to handle the tabulation of a more realistic combustion chemistry than other conventional tables. Therefore, the dynamical evolution of the chemical composition can be computed more efficiently in ANN without the need for real-time chemistry integration. The ANN methodology proposed by [35] is conditioned on the prerequisite that data sets representing the thermo-chemistry field of the real reactive flow are available in advance. They must also be valid and all-inclusive

representatives of the real reactive flow under consideration as they are used to train the ANN model. These representative data equip the ANN model with information and prepare it to predict the chemical composition of the actual reactive flow problem. In other words the ANN model has to acquire an intensive comprehension of the problem that makes it capable of estimating the temporal advancement of any thermo-chemical state point that may occur in the actual flow. The ANN method would provide as an ultimate goal a prediction very close to that attainable by the original chemical integration.

Recently, in the interest of more CPU time-saving, the ANN tabulation technique has been applied with RCCE methods. Reduced systems like RCCE are favourable for combination with tabulation techniques because of their moderate dimensionality which produces tabulations with manageable memory requirement. A combination of chemistry reduction with RCCE and ANN methods was employed by [35] allowing for large CPU time-saving in the chemistry computations as compared to direct chemistry integration. The training data set was produced using RCCE computations of an ensemble of non-premixed laminar flamelets which provide representation of the chemical layers in the turbulent diffusion flame under consideration. Their ANN-RCCE predictions gave encouraging predictions compared to the real-time integration with RCCE.

3.8 Background on theory and modelling of soot formation

3.8.1 Introduction

Soot refers to carbonaceous solid particles, containing numerous carbon atoms. Soot particles form during the pyrolysis and incomplete combustion of hydrocarbon fuels, particularly in fuel rich conditions. Soot is released to the atmosphere and exposure to soot particles may cause adverse health effects. One of the desirable effects of soot is that it strongly enhances radiative heat transfer in boilers, furnaces and

combustors. The soot formation process involves complex chemical and physical processes that convert hydrocarbon molecules to heavy soot particles. It involves the transition from the gas phase to the solid phase. The overall physical processes and chemical kinetics related to soot formation have not been fully formulated even for simple fuels despite the existence of a considerable knowledge on the mechanisms of some elements of these processes [166]. At least, some of the rate-limiting and controlling chemical pathways are quantitatively established and to some extent agreed on. On the other hand, the accuracy of any model for soot formation relies as well on the accuracy of gas-phase chemistry and relevant species profiles. Recently, information on the particle size distribution has become as important as the soot volume fraction [22].

Soot formation is connected to Polycyclic Aromatic Hydrocarbons PAH and is controlled by chemical kinetics as well as by particle dynamics [103]. Some of the PAH have also been identified as significantly carcinogenic and may pose other serious health risks. Soot formation was also linked to the appearance of ions in flames. After soot is formed and if the fuel rich parcels containing soot are allowed to mix with oxygen or any other oxidiser, some of the soot particles will burn out. New soot particles can still be formed in the oxidation regions due to the existence of sufficient concentrations of soot precursors such as C_2H_2 and PAH [140].

There are several routes and theories that have been put forward to describe the formation of soot particles. They range from global simplified routes to routes which include multiple chemical kinetic schemes, with every scheme involving several elementary reactions of PAH formation. The routes with detailed chemical kinetic schemes require reliably accurate rate constants and other kinetic data for a large number of elementary reactions or at least for the most significant reactions. This is an area of research which is currently subject to an extensive body of experimental and theoretical effort. Commonly, the mechanism of soot formation is represented by four processes: nucleation, surface growth, oxidation and finally coagulation and agglomeration.

3.8.2 Soot precursors

The outset of soot formation is usually described by the formation of primary incipient particles. It is widely agreed that these incipient particles are mainly formed by the growth and collision of Polycyclic Aromatic Hydrocarbons PAH [10, 103]. In fuels that do not contain aromatic rings, PAH are by-products that are generated from the chemical conversion of smaller hydrocarbons such as acetylene. The latter occurs as an intermediate species of combustion and fuel pyrolysis. It is commonly stated that in the initial stage, lower aromatic rings are formed by gas-phase chemistry mainly from acetylene, but other hydrocarbons and hydrocarbon radicals also contribute to this [225]. Large PAH are then produced by condensation and recombination of several small aromatic rings as well as by the so-called hydrogen-abstraction-acetylene-addition (HACA) mechanism [62, 61].

HACA mechanism involves two reaction steps. First, a gaseous hydrogen radical re-activates the aromatic molecule and creates a radical site on it by abstraction of one of its hydrogen atoms. This is followed by the second step which is the addition of an acetylene molecule to the radical site formed on the aromatic molecule. It is one of the main pathways for growing and forming higher aromatics which produce soot. In addition, it is widely recognised that the HACA mechanism is also dominant in soot particle surface growth reactions. There is evidence that the H-abstraction re-activation of soot particles and PAH are also caused by reactions with other species like the OH radical and some hydrocarbons [51, 5]. Although it has been observed that methyl (CH_3) and propargyl (C_3H_3) are also converted to benzene and other aromatics in some flames [60, 225], it is reported that further growth of these aromatics continues mainly by acetylene addition [60]. It has been reported that the radical pool, and specifically H radical has a strong effect on soot formation [60]. However, conventional soot models incorporate only the role of main precursors which provide carbon.

This explains the wide consensus that at least for lower hydrocarbon flames, acetylene C_2H_2 represents a main indicative precursor species for soot nucleation

and surface growth. This has a computational advantage in the joint PDF models since reduced chemical models with a small or moderate number of species which include C_2H_2 chemistry will be sufficient for soot flame simulations. Benzene, which is a basic single-ring aromatic, and other small aromatics, have also been regarded as indicative species and precursors of soot in some hydrocarbon fuels. The formation of benzene from small aliphatics has long been regarded as a rate-limiting step to the formation of PAH. However, other chemical kinetic pathways which bypass this step and directly form two- and three-ring aromatics have also been observed [60]. Predictions of PAH concentrations are associated with several computational problems and large errors which have prohibited the inclusion of large PAH in models of soot formation. However, quantitatively good accuracy in predicting lower PAH has been reached recently. Based on this, two- to four-ring PAH such as naphthalene (C_{10}H_8) and pyrene ($\text{C}_{16}\text{H}_{10}$) have been recently used as nucleating species in heavy hydrocarbon fuels [16]. In a DNS study of n-heptane flame by [22], nucleation of soot and condensation of dimers were assumed to be dominated by the formation of naphthalene (C_{10}H_8) while acetylene C_2H_2 is assumed to govern the surface growth reactions via the (HACA) mechanism.

3.8.3 Modelling of soot in turbulent flames

Early models of soot formation in non-premixed flames utilised mixture fraction as an indication of soot formation. Some models empirically related the soot yield directly to mean mixture fraction, without considering any residence time effects or any influence of turbulent mixing rates on soot chemistry. Kennedy et al.[104] pointed out that to incorporate the dynamic effects, transport equations of soot need to be solved, and proposed that surface growth rate should be a function of mixture fraction. However, the same study also indicated the sensitivity of surface growth reactions to heat loss by radiation as well. Moss et al. [151] developed a semi-empirical soot model represented by the rate equations for particle number density and soot volume fraction. The model comprised nucleation, surface growth and coagulation processes all of which were assumed to be functions of the mixture fraction. This provided a significantly easy approach for the coupling of turbulence

and soot with gas-phase chemistry through the laminar flamelet approach. Laminar ethylene diffusion flame experiments were utilized for the model validation. Later, they [207] applied the soot model to predict turbulent methane diffusion flames in the context of the laminar flamelet approach. The radiation heat loss was treated by perturbing the temperature-mixture fraction profile. The parameters of the soot mechanism were established by comparison with laminar methane flame experiments. The model for the surface growth term was modified to be linearly dependent on the aerosol surface area instead of the dependence on particle number density in the earlier formulation of Moss et al. [151]. The model of [207] was criticised for exaggerating the role of parent fuel represented by mixture fraction as an indicative variable for soot formation and also for overestimating the dependence of surface growth on the total particle surface area. The latter is, though an issue of wide controversy.

It has been widely argued that simplified models that correlate soot as a unique function of mixture fraction in non-premixed combustion are inadequate. This is supported by the common idea that soot chemistry is slow and its diffusion rates are also much less than those of gaseous molecular species, whereas the mixture fraction theory is based on fast chemistry and equal diffusivities assumptions [103]. It has been argued that there is neither a direct correlation between soot concentration and the mixture fraction space, nor is there a strong correlation between mixture fraction and growth species since they vary widely even across the rich side of stoichiometry. Brookes and Moss [27] however, found that OH, as a main oxidiser for soot, exists over a small range of mixture fraction and hence OH correlation with soot can be linked to mixture fraction.

Alternatively, Leung et al. [123] proposed a simplified mechanism for soot formation based on the fact that nucleation and surface growth are initiated and dominated by acetylene instead of the parent fuel. Nucleation and surface growth were treated as first order in acetylene rather than a function of the mixture fraction itself. They implemented a surface growth model which is expressed as a function

of the number of active sites instead of total surface area to avoid the excessive dependence of the soot surface growth on the surface area. The number of active sites, however, is assumed to be proportional to the square root of surface area. Nucleation mechanism was assumed to be a 1-step acetylene conversion to soot and hydrogen. This soot mechanism was verified with data for coflow and counterflow laminar diffusion flames. Their model accounts only for oxidation by O_2 and neglects oxidation by OH. An ad hoc adjustment was applied on the oxidation rate to match the experimental measurements. Fairweather et al. [55] applied the soot mechanism of [123] to turbulent coflowing soot flames by coupling it to the laminar flamelet model. Moss et al. proposed that oxidation is by reaction with OH as the only oxidiser in [151, 207] while they incorporated oxidation with both O_2 and OH in [152].

Later, Moss and co-workers [27, 6] incorporated the non-adiabatic effects of the radiation heat loss on soot variables by choosing the radiative loss as an extra independent flamelet parameter in addition to the mixture fraction. C_2H_2 was assumed to be the soot precursor while OH was the main oxidant. Brookes and Moss [27] closed the solution using the presumed PDF of the mixture fraction only while the soot variables were assumed either uncorrelated or perfectly correlated with the gas phase (mixture fraction). This approach does not account for the statistical correlation between the gas phase and soot and as a consequence competition between soot surface growth and oxidation was not well captured. Aksit and Moss [6] tried to resolve this issue by solving the joint scalar PDF of mixture fraction, heat loss fraction and soot parameters, namely particle number density and soot mass fraction. The joint scalar PDF equation was solved using a Monte Carlo particle method in the context of a hybrid solver. Statistics of the remaining scalars were not calculated directly by the Monte Carlo solution; rather they were extracted from libraries of non-adiabatic flames tabulated with respect to the heat loss value. Discrepancy in the soot predictions were attributed to an underlying discrepancy in the prediction of the scalar field.

The transported PDF approach has been exploited for the interaction between soot formation and turbulence just as the model accounts for the interaction between turbulence and gas-phase chemistry. Early studies that perform coupling between soot models and the transported PDF approach include the work of Kollmann et al. [108]. Lindstedt and Louloudi [128] also performed soot modelling in turbulent non-premixed ethylene-air flames using transported PDF of the scalar field. Recently Stoellinger and Roekaerts [203] presented a study of methane soot flames in which unsteady non-adiabatic flamelet solutions are used to construct chemistry libraries inserted into the solution of then transported PDF equation of five scalar variables. The five independent variables are mixture fraction, progress variable, enthalpy, soot mass fraction and the normalised soot number density.

Chapter 4

The Joint Scalar PDF methodology with RCCE chemistry reduction

The transport equation of the scalar PDF can be derived from the instantaneous conservation equations by taking the ensemble average of the fine-grained density function as in [164] and [75]. The joint scalar PDF ($\tilde{\mathcal{P}}(\underline{\psi})$) equation can be written in the following form:

$$\begin{aligned} \frac{\partial \bar{\rho} \tilde{\mathcal{P}}(\underline{\psi})}{\partial t} + \frac{\partial}{\partial x_l} \left\{ \bar{\rho} \tilde{u}_l \tilde{\mathcal{P}}(\underline{\psi}) \right\} + \bar{\rho} \sum_{s=1}^{N_{sc}} \frac{\partial}{\partial \psi_s} \left\{ \left(\frac{\dot{\omega}_s}{\rho} \right) \tilde{\mathcal{P}}(\underline{\psi}) \right\} - \bar{\rho} \frac{\partial}{\partial h^*} \left\{ \left(\frac{\dot{q}_{rad}}{\rho} \right) \tilde{\mathcal{P}}(\underline{\psi}) \right\} \\ = - \frac{\partial}{\partial x_l} \left\{ \bar{\rho} \langle u'' | \underline{\psi} \rangle \tilde{\mathcal{P}}(\underline{\psi}) \right\} + \sum_{s=1}^{N_{sc}} \sum_{s'=1}^{N_{sc}} \frac{\partial^2}{\partial \psi_s \partial \psi_{s'}} \left\{ \frac{\mu}{Sc} \left\langle \frac{\partial \phi_s}{\partial x_l} \frac{\partial \phi_{s'}}{\partial x_l} | \underline{\psi} \right\rangle \tilde{\mathcal{P}}(\underline{\psi}) \right\} \end{aligned} \quad (4.1)$$

This equation is based on similar approximations that we have applied to the averaged conservation equations in chapter (2). In particular, the term representing molecular diffusion in physical space was neglected assuming high Re . As for molecular diffusion in scalar space, this term can not be neglected and multi-species Fickian diffusion assumption was invoked. In addition, the diffusivities were assumed

to be equal with unity-Lewis-number and uniform mixture viscosity μ throughout the solution domain. Another approximation is that the radiative emission $\dot{q}_{rad}$ is the only source or sink term to appear in the enthalpy equation when assuming optically-thin flames. The chemical source term $\dot{\omega}_s$ for production of reactive species and other non-conserved scalars can be expressed in the exact original form.

Terms on the left-hand side are all in closed forms and they represent respectively: the time rate of change in physical space, convection by mean velocity, transport by chemical reaction and, finally, sink term by radiation emissions of the enthalpy. The unclosed terms in the PDF equation are only the terms on the right-hand side which represent, respectively, turbulent transport in physical space (turbulent diffusion) and micromixing in scalar space.

There is no information on velocity statistics that can be obtained from the scalar PDF and for this reason the turbulent transport term (i.e. the term involving conditional fluctuating velocity) is one of the unclosed terms that need modelling. The micromixing term also requires modelling and it represents a main closure difficulty in all classes of transported PDF approaches. This term involves diffusion coefficients and conditional expectations of scalar gradients. Differential diffusion is commonly neglected in the PDF modelling of turbulent reactive flows.

4.1 Turbulent transport modelling

When an eddy-diffusivity model is applied for the flow field, this term is commonly modelled using gradient diffusion which can be written:

$$\bar{\rho} \langle u'' | \underline{\psi} \rangle \tilde{\mathcal{P}}(\underline{\psi}) = -\bar{\rho} \left(\frac{\nu_t}{\sigma} \right) \left(\frac{\partial \tilde{\mathcal{P}}(\underline{\psi})}{\partial x} \right) \quad (4.2)$$

This form is consistent with the $k - \varepsilon$ model and ν_t is obtained from Eq.(2.36). In situations where transport by molecular diffusivity is not neglected, an effective diffusivity D_{eff} which is equal $\left(\frac{\nu_t}{\sigma} + \frac{\nu}{Sc} \right)$ is employed instead of the turbulent diffusivity $\left(\frac{\nu_t}{\sigma} \right)$. However, in joint velocity-scalar PDF's, it is noted that the gradient

diffusion approximation is avoided since velocity fluctuations are included in the PDF information and obtained directly from the PDF field itself.

4.2 Scalar micromixing Modelling

This term represents the process responsible for the evolution of the scalar or composition field by mixing occurring at the small scales and that is why the name micromixing is commonly adopted. In the presence of a scalar gradient, turbulent straining generates complex small-scale gradients and fluctuations in the scalar field and then molecular diffusion acts against this process and causes the decay of these scalar fluctuations. At high Reynolds numbers and high Peclet numbers ($Pe = Re.Sc$) (e.g. at $Sc = 1$), the process can be considered as independent of the molecular diffusivity since it is the large-scale turbulent motion which acts on the mean scalar gradient and controls the amount of molecular mixing.

The term representing scalar micromixing is unclosed in the single-point joint PDF equation and a model like the IEM, Curl's model or another model is usually needed to approximate this term. It has been pointed out that higher level closure of the PDF such as the derivation of the two-point joint scalar PDF equation or alternatively inclusion of scalar gradients in the single-point joint PDF should provide a more accurate description of mixing as this term appears in a closed form [90, 170]. Effects of small scales, differential diffusion and other multi-scalar effects would be accounted for in these closures. These options, however, have only been explored in simplified problems as they lead to extra mathematical and numerical complications. Babenko and Stavrov [11] presented a solution for the PDF equation of the mixture fraction and its gradient in a flow with a homogeneous and isotropic turbulence. This PDF contained the information required to compute the scalar dissipation rate, a quantity which represents the rate of mixing.

The common practice that has been followed to deal with this term is the construction of a suitable micromixing model in the single-point single-time PDF. There

are many constraints and guiding principles that usually direct the numerical modelling of the term to achieve an efficient representation of the molecular mixing process. It has been argued that any mixing model should adjust to these regulating principles in order to reproduce the correct behaviour of the phenomena in the real flow. While this is generally clear and proven for some of the conditions, a desirably efficient mixing model may be achieved without complying with all of the conditions mentioned here. Detailed discussions on these constraints can be found in [90, 179, 205, 184]. Essentially, the model should not produce values that are physically unrealisable or results that contradict the experimental and mathematical observations. From the physical realizability conditions, the probability that a mass fraction of any chemical species is negative or more than one is zero. The mass fractions of all species in a mixture must sum to one and the mean should not be altered by the mixing process alone.

Pope [179] discussed in detail the independence and linearity conditions for mixing a set of conserved, passive scalars, when the equal-diffusivities assumption is imposed. The implication of independence is that mixing should leave each passive scalar quantity to evolve independently and not be affected by the statistics of any other scalar. In the Lagrangian PDF methods mixing causes each scalar quantity of the particle to interact only with its counterparts in other particles and should not be affected by other properties or scalars of the particle. The linearity principle implies that when a single (or a set of) scalar(s) are linearly transformed, the governing equations of these scalars are preserved for the resulting transformed quantities.

4.2.1 Constraint by Scalar Dissipation Rate

Another principle that must be imposed in the mixing model is that the molecular mixing must yield the correct scalar dissipation rate, which is the decay rate of scalar variance. The scalar dissipation rate is a quantity of central importance in reacting flows because it represents the rate of scalar micromixing and consequently it plays a dominant role in the turbulence-chemistry interaction. If mixing is the rate-limiting process such as in combustion with fast chemistry, then the chemical

reaction rate maybe determined from this quantity [28]. As has been mentioned earlier [eq (2.45) and eq (3.12)], the mean scalar dissipation rate is commonly modelled by prescribing a mixing time scale:

$$\tilde{\chi}_s = \frac{\widetilde{\phi_s''^2}}{\tau_\phi} \quad (4.3)$$

In the above equation τ_ϕ is the scalar mixing time scale. In PDF methods, mixing models make use of this time scale which is commonly assumed to be linked to the turbulence field.

4.2.1.1 Models with constant time scale ratio

It is quite common to determine τ_ϕ solely from the integral mechanical time scale of the turbulent flow $\frac{k}{\varepsilon}$, particularly when scalar eddies are entirely produced by turbulent velocity fluctuations acting on mean scalar gradients. An analogy is usually drawn between the dissipation rate of scalar and the dissipation rate of turbulent kinetic energy and the two time scales. Eq. (4.3) can then be re-written as:

$$\tilde{\chi}_s = \frac{1}{2} C_\phi \frac{\varepsilon}{k} \widetilde{\phi_s''^2} \quad (4.4)$$

A common practice in *RANS* simulations is to assume that the time scales are comparable and thus assign the time scale ratio C_ϕ a constant value close to 2.0. This may be regarded as a justifiable simplification at least for the mixing of binary conserved scalars in flows with turbulence in approximate equilibrium [93] and in flows where micromixing is controlled by the large scales of turbulence. Fox [59] demonstrated that energy containing eddies of turbulence are responsible for creating scalar fluctuations. The intensity of the scalar fluctuations is proportional to the intensity of turbulence and for this reason it is assumed that scalar integral length and time scales are equal to those of the turbulent field.

There are, however, some issues that raise uncertainty regarding the applicability, validity and accuracy of this global approximation to multi-scalar reactive flows. There are observations which indicate that the value of the time scale ratio C_ϕ is

not constant even for temperature fluctuations in inert flows [224]. Furthermore, the presence of differential diffusion in multi-scalar flows (i.e. presence of species with non-equal diffusivities) which causes different mixing rates of these species. It is observed, for example, in turbulent jet diffusion flames, that a laminar mixing layer occurs in the near field region (close to the nozzle) where molecular diffusion effects become dominant. The flame evolution will be influenced by the differential diffusion both in this region and away from it [175]. Another issue is the variation of the time-scale ratio with the type of flow and flow configuration, possibly due to its sensitivity to the dominant flow processes like buoyancy effects [196, 48], momentum, diffusion or reaction, or to the interaction between several flow processes [187]. In addition, the observation of very small reaction layers, particularly in premixed combustion regimes implies the existence of mixing scales which are much smaller than the smallest scales of turbulence [204].

4.2.1.2 Performance of mixing models with constant C_ϕ

To some extent, the single time scale (constant coefficient) assumption furnishes the transported PDF methods with a significant simplification. This explains the widespread adoption of this approximation when using simplified mixing models in multi-scalar reactive flows, including turbulent combustion calculations. Recently, there has been an extensive amount of research dealing with this aspect and there appears to be a blend of attitudes towards the performance of the constant coefficient. In simple geometry combustion problems such as jet flames, reasonable predictions have been reported with the constant time scale coefficient, though it is frequently altered from 2.0 to get best flame predictions.

From the computational view, it is not clear how much this single time scale approximation contributes to the inaccuracy of micromixing models or to the whole PDF simulation. Since the errors introduced by this and other simplifications can not always be estimated, it is not known how these limitations affect each other. From the published research, one notices that similar PDF algorithms with the same mixing model require different values for this coefficient even when the same flame

is being calculated. It is possible that this complicated behaviour is caused by differences in the modelling of other processes such as transport in physical space, its interpolation schemes, or the chemical reaction model. In addition, there is no indication that a certain class of the PDF would need a certain value, or that every mixing model has a universal and distinguishable value. There might be an indication of coupled sensitivity and influence between the use of a single time scale with several components of the modelling, including the type of mixing model, other elements of the PDF implementation, the chemical mechanism and errors in the turbulent time scale estimation.

Cao et al. [30] had to use higher values for this coefficient (i.e. 3.3 with the IEM model and 3.8 with the MCD model) to reproduce Sandia Flames D, E and F with a detailed chemical mechanism GRI-3.0 [2] in the velocity-turbulence frequency-composition PDF closure. The EMST model, which is discussed more in the next section, showed some advantage over the other two mixing models as it produced better results at lower C_ϕ value, i.e. 1.5. It was observed that the higher values used with the IEM and MCD models resulted, from one side, in producing a reasonable amount of scalar scatter in mixture fraction space, though from another side it caused under-prediction of mean rms of the mixture fraction and the reactive scalars in the real physical space. The latter observation suggests that too much mixing was enforced with the IEM and MCD models to obtain burning flames. Lindstedt and coworkers solved the joint-scalar PDF in the context of a second moment closure for piloted turbulent diffusion flames [130, 129] and stated that $C_\phi = 2.3$ was the best choice for their simulation, though this value may not be universal or unique. Finite-rate chemistry of 20 species was retained in these studies and reasonably good results were predicted. The same C_ϕ value was adopted for the non-piloted diffusion flames [131], though an artificial ignition was applied in order to keep the non-piloted flames burning.

In premixed flames, the value of time scale ratio poses similar or maybe more challenging difficulties, where changing the value is also commonly practised or a

model for time scale variation is employed [133, 204]. Vaos and Lindstedt [133] performed an analysis of the influence of changing the value of the constant C_ϕ as well as of using models with variable time scale ratio on the burning of turbulent premixed flames. The study included a challenging case for a flame with low Da which is regarded as close to global extinction. Constant values as high as 8 were tried for C_ϕ with the modified Curl's model (MCD). Some of their simulations showed sensitivity to both mixing and chemistry as well as to the specification of the pilot boundary conditions. A similar procedure was reported by [204], though the constant ratio was increased up to 12 in testing the performance of several mixing models for premixed flames.

4.2.1.3 Alternative models with variable time scale ratio

One of the alternatives to the constant C_ϕ is to solve a transport equation for the mean scalar dissipation rate (or by using an algebraic model). This is usually appropriate when second moment equations are already being solved as in [83]. The conditional mean scalar dissipation rate is a central quantity in CMC and MMC closures. Sanders and Gokalp [196] solved a transport equation for the scalar dissipation rate of the mixture fraction in the context of a second-moment closure to analyse the variation of mixing time scale. A model with a constant time-scale ratio and another with algebraic variable time-scale were also examined. These time-scale models were employed to compute turbulent jet flames. They highlighted that although major characteristics of the flow studied were reasonably reproduced by the constant-ratio model, accurate computations of detailed flow phenomena require knowledge of the detailed distribution of the time scale ratio. Therefore, they recommended that a model with a transport equation for the scalar dissipation rate or an algebraic variable-scale model should be included.

Alternatively, a quantity which has information on variation of mixing time scale can be included in the PDF model. The option of including mixing-time-scale information in the PDF equation applies for example to the PDF of gradient quantities [11]. A different approach was adopted by [32], who applied a mapping closures

model in the framework of flamelet computation and calculated the time scale ratio for reactive flows. It was suggested that the approach can straightforwardly be extended to micromixing modelling in the transported PDF equation. Further, they noted in the same study [32] that the time scale ratio was found to be affected by reaction. The time scale ratio is considerably reduced as stoichiometric locations are approached, implying that micromixing is enhanced in the reaction zone.

For premixed flames simulations, an advanced combined mixing model was proposed by [204] which takes into account the variation in C_ϕ . This model is based on switching between two regimes of combustion in premixed flames. A model was proposed for the distributed thickened regime and another model for the flamelet regime. For the distributed thickened combustion regime, a transport equation of the scalar dissipation rate (of the reaction progress variable) is solved, while an algebraic model was applied for the scalar dissipation rate in the flamelet (high Damkohler number) regime. Applying different closures for each combustion regime (distributed vs flamelet) produces two limiting values for the scalar dissipation rate which can be inserted in the combined mixing model. The model essentially combines these two values using a linear blending function to compute the effective scalar dissipation rate while preserving the limits at these two extreme values. The combined-regime mixing with linear blending idea was first introduced by Mura et al. [154], though a constant C_ϕ was used then. A single algebraic formula for variation of time scale ratio was applied in [133] for premixed flames and reported some improvements over the constant C_ϕ setting.

On the other hand, Richardson and Chen [190] proposed a model that accounts for differential diffusion effects in the PDF modelling of premixed flames. Furthermore, Mura et al. [153] introduced the so-called flamelet-PDF-unified model for turbulent combustion.

4.2.2 Localness Character of the mixing model

The principle of localness or proximity of scalar mixing is introduced to improve the performance of molecular mixing models in non-premixed combustion problems in a relatively simple way rather than introducing mathematical complications from the explicit resolution to small scales or direct inclusion of differential diffusion effects. It has been pointed out [205] that the semi-smooth and continuous behaviour of the composition field in the physical space implies that a scalar mixing model should be local in composition space. Molecular mixing is a microscale process by which an exchange occurs within small scales. It occurs between neighbouring fluid particles at the molecular level [184].

This was a main motivation for developing models which enhance the localness in composition space, as some conventional mixing models were accused of allowing particles with extremely distinct compositions to mix while they should ideally be set apart and isolated by thin reaction layers in the physical space. Numerically, in mesh-based simulations, micromixing is limited only between particles in the same cell. Particles with two broadly different compositions may coexist in the same cell and interact for example in regions of very high scalar gradients and intense turbulence, such as near mixing layers and reaction zones where macromixing is strong. The occurrences of this situation may, however, be exaggerated by poor implementation such as using a low number of particles or a too coarse grid such that some cells extend into the regions of markedly different compositions. Another situation is when the time step is not small enough that particles skip cells and move quickly to another region of different composition before they mix with previously closer particles (old neighbours). The particle may also jump and skip cells if there is an abnormally large numerical error in the particle motion model (turbulent diffusion) which would cause unreasonable macromixing behaviour. This implies that improved grid resolution and small time steps with a large number of particles are required to improve the representation of micromixing process. However, this is restricted by the fact that finer grids may require even smaller time steps and an extremely large number of particles, which would make the simulation computation-

ally unaffordable.

The intention of forcing this condition on the mixing term in PDF methods is to confine the interaction to particles which are considered neighbours in the composition space (or more generally the scalar space). The prospective result is to improve the resolution in scalar space and effectively to reduce numerical errors introduced by poor micromixing such as mixing particles with two distinct compositions.

The IEM model, Curl's CD model and its conventional modified versions (MCD) do not ensure observance of the localness property, while there are several other mixing models that actually do. The models which satisfy the localness in composition space are the Mapping Closures, EMST model and Multiple Mapping Conditioning approach. EMST can be viewed as an extension of mapping closures and is based on a similar concept. Actually, the Multiple Mapping Conditioning (MMC) approach is not a mixing model; rather, it is a framework on which various models are formulated and it provides implicitly a closure for the micromixing of the scalar field.

4.2.3 Interaction with the Mean

The principle of the interaction with the mean (IEM) model is to perform mixing of the individual entities of the PDF by allowing their properties to interact with their local ensemble means. The first version of the IEM was proposed by Villiermaux and Devillon [213]. The linear mean square estimation (LMSE) which was introduced by Dopazo and O'Brien [49] is a version of the IEM and is based on the same principle. In Lagrangian representations of reactive flows, chemical species concentrations and other transported scalars are properties of the notional particles. These properties are changed by interaction with an appropriate estimation of its local ensemble mean. For example, the mean can be appropriately evaluated over all particles located inside the FV cell. The scalar field is relaxed towards the local mean at a rate proportional to the mixing time scale τ_ϕ . Accordingly, the mixing contribution to the evolution of the scalar θ_s^{mix} can be expressed:

$$\theta_s^{mix} = -\frac{\rho(\psi_s - \tilde{\phi}_s)}{2\tau_\phi} \quad (4.5)$$

Based on an analysis of the balance of the scalar flux resulting from micromixing by the IEM model, Pope [180, 181] noted the need for a modification of the model to ensure that it remains consistent with the local isotropy of high- Re turbulent flows. On this basis, it was proposed that the velocity-conditioned scalar mean is employed for the mixing instead of the unconditional mean which is equivalent to the interaction by exchange with the conditional mean IECM model. Fox [58] introduced a general formulation for velocity-conditioned scalar mixing models from which versions of the IECM model were deduced and employed for inhomogeneous scalar field mixing [58, 12]. Fox [58] stated that it is crucial that the mixing model accounts for the effects of local anisotropy persisting at moderately high Reynolds numbers in turbulent shear flows. Therefore, his version of the IECM involved multiplication with a Reynolds-number-dependent factor representing the extent of local anisotropy.

4.2.4 The Curl model and the modified versions

Curl's original model [45] is also called the coalescence-dispersion (CD) model, which was primarily devised for the mixing of liquid droplets in chemical reactors. It is a pairwise exchange model which is based on randomly selecting a number of Particle pairs N_{pp} with a probability that is equal to $C_\phi N_{pc} \omega dt$. The scalar dissipation rate implied by Eq. (4.3) is also maintained by this model through the use of the time scale. Every pair of particles among the N_{pp} pairs are mixed by changing the scalar values to the mean of their original values. The Curl model is thus discontinuous in scalar space, though it has been found to modify the original shape of the PDF. Modified versions of the model have been developed by Janicka et al. [79] and Dopazo [50] in which particle pairs do not necessarily mix to their mean values. Rather, mixing may produce any values lying on the line between the original values of the two particles. This is commonly introduced using a new random parameter to control the degree of mixing in the interaction event between the pair of particles.

$$\phi_s^{(p)}(t + \Delta t) = \phi_s^{(p)}(t) - \frac{1}{2}\epsilon (\phi_s^{(p)}(t) - \phi_s^{(q)}(t)) \quad (4.6)$$

$$\phi_s^{(q)}(t + \Delta t) = \phi_s^{(q)}(t) + \frac{1}{2}\epsilon (\phi_s^{(p)}(t) - \phi_s^{(q)}(t)) \quad (4.7)$$

If particles do not have equal weights, the model needs to be modified to account for the variation in particle mass. One way of doing this will be discussed in the Lagrangian particle implementations. Explicit dependencies of mixing on the particle velocities has also been suggested [58], particularly for velocity-composition PDF methods.

This category of models does satisfy some of the basic conditions of micromixing such as linearity, independence, preserving the mean and scalar dissipation rate. The model has the same limitations as the IEM model, such as violating the localness in scalar space, though the PDF produced by the two models is not the same. The MCD model in current PDF implementations for turbulent flames has been reported to require large values for C_ϕ . As has been discussed in Section 4.2.1, values as high as 3.8 have been reported for non-premixed flames and 8 and 12 for premixed flames.

4.2.5 Mapping Closures Model

Chen et al. [36] proposed a scalar mixing model called the mapping closures, which have subsequently been formulated for particle methods by Pope [185]. Mapping closures employ a mapping function to develop correspondence or a map between the unknown physical scalar field and a Gaussian reference field whose PDF is prescribed. The statistics of this Gaussian reference field are utilised to model the PDF of the real scalar field through the mapping function. Unclosed two-point processes like micromixing are implicitly obtained from the statistics of the Gaussian reference field. In particular, the conditional scalar dissipation rate in physical scalar space is expressed in terms of the conditional scalar dissipation rate in reference space [214]. Arbitrary initial conditions of the PDF can be applied in this model including those relevant to turbulent combustion.

In the mapping closure particle model, particles interact with those close to them in composition space via the specification of a bandwidth for the particle interaction matrix to enhance the localness condition [205]. In addition to the localness of mapping closure, they satisfy the relaxation to a Gaussian distribution of conserved scalars in statistically homogeneous systems [75]. The boundedness and scalar dissipation rate constraints are also preserved. Analytical solutions for mapping functions have been obtained using a reference field whose distribution is Gaussian, and applications to conserved and reactive scalars in homogeneous turbulence have been performed successfully (see e.g. [64, 69] and others cited there). Direct extension of mapping closures applications to inhomogeneous turbulence introduces mathematical complications. Alternatively, Mortensen and Andersson [150] used the mapping closure solution for a homogeneous flow as a presumed mapping function PMF that can be generalised for inhomogeneous turbulence. This generalised PMF model can take any combination of initial delta functions and can describe mixing from multiple injections. The presumed mapping function (PMF) model has similar features to the presumed-shape PDF approach, though comparison with DNS data shows that PMF has advantages over the presumed β -PDF approach, particularly, in terms of generating better models for conditional statistics.

4.2.6 The Euclidean Minimum Spanning Tree (EMST) Model

The EMST model is an extension the single scalar mapping closures approach [185] to multi-dimensional scalar mixing by applying a generalisation on the coefficient of the particle evolution equations to account for a multiple number of scalars. The model then enforces the localness in composition space criterion by constructing a minimum spanning tree on the ensemble of particles which determines the relation governing the interaction between particles due to mixing. Thus an Euclidean Minimum Spanning Tree in this model replaces the one-dimensional ordering in conventional Mapping closures. The appearance of particles in stranding patterns in some instances is remedied by the intermittency feature of the EMST model. This feature is established by introducing an age property for the particle such that, for

every time step, the EMST is constructed only on a subset of the ensemble of particles in the cell, while the rest of the particles are in a nonmixing state. Like other mixing models, the EMST model satisfies the primary principles of mixing such as boundedness, the conservation of the mean and the scalar dissipation rate condition. Despite the apparent merits of the EMST model, which lie mainly in its localness, it does not allow the scalar field to abide by both the linearity and independence principles since the particle scalars evolve according to the tracing and ordering in the EMST which is dependent on the scalar field itself.

Recently the performance of the EMST has been frequently compared with other mixing models such as IEM and MCD in calculations of turbulent combustion, by which the improved predictions by the EMST is allegedly attributed to its localness property. As we discussed in the previous section, the model has been found to be capable of producing a burning turbulent non-premixed flame with extinction and re-ignition without having to use high values for C_ϕ as in the study of Cao et al. [30].

Merci et al. [143] assessed the EMST model by comparing it with the MCD at similar values for C_ϕ . They analysed the coupled interaction between micromixing and chemistry by performing transported scalar PDF simulations with three different chemical mechanisms. Despite the observed strong effect of these reduced chemical mechanisms on the simulations, the two mixing models seemed to respond differently. This can be seen from the presented results at $C_\phi = 2$ which indicates the coupled interaction between the two processes (mixing and reaction) which dominates the calculations. The MCD model did not perform well with the flame that has a measured local extinction as this model leads to excessive extinction of this flame at $C_\phi = 2$. While this bad performance of the MCD model was attributed to the absence of the localness constraint, more investigations are needed to examine the influence of the chemistry. In addition, effects from other simplifications in their modelling could only be analysed if a comprehensively detailed chemical mechanism was used to reduce the limitation of the chemistry. The simulations with EMST showed the flame is burning but neither of them predicted the local extinction as

minimal scatter is observed in the calculations. Variances of combustion products were strongly under-predicted by the EMST despite showing high levels of mixture fraction variance. The influence of changing the chemistry with the EMST model in their simulation can only be observed in the CO predictions. In a more recent study by the same group (De Meester et al. [47]), a transported scalar PDF simulation was performed for a different swirling bluff-body flame, though this flame exhibits local extinction as well. The MCD model's behaviour was remedied to some extent by increasing C_ϕ to 3. The model now predicts a burning flame with some degree of extinction, though the amount of scatter still seems to be more than what is reported experimentally. The EMST model calculations with $C_\phi = 2$ of the latter flame showed similar behaviour to the previous study [143] despite the fact that a different chemical mechanism was employed. The typical outcome with EMST in both studies [143, 47] was that it did not predict the extent of local extinction which is experimentally observed and can be identified by the scatter in the instantaneous scalar measurements. It is puzzling that the two models (MCD and EMST) interacted in a nearly opposite way with the chemistry models. Several aspects of the modelling could contribute to this incompetent performance of both the mixing models including the chemistry, adoption of constant C_ϕ approximation and other submodels in the particle equations.

4.2.7 Multiple Mapping Conditioning

More recently, a new tool based on the mapping closures and which retains some of its properties has been developed. It is called the multiple mapping conditioning approach (MMC) [106] which is also based on introducing a mathematical reference field whose PDF is prescribed. MMC can be viewed as a generalisation of mapping closures by which the merits of transported PDF and CMC models are combined together in a consistent and conformable way into one methodology. This generalisation is achieved through the use of multi-dimensional reference space to formulate the modelling equations with the aid of mapping functions.

In common with mapping closures, turbulent fluctuations and micromixing in

the reference field are utilised to describe turbulent fluctuations and micromixing of the real scalar space. In the original proposition of MMC by Klimenko and Pope [106], the dimensionality of the reference field is taken as a subset of the total number of scalars. These were named the major species which are selected such that they can specify all the allowed fluctuations and thus a representative composition manifold can be constructed. Consequently, the rest of the species (minor species) are assumed to have no fluctuations around their conditional means conditioned on the major species and accordingly the minor species are fully characterised by their conditional means. The formalism of MMC provides a generalised framework of multiple conditioning on major variables similar to the CMC approach while those major variables and their conditional dissipation rates are determined consistently from the joint PDF by utilising a multi-dimensional reference field. As a consequence, a closure is implied for molecular mixing in identical manner to mapping closures but the closure here in MMC is applicable to multi-dimensional scalar field and inhomogeneous flows.

All of the following principles of micromixing are satisfied in the MMC approach: boundedness, conservation of the mean, scalar dissipation rate, localness, independence and linearity. It is interesting that MMC compliance with the last two principles, independence and linearity, is the result of enforcing the localness through the reference variable space rather than directly through the real composition space. This merit of MMC is regarded as one of its advantages over the EMST model which violates both of these principles. Another feature of the MMC approach is that both Gaussian and non-Gaussian distributions for the reference field can be employed.

Vogiatzaki et al. [216, 215, 217] applied deterministic and stochastic MMC methodologies on turbulent diffusion flames with the mixture fraction being the only major scalar that is solved with a Gaussian reference field, while the equations of all other scalars are obtained using a coordinate transformation from the mixture fraction reference field. The equations for the conditioned reactive species in the case of a one MMC reference variable have the typical form of singly conditioned

moment closure CMC; however, their conditional scalar dissipation rate terms were implicitly modelled with the MMC approach which is a major difference from conventional CMC closure. In their latter work [217] for example, the stochastic MMC formalism were employed and the molecular mixing was modelled with an IEM-type model in which the localness of mixing is controlled by ordering according to the reference variable of the mixture fraction.

Wandal and Lindstedt [219, 220] combined the MMC for all scalars with the binomial Langevin model which solves joint statistics and the mixture fraction only; to avoid the problem of reactive scalar bounds in the binomial Langevin model. In accord to MMC ensured observance of the localness property by the modified Curl’s model (MCD) by employing a criterion controlling the selection of pairs of particles to be close in reference space. The methodology was first [219] applied to flame D and in the second work [220], flame E was simulated and both were with encouraging results. Cleary, Klimenko and coworkers [40, 39, 68] integrated LES with a stochastic MMC methodology called sparse-Lagrangian-MMC which is characterised by use of a relatively low number of particles (e.g. less than one particle per cell in fine LES grid). The generalised MMC mixing model which guaranteed localness in the scalar field ensured good-quality mixing despite the low number of particles employed.

4.3 Chemistry Reduction by the Rate-Controlled-Constrained Equilibrium

4.3.1 The Concept of RCCE

The concept of RCCE was first introduced by [101]. The methodology was developed further by Keck and co-workers (e.g. [100, 73]) and others (e.g. [86, 87]). It is one of the systematic methods of mechanism reduction that has the advantage of time scale separation. It provides a generalised differential-algebraic formulation that can be applied instantly to any set of reacting species without any modification to the formulation or to the original mechanism which is being reduced by RCCE.

In RCCE methodology, retaining the influence of important reactions is manifested by constraining the species controlled by these reactions. These kinetically-controlled species are determined by their original rate equations as in the original detailed mechanism, i.e. they evolve according to their chemical kinetics in the detailed mechanism without any approximation or mathematical truncation. The remaining species which are assumed to be kinetically less important are approximated by an equilibration of the system constrained to the kinetically-controlled species. This constrained equilibrium state is computed by minimisation of the Gibbs free energy subject to the conservation of elements and to the concentration of the kinetic species as additional constraints. So the composition is not relaxed to full equilibrium state, since finite rate chemistry is incorporated by imposing the concentration of kinetic constraints which are obtained directly from their chemical kinetics. If an appropriate subset of the reactive chemical species is chosen as kinetic constraints, the integration of the new chemical system should ideally exhibit less stiffness and require less CPU time than the full detailed mechanism. In RCCE, the set of constraint species may vary from a basic one which comprises the most important and significant species only, to a relatively detailed one which includes several minor species whose kinetics have an effect on the computation. If a basic set of constraints is implemented, the accuracy of the mechanism will probably be compromised by this relatively excessive system reduction in RCCE, in a similar manner to other globally reduced mechanisms by QSSA. In the interest of accurate predictions of chemistry and other combustion processes, the RCCE system is required to reasonably preserve the important structure of the detailed mechanism and to give accurate rates of formations for global species as well as dominant radicals affecting the flame burning rates. In turbulent flame simulations, if the RCCE system produces unreasonable concentrations of radicals which control flame ignition, this might cause either flame extinction or its contrary: excessive burning rates of fuel.

4.3.2 Fundamental thermodynamic relations

The Gibbs free energy (g) is a thermodynamic quantity of central importance which determines the location of chemical equilibrium at a certain temperature and pressure. It is an extensive property which is defined by the following equation:

$$g = h - Ts \quad (4.8)$$

Using the definition of the total enthalpy, the differential form for g is written:

$$dg = de + pdV + Vdp - Tds - sdT \quad (4.9)$$

and applying the definition of the first law of thermodynamic and definition of entropy of a reversible process we get:

$$dg = Vdp - sdT \quad (4.10)$$

If a chemical reaction is not in equilibrium state, it will proceed spontaneously in the direction which decreases the free energy ($\Delta g < 0$). The change in the Gibbs free energy (Δg) is the difference between the free energies of the products and the reactants. The Gibbs free energy of the mixture depends on the composition and can be evaluated from the chemical potential of individual species μ_s which is the same as its partial molar Gibbs free energy G_s . Both G_s and μ_s are functions of temperature and pressure, though the μ_s is an intensive thermodynamic property of the species:

$$g = \sum_{s=1}^{N_s} (\mu_s n_s) \quad (4.11)$$

The chemical potential μ_s for a species in a multi-component mixture is:

$$\mu_s = \mu_s^o + RT \ln \frac{n_s}{n} + RT \ln \frac{p}{p_0} \quad (4.12)$$

μ_s^o is the chemical potential at the standard state (or reference) pressure and it depends on temperature only. An important relation is the partial temperature dependence of the g/T at constant pressure:

$$\frac{\partial(g/T)}{\partial T} = -\frac{h}{T^2} \quad (4.13)$$

The derivation of this relation can be found in [102]. For a single species at the standard pressure, g may be replaced with μ_s^o and the partial derivative may be converted to the ordinary derivative (since p is constant and μ_s^o is a function of temperature only) which gives:

$$\frac{d(\mu_s^o/T)}{dT} = -\frac{H_s^o}{T^2} \quad (4.14)$$

This relation will be used in the derivation of the differential RCCE equations.

4.3.3 Derivation of RCCE Equations

The equilibrium state of the constant pressure combustion system is conveniently evaluated by maximising the entropy or minimising the Gibbs free energy. This method of equilibrium state calculation has the merit that it does not require knowledge of individual reactions of the chemical mechanism while this is a prerequisite in the equilibrium constants method. The minimisation of the Gibbs free energy is expressed by the following equation:

$$\frac{\partial g}{\partial n_s} = 0 \quad (4.15)$$

Since the elements are conserved during combustion reaction, enforcing the conservation of elements is a main condition for defining both full and constrained equilibrium states. The difference between the two states is that the elements are the only mass-balance constraints imposed on the composition in full equilibrium state while the constrained equilibrium requires additional constraints for composition. The elements composition maybe determined from the species composition through the atomic elements matrix which contains the number of atoms of each

element β in each species s .

$$E_\beta = \sum_{s=1}^{N_s} (a_{\beta s}^e n_s) \quad (\beta = 1, \dots, M_e) \quad (4.16)$$

The ideal gas equation of state as well as the enthalpy equation are both applied:

$$p = n\rho RT \quad (4.17)$$

$$h = \sum_{s=1}^{N_s} (n_s H_s^o) \quad (4.18)$$

Evaluation of chemical equilibrium by minimisation of the Gibbs free energy (constrained minimisation) has been widely solved by the method of Lagrange Multipliers in which one introduces the element potential λ_β^e to constrain the elements composition. The rate-controlled constrained equilibrium state has been viewed as an extension of the full equilibrium and hence it can be performed in a similar way using the method of Lagrange Multipliers once the additional kinetic constraints are imposed. The derivation of constrained equilibrium equations by Lagrange Multipliers was first achieved by Keck [100]. Jones and Rigopoulos [86, 87] also accomplished the solution of the constrained equilibrium by extending the methodology of Gordon and McBride [70] for full equilibrium.

Therefore, the first step in the RCCE is the specification of the kinetic constraints which together with the elements constraints, pressure and enthalpy define the constrained equilibrium state. The kinetic constraints can be expressed as follows:

$$C_\alpha = \sum_{s=1}^{N_s} a_{\alpha s}^c n_s \quad (\alpha = 1, \dots, M_c) \quad (4.19)$$

where $a_{\alpha s}^c$ is the constraints matrix defining the contribution of species s in constraint α . The number of kinetic constraints is M_c and they can be either single or a combination of species or a mixture of the two. If all the kinetic constraints are single species, then only the rows of these species have one non-zero value (which is equal to one) and the rest are all zeros. The Lagrange multipliers parameters which

appear here are the elements potentials λ_β^e as well as the constraint potentials λ_α^c . They are introduced in the following function which needs to be minimised:

$$g' = g + \sum_{\beta=1}^{M_e} \lambda_\beta^e (E_\beta - a_{\beta s}^e n_s) + \sum_{\alpha=1}^{M_c} \lambda_\alpha^c (C_\alpha - a_{\alpha s}^c n_s) \quad (4.20)$$

The following system of equations is then obtained for the constrained equilibrium state:

$$\mu_s + \sum_{\beta=1}^{M_e} \lambda_\beta^e a_{\beta s}^e + \sum_{\alpha=1}^{M_c} \lambda_\alpha^c a_{\alpha s}^c = 0 \quad (s = 1, \dots, N_s) \quad (4.21)$$

Alternatively, by substituting the equation for the chemical potential i.e. Eq (4.12) and re-expressing the RCCE system of equations (4.21) along with $(1/RT)$ scaling of $(\lambda_\beta^e$ and $\lambda_\alpha^c)$ yields the following equation for constrained equilibrium composition:

$$n_s = \frac{p}{\rho RT} \exp \left[\frac{-\mu_s^o}{RT} \right] \exp \left[\sum_{\beta=1}^{M_e} (\lambda_\beta^e a_{\beta s}^e) \right] \exp \left[\sum_{\alpha=1}^{M_c} (\lambda_\alpha^c a_{\alpha s}^c) \right] \quad (s = 1, \dots, N_s) \quad (4.22)$$

The importance and advantages of the constraints matrix $a_{\alpha s}^c$ in RCCE formulation can be easily perceived. Once this matrix is specified, the RCCE system is automatically formulated. It also allows that the constraints could be either single species or a combination of species. The differential equations for the dynamic evolution of the kinetic constraints which is obtained from the ODE's of single species can be written:

$$\frac{dC_\alpha}{dt} = \sum_{s=1}^{N_s} \left[a_{\alpha s}^c \frac{dn_s}{dt} \right] = \sum_{s=1}^{N_s} \left[a_{\alpha s}^c \left(\frac{\sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k)}{\rho} \right) \right] \quad (\alpha = 1, \dots, M_c) \quad (4.23)$$

Here, the differential equations are written in an ordinary form although the constraint species are originally described by PDEs because the fractional step method is employed, in which the evolution by chemical reaction is performed independently from other processes such as transport and mixing. It is evident from this equation that RCCE chemistry requires the solution of the ODE's of the species which are kinetically controlled only, and ODE's of the equilibrated species are excluded. The system of differential equations (4.23) is combined with the system of alge-

braic equations for equilibrated species (4.22) to construct the complete system of differential-algebraic equations (DAE) for RCCE. However, it is usually more convenient to transform this combined DAE formulation into an implicit pure ODEs set of equations using the index reduction technique to derive the corresponding differential equations which are easier to implement with CFD codes. The pure ODEs set is an index zero formulation for RCCE in which the Lagrange multipliers, temperature and density are taken as independent variables to compute the composition of the mixture. This method is employed in this study and its derivation is outlined in Appendix (A). The final ODEs are written here:

$$\begin{aligned}
& - \sum_{s=1}^{N_s} (a_{\alpha^*s}^c n_s) \frac{1}{\rho} \frac{d\rho}{dt} + \sum_{s=1}^{N_s} \left[(a_{\alpha^*s}^c n_s) \frac{1}{T} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\
& + \sum_{s=1}^{N_s} \left[(a_{\alpha^*s}^c n_s) \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_{\beta}^e}{dt} \right) \right] + \sum_{s=1}^{N_s} \left[(a_{\alpha^*s}^c n_s) \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_{\alpha}^c}{dt} \right) \right] \quad (4.24) \\
& = \sum_{s=1}^{N_s} \left[a_{\alpha^*s}^c \left(\frac{\sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k)}{\rho} \right) \right] \quad (\alpha^* = 1, \dots, M_c)
\end{aligned}$$

$$\begin{aligned}
& - \sum_{s=1}^{N_s} (a_{\beta^*s}^e n_s) \frac{1}{\rho} \frac{d\rho}{dt} + \sum_{s=1}^{N_s} \left[(a_{\beta^*s}^e n_s) \frac{1}{T} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\
& + \sum_{s=1}^{N_s} \left[(a_{\beta^*s}^e n_s) \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_{\beta}^e}{dt} \right) \right] \quad (4.25) \\
& + \sum_{s=1}^{N_s} \left[(a_{\beta^*s}^e n_s) \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_{\alpha}^c}{dt} \right) \right] = 0 \quad (\beta^* = 1, \dots, M_e)
\end{aligned}$$

$$\begin{aligned}
& - \sum_{s=1}^{N_s} \left(\frac{H_s^o n_s}{\rho} \right) \frac{d\rho}{dt} + \sum_{s=1}^{N_s} \left[n_s \frac{\partial H_s^o}{\partial T} + \left(\frac{H_s^o n_s}{T} \right) \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} + \\
& + \sum_{s=1}^{N_s} \left[(H_s^o n_s) \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_{\beta}^e}{dt} \right) \right] + \sum_{s=1}^{N_s} \left[(H_s^o n_s) \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_{\alpha}^c}{dt} \right) \right] = 0 \quad (4.26)
\end{aligned}$$

$$\begin{aligned} & \frac{p}{T} \sum_{s=1}^{N_s} \left[1 + \frac{n_s}{n} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\ & + \frac{p}{n} \sum_{s=1}^{N_s} \left[n_s \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_{\beta}^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_{\alpha}^c}{dt} \right) \right] = 0 \end{aligned} \quad (4.27)$$

4.3.4 Selection of Constraints

In the original derivation of RCCE, Keck [101, 100] proposed that the kinetic constraint can be either a species or a linear combination of species. In the recent derivation by Rigopoulos and Jones, the formulation was based on selecting all constraints as single species. In [73], the kinetic constraints are a linear combination of reactive species. They pointed out some conditions which need to be obeyed by the constraints, such as the requirement that the constraints are linearly independent, to avoid singularity in the RCCE matrix.

Although the RCCE formulation implemented here is general, which means that any set of constraints can be applied without any manipulation, it does not have a built-in criterion for analysing the species importance or time scales and thereby facilitating the picking up of constraints. So, the RCCE user needs to look for a means for selecting the optimal set of constraints. This can be done optionally by combining RCCE with one of the species determination methods that are based on the same principle of time-scale separation, for example the species ranking method with level of importance (LOI) [134] or the computational singular perturbation (CSP) method. The RCCE simulation can, however, be performed without the need for these methods given that the set of constraints are manually chosen before the calculations are started. This has been the traditional procedure in most RCCE studies in which the researchers would rely on some heuristic analysis and previous experience of similar combustion problems.

It should be noted that, given the complexity of chemical kinetics of combustion, there is the possibility that the influence of some species and reactions will vary

considerably when the combustion process occurs in quite different environments or different thermodynamic states [118]. Bibrzycki et al. [17] who investigated predictions of laminar flame speed with reduced mechanisms pointed out that these reduced mechanisms would work differently if the composition of the oxidiser was changed from air to O_2/CO_2 mixture. Although the optimal list of constraints for a certain fuel may possibly vary from one combustion problem to another, for example those associated with premixed and non-premixed combustion, the most significant and global species can be identified without difficulty. In essence, however, more reactions and species need to be preserved in the reduced system in order for the reduced mechanism to accurately resemble the structure of the full mechanism in a wide range of conditions and to be an efficient chemical model. The difference between the optimal RCCE sets of constraints for different problems would be, essentially, in the extra intermediate and minor species which need to be included to obtain a better prediction of the problem. For example, the same 9 constraints were employed successfully in RCCE simulations of three different combustion problems of methane-air mixtures [86, 85]. This set comprised the 9 global species which are retained in most methane-air RCCE reduced systems, e.g. [159]. Furthermore, increasing the number of constraints in RCCE has been shown to improve the accuracy of laminar combustion predictions without introducing much computational problems or losing much of the savings in CPU time [88].

In turbulent combustion the choice of the additional constraints is more challenging due to more overlapping between flow and chemistry scales, which results in a strong interaction between some reactions and small scales of turbulence. If the production rates of important radicals are not accurately computed by the RCCE procedure, the flame calculations may result in a quenched flow or too much burning of the fuel.

In parallel to using RCCE alone for chemistry reduction of combustion problems, there has been some focus recently on integrating some techniques of automatic determination of constraints with RCCE such as the CSP and the LOI methods. A

potential research area which is being explored [202] is to couple the RCCE with the CSP method which has also received considerable developments and refinements. With regard of using CSP for methane-air flames, Belcadi et al. [4] performed an analysis based on an integrated CSP criterion applied to reduce $CH_4 - NO_x$ chemistry by providing ordering of all the species. A ten-step mechanism was tested on lean and rich premixed methane-air mixtures with equivalent ratios (0.6 to 1.4) and at a range of pressures (1 to 30 atm).

The level of importance (LOI) method [134] provides a ranking for species in terms of combined criteria that are based on the species time scales and a measure of species sensitivity. The LOI was devised to furnish the QSSA system with the list of steady state species which would then be computed by the algebraic equations. The rest of the species are the ones solved kinetically. In a similar manner, the LOI has also been employed to supply the RCCE with the list of constraints for laminar premixed flames [192] and for turbulent non-premixed flames [135]. The leading species in the LOI matrix which have more chemical importance and slower time scales were used as constraints for the RCCE. In the later implementation for turbulent non-premixed flames by Løvas et al. [135], the reduced chemical system computed by RCCE was allowed to adapt to local flow conditions by adjusting the LOI lists according to variations in the mixture fraction. Hiremath et al. [76] implemented a method called the Greedy Algorithm with Local Improvement to automatically choose the set of constraints.

4.4 Soot mechanism and modelling

4.4.1 Soot nucleation and Surface Growth

Nucleation is the production of the smallest visible (radiant) soot particles with diameters usually of the order of 1 nm and with masses of the order of 1000 amu, presumably containing a cluster of PAH molecules. So, they lie in the range that is too heavy to identify by gas chromatography which is limited to molecular mass less than 300 amu and too small to be observed by high resolution microscopes. This

explains the lack of detailed knowledge of nucleation chemistry [191]. The primary incipient particles can not be regarded as solid carbon as they comprise, in addition to carbon, a considerable amount of hydrogen atoms. As we have stated, there is a wide recognition that the nucleation and growth of soot particles are the result of the recombination and growth of PAH.

For nucleation, smaller PAH grow to larger PAH as they react with other species, including C_2H_2 and other aromatic rings. Growth and combination of large PAH produce PAH dimers, PAH trimers and PAH tetramer. Further coagulation and condensation of PAH leads to the formation of primary semi-solid incipient soot particles [191]. Nucleation is, thus linked to PAH and C_2H_2 .

Growth by surface reactions is commonly assumed to be governed by the (HACA) mechanism. The implication of surface growth by HACA is that the C – H bonds become active radical sites by the H atom abstraction. Subsequently, the active radical sites on the particle surface react with the dominant growth species, e.g. C_2H_2 [60]. It is believed that other reactants such as stable PAH also react with radical sites on the soot particle surface [191]. Acetylene C_2H_2 can thus be regarded as a central species for surface growth of soot particles in addition to its role in soot nucleation in smaller hydrocarbon flames. In this study we assume that nucleation and surface growth occur by addition of C_2H_2 only. The mechanism is implied by the following reaction occurring between a molecule of C_2H_2 and a soot particle $C(s)_i$ containing (i) carbon atoms:



Surface growth reactions are strongly dependent on temperature. It is common that surface growth is linearly related to surface area [103, 127, 16]. However, the role of active sites on particle surface and the observation of different growth rates in similar-size aerosols due to ageing effects suggested the use of modified relations [103]. Some approaches proposed that dependence of surface growth rate on total soot surface area should be weakened [123]. The nucleation and surface growth rates

are given by:

$$\hat{\omega}_n = k_n (T) [\text{C}_2\text{H}_2] \quad (4.29)$$

$$\hat{\omega}_G = k_G (T) A_{st} [\text{C}_2\text{H}_2] \quad (4.30)$$

where molar concentration of acetylene per unit volume of the mixture $[\text{C}_2\text{H}_2]$ is equal to $(\rho n_{(\text{C}_2\text{H}_2)})$. The $(n_{(\text{C}_2\text{H}_2)})$ is acetylene's specific mole number. As can be seen the linear proportionality between surface growth and soot surface area is taken in this model. The soot surface area per unit volume of spherical particles is obtained from:

$$A_{st} = \pi d_{st}^2 \rho \text{Np}_{st} \quad \text{and} \quad d_{st} = \left(\frac{6Y_{st}}{\pi \rho_{st} \text{Np}_{st}} \right)^{\frac{1}{3}} \quad (4.31)$$

where Np_{st} is the soot particle number density per mass of the mixture and d_{st} is the soot particle diameter. The density of soot ρ_{st} is given the value 2000 kg/m³.

4.4.2 Oxidation

Oxidation of soot particles occurs by O₂, OH and O. OH is the dominant soot oxidiser inside the flame while burning by the O₂ usually becomes important in the post-flame fuel-lean zones. [166]. Oxidation is the only process that reduces the amount of soot in the flame by transforming it to CO and subsequently to CO₂. Lee et al. [120] developed an empirical model for O₂ oxidation rate of soot based on measurements of dependence of this reaction on temperature and O₂ concentration on the assumption that kinetics of surface reactions are dominant. The soot oxidation process is commonly represented by the following reactions:



Oxidation by the O radical is not included explicitly in soot mechanism adopted here. The oxidation reaction by O has been recently included as an independent oxidation step in detailed schemes [16];

$$\dot{\omega}_{ox} = k_{O_2}(T) A_{st} [O_2] + k_{OH}(T) A_{st} [OH] \quad (4.35)$$

4.4.3 Coagulation and agglomeration

Collisional processes like coagulation and agglomeration become important when the particle number density is large. Coagulation and agglomeration increases the particle size and results in a reduction of the particle number density, though the total soot mass is not affected by these processes.

In the coagulation process, primary particles coalesce to form one larger particle, usually assumed to preserve the spheroid shape. Agglomeration usually occurs among older particles as they tend to form aggregates with fractal-like geometries [103, 128]. Bisetti et al. [23] stated that the typical size of a soot particle ranges from 1 to 100 nm, while the number of primary particles in an aggregate ranges from 10 to 1000. The source term of the particle number density increases by nucleation and decreases with agglomeration and coagulation.

$k_k(T) =$	$B \cdot T^a \cdot \exp(-E_r/RT)$
$k_n(T) =$	$6.3 \times 10^3 \cdot \exp(-21000/T)$
$k_G(T) =$	$7.5 \times 10^2 \cdot \exp(-12100/T)$
$k_{O_2}(T) =$	$7.15 \times 10^2 \cdot T^{1/2} \cdot \exp(-19800/T)$
$k_{OH}(T) =$	$0.36 \cdot T^{1/2}$

Table 4.1: Rate-constants of soot reactions [24, 127, 111, 120]

4.4.4 Net soot source terms

The overall source terms of soot variables i.e soot mass fraction (Y_{st}) and soot particle number density ($N_{p_{st}}$) are obtained from the equations:

$$\dot{\omega}_{Y_{st}} = (2\hat{\omega}_n + 2\hat{\omega}_G - \hat{\omega}_{ox}) W_C \quad (4.36)$$

$$\dot{\omega}_{N_{p_{st}}} = 2\hat{\omega}_n \frac{N_A}{N_{i,min}} - 2C_a d_{st}^{1/2} \left(\frac{6\kappa_B T}{\rho_{st}} \right) (\rho N_{p_{st}})^2 \quad (4.37)$$

where $W_C = 12.011$ is carbon atomic weight. N_A is the Avogadro number (6.022×10^{26} 1/kmol) which represents here the number of carbon atoms per 12kg of carbon. $N_{i,min}$ is the minimum number of carbon atoms required for the nucleation of a new soot particle. The agglomeration constant $C_a = 9$ and the Boltzmann constant ($\kappa_B = 1.38065 \times 10^{-23}$ J/K)

4.5 Lagrangian solution of the Scalar PDF equation in a Hybrid Framework

In this approach, turbulent non-premixed flames are simulated by devising a hybrid algorithm in which the integration between flow field modelling and the chemistry calculation is done interactively with the use of the Lagrangian Monte Carlo model. The Lagrangian Monte Carlo model provides a solution for the transported joint scalar PDF equation. The implementation is based on the work of Di Veroli and Rigopoulos [212] and we follow their methodology in several parts of the simulation. Their original implementation was developed for constant-density flows, so their code was first modified to account for density variations in turbulent combustion flows. The flow field computations is done with a RANS code called BOFFIN which is a finite volume CFD solver simulating the velocity field of the turbulent jet using a RANS $k - \varepsilon$ modelling. The configuration of the hybrid algorithm is devised so that different chemistry models (either reduced or detailed chemical mechanism) can be employed and integrated into the solver with the same setting of the boundary conditions.

4.5.1 Finite Volume Algorithm for the Flow Field

The Reynolds averaged NavierStokes equations (RANS) Eqs. (2.26) and (2.27) are solved using a finite volume algorithm as implemented in the BOFFIN code. The code incorporates the Favre-averaged form of $k - \varepsilon$ model to compute the turbulent quantities which are required in the RANS solver as well as the PDF model. The equations of k and ε (Eqs. 2.38 and 2.39 respectively) are in the standard form except the well-known modification of $C_{\varepsilon 2}$ to 1.8 instead of 1.92 to correct the turbulent jet spread rate.

The finite volume approximation of the partial differential equations is implemented by applying the standard finite difference methods in a transformed rectangular domain which is then mapped back to the actual physical geometry. The transformation into a rectangular domain is applied on the discretised conservation equations although the dependent variables [velocity components and turbulent quantities] are not themselves transformed. Rather, extra geometric coefficients such as the Jacobian factor and other transformation coefficients are introduced into the discretised equations. This allows the applicability of the BOFFIN code to any complex geometry.

In this version of RANS code (BOFFIN), a preconditioned conjugate gradient method is applied to compute the pressure increment and the preconditioned Bi-conjugate gradient method is applied to other dependent variables. The Total Variation Diminishing (TVD) scheme developed by Van Leer [122] is applied to the convection terms as it is known to give a second order accuracy for the differencing and prevents spatial oscillations. Cell face values which are required in the TVD scheme are obtained from an upwind interpolation with the correction and limiter of Van Leer [122].

4.5.2 Lagrangian particle solver

In the Lagrangian particle model, the increment over the time step of each physical process are computed sequentially using the so-called operator splitting or frac-

tional step method. The numerical operation of each term which corresponds to one physical process like transport, mixing or reaction is decoupled from the numerical operation of other terms.

The time step of the finite volume CFD solver (Δt) may not be suitable for the particle field. The time scales of the particle are defined by the local flow field quantities such as mean velocity and turbulent quantities. Therefore, a new global time step (Δt^*) is defined for the PDF model so that the CFD time step can be divided into an integer number of PDF sub-steps N_{pdf} . Alternatively, adaptive local time stepping has been recommended and applied [155, 189] where every particle has its unique time step but this has not been considered in this study. Rather, a global number of PDF steps N_{pdf} per one CFD time step is applied for all particles which relates the two time steps by the relation:

$$N_{pdf} = \frac{\Delta t}{\Delta t^*} \quad (4.38)$$

This number of sub-steps is computed so that the PDF time step satisfies the three following criteria:

- Courant (CFL) number is less than unity so that mean convection does not cause particles to skip the neighbouring cell on the side relevant to its direction of motion
- Diffusion number is less than unity implying that transport by turbulent and molecular diffusion does not cause the particle to skip the neighbouring cell on the side relevant to its direction of motion
- PDF time step is shorter than the turbulence integral time scale

The above three criteria should be satisfied for all particle locations in the solution domain. For simplicity, the number of PDF sub-steps N_{pdf} are computed based on the variables at the centre of all FV cells. The maximum value of N_{pdf} over all cells and from the three criteria is taken so that the minimum time step is employed as a global time step Δt^* for the particle field calculations. Therefore, N_{pdf} is the

nearest integer to:

$$N_{pdf} = \max \left\{ \left(\Delta t \cdot \frac{u_l}{c_l \Delta x_l} \right), \left(\Delta t \cdot \frac{D_{eff}}{df_l (\Delta x_l)^2} \right), \left(\Delta t \cdot \frac{C_\phi \varepsilon}{c_{mix} k} \right) \right\} \quad (4.39)$$

Since the subscript l refers to the spatial dimensions, the first two criteria are usually repeated for the three dimensions of the physical space in three-dimensional simulations. In this two dimensional axi-symmetric implementation, the criteria is performed for two dimensions which are the axial and radial directions. Convection number (c_l) and diffusion number (df_l) are assigned a value of 0.5 while even a lower value is taken for $c_{mix} = 0.25$. In all the simulations, it was noticed that the small Δx_l in the shear layer zone made the diffusion criterion the strongest and gave the smallest Δt^* which would be considered.

4.5.2.1 Particle initialisation and motion

The joint scalar PDF equation is represented by an ensemble of particles. Each particle carries a set of quantities such as mass m^* , position $\underline{x}^*$ and a set of scalar variables $\underline{\phi}^*$ which includes composition and enthalpy. Velocity is also interpolated to the particles locations from the cell centre values which are provided by coupling with the Eulerian $k - \varepsilon$ CFD solver. Although every particle is assigned its unique (interpolated) velocity components, the later are not modified by the PDF model since velocity is not a transported quantity. The particle system is initialised with an equal number of particles per cell N_{pc}^o . Particle masses m^* are initialised according to the finite volume cell mass m^{cell} such that ($m^* = m^{cell}/N_{pc}^o$). Particles within a cell are thus initialised with equal masses but there is variation from cell to another in particle masses due to the variation in cell volumes and mean flow field density $\bar{\rho}$.

Particles move in the physical space according to the a modelled stochastic differential equation which is consistent with gradient transport formulation. The equation includes both a deterministic convection (drift) process and a random walk

stochastic (diffusion) process and can be written:

$$\Delta x_i^* = \left(\tilde{u}_i^* + \frac{1}{\bar{\rho}} \frac{\partial}{\partial x_i} \left(\frac{\mu_t}{\sigma} \right) \right) \Delta t^* + \left[\frac{2}{\bar{\rho}} \left(\frac{\mu_t}{\sigma} + \frac{\mu}{Sc} \right) \right]^{1/2} \Delta W \quad (4.40)$$

where $\tilde{u}_i^*$ is the mean velocity interpolated to the location of the particle. There are several interpolation schemes that have been employed for this purpose. One common procedure is to perform a linear interpolation scheme [90] which will be employed in some of the calculations. The original implementation by Di Veroli and Rigopoulos [212] applies an interpolation scheme similar to that of Jenny et al. [80] for mean velocity components which is also used for some of the calculations here as well. The Jenny et al. scheme [80] is based on the principle that each velocity component has quadratic variation in its own direction and a linear variation in the direction normal to it.

Like mean velocity, the turbulent diffusivity μ_t is also obtained from the flow field CFD solver using $(\mu_t = \bar{\rho} C_\mu \frac{\tilde{k}^2}{\tilde{\varepsilon}})$. The turbulent Schmidt or Prandtl number σ is taken to be 0.7. The second term on the right hand side of Eq. 4.40 represents the stochastic diffusion process. ΔW is the increment of an isotropic Wiener process during the PDF time step which involves a normal random variable with zero mean and unity variance. ΔW is thus a random variable with zero mean and a variance equal to the PDF time step Δt^* [90].

4.5.2.2 Particle tracking and control

Particles change their cell as they move in the physical space. New particles are also introduced to the cells adjacent to the inlet boundary according to the flow rates and composition of the different inlet streams. Thus, they become unsorted and need tracking. This also causes that particles with different masses to exist in one cell and the initial number of particles in the cell N_{pc}^o is not preserved for individual cells. A particle tracking and control scheme is employed to sort the particles in cells and limit the variation in particles masses within one cell. The particle masses are driven towards the average particle mass in the respective cell by splitting particles with

larger masses and clustering the ones with smaller masses. The targeted particle mass $m_{p,tar}^*$ in a cell is set according to the following range:

$$\frac{1}{2N_{pc}^o} \sum_{p=1}^{N_{pc}} m_p^* < m_{p,tar}^* < \frac{2}{N_{pc}^o} \sum_{p=1}^{N_{pc}} m^* \quad (4.41)$$

N_{pc} is the current number of particles in the cell before splitting and clustering is applied. As a consequence, the scheme controls the variation in the number of particles per cell N_{pc} which would be within the range ($0.5N_{pc}^o < N_{pc} < 2N_{pc}^o$) and with a targeted average number of particles per cell that is very close to the initialising value N_{pc}^o .

4.5.2.3 Mixing and Chemical reaction

The evolution of the scalar field by molecular mixing and reaction are performed one at a time by the fractional step method. The molecular mixing is treated by implementing the IEM and the MCD models. Mixing between particles is confined to those in the finite volume cell. In the IEM model, this is achieved by estimating the mean of the scalar quantity from the ensemble of all particles present in that cell. This ensures that the weighted mean of composition and other scalars based on the cell are not modified by mixing.

The change in particle scalar variables by IEM mixing over one PDF time step is given by the following relation:

$$\phi_s^*(t + \Delta t^*) = \phi_s^*(t) - \frac{C_\phi \varepsilon}{2k} \left(\phi_s^*(t) - \tilde{\phi}_s \right) \Delta t^* \quad (4.42)$$

In the modified Curl's model (MCD), the mixing is performed so that the cell weighted ensemble mean is preserved by accounting for the unequal masses of particles. This is achieved by including the weighted average of the pair of particles (p) and (q) which is estimated before mixing $\phi_s^{(pq)}(t)$.

$$\phi_s^{(pq)}(t) = \frac{m^{(p)} \cdot \phi_s^{(p)}(t) + m^{(q)} \cdot \phi_s^{(q)}(t)}{m^{(p)} + m^{(q)}} \quad (4.43)$$

The new scalar values for the pair of particles after MCD mixing over one PDF time step is written here following [90]:

$$\phi_s^{(p)}(t + \Delta t^{(p)}) = \phi_s^{(p)}(t) - \epsilon (\phi_s^{(p)}(t) - \phi_s^{(pq)}(t)) \quad (4.44)$$

$$\phi_s^{(q)}(t + \Delta t^{(p)}) = \phi_s^{(q)}(t) - \epsilon (\phi_s^{(q)}(t) - \phi_s^{(pq)}(t)) \quad (4.45)$$

As it has been mentioned in section 4.2.1 that there is no universal value for C_ϕ . Here we give it the value 2.2 which works well for several turbulent jet flames of hydrocarbon fuels. Turbulent quantities k and ε are obtained by the turbulence model. From the criterion of the PDF time step by the integral time scale, Δt^* is much smaller than turbulence integral time scale ε/k . This ensures that mixing does not violate the decay of the scalar variance, preserves the mean and that the fractional step method is justified. As for the chemical reaction, the PDF model is coupled with both the direct integration (DI) of the detailed mechanism and with the RCCE reduced mechanisms. Here, the DVODE solver was employed in the RCCE simulations. The simulations with DI of the detailed GRI-3.0 mechanism [2] were not obtained with the DVODE solver as some simulations experienced several crashes and for this reason the DLSODE solver was employed in the full GRI-3.0 simulations.

For, adiabatic non-sooting flame simulations, the dimensionality of the scalar field N_{sc} equals $N_s + 1$ in the case of DI chemistry and equals $M_c + 1$ in the case of RCCE chemistry. Each particle carries these N_{sc} scalars of which N_s or M_c is the number of gaseous species or constraints which are controlled by chemical kinetics. The additional one refers to mixture fraction z which is used to compute the specific enthalpy h for adiabatic flames and the atomic element composition. h is a conserved scalar in adiabatic flame simulations and does not need to be transported since it is represented by the mixture fraction. In the case of calculations with RCCE mechanisms, the rest of the species $N_s - M_c$ are in the constrained equilibrium state.

4.5.2.4 Coupling with radiation and soot models

Extension of the methodology to incorporate thermal radiation and particulate formation are straightforward here. This is due from one side to the simplified models adopted for these processes that do not generate complicated mathematical problems. The main procedure is to include enthalpy and soot parameters as additional properties for the Lagrangian particles. Transported soot parameters which are carried by the Lagrangian particles in the current PDF simulations of sooting flames are soot mass fraction Y_{st} and soot particle number density $N_{p_{st}}$. We emphasize here that the term *Lagrangian particle* which is a notional entity in Lagrangian PDF methods is different from the term *soot particle* which is a tangible solid particles formed during combustion.

For soot formation mechanism, the simple semi-empirical model which is outlined in section (4.4) for the source terms of Y_{st} and $N_{p_{st}}$ is also coupled with the PDF algorithm. The evolution of h by radiative emissions is accounted for by coupling the simplified optically-thin model (RADCAL model) [72] with the PDF algorithm. The radiative emissions by soot are also incorporated with the constant of the soot Planck mean absorption coefficient $C_s = 2370\text{m}^{-1}\text{k}^{-1}$ [226]. The total radiative heat loss rate is:

$$\dot{q}_{rad} = 4\sigma \left[C_s f_v (T^5 - T_o^5) + \sum_{s=1}^{N_s} \gamma_s X_s (T^4 - T_o^4) \right] \quad (4.46)$$

where γ_s is the Planck mean absorption coefficient of the gaseous species (s). The values of γ_s for CH_4 , CO_2 , H_2O and CO were taken from fits to results from the RADCAL program [72] which were presented on the TNF website [1]. In the propane flame simulation, the plank mean absorption coefficient for propane (C_3H_8) was taken from [218].

Chapter 5

PDF-RCCE Simulation of Piloted Methane-Air Turbulent Diffusion Flames

5.1 Introduction

In this study, the coupled PDF-RCCE methodology is applied for turbulent diffusion flames by integrating it with a RANS algorithm. The transported scalar PDF equation, which is solved by implementing a Monte Carlo particle method, is exploited for the turbulence-chemistry interaction. Thus the Lagrangian PDF particle model provides the coupling between the $k - \varepsilon$ RANS model which computes the velocity and turbulent fields and the RCCE mechanism which computes the chemical source term. Actually, this numerical setup is developed for the computation of turbulent jet flames with both detailed and reduced chemical systems. The simulations were performed for three piloted turbulent diffusion flames which are Sandia Flames D, E, and F. Every flame is computed with both the detailed mechanism and with RCCE system derived from the same detailed mechanism to enable the evaluation of RCCE predictions relative to the detailed mechanism. The phenomena of local flame extinction increases gradually in these flames from flame D to flame F. Quite limited local extinction is observed in flame D measurements and becomes more noticeable and perceptible in flames E and even more in flame F which is close to

global extinction. Accordingly the re-ignition phenomena is also more clearly observed in flame F than the other two flames.

Both the CFD and chemistry approaches need to account efficiently for these phenomena, particularly in flames E and F. An accurate computation of the turbulence field and its interaction with chemistry need to be accurately configured so that strengths and weaknesses of the chemical model are evaluated with less uncertainties. An accurate chemical kinetics mechanism should be capable of showing the right dynamic response to the turbulence field. In this study we test the strength of the RCCE approach in the context of transported PDF method because the latter is well known for its capability to incorporate detailed and satisfactory representation of finite-rate chemical kinetics and its interaction with turbulence.

The combination of RANS and PDF adopted in this study is considered to be an appropriate setting for testing the RCCE approach on these relatively simple flame configurations at a moderate computational cost. The reason for choosing RANS-PDF methods here that they involve a good balance between accuracy and computational cost. They have been widely applied for turbulent jet flames that the sources of their strengths and weaknesses are mostly identified and understood to some extent. The RANS-PDF setup with the considered experimental flames and similar test cases have been a focal area under intensive investigations with many chemical mechanisms and several mixing models which have been published recently that should aid the understanding of the present results.

5.2 Test Case Configuration

The experimental test cases under consideration here are the well known piloted methane-air turbulent jet flames, namely Sandia Flames D , E and F [3]. The Sandia piloted flames have the same geometric configuration and with the same composition of the jet, pilot and co-flow streams but they differ in the jet and pilot velocities. These three flames are a part of a series of six piloted non-premixed flames

[A, B, C, D, E and F] which has been studied experimentally by Barlow and coworkers [13, 14] who provided detailed measurement of the scalar field. Laser Doppler Velocimetry (LDV) measurements for the flow field were published by Schneider et al. for the flames D, E and F [197]. The jet Reynolds numbers of the flames span from 1,100 (for the A which is a laminar flame) to 44,800 (for the F flame which is turbulent with global extinction and reignition).

The unconfined flames were established on a piloted burner setup which had been developed at Sydney University [141]. The burner has a nozzle diameter of $d=7.2$ mm and a premixed pilot that extends to a diameter of 18.2 mm. The main fuel jet is a partially premixed methane-air mixture with composition of 25% CH_4 and 75% air by volume which produces non-sooty flames. This partial premixing with air also enhances flame stabilisation at a higher Reynolds number than that which a pure CH_4 flame can be stabilised at, thus allowing for testing combustion at high turbulence levels [13, 14]. This also minimises the formation of soot and soot precursors which interfere with the Raman signals and affect the scalar measurement. In addition, from the computation point of view, the non-sooty flames are favoured for the study of gas-phase chemistry and turbulent-chemistry interaction without having to incorporate models for radiation and soot formation.

The pilot burns a lean ($\Phi = 0.77$) pre-mixture of C_2H_2 , H_2 , O_2 , CO_2 , and N_2 with the same nominal enthalpy and equilibrium composition as methane-air at this equivalence ratio. The energy release of the pilot is approximately 6% of the main jet. Barlow and Frank stated that during the scalar field measurement, the burner exit is set approximately 150 mm above the exit of a vertical wind tunnel while during the flow field measurement by Schneider et al. [197] it was aligned 20 mm above the exit of the co-flow nozzle.

5.3 Previous Simulations of Sandia Flames

An exhaustive survey of the studies that have been performed for these flames is not intended here, but we point to examples of relevant studies that apply some of the components of the current methodology. Some studies apply a different class of the PDF such as the velocity turbulent frequency and composition but the details of the chemistry or type of mixing model might be similar. Other studies apply the scalar PDF class but may differ in the CFD closure, in the chemical mechanism or in the mixing model. Examples of studies employing an essentially different methodology are also mentioned at the end of this section. Extra examples have been discussed in previous chapters.

The three flames have been computed with the joint PDF of the velocity, turbulent frequency and composition with an augmented reduced mechanism (ARM) by Tang et al. [209] and Xu and Pope [232] and later with the full GRI-3.0 mechanism by Cao et al. [30]. Lindstedt and coworkers [129, 130] implemented the transported scalar PDF in the context of second moment closure of the flow field and applied it to flames B, D and F. Jaishree and Haworth [78] computed every flame of these three with three different Monte Carlo methods to solve the composition PDF equation in the hybrid RANS-PDF context. These three methods are the Lagrangian particle method, the stochastic field method and finally the multi-environment MEPDF method. The MEPDF method is a direct-quadrature-method-of-moments closure in which there are no stochastic terms added in the PDE's in contrast to the stochastic field method. The simulations of the three flames have been utilised to compare the computational efficiency of these three methods in terms of capturing the extinction and re-ignition phenomena. Comparable results were obtained for the two stochastic methods and poor results for the MEPDF.

In LES, the stochastic field method has been recently developed to solve the sub-grid PDF. Jones and Prasad [96] employed the stochastic field method for LES-PDF and computed the three flames (D, E and F) successfully. The MMC representation of mixing has also been tested on these flames both in the RANS and LES context.

Examples of the RANS-MMC simulations are those by Vogiatzaki et al. [217] and Wandel and Lindstedt [219, 220]. The LES-MMC methodology has also been introduced. Cleary and Klimenko [39] utilised the sparse-Lagrangian filtered density function to perform LES-MMC computation of flame D. A Similar approach has been employed to compute the three flames with the GRI-3.0 mechanism by Ge et al. [68].

Pitsch and Steiner [174] implemented the flamelet model with LES and applied it to Flame D and later Ihme and Pitsch [77] performed LES of flames D and E with the flamelet-progress variable model for combustion. The CMC model was applied in the context of LES in the study of these flames such as the LES-CMC study of flames D and F by Garmory and Mastorakos [65, 66].

5.4 Numerical Implementation

These turbulent diffusion flames are simulated with a hybrid algorithm in which integration between the flowfield and the chemistry is done interactively with the use of a Lagrangian Monte Carlo implementation for the PDF model. The flowfield computations is done with the BOFFIN code while the chemistry of these methane flames is computed with the both direct integration of the GRI-3.0 mechanism [2] and with applying RCCE reduction on this mechanism. Details of the RANS-PDF hybrid algorithm have been described in Section 4.5.

The quality of the RCCE predictions are assessed mainly by comparison with those obtained by DI of the detailed mechanism. The only difference that could have been avoided is the mathematical integration solver. Here, a solver called DL-SODE was exploited for the integration of the detailed GRI-3.0 mechanism [2] while another solver called DVODE was used in all RCCE computations.

5.4.1 Initialisation and Calculation procedure

The Monte Carlo Algorithm applies the Lagrangian particle method to solve the scalar PDF equation. The PDF equation is represented with a large number of particles distributed over the whole FV solution domain. Before initialising the particle field, the velocity field was initialised by running a cold jet computations with the RANS code alone. The particle distribution was then initialised on this initial flowfield and all particles were initialised using the composition and density of the oxidiser stream. Each particle carries a set of quantities such as mass, position in physical space and composition. The scalar field, which comprises in this study all independent composition variables, is transported by applying transport, mixing and reactions on each particles.

It has been stated earlier that the dimensionality of the scalar field N_{sc} equals $N_s + 1$ in the case of the DI of the detailed mechanism. In the case of RCCE reduced mechanisms, N_{sc} is reduced to $M_c + 1$ where the number of constraints M_c is a subset of the N_s species present in the original mechanism.

For the purpose of consistency and systematic comparison, a complete set of simulations for the three flames that compare RCCE mechanisms and the DI of the GRI-3.0 mechanism [2] were obtained using the Jenny et al. [80] scheme. The second particle spatial evolution submodel which applies a linear interpolation scheme for both the mean velocity and turbulent quantities has been applied to Flame D only.

5.4.2 Grid Generation

In this study, all generated grids are axisymmetric with orthogonal cells in the x-r plane of the physical cylindrical geometry of the round jet [i.e. cells are rectangular in the plane of the axial and radial directions]. The current PDF model is implemented for two-dimensional orthogonal grids although extension to three-dimensional non-orthogonal grids can be applied in future if required. These orthogonal grids are not uniform as they are generated with a weak expansion ratio around [1.02] in both the axial and radial directions. This results in grids with relatively finer resolution

in the near-field region (i.e. near the jet and pilot nozzles). This is an important feature to provide improved discretisation of the thin shear layers which involves very high gradients as well as very fine turbulent length scales and small-scale scalar mixing.

A grid with a solution domain extending to 100 jet diameters ($100D$) in the axial direction and 15 diameters ($15D$) in the radial direction was generated. This grid has 100 X 80 orthogonal cells in the axial and radial directions respectively which are not equally spaced because of the expansion ratio just mentioned above. Solutions with the full GRI-3.0 [2] mechanism were obtained using this grid for the three flames. However, another grid in which the stream-wise length of the solution domain is reduced to ($55D$) and with (70 X 80) cells was generated for flame D. This grid has similar resolution of the first longer (100 X 80) grid to the extent that it appears as if the bigger mesh was clipped to 70 axial cells.

Axial Location	$x = 0$	$x = 15D$	$x = 30D$	$x = 45D$	$x = 60D$
spacing (Δx)	2.38 mm	4.54 mm	6.77 mm	9 mm	10.8 mm

Table 5.1: Axial spacing of Sandia flames grid

Radial	$r = 0$	$r = 0.5D$	$r = 1.25D$	$r = 3D$	$r = 15D$
Location	jet inner	jet-pilot	pilot-coflow	coflow	coflow outer
spacing (Δr)	0.59 mm	0.65 mm	0.75 mm	1.01 mm	2.7 mm

Table 5.2: Radial spacing of Sandia flames grid

5.4.3 Setting of the Flow Field Boundary Conditions

At the inlet boundary, the values of the dependent variables need to be specified explicitly. A careful specification of the mean flow and turbulence field is an important element for the turbulent jet flame simulation. Unrealistic values for the

turbulent kinetic energy or its dissipation rate may result in a wrong behaviour in the evolution of turbulence in the near field which might affect the whole solution. As we have pointed out in (4.2.1), the mixing and reaction are strongly sensitive to the prediction of the turbulent time scale (k/ε) since it determines the rate of micromixing. In this work, the flow field quantities that need to be specified at the boundary are the mean velocity components, turbulent kinetic energy and its dissipation rate. There are two options for the profiles of mean velocity and turbulent kinetic energy at the boundary for these boundary conditions. The first option is to use the preliminary data provided by Barlow and Frank. However, the detailed flowfield experimental data by Schneider et al. [197] include a file for profiles at an axial distance of 1 mm from the jet exit. So the inlet profile for mean axial and radial velocity and turbulent kinetic energy can be taken from this set of data. According to [197], turbulent kinetic energy is computed, with the assumption of axial symmetry, from axial and radial Reynold stress components. The dissipation rate ε is not explicitly provided and has to be carefully estimated. It can be approximated from the turbulent kinetic energy using the mixing length hypothesis to specify the mixing length [89].

$$\varepsilon_{jet} = C_{\mu}^{\frac{3}{4}} \frac{k^{\frac{3}{2}}}{l_m} \quad (5.1)$$

There are many forms for the profile of the mixing length that can be applied used for the turbulent fuel jet. From these which have been suggested in the literature is the ramping function of [53] ($l_m = \min(\kappa y, 0.09R)$) where y here is the distance from the nozzle wall. This form applies variation in mixing length with y only in the cells next to the wall when y ($y < .22R$). Both Nikuradse and Merci et al. [145] proposed alternative expressions which incorporate variation of the mixing length with y for all the jet radius (see Merci et al. [145]). Alternatively, constant mixing length assumption has been also used (e.g. [149] with $l_m = 0.075R$) and ε_{jet} would only vary with k . The constant l_m approximation has been used here. The inflow boundary conditions for flame D are shown in figure (5.1) as an example.

5.4.4 Setting of the Scalar Field Boundary conditions

It is essential to specify values of scalar quantities at the inlet boundary. At least, the mixture fraction mean and variance are needed so that the composition of the inlet streams can be specified. Mean mixture fraction values are specified by classifying the cells at the inlet boundary according to the stream region they are physically positioned in (fuel jet, pilot or oxidant coflow inflow). Mixture fraction variance is set to zero in all streams. Mean mixture fraction values are sufficient to determine the composition at the inlet boundaries. Pressure is set to the atmospheric value while temperature of the fuel and coflow are also specified according to [15].

The composition of the pilot can be approximated by full equilibrium which would be a consistently appropriate boundary condition for the RCCE simulation. However, detailed species concentrations for the pilot of flame D were also provided by Barlow and Frank [15]. This measured pilot composition has been used in all computations of the three flames to minimise the uncertainties from the pilot. Despite that the pilot was nominally chosen to be with the same enthalpy and equilibrium composition of methane/air mixture with $\Phi = 0.77$, the composition provided in [15] does not ensure a complete and accurate conservation of elements and consistency with the CH_4/Air mixture. Although the disagreement in element composition is not very high, the species concentrations have been modified to improve the consistency. Alternatively, the composition of the flamelet at the same Φ can be used for the pilot. Actually, the modified composition which is employed in the simulations is found to be very similar to data of the strained CH_4/Air flamelet with ($z = 0.273$) at 80 s^{-1} strain rate.

5.4.5 Selection of Constraints for the Sandia Methane-air Diffusion Flames

In this study, the determination of the optimal sets of constraints for the PDF simulation is based on assessing them using an independent code with the aid of

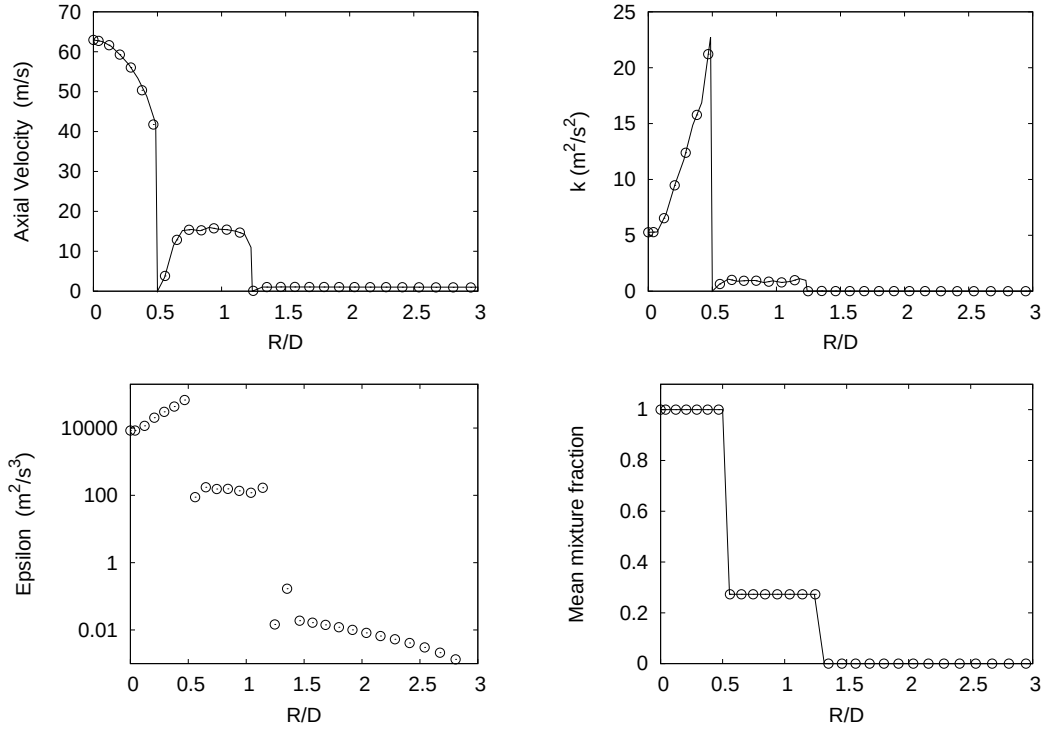


Figure 5.1: Flame D inflow: axial velocity (top left), turbulent kinetic energy (top right), dissipation rate (bottom left) and mixture fraction (bottom right)

experience from previous simulations [86, 87]. The code which we exploited for preliminary assessments performs a numerical solution of the one-dimensional steady laminar flamelet equations at different strain rates. The reasoning behind choosing this method is that these flamelet computations can be performed in a much shorter time than the PDF simulations. It is noted that turbulence-chemistry interaction (TCI) is incorporated in a simplified and parametric mode in the steady strained flamelet which assumes that chemistry responds instantaneously to rapid variations in scalar field fluctuations. Despite this fact, flamelet-like regimes are observed in moderately turbulent flames and a considerable degree of agreement and similarity has been predicted in the evolution of composition of these flames. The effect of the turbulent flow field on combustion can be resembled, though not in a rigorous manner, with straining of the laminar flamelet.

In parallel, preliminary tests were performed by applying simplified RCCE sets in PDF simulations of Sandia D flame. A global RCCE set comprising the same 9 constraints which were used in the laminar flame simulation [86] failed to produce a

burning flame. These global RCCE systems contain the major species and the most important minor species for methane combustion. Determination of more dominant intermediate species is needed for stronger RCCE systems which can handle the problem of these turbulent flames. We determine the additional constraint species from the DI of the flamelet chemistry and from the PDF solution of flame D with DI. This gave ordering of the species of the GRI-3.0 mechanism which did not differ much from the ordering given by the integrate CSP pointer reported by Belcadi et al. [4] for premixed methane flames.

Firstly, the addition of the three dominant C_2 species (C_2H_2 , C_2H_4 and C_2H_6) as well as CH_2O and CH_3 did not lead to successful simulation of these flames. In flamelet calculations, this set was found to extinguish at a lower strain rate than the extinction strain rate of the full mechanism. CH_3 is known to be an important intermediate species in finite-rate oxidation of methane and its concentration increases when the strain rate is increased or when turbulence is intensified. However, it tends to make the PDF-RCCE simulations of turbulent flames more difficult to ignite while constraining CH_3OH was found to increase the extinction strain rate of the flamelet considerably and to make the PDF-RCCE simulation easier to ignite. In spite of this, no extinction would be observed when CH_3OH was included in the constraints but not CH_3 because the flamelet would give a burning flame even at very high strain rates. Thus, the investigation indicates that CH_3 is needed as a constraint to get local extinction in the flames. CH_2 and $CH_2(s)$ were also included because they make the extinction strain rate closer to the DI value.

More particle failures in the PDF-RCCE simulation were experienced when one or both of HO_2 and H_2O_2 were added to the constraints and so they were excluded. Some sets of constraints were found to perform better with the so-called constraint-removing feature. This feature temporarily removes the species whose concentration is zero or vanishingly small ($n_s < 10^{-8}$) from the RCCE.

The performance of different RCCE sets was analysed and evaluated using the

flamelet calculation. Here we compare three potential sets which are (RCCE-18 , RCCE-19, RCCE-16) against DI of the detailed mechanism at different strain rates as shown in the figures (5.2 - 5.6). High strain rates are employed for this investigation which are more representative of the Sandia flames.

The following 15 species constitute the 15 constraints which are present in all these RCCE sets:

CH_4 , O_2 , CO_2 , CO , H_2O , N_2 , H_2 , H , OH , O , CH_2O , C_2H_2 , C_2H_4 , C_2H_6 and CH_3OH .

The additional constraints for each set are as follows:

- RCCE-18: CH_3 , CH_2 , $\text{CH}_2(\text{s})$
- RCCE-19 : CH_3 , CH_2 , $\text{CH}_2(\text{s})$, CH_2CO
- RCCE-16: HCO only

The first two sets (RCCE-18 and RCCE-19) showed good agreement in the flamelet over all strain rates. These two sets, though extinguish at about 1970 s^{-1} strain rate which is slightly less than the extinction strain rate with the full GRI-3.0 mechanism which is about 2120 s^{-1} . On the other hand, the RCCE-16 did not appear to be a very successful set of constraints for the problem investigated here. It did not show sensitivity to strain rate and no extinction is observed upto 2800 s^{-1} strain rate. The CO profiles at high strain rates obtained using this set have considerable discrepancy on the fuel-rich side.

Thus, PDF-RCCE calculations of Sandia flames were performed using the (RCCE-18 and RCCE-19) sets. Since they differ in the CH_2CO species, the analysis of the results would provide us with understanding of influence of constraining this species or equilibrating it.

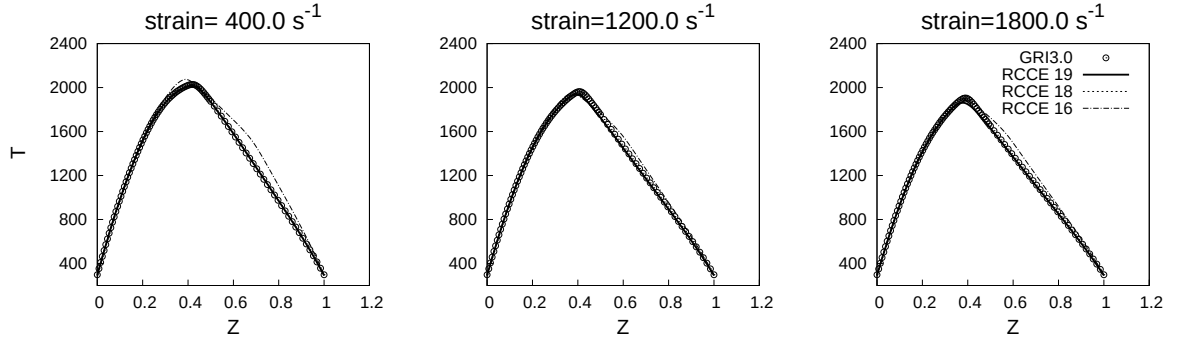


Figure 5.2: Flamelet mean temperature. key: small circles : GRI-3.0, dashed line: RCCE-18 , solid line: RCCE-19, dash-dotted line : RCCE-16

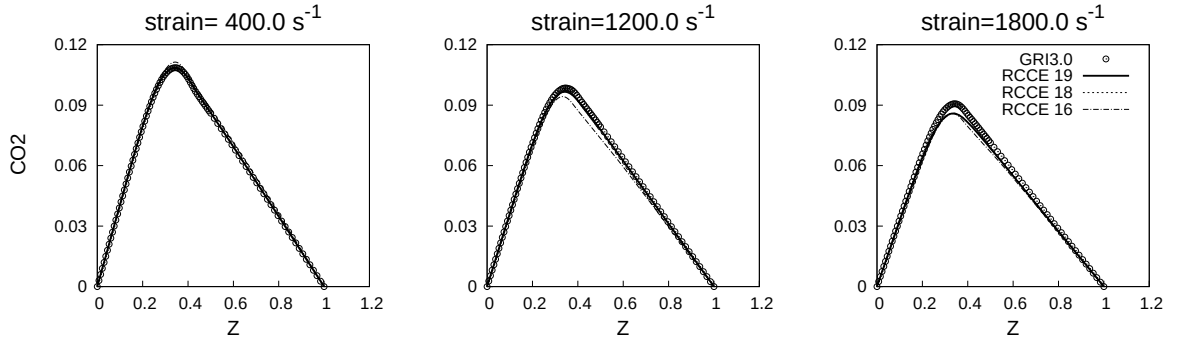


Figure 5.3: Flamelet mean CO₂. Legend as in fig(5.2)

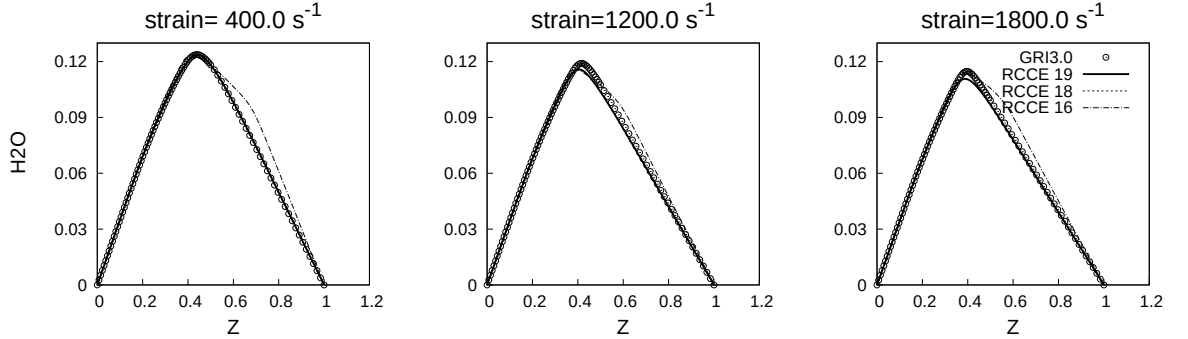


Figure 5.4: Flamelet mean H₂O. Legend as in fig(5.2)

5.5 Results of Sandia Flames

The setting of various parameters in the flow field and the PDF algorithms are identical in the simulation of the three flames. Three sets of results are produced for each of the three flames which include one simulation with DI of the GRI-3.0 [2] mechanism and two RCCE simulations with the 18-constraint and 19-constraint

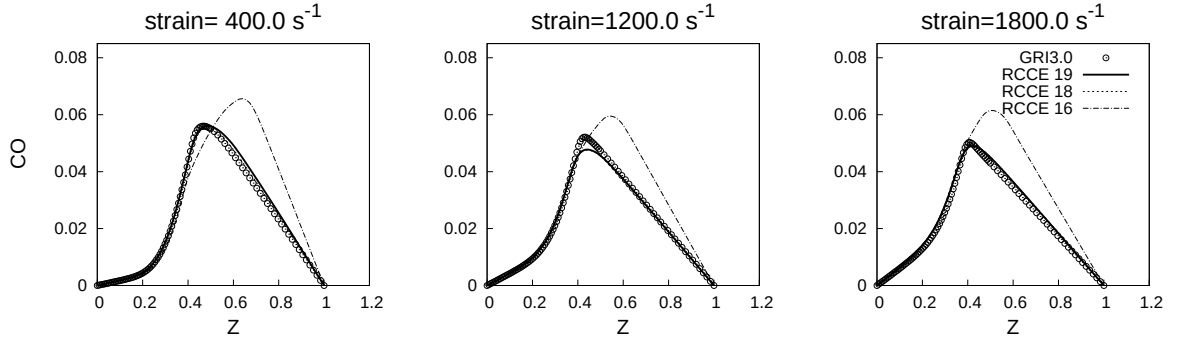


Figure 5.5: Flamelet mean CO. Legend as in fig(5.2)

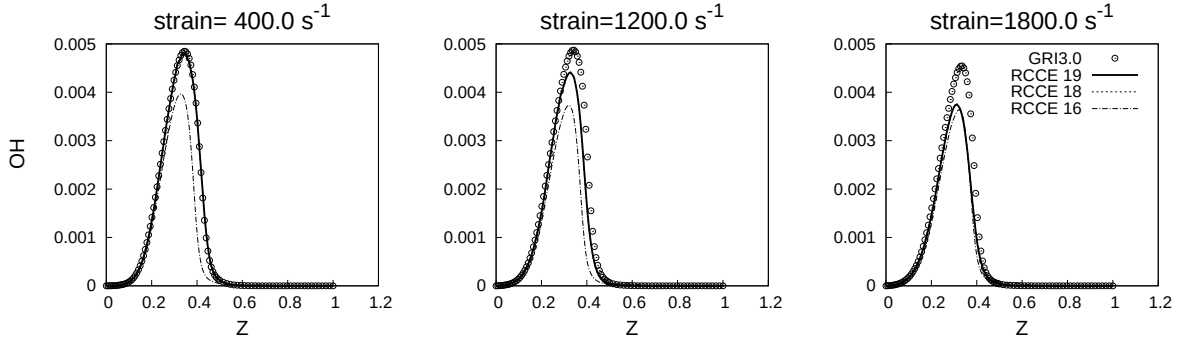


Figure 5.6: Flamelet mean OH. Legend as in fig(5.2)

sets. The boundary conditions of the flames differed in the inlet profiles of mean axial velocity and mean turbulent kinetic energy $\tilde{k}$. The TVD scheme [122] in BOF-FIN is employed in the simulations of flames D and E but not in flame F. When TVD was activated in the simulations of flame F, it produced large errors in the flow field and the calculation would crash.

Overall, the calculations produced the three flames with encouraging results. The general characteristics of flow field of the three flames are reasonably reproduced. There are, though some inaccuracies in the predicted $\tilde{k}$ that might have contributed to the uncertainties in the combustion calculations. The trends of the scalar fields are reasonably predicted despite the fact that the computed centreline mean mixture fraction indicates underprediction of the flame length when particle motion in the PDF is modelled using Jenny et al.'s model [80]. The centreline mean mixture fraction is comparable upto $x = 30D$ but is considerably underpredicted at higher

axial distances. In addition, the initial radial spreading of the fuel (e.g. at $x = 7.5D$ and $x = 15D$) is overpredicted. This is caused by uncertainties in turbulent diffusion modelling or from overprediction of $\tilde{k}$ in the near-field region since it is used to calculate the apparent turbulent diffusivity for notional particles. The RCCE simulations consumed approximately 40-60% of the computational time required by the original mechanism which is not a big time-saving.

5.5.1 Flow Field Predictions

The mean axial velocity and turbulent kinetic energy $\tilde{k}$ profiles are plotted in figures (5.7-5.10). The profiles of mean axial velocity are in good agreement with measurements. There is some uncertainty in estimating the experimental $\tilde{k}$ from the measured normal Reynolds stresses $\widetilde{u_1''^2}$ and $\widetilde{u_2''^2}$. Data for the azimuthal normal stress $\widetilde{u_3''^2}$ are not available. It can be approximated from the other two components such as assuming that ($\widetilde{u_3''^2} = \widetilde{u_2''^2}$). Alternatively, it could be assumed that ($\widetilde{u_1''^2} = \widetilde{u_2''^2} + \widetilde{u_3''^2}$) which leads to the approximation that $k = \widetilde{u_1''^2}$. The first approximation which implies that ($\tilde{k} = 0.5\widetilde{u_1''^2} + \widetilde{u_2''^2}$) was adopted in this thesis. Based on this, the computed mean turbulence kinetic energy is predicted with reasonable agreement with measurements. However, the plots show some overprediction of the maximum $\tilde{k}$ close to the nozzle as well as at $x = 7.5D$ for flame D and at $x = 15D$ for flame F. It noted that in most of these locations where it does not agree with the adopted definition of ($\tilde{k} = 0.5\widetilde{u_1''^2} + \widetilde{u_2''^2}$), it approaches the value of the other one (i.e $\tilde{k} = \widetilde{u_1''^2}$). Another issue was observed in the simulation of flame D that $\tilde{k}$ on the centreline was underpredicted.

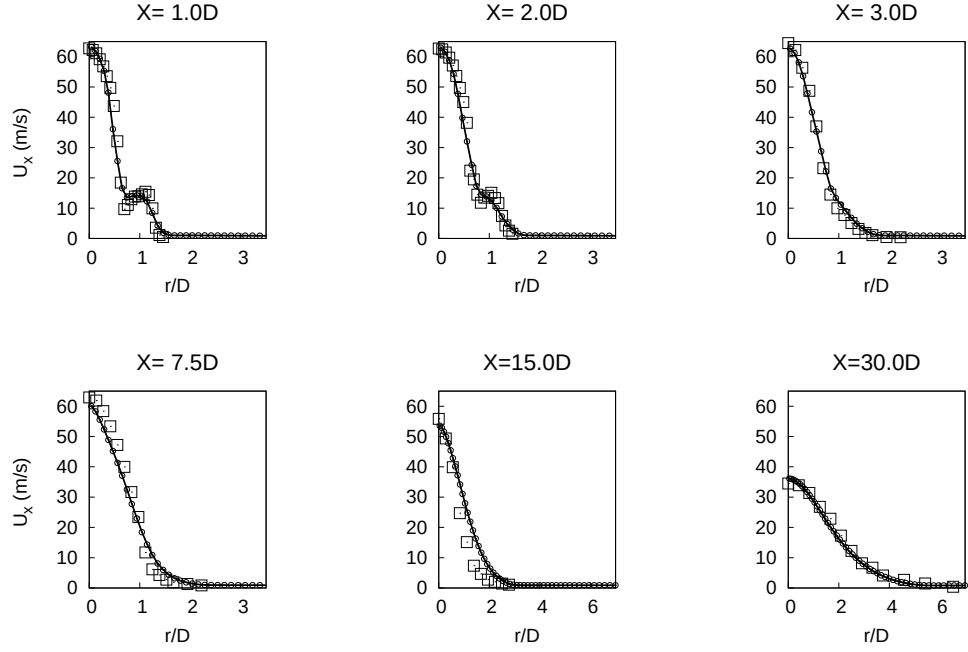


Figure 5.7: Flame D: Axial Velocity. Key: squares: measurements , circles : GRI-3.0 direct integration, dotted line : RCCE-18, solid line: RCCE-19

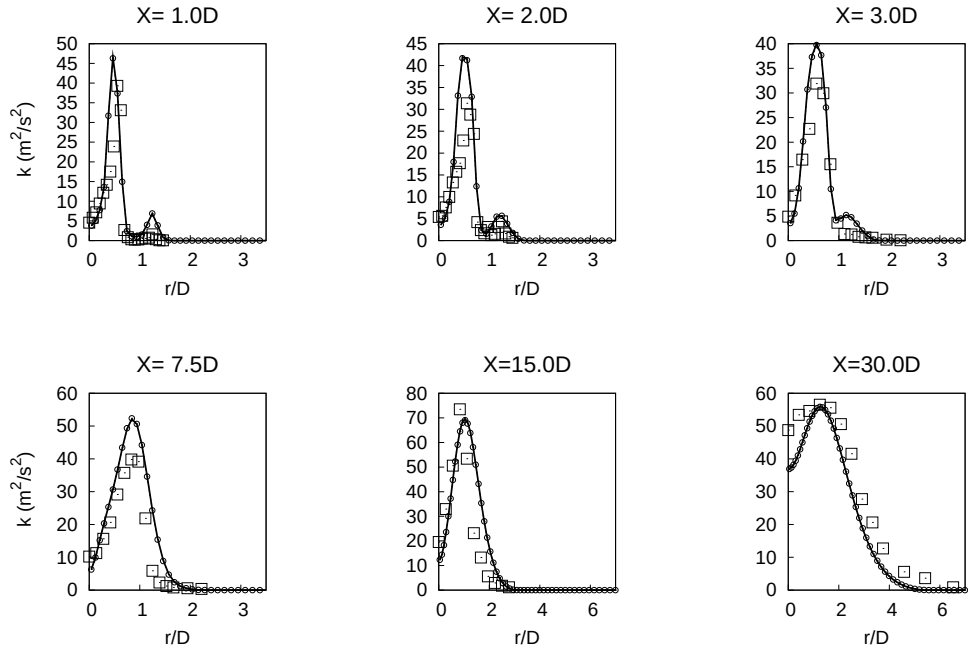


Figure 5.8: Flame D: turbulent kinetic energy (k). Legend as in fig (5.7) caption

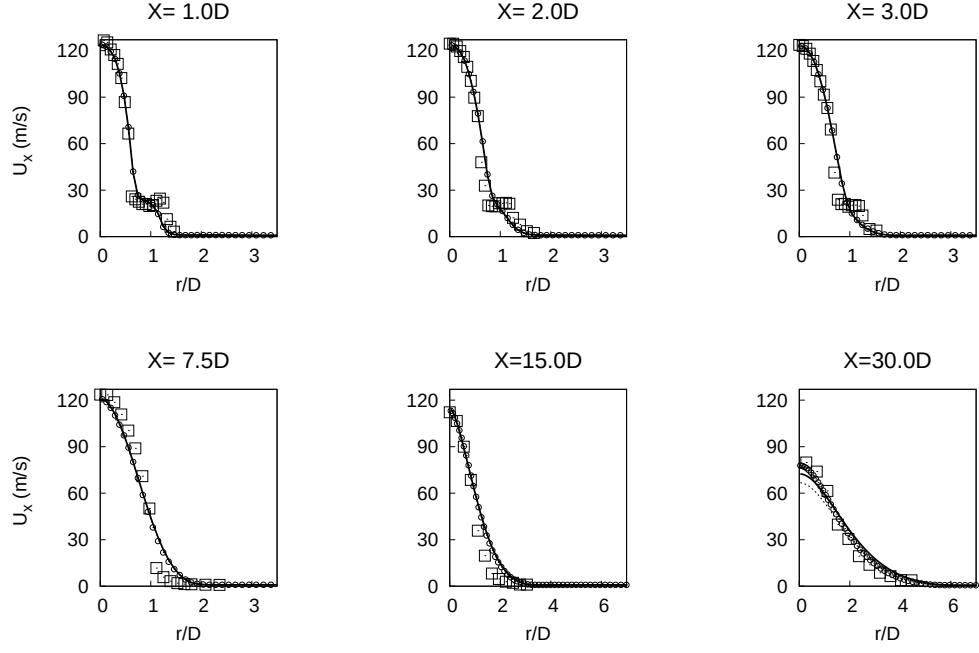


Figure 5.9: Flame F: Axial Velocity. Legend as in fig (5.7) caption

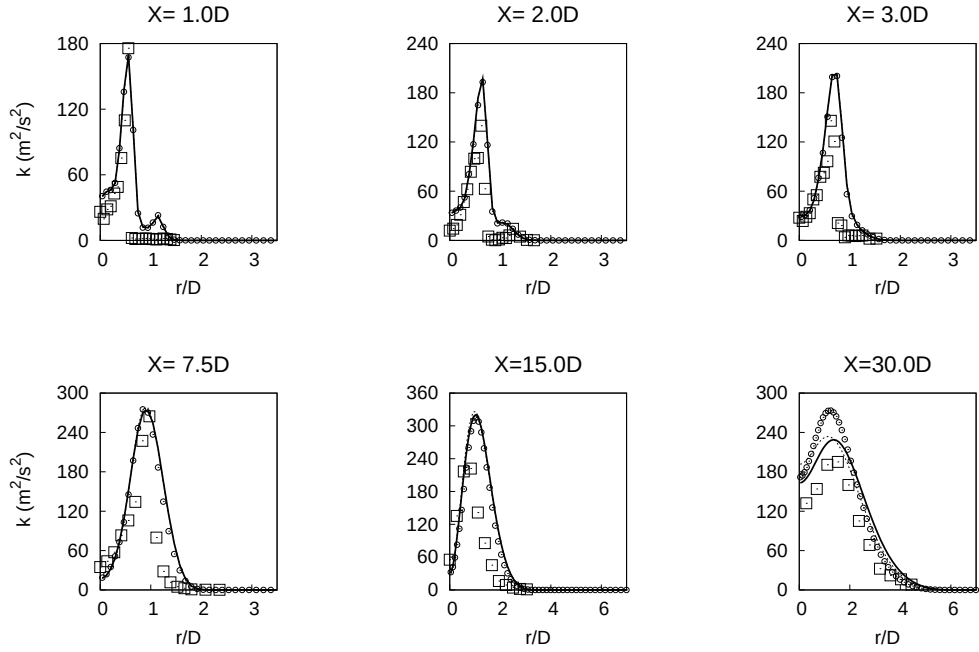


Figure 5.10: Flame F: turbulent kinetic energy (k). Legend as in fig (5.9) caption

5.5.2 Scatter Plots

Micromixing is an important process which has to be modelled efficiently in order to obtain accurate prediction of the flames. The effect of micromixing models on the prediction of extinction and reignition in these flames has been addressed by several PDF studies such as [30, 78, 222]. The most relevant to us here from these studies are the predictions by the IEM model in all three studies and particularly the composition PDF calculation in [78]. The values of C_ϕ adopted in these studies are higher than the value used in the present study except for the flame D simulation of [78] where a value of 2.1 was used. These higher values are usually the minimum value required to obtain a burning flame but it resulted in underprediction of mixture fraction variance. Preliminary calculations suggested that $C_\phi = 2.2$ is a good value for the three flames.

The scatter plots of the three flames (figures 5.11-5.16) are plotted with each figure containing scatter plots for the three flames of one variable (e.g. temperature or CO). The top row of plots are the measured data with flame D on the left and flame F on the right. The calculations are in the three lower rows with consistent sorting of flames (left to right). For example, the second column of plots is for flame E starting from its measured data in the top-middle, its DI of GRI-3.0 computations is middle of the second row, its RCCE-19 computation is middle in the third row and its RCCE-18 computations is middle in the bottom row.

Overall, the scatter plots (figures 5.11-5.16) show that both the detailed mechanism DI and RCCE are capable of producing an amount of extinction in the three flames. In all calculations, the extinction predicted in flame D is less than in flames E and F which is qualitatively in agreement with the measurements. However, the calculations seem to produce too much local extinction in flame E to the extent that some of flame E scatter plots are hardly distinguishable from those of flame F calculations. It might be seen that the DI scatter plots of flame E are slightly more successful than the RCCE simulations of the same flame because the RCCE tends to predict excessive amount of local extinction in the fuel lean particles. In other

words the fuel-lean measured snapshots show little extinction in flame E and the DI predicts some amount of extinction of fuel-lean particles but less than the amount predicted by the RCCE.

Furthermore, there is a non-physical irregular behaviour resulting from the fact that particles follow certain trajectories making them not well distributed in composition space. This is identified in the computed scatter plots mainly by two detached patterns or pockets of particles which are more evident on the fuel rich side (see e.g. figure 5.12). In other words notional particles which have similar amount of fuel appear to exhibit either of two different scalar states (composition and temperature) with lack of predicting the intermediate states. This behaviour resembles the stranding problem encountered in the EMST model which refers to accumulation of notional particles on different distinct lines structures in scalar space like the branches of a tree [146, 205, 221]. It is thought that the simplified representation of mixing by the IEM model with single-time scale for scalars has a significant contribution to this.

The scalar plots themselves do not provide definite and a clear interpretation for the mechanism leading to this behaviour. However, it is agreeable in the terms that they indicate the existence of particles with the same mixture fraction that their compositions evolve differently in flames with strong turbulence-chemistry interaction. Gaps are noticed in composition and temperature scatter plots which are more visible in flames E and F but are also present in flame D plots at $30D$. They become wider at axial distance higher than $x = 7.5D$ and in particular at locations of strong flame extinction ($x = 15D$). This suggests to us that this unrealistic observation is linked to the extinction and ignition of particles which are influenced by mixing and chemical reaction or more probably by the interaction between mixing and reaction.

It is apparent that accurate representation of extinction and reignition in the flames is a major challenge to the current relatively simplified PDF implementation. In particular, it is noticed that some of the experimentally observed trajectories and

paths of the moderately fuel-rich mixtures in flames E and F are not well captured. Measured temperature scatter data show that points with the same mixture fraction are (at least in a qualitative manner) uniformly dispersed between the two extreme measured temperatures at that mixture fraction value. This is more recognisable in flames E and F, though the range of variation in measured temperatures differs in the two flames depending on the degree of extinction. The calculations seem to show different behaviours in these regions (i.e fuel-rich particles) despite the positive point that some realistic degree of extinction is predicted in flame F.

This issue may be understood qualitatively by analysing the evolution of the scalar field of these fuel-rich particles which exhibit this pattern. As the stoichiometry is approached from the fuel-rich side, the temperature profile starts to break into the two patterns mentioned above with very little particles in the intermediate states. The upper temperature portion refers to particles with sustained burning and the other points to those undergoing a relatively strong degree of extinction but not completely quenched.

The $x = 15D$ temperature scatter plot of flame F (figure 5.12 top-right), measurements fill the range from 600 to 2000 K while computations are concentrated in two ranges which are [1000,1400] and [1900,2100] K. So, the observed quenching shots with temperatures less than 1000 K and the intermediate region with temperature range [1400,1900] were scarcely predicted. Both numerical errors from turbulent diffusion transport and weakness of the mixing model possibly have caused inaccurate representation of entrainment and lack of efficient micromixing between PDF particles. The same trend is observed in the CO (figures 5.14- 5.16) and similarly in other species scatter plots.

Insight can also be gained by focusing on how mixture fraction, temperature and composition of particles evolve in physical space. For example, many of the particles with lower temperature (e.g. in 5.11) are probably formed by mixing between hot and cold particles without residing enough time or mixing well in the reaction zone

to ignite them. These particles seem to diffuse away from the reaction zone due to excessive turbulent diffusion. It could be also that improper micromixing causes inaccurate molecular diffusion of some species. Furthermore, mixing between particles with very diverse compositions is physically improbable. However, the present calculations do not guarantee this due to the lack of localness in the IEM mixing and rapid macromixing which excessively brings those particles into physical neighbourhood. Mixing and reaction should ideally result in a variety of ignition or extinction scenarios since particles experience different histories and scalar trajectories. This should result in spreading them over the allowable temperature and composition range. The apparent scenario in the present simulations which follows the above unrealistic mixing of such particles is that ignition of considerable percentage of them seem to be deferred for longer time. There appears to be a strong likelihood, in the simulations of flame F that ignition of these particles is even delayed until they reach the fuel-lean side and diffuse back to the reaction zone. The ignition would occur later by mixing with burning particles at higher axial distances despite that mixing rates are lower than closer to the nozzle.

The measurements show that a considerable amount of reignition occurs at 30D axial distance particularly in the samples close to stoichiometric composition. This is best recognised by comparing the experimental scatter data of flame F at 15D (figures 5.12 and 5.15) and 30D (figures 5.13 and 5.16). The computations, reignition has been predicted qualitatively well at 30D. However, it might be argued that the amount of reignition is not in good quantitative agreement with the measurements especially when taking into account that extinction at 15D was less in the computations. It has been pointed out [222] that reignition of particles proceed in these flames by several mechanisms.

It is concluded that IEM mixing does not perform in an efficient way as it causes ignition delay for too many particles. It also looks that accurate transport in physical space is a prerequisite for efficient PDF calculations. The weaknesses are usually remedied in PDF methods by increasing the mixing rate coefficient to

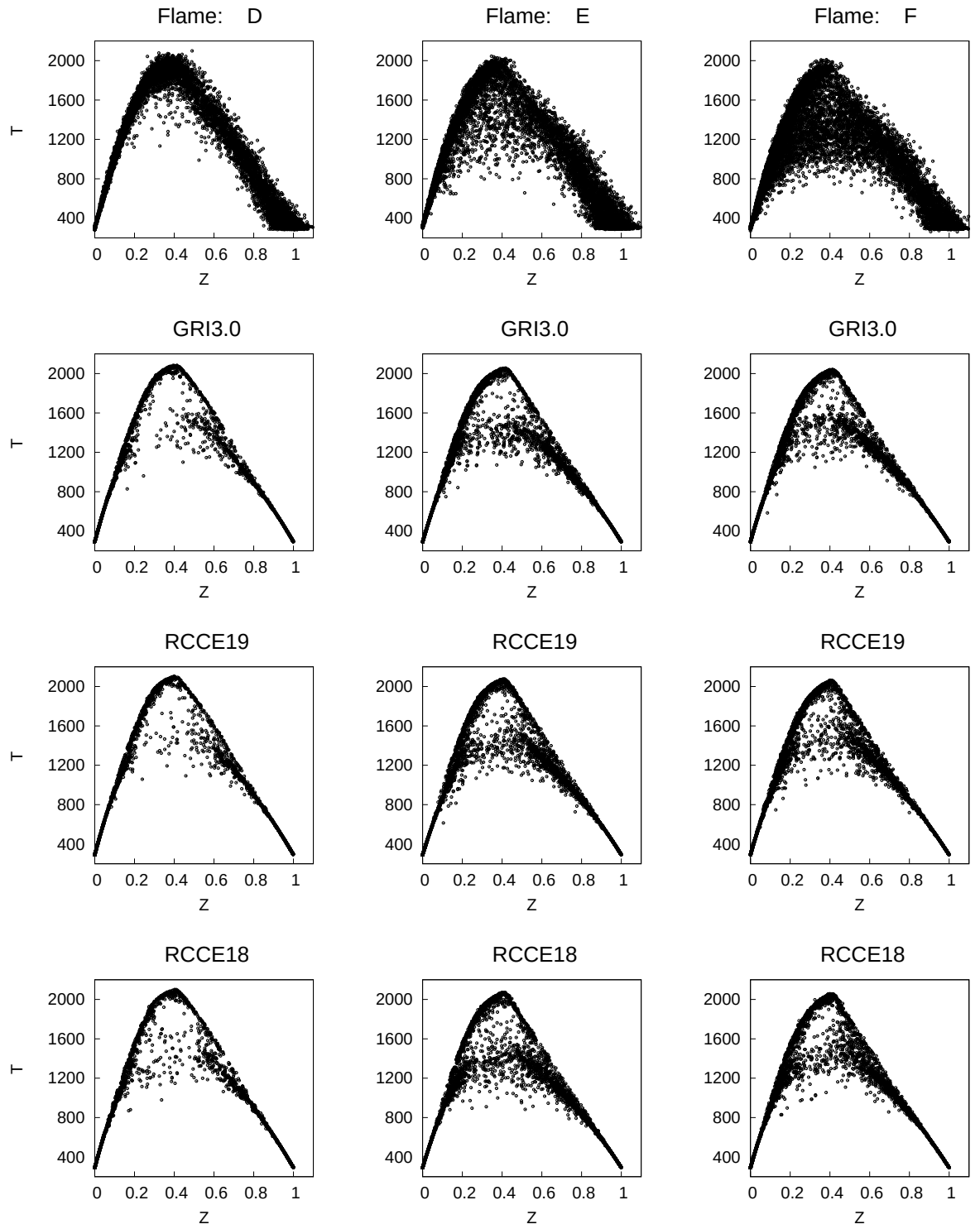


Figure 5.11: Temperature Scatter at $x=7.5D$

produce a burning flame. This also encourages for examining the methodology with LES where the fine details of the flow are captured.

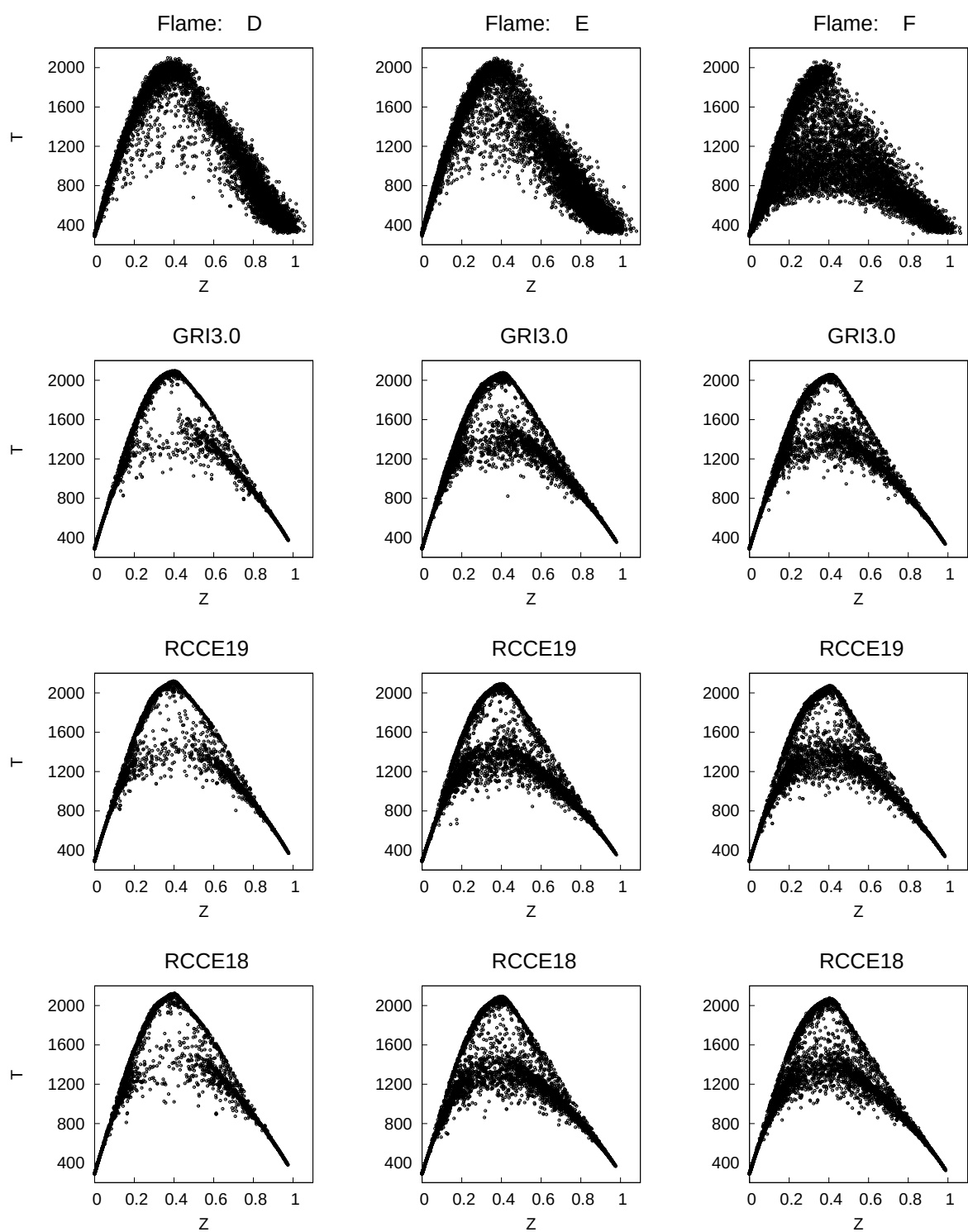


Figure 5.12: Temperature Scatter at $x=15D$

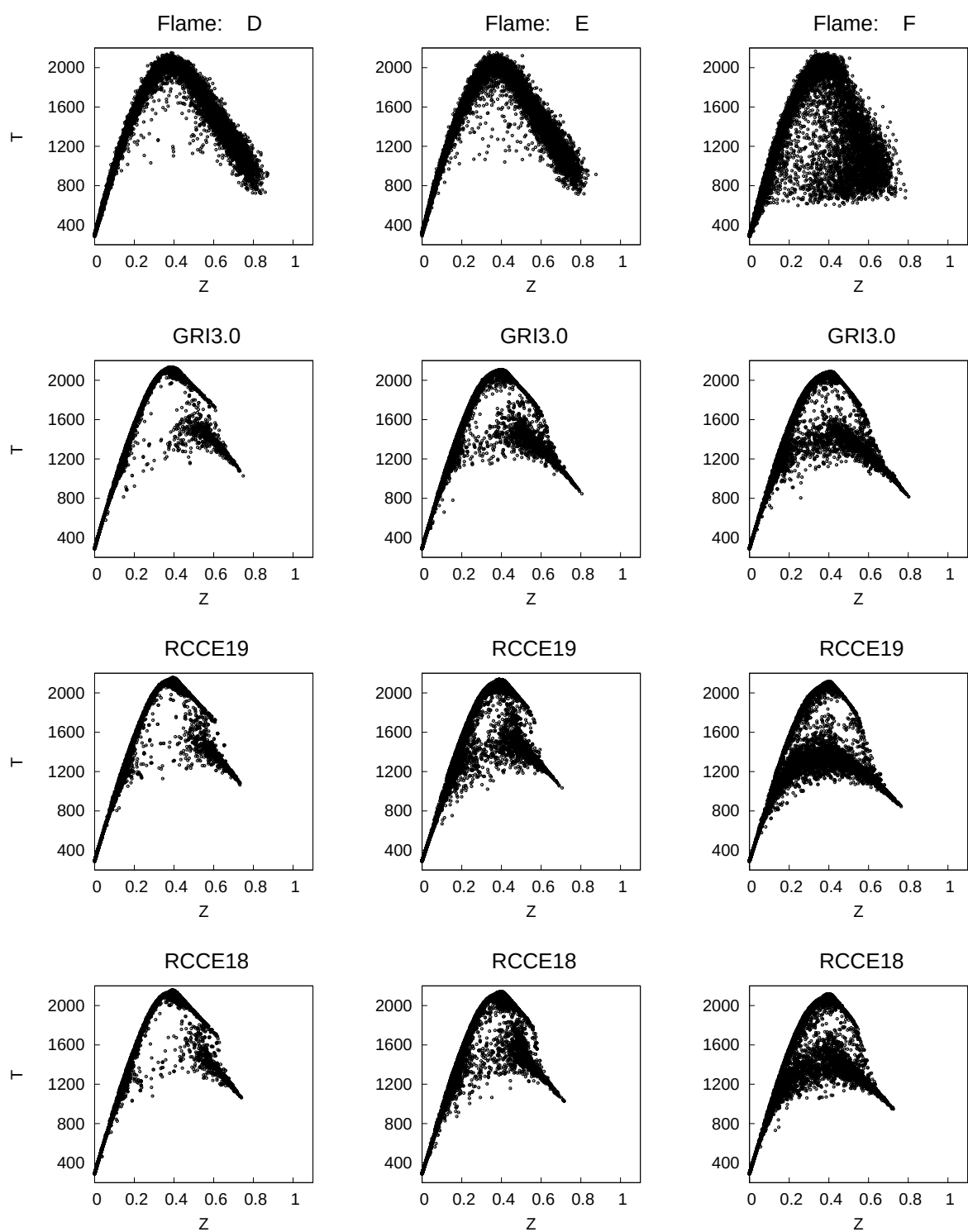


Figure 5.13: Temperature Scatter at $x=30D$

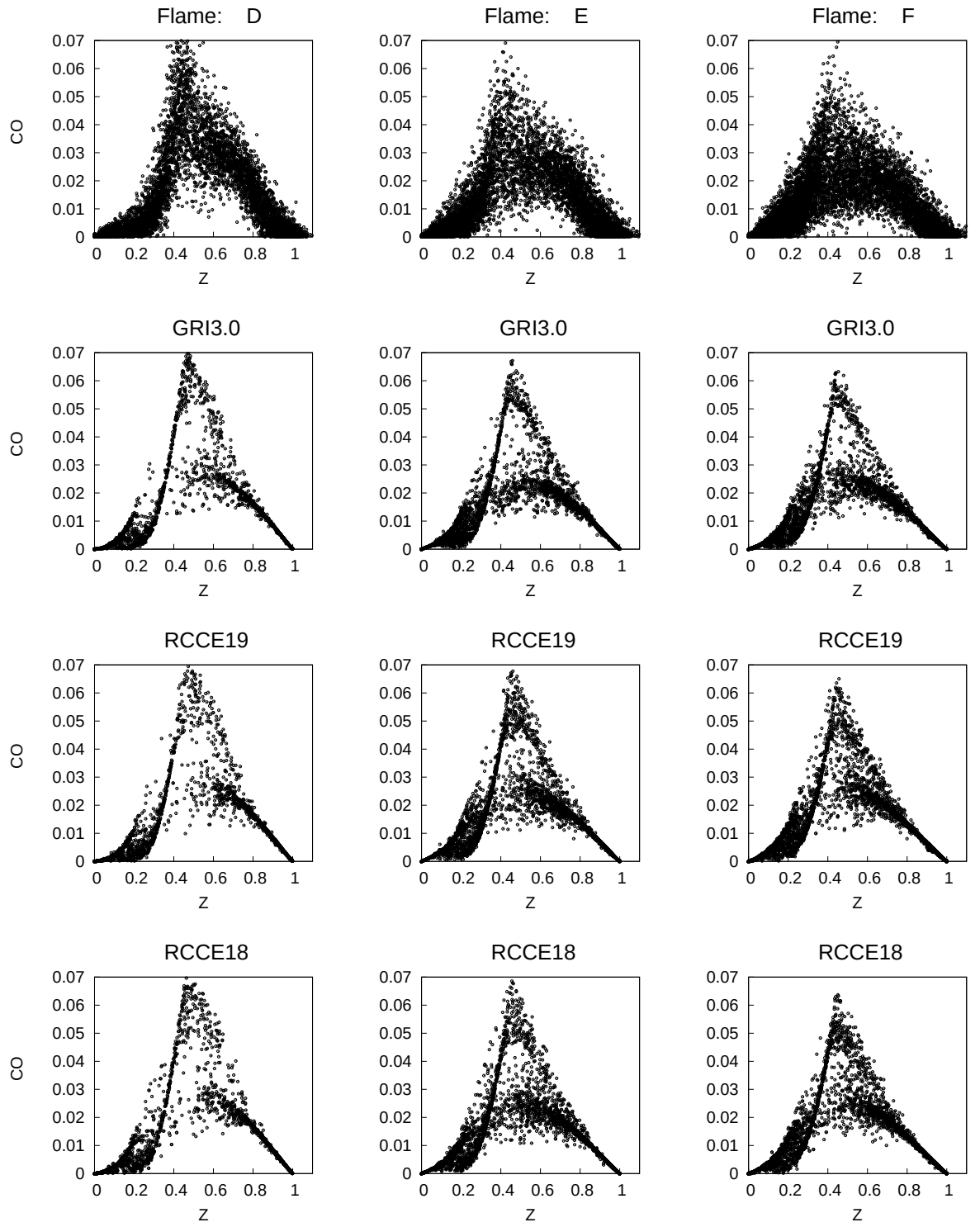


Figure 5.14: CO Scatter at $x=7.5D$

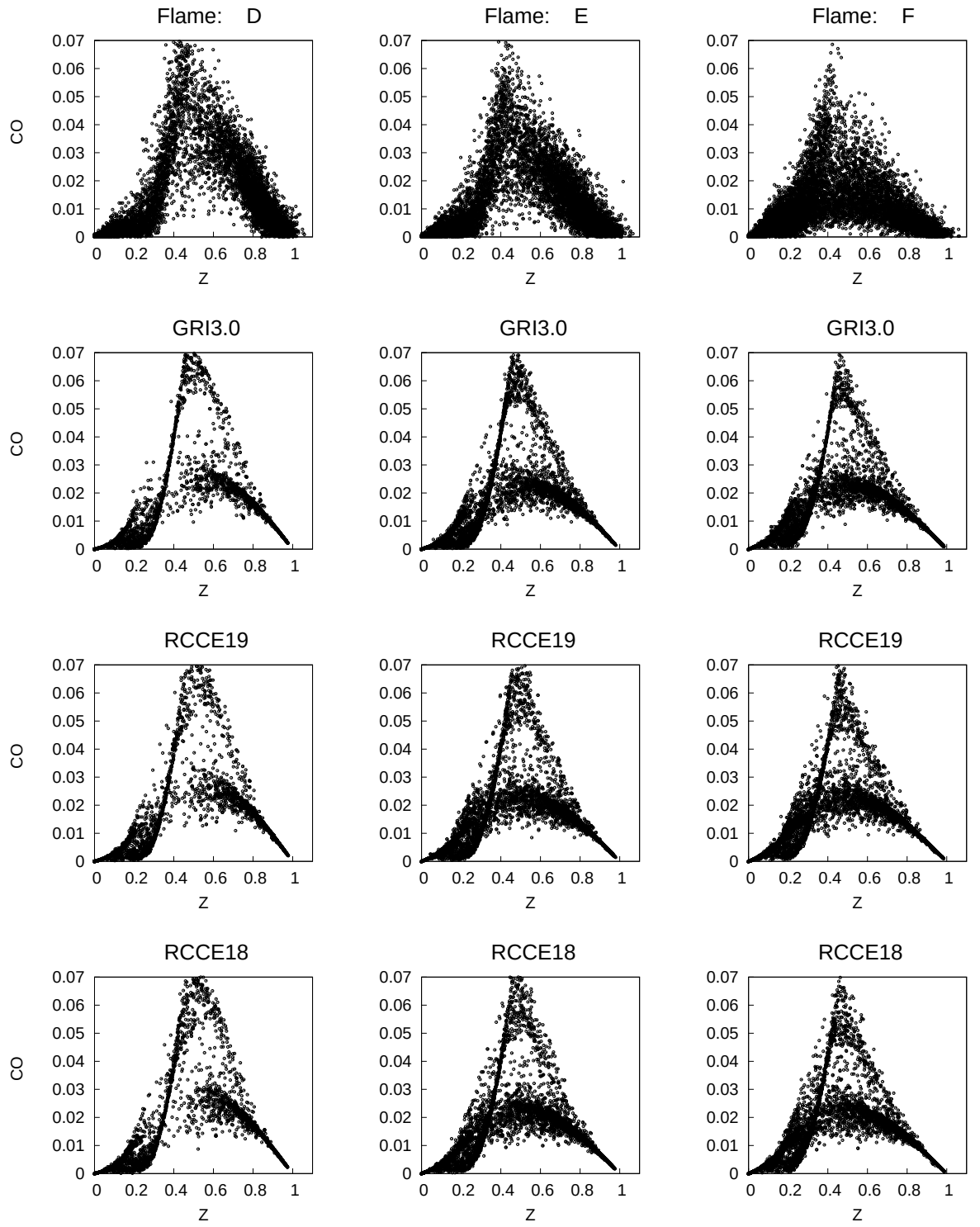


Figure 5.15: CO Scatter at $x=15D$

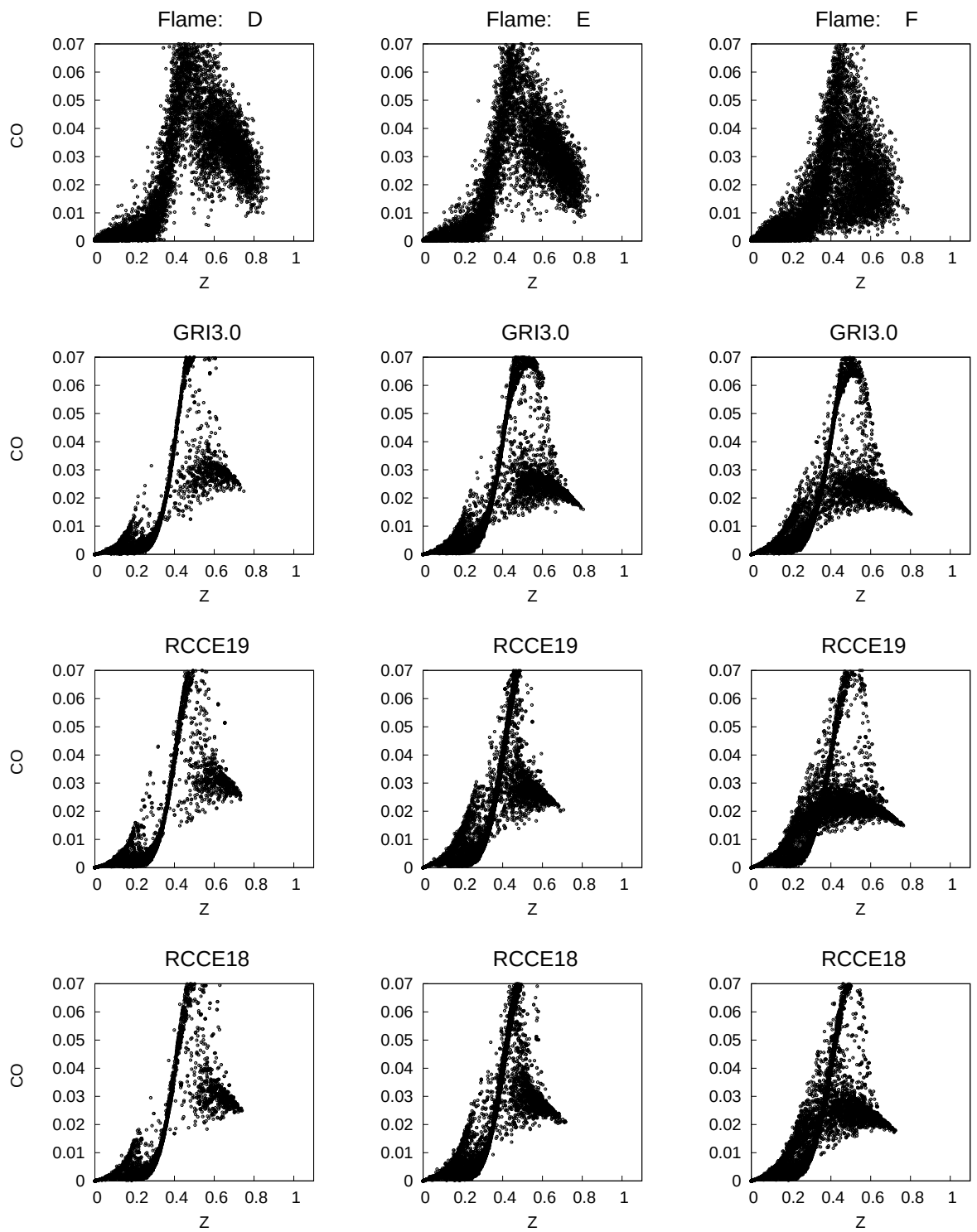


Figure 5.16: CO Scatter at x=30D

5.5.3 Discussion of scalar field results of flame D

In this section, general observations on the scalar field predictions of the three flames are discussed with concentration on the quality of flame D results. The unconditional scalar field results of flame D are shown in the figures (5.17 to 5.34). As has been pointed out, the particle motion model of Jenny et al. [80] for particle motion leads to early decay of the centreline mean mixture fraction in the three flames. The underprediction is recognisable in centreline values starting from $x = 25D$. The underprediction is visible near the centreline of the mean mixture fraction profile at $30D$ as in figure (5.17) for flame D and figure (5.35) for flame E. On the other hand, the radial profiles of mean mixture fraction upto $x = 15D$ are reasonable near the centreline with overpredictions in the outer regions of the $7.5D$ and $15D$ profiles indicating early radial overspreading of the jet. The accuracy of mixture fraction rms (e.g. figure 5.18) is not good as it is overpredicted in several locations. These overpredictions coincide with the overpredictions of turbulence kinetic energy $\tilde{k}$ and some of them appear in locations with considerable discrepancy in mean mixture fraction. It is apparent that notional particles spread radially in a rapid way leading to overprediction of mean and rms of mixture fraction in near-field jet-pilot layer and in the outer regions of $7.5D$ and $15D$ profiles.

In this diffusion flame, the scalar field is strongly correlated with the mixture fraction that the discrepancy in the mixture fraction affects the species and temperature profiles. The radial profiles of mean temperature in physical space 5.19 shows that discrepancy in mean temperature correspond to those in mixture fraction. This is visible in the fuel-lean side (outer region) in the $7.5D$ and $15D$ profiles and in the fuel-rich side (inner centreline region) in the $30D$ profile. The trend of rms of temperature (5.20) is qualitatively reasonably reproduced with some discrepancies in the values of rms. Temperature fluctuations are mainly produced by the turbulent flow field but chemical kinetics play an important role in these flames due to the interaction between turbulence and chemistry. This is demonstrated more in the results of flame E and F. The overpredictions in the rms of temperature in the fuel-rich side may be connected to the trends of scatter plots that have been discussed

in section 5.5.2.

Since the discrepancy in scalar field are to a large extent induced by disagreement of the mixture fraction predictions with measurements, mean temperature and species profiles are plotted against mixture fraction. This should facilitate the analysis of the pure effects of chemistry on the scalar field. It is noted here that the trends of scalar profiles in mixture fraction space are equivalent to their respective profiles in physical space drawn with decreasing radial position. This is clear because mean mixture fraction decreases with r/D . Overall, the predictions of both RCCE simulations are undistinguishable from the direct integration of the detailed mechanism particularly for mean mixture fraction, temperature and major species. The comparison of RCCE predictions of mean minor species with the respective direct integration calculations shows reasonable agreement with very slight disagreement. This is an indication of the excellent performance of RCCE and capability to reproduce the finite chemistry effects of the original mechanism in this turbulent flame. It is apparent that inaccuracies in the lower radial profiles i.e $[D, 2D, 3D]$ are in general due to boundary condition effects. In addition, this region needs better grid resolution or even better turbulence simulation due to the presence of a thin shear layer with strong anisotropy and very fine scales.

The predictions of mean of major species are consistent with mean temperature prediction and indicate excellent agreement between RCCE and detailed mechanism. However, the measured stoichiometric values of these species on the $7.5D$ profile are not accurately reproduced by the simulations. In other words maximum mass fraction of both of CO_2 and H_2O are underpredicted with overprediction of the minimum value (consumption) of O_2 . It is thought that the particle field encounters excessive macromixing caused by overestimated turbulent diffusion. This can be recognised from the overprediction of $\tilde{k}$ as well as mixture fraction and temperature fluctuations in this location. It should be noted that inaccuracy in the particle motion does not necessarily originate from the flow field calculations as there is an uncertainty in the particle model itself, particularly turbulent diffusion representa-

tion. In other locations where these major reactants and products are accurately predicted, the mean temperature shows an average overprediction of around 100 K which is perhaps caused by neglecting the radiation of heat. The levels of mean CO and H₂ against mean mixture fraction are accurately captured implying that the 18- and 19-set of constraints are successful.

The accuracy of OH have some 25% to 50% disagreement and while the trend is reproduced, its time evolution is not well captured. The pattern and values of measured mean OH mass fraction show that its maximum value occurs in the pilot region close to the inlet boundary. It is actually close to pilot inlet value (2.8×10^{-3}) which is preserved for $3D$ axially or more. The present PDF calculations, on the other hand, show either rapid depletion of this species from the pilot zone or not enough production rate possibly due to inaccurate turbulent diffusion (entrainment) and mixing. The measured OH is consumed after $3D$ to reach steady-state values only at around $15D$. These issues are in major disagreement with steady strained flamelets predictions which exhibit increase of OH to around 5×10^{-3} at high strain rates. In this near-field region with small turbulence time scales, non-steady effects can not be represented accurately by steady flamelets. Despite that OH is not well reproduced by the flamelets, there is some qualitative resemblance between PDF-RCCE and flamelet-RCCE as they both produce values lower than their respective direct integration values. H is also slightly less with RCCE than with direct integration of the detailed mechanism. Furthermore, the level of agreement for C₂H₂ between RCCE and direct integration is reasonable and similar to other minor species. C₂H₂ is usually the most dominant intermediate hydrocarbon product of fuel-rich pyrolysis. It is noted here that the amount of C₂H₂ produced in these turbulent flames is much less than in sooting methane flames due to the partial premixing and intense turbulence in these flames. The last two species plotted are CH₂O and CH₃ whose RCCE predictions show some disagreement with direct integration but still encouraging like other minor species.

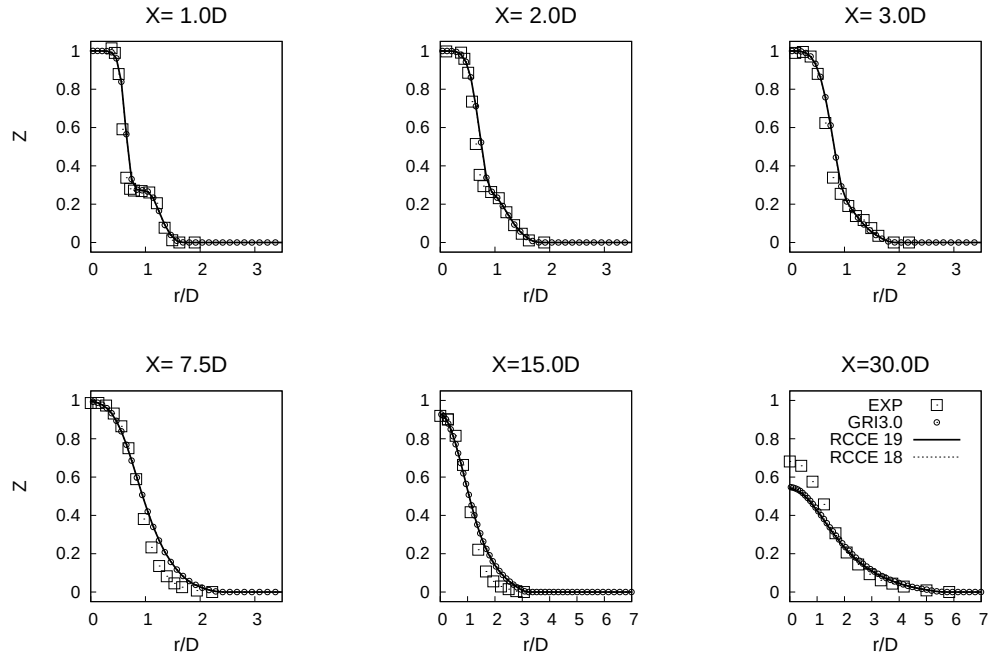


Figure 5.17: flame D: mean mixture fraction. Key: squares: measurements , circles : GRI-3.0 direct integration, dotted line : RCCE-18, solid line: RCCE-19

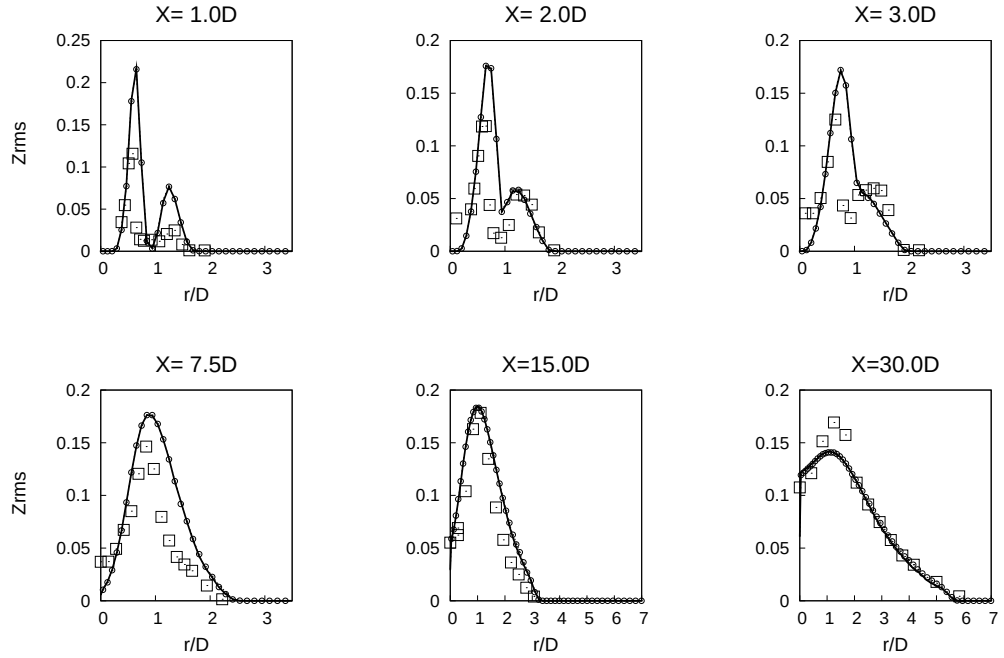


Figure 5.18: flame D: rms of mixture fraction. Legend as in fig (5.17) caption

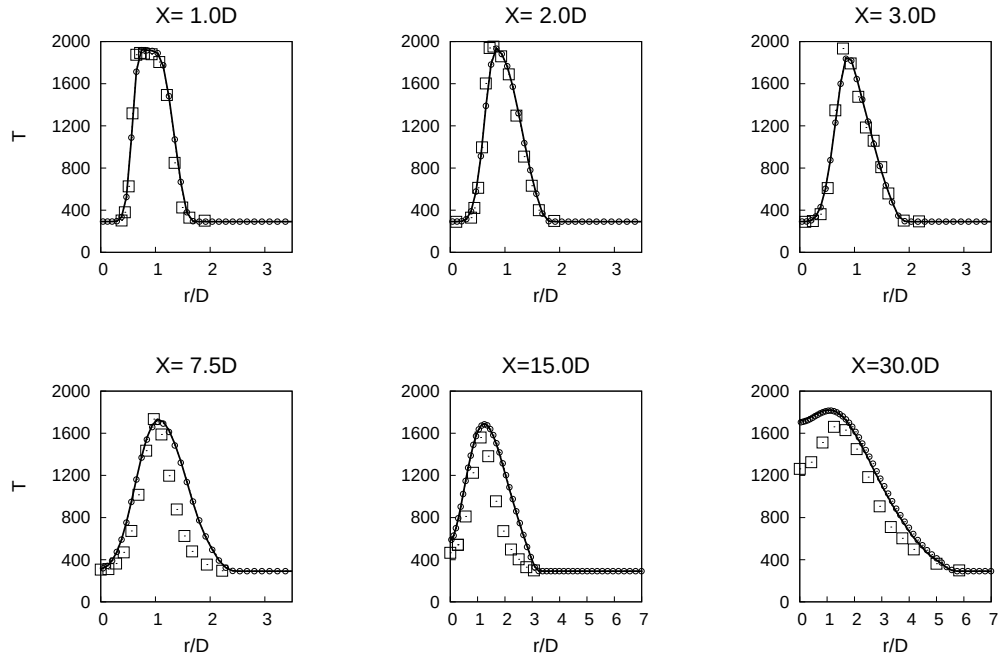


Figure 5.19: Flame D: mean temperature. Legend as in fig (5.17) caption

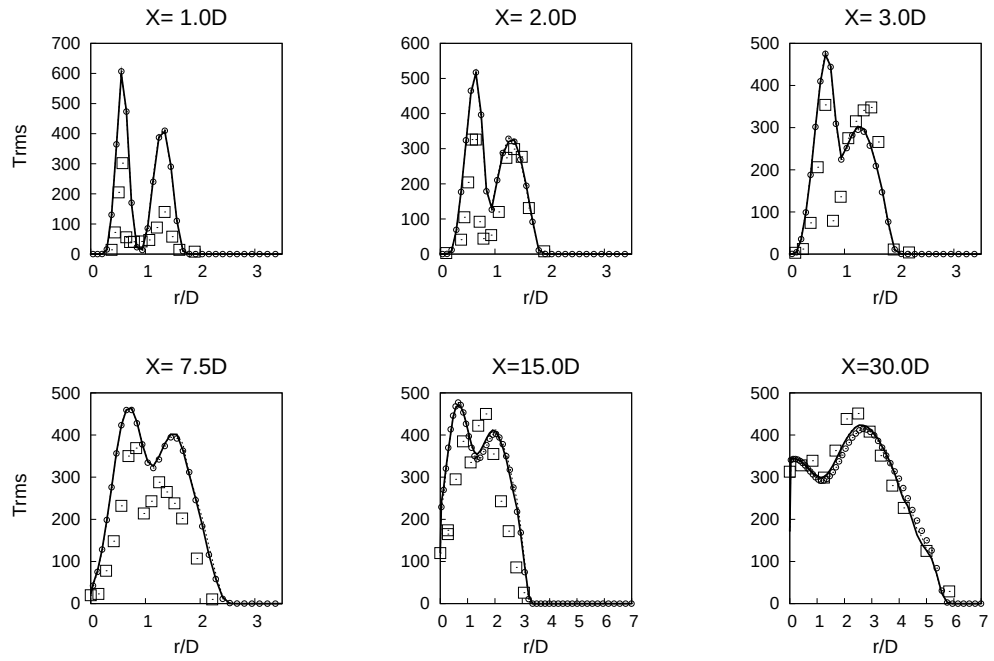


Figure 5.20: Flame D: rms of temperature. Legend as in fig (5.17) caption

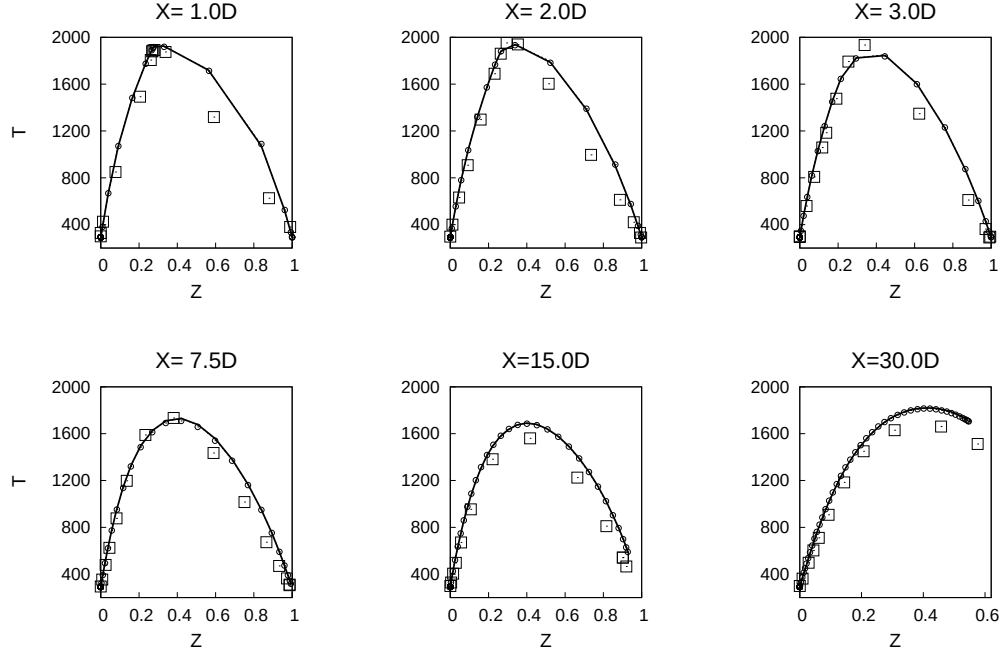


Figure 5.21: Flame D: mean temperature in mixture fraction space. Legend as in fig (5.17) caption

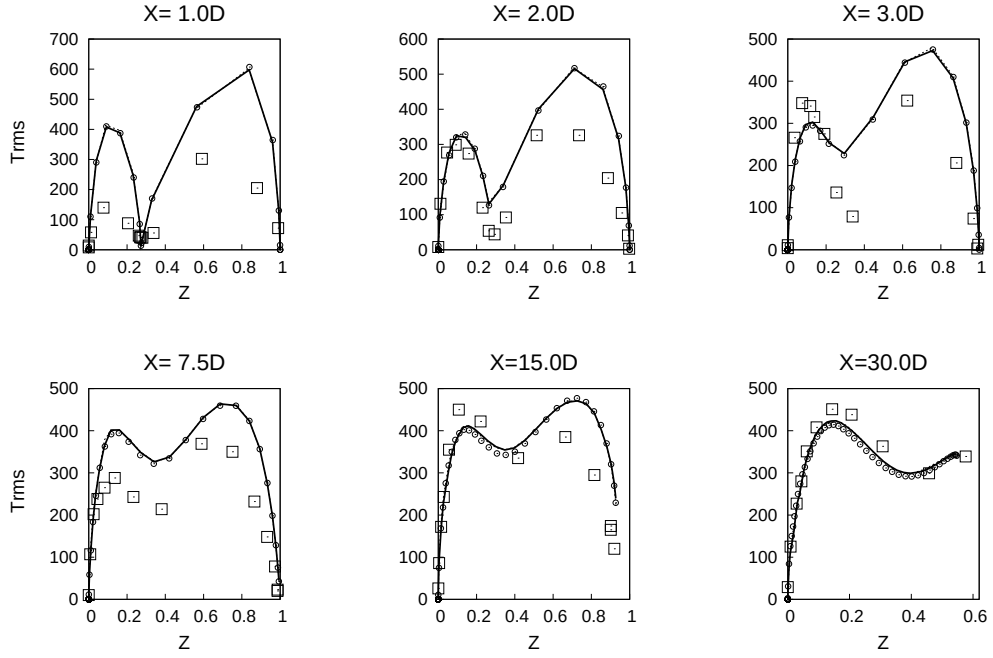


Figure 5.22: Flame D: rms of temperature in mixture fraction space. Legend as in fig (5.17) caption

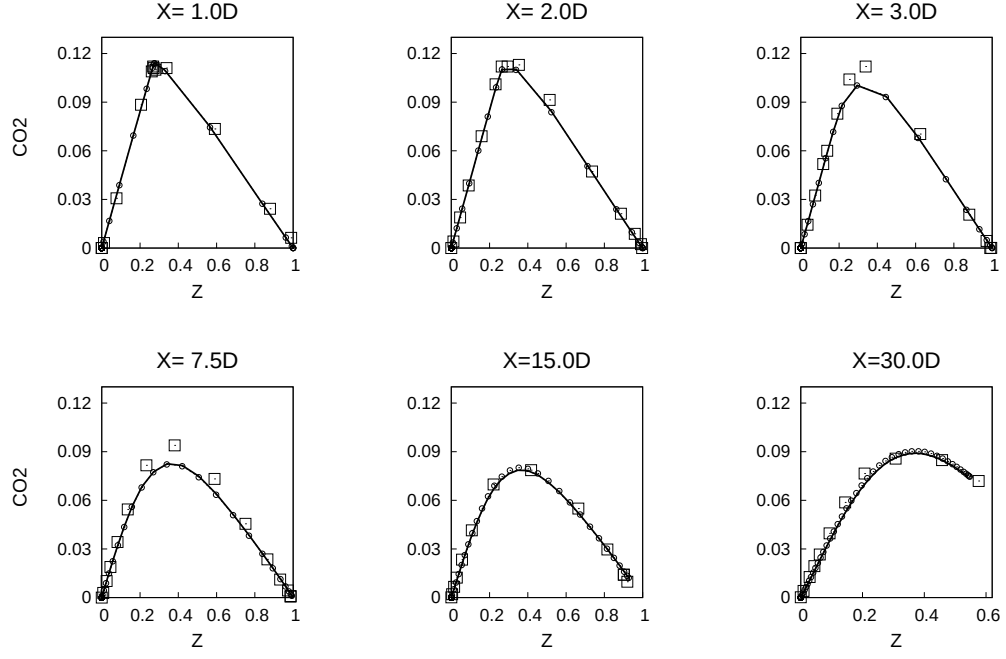


Figure 5.23: Flame D: mean mass fractions of CO_2 in mixture fraction space. Legend as in fig (5.17) caption

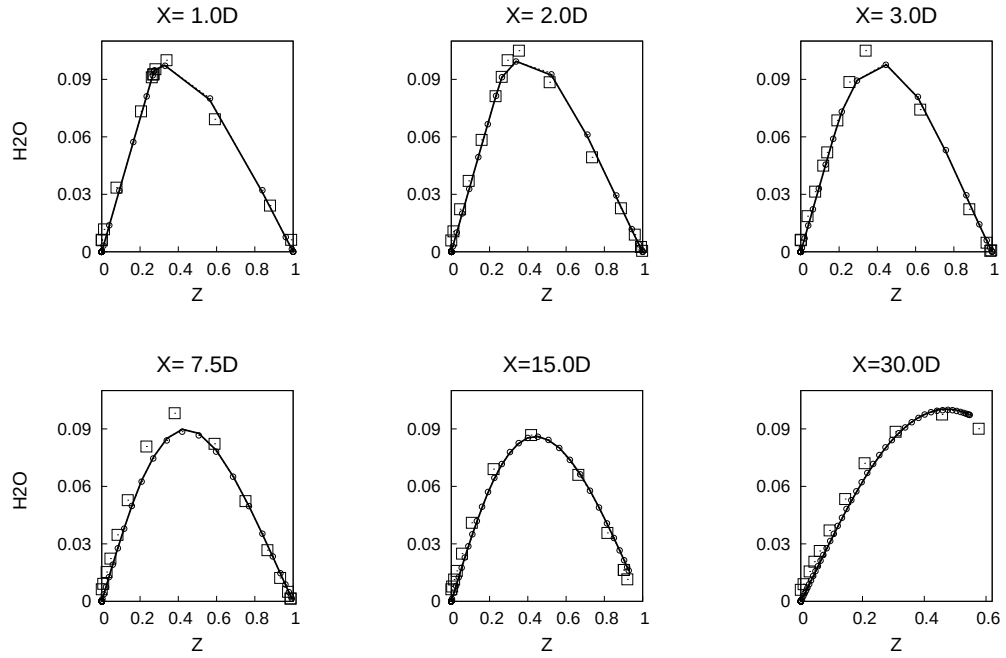


Figure 5.24: Flame D: mean mass fractions of H_2O in mixture fraction space. Legend as in fig (5.17) caption

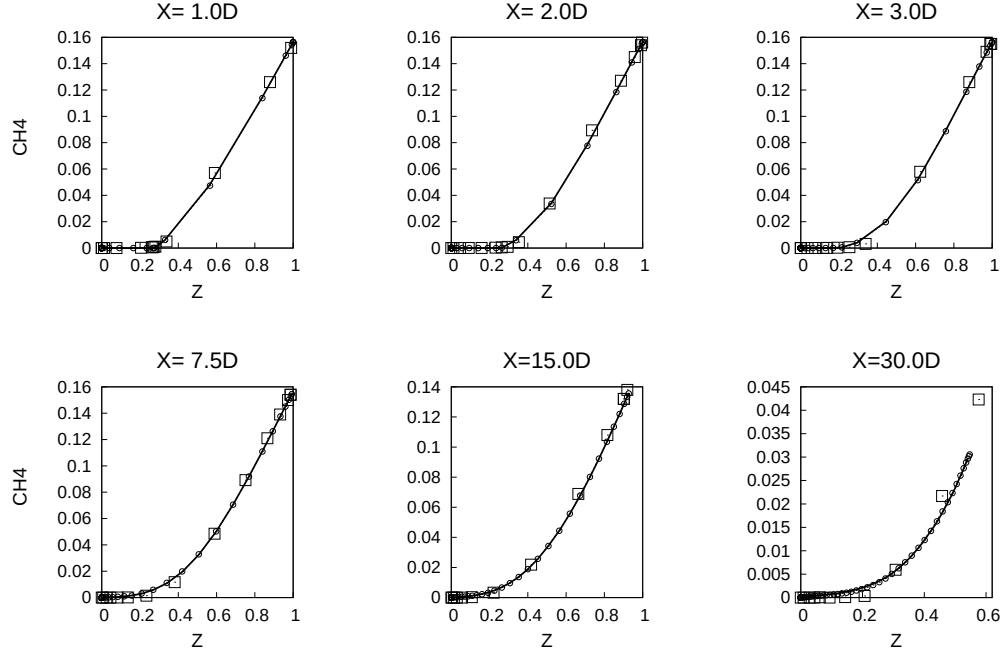


Figure 5.25: Flame D: mean mass fractions of CH_4 in mixture fraction space. Legend as in fig (5.17) caption

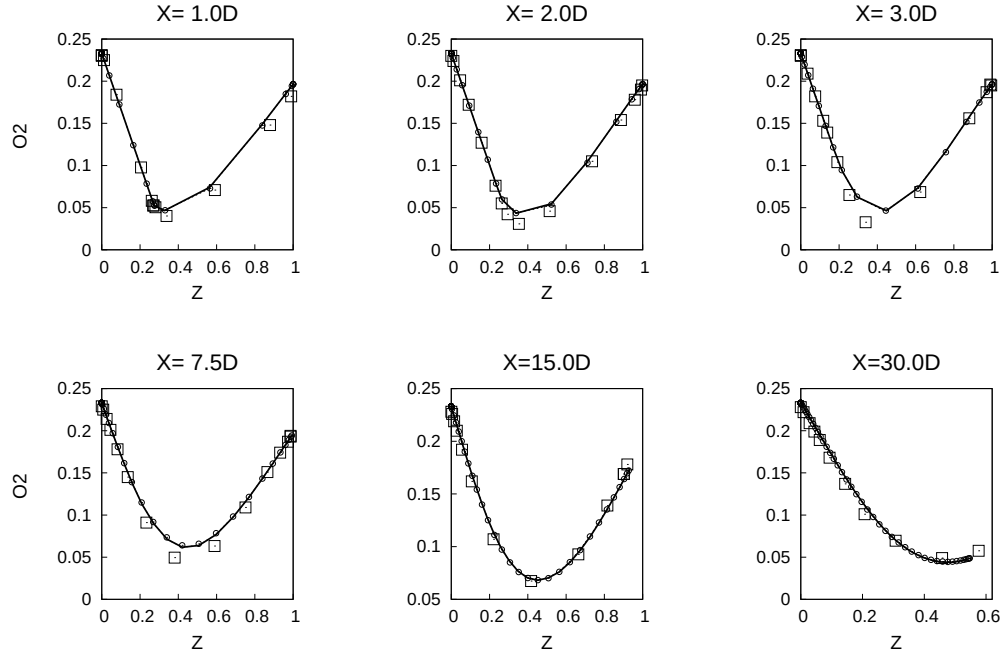


Figure 5.26: Flame D: mean mass fractions of O_2 in mixture fraction space. Legend as in fig (5.17) caption

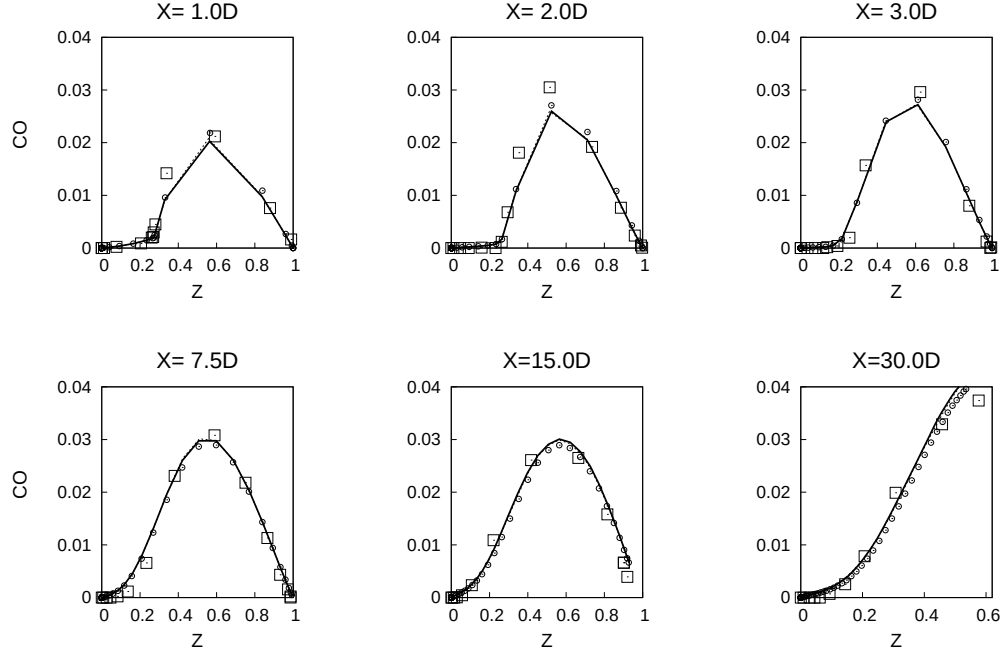


Figure 5.27: Flame D: mean mass fractions of CO in mixture fraction space. Legend as in fig (5.17) caption

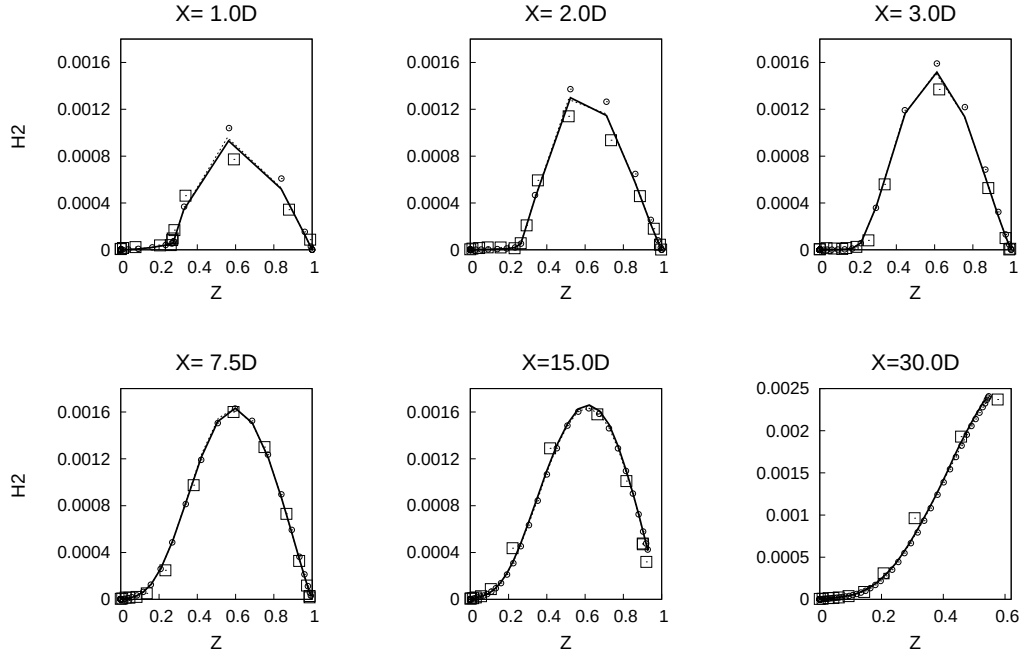


Figure 5.28: Flame D: mean mass fractions of H_2 in mixture fraction space. Legend as in fig (5.17) caption

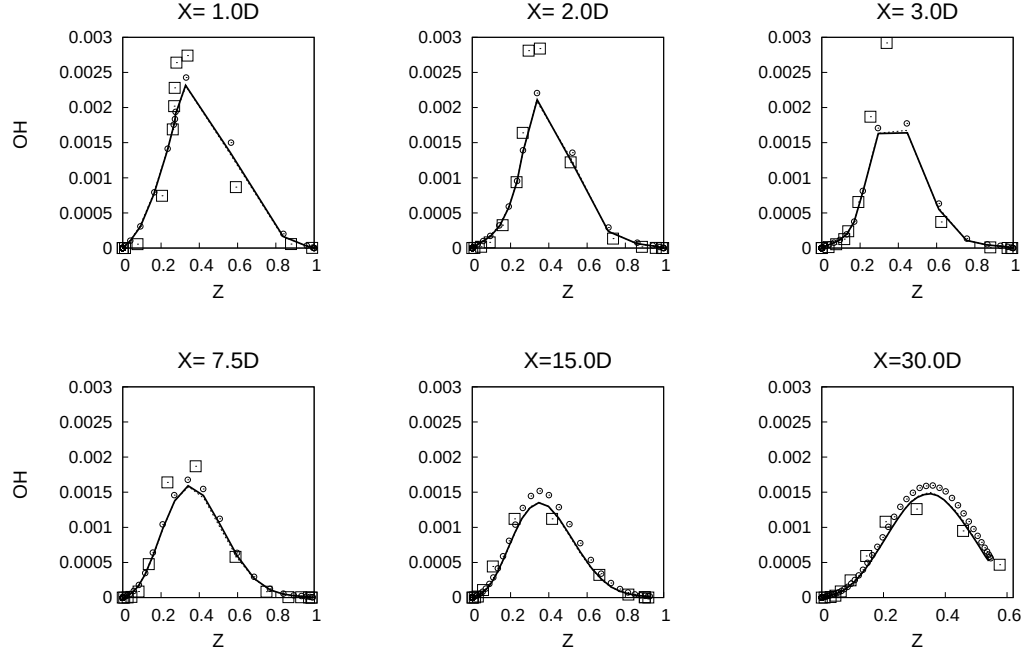


Figure 5.29: Flame D: mean mass fractions of OH in mixture fraction space. Legend as in fig (5.17) caption

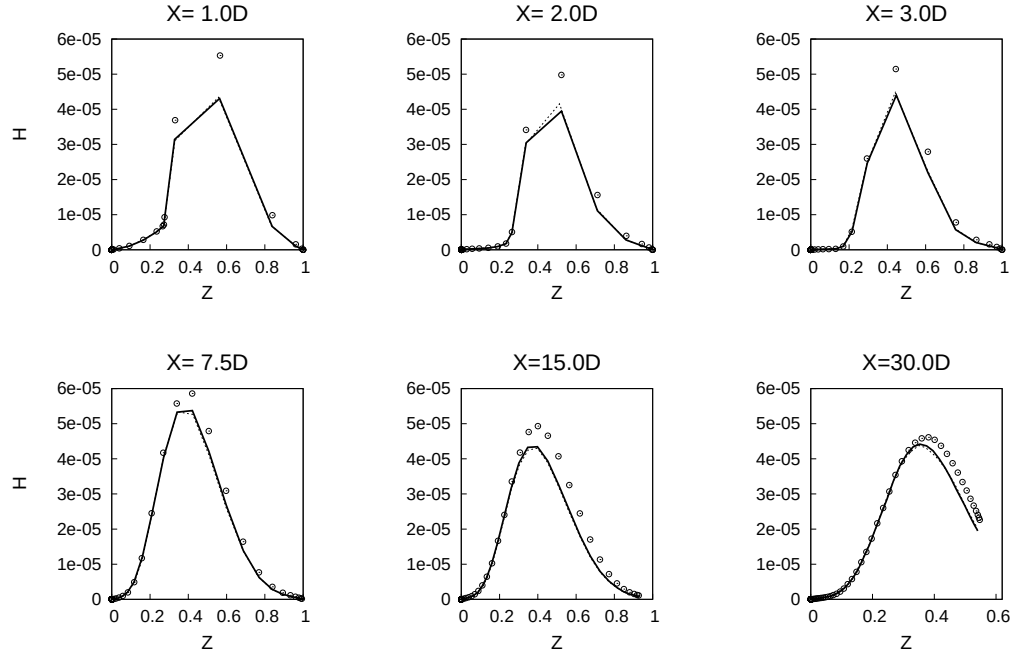


Figure 5.30: Flame D: mean mass fractions of H in mixture fraction space. Legend as in fig (5.17) caption

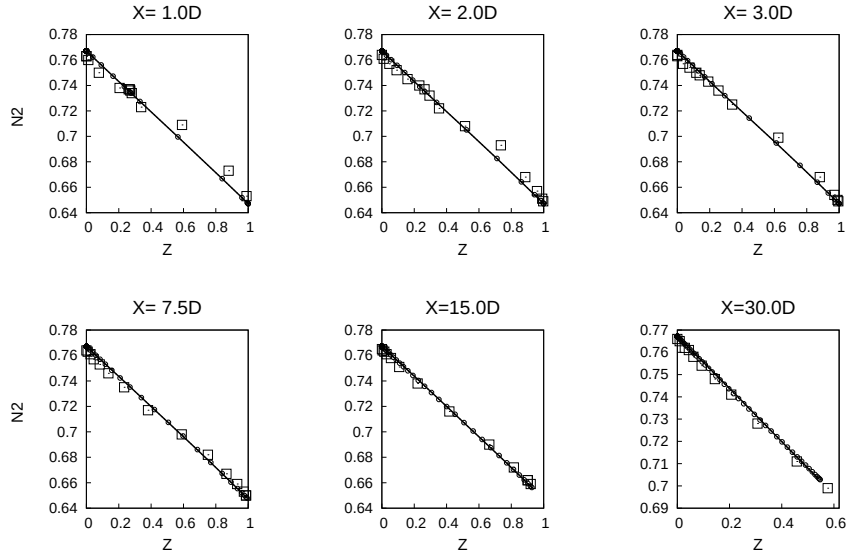


Figure 5.31: Flame D: N_2 in mixture fraction space. Legend as in fig (5.17) caption

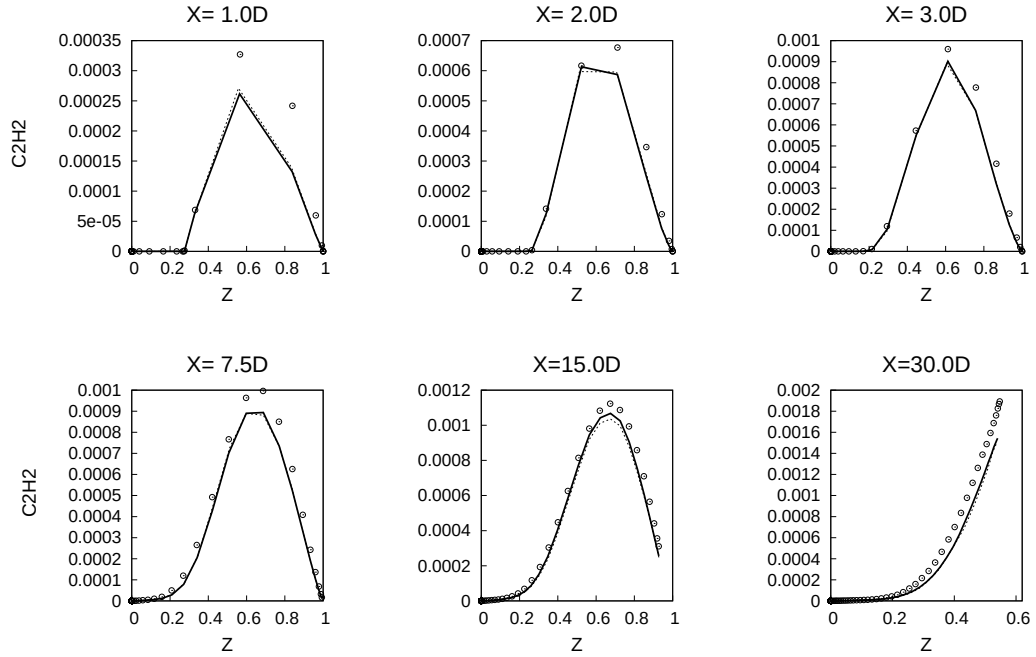


Figure 5.32: Flame D: mean mass fractions of C_2H_2 in mixture fraction space. Legend as in fig (5.17) caption

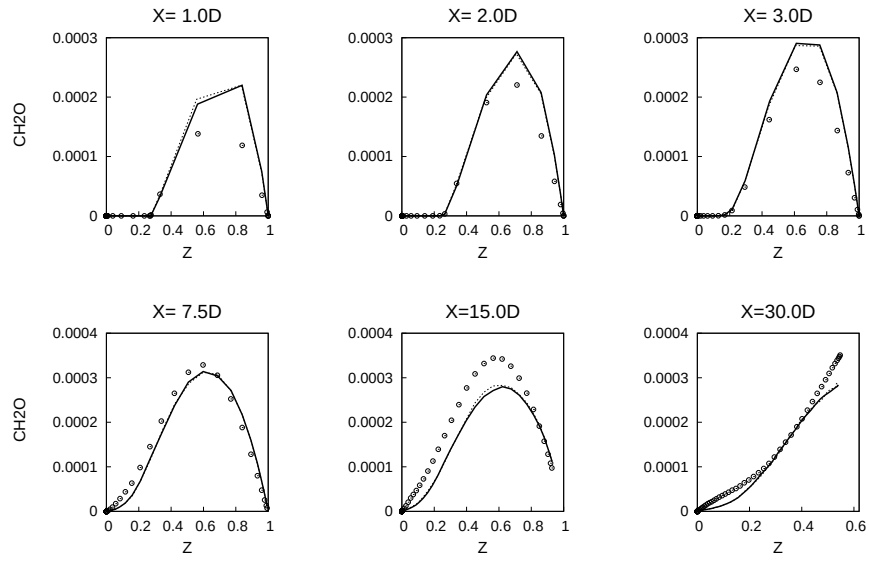


Figure 5.33: Flame D: mean mass fractions of CH_2O in mixture fraction space. Legend as in fig (5.17) caption

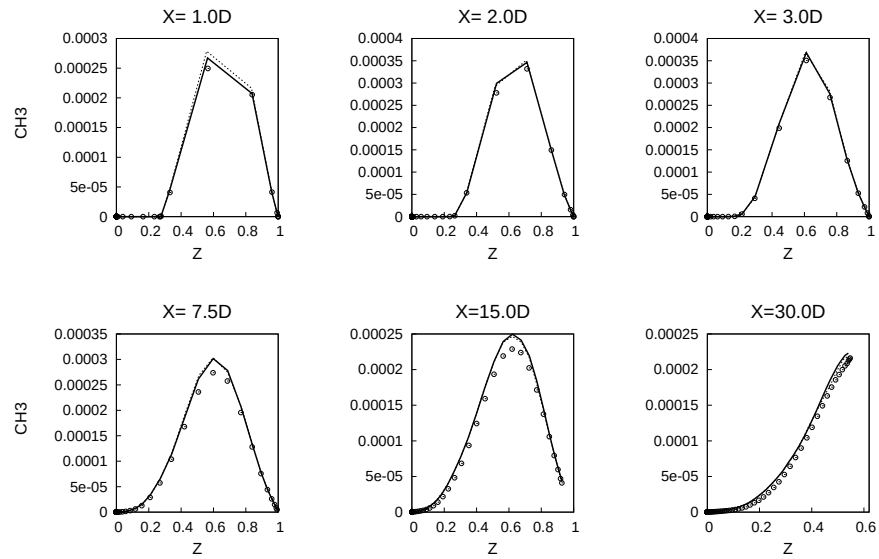


Figure 5.34: Flame D: mean mass fractions of CH_3 in mixture fraction space. Legend as in fig (5.17) caption and in the 30D plot here

5.5.4 Further discussion of results of flame E

The unconditional scalar field results of flame E are shown in the figures (5.35 to 5.51). Some of the observations that have been stated in the discussion of flame D are present in flame E particularly those related to mean mixture fraction and its rms. There is some discrepancy in the temperature and species profiles particularly in locations where mean and rms mixture fraction predictions are in disagreement with the measurements. In general the unconditional scalar field of flame E are reproduced with reasonable accuracy. For instance, it can be shown that peak values of temperature and chemical products are relatively lower in this flame than in flame D which is consistent with the trend of the measurements. This demonstrates both the applicability of the PDF method in reproducing the TCI phenomenon and the accuracy of the chemical mechanisms.

It is noted, however, that maximum temperature at $7.5D$ is overpredicted in flame E by an amount of 200 K which may imply that not enough local extinction is predicted in the stoichiometric zone at $7.5D$ axial distance from the nozzle. This can not be perceived accurately by the scatter plots of this flame in which a considerable number of particles fall in the extinction region (see middle graphs in figures 5.11 and 5.14). We also recollect that no thermal radiation is incorporated in the calculation of these flames. Although heat emissions by radiation in these flames are not significant, it is thought that inclusion of radiative effects would improve the accuracy of mean temperature at this location. The mass fractions of major species against mean mixture fraction are in good agreement with measurements. Specifically, the consumption rates of O_2 and CH_4 are reproduced with excellent accuracy which indicates the strength of the detailed and RCCE chemistry employed in this study.

On the other hand, there is considerable disagreement in the turbulent scalar fluctuations as seen in the temperature rms profiles mainly on the fuel-rich side at $7.5D$ and $15D$. In fact, it is apparent that these overpredictions in temperature fluctuations originate from the near-field fuel regions. This implies the inefficient

performance of the mixing model in the near-field region. In the calculations, this issues may be related to some extent to problems in the scatter plots that have been discussed in a previous section (5.5.2). This is despite the fact that predictions of mean temperature and mean chemical species in these fuel-rich regions are in better agreement with measurements than temperature rms. This observation on the fuel side is not distinct from the results of flames D and F as this behaviour has been common in all simulations although with different degrees in the three flames. Furthermore, other studies have also suffered from discrepancies in the turbulent scalar field of these flames implying the strong challenge presented on TCI and chemistry models. Further details will be concluded in the comparisons with other studies in a forthcoming section. It is thought that better representation of mixing would improve the predictions in these regions but the influence of chemistry here is not clear.

It can be observed that the level of accuracy at $15D$ is higher for mean temperature and major species like CO_2 , H_2O , O_2 and CH_4 than at the lower location $x = 7.5D$. The increase in the amount of local extinction in flame E relative to flame D can be realised very well by predictions at this location. One of the remarkable observations is the fact that mean CO mass fraction is well predicted by both the DI chemistry and RCCE at several locations. The commonly experienced overprediction of CO in fuel-rich regions in several previous studies is relatively small in the present predictions of this flame. H_2 is slightly underpredicted by the RCCE in comparison with DI. The rest of the plotted minor species also show different degrees of underprediction by the RCCE models. Although we start to distinguish between the two RCCE calculations in flames E and F but the difference is quite minimal. This still indicates that adding the CH_2CO species to the set of constraints has no or very little effect.

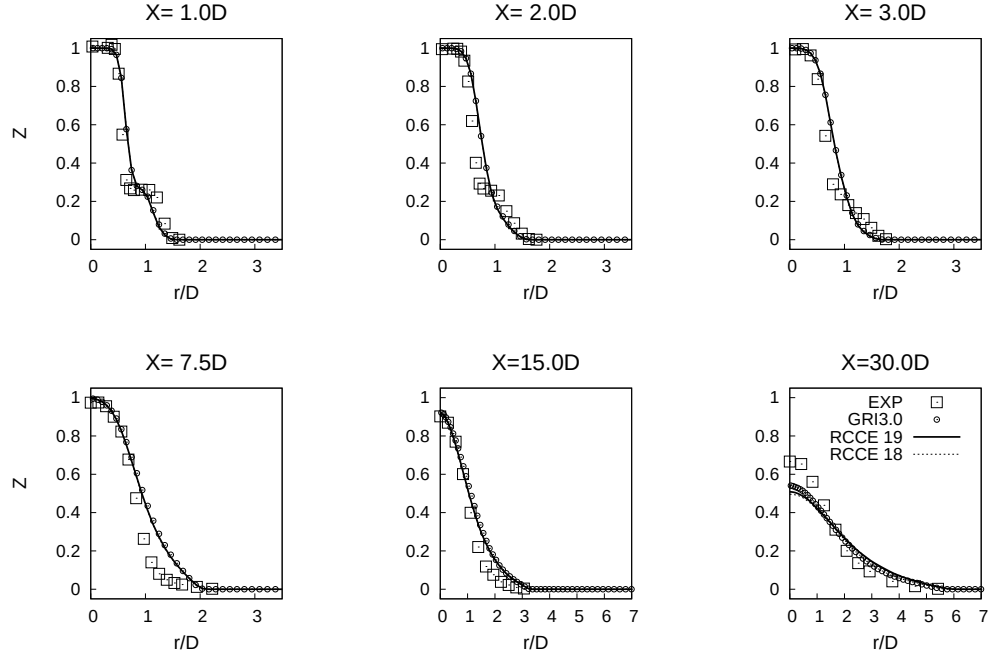


Figure 5.35: flame E: mean mixture fraction. Legend as in fig (5.17) caption

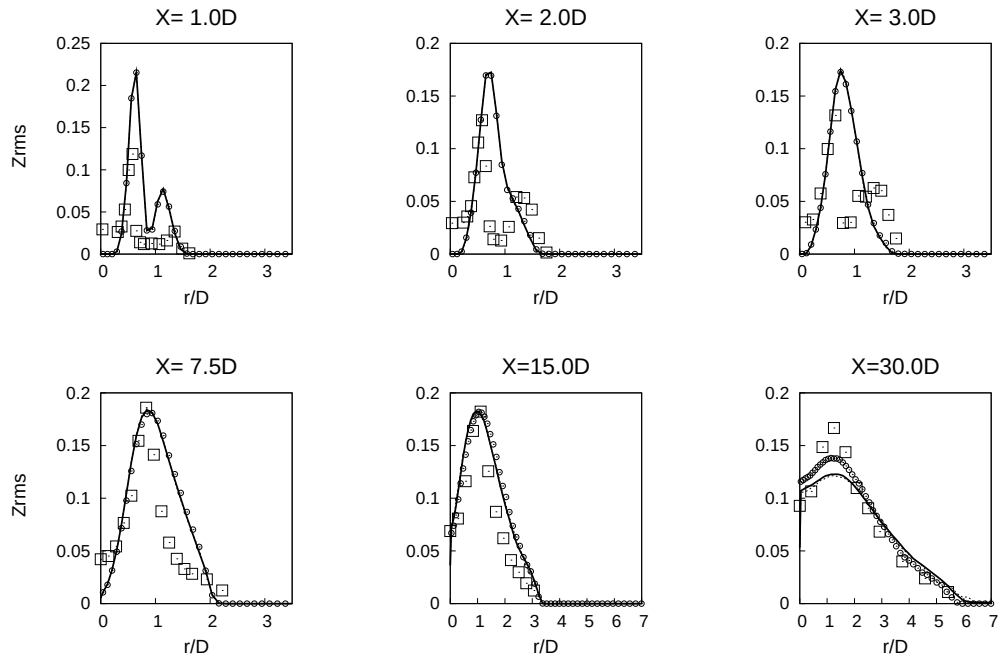


Figure 5.36: flame E: rms of mixture fraction. Legend as in fig (5.17) caption

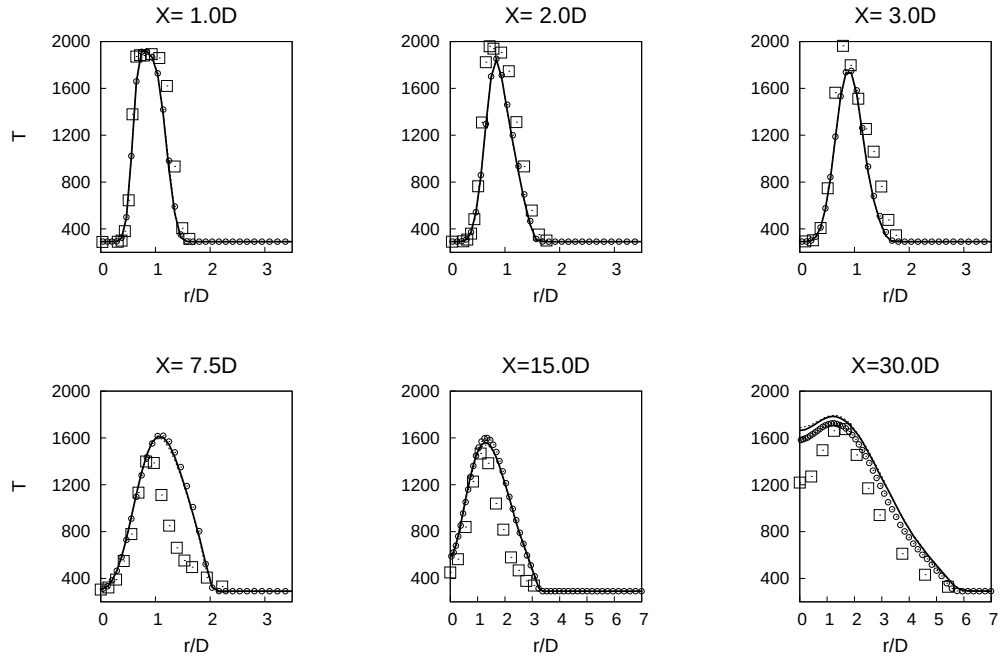


Figure 5.37: Flame E: mean temperature. Legend as in fig (5.17) caption

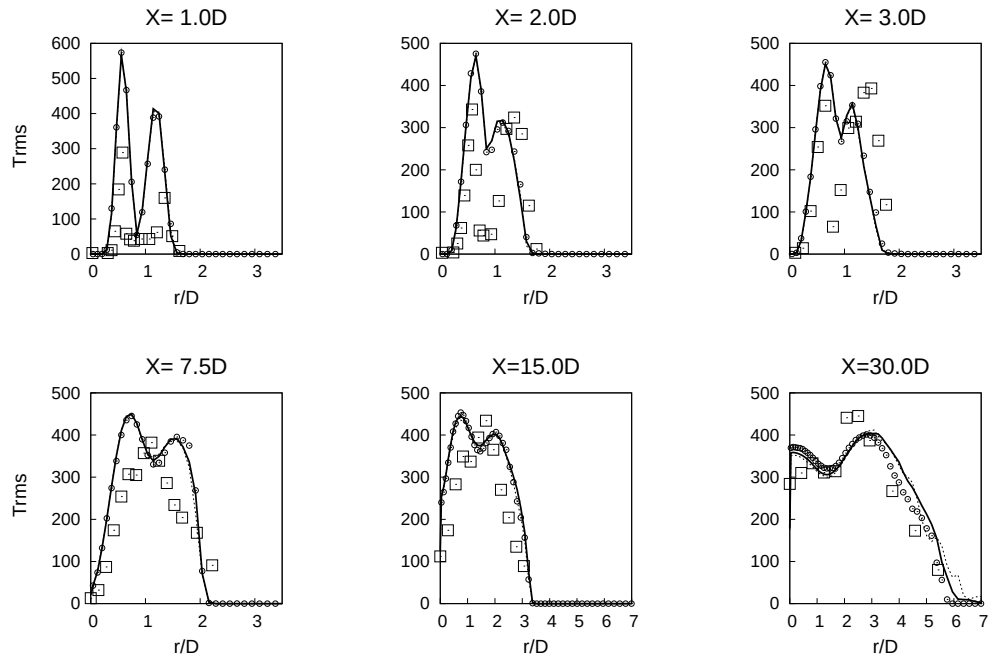


Figure 5.38: Flame E: rms of temperature. Legend as in fig (5.17) caption

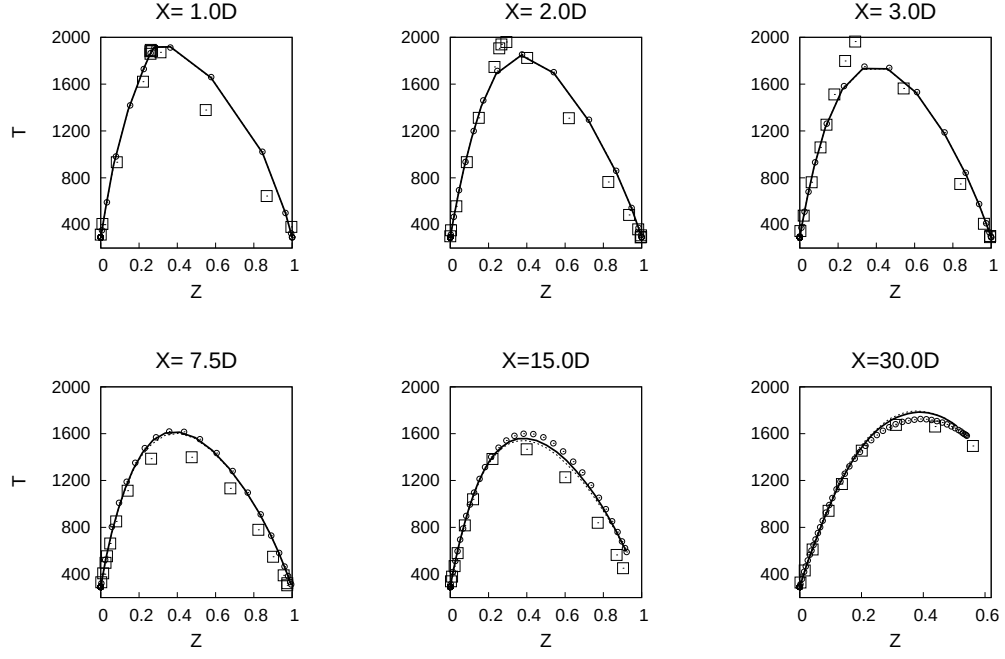


Figure 5.39: Flame E: mean and rms of temperature in mixture fraction space. Legend as in fig (5.17) caption

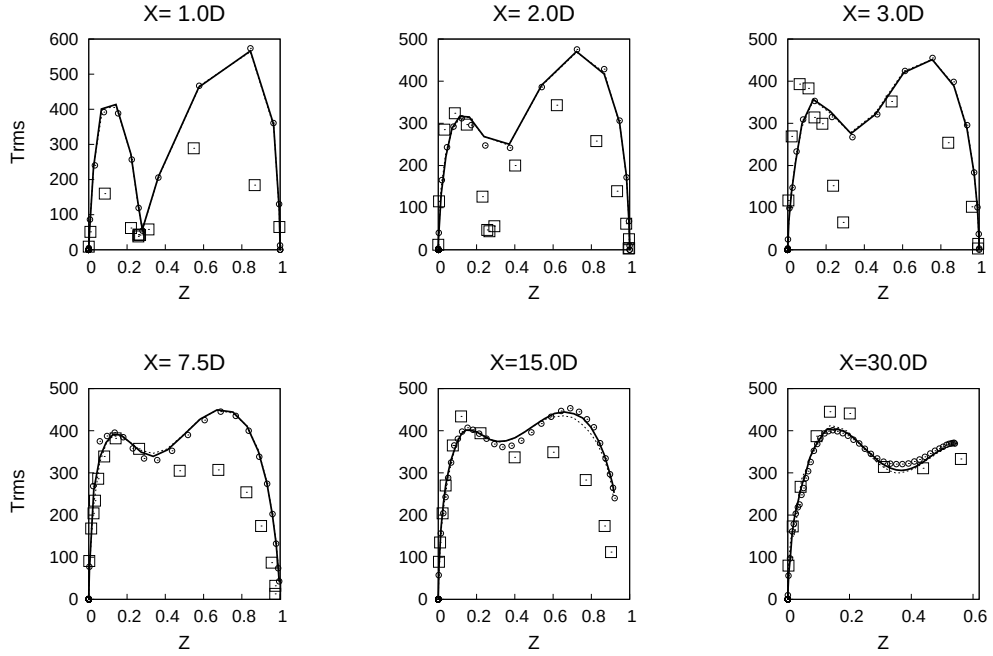


Figure 5.40: Flame E: rms of temperature in mixture fraction space. Legend as in fig (5.17) caption

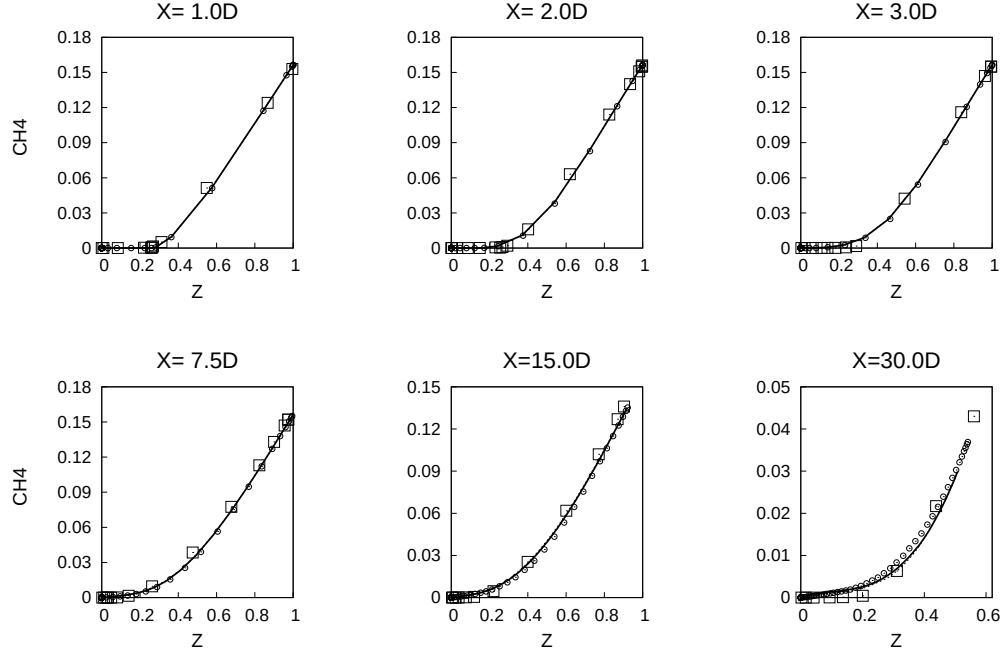


Figure 5.41: Flame E: mean mass fractions of CH_4 in mixture fraction space. Legend as in fig (5.17) caption

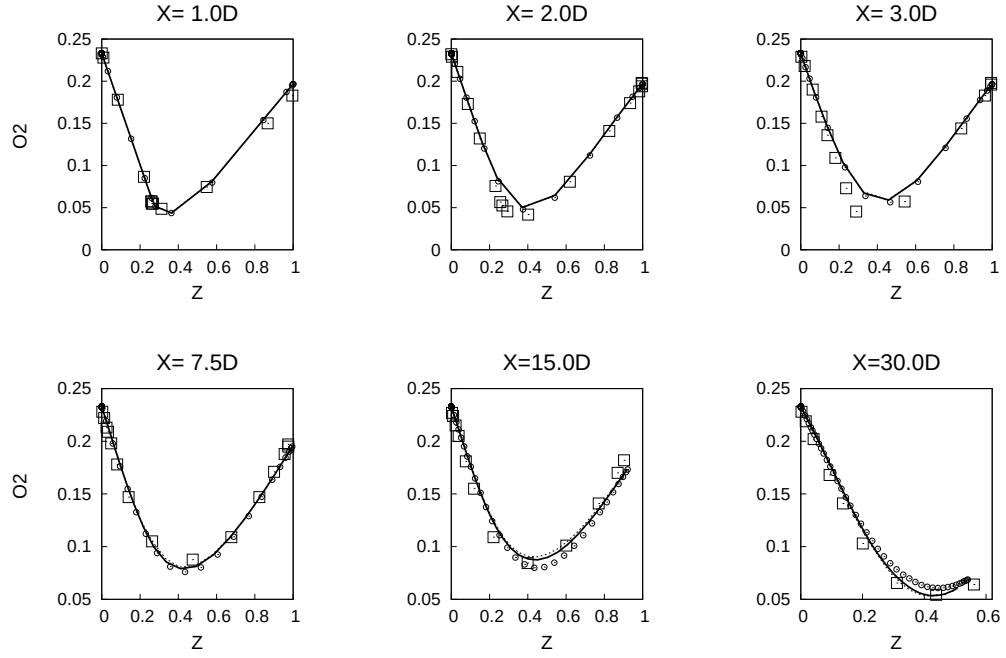


Figure 5.42: Flame E: mean mass fractions of O_2 in mixture fraction space. Legend as in fig (5.17) caption

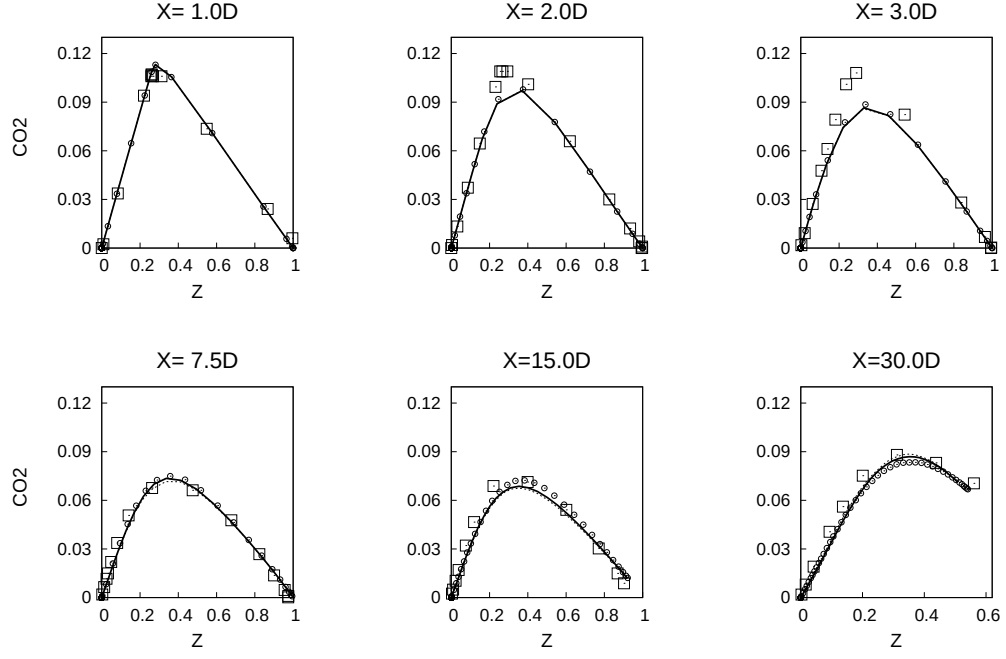


Figure 5.43: Flame E: mean mass fractions of CO_2 in mixture fraction space. Legend as in fig (5.17) caption

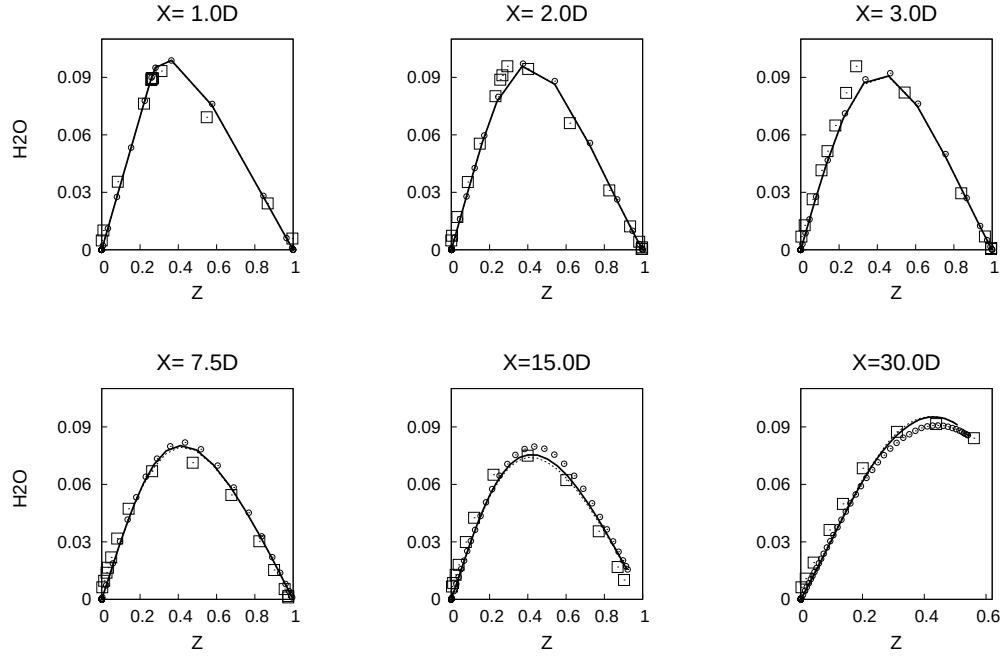


Figure 5.44: Flame E: mean mass fractions of H_2O in mixture fraction space. Legend as in fig (5.17) caption

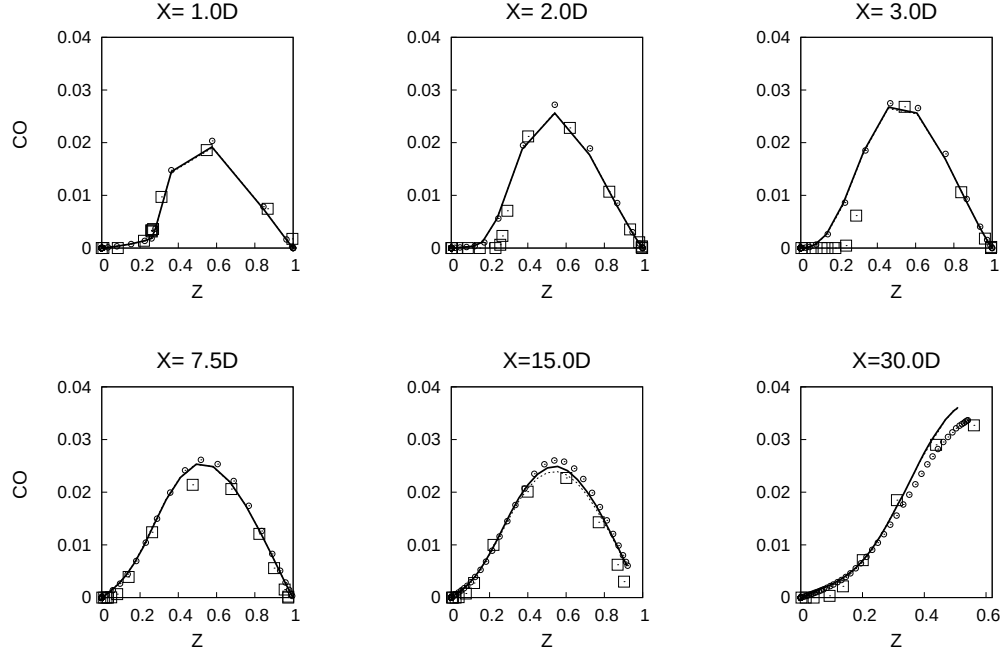


Figure 5.45: Flame E: mean mass fractions of CO in mixture fraction space. Legend as in fig (5.17) caption

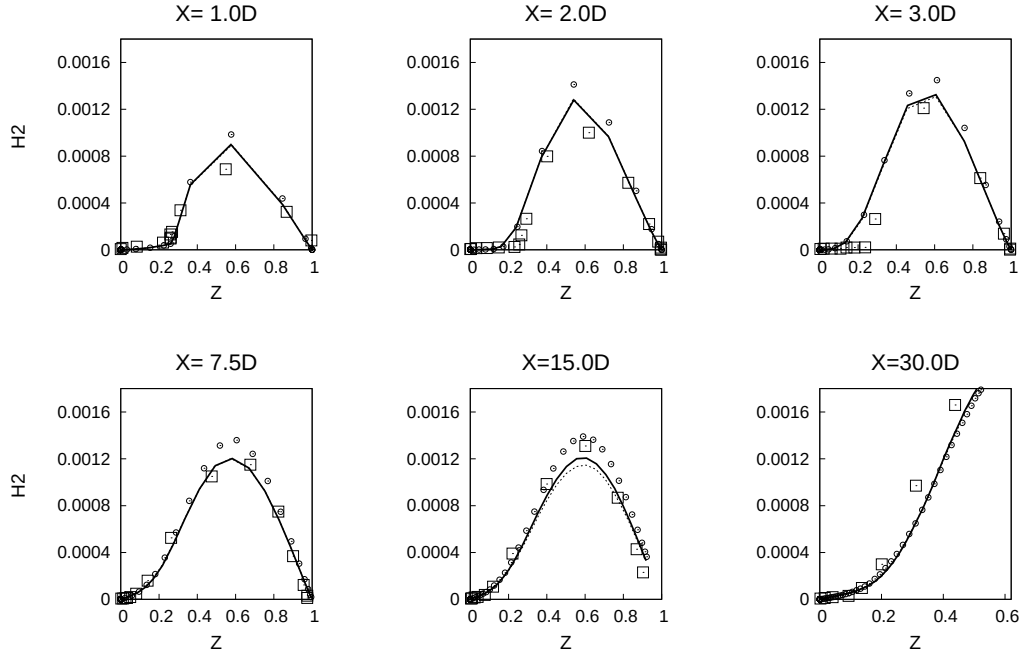


Figure 5.46: Flame E: mean mass fractions of H_2 in mixture fraction space. Legend as in fig (5.17) caption

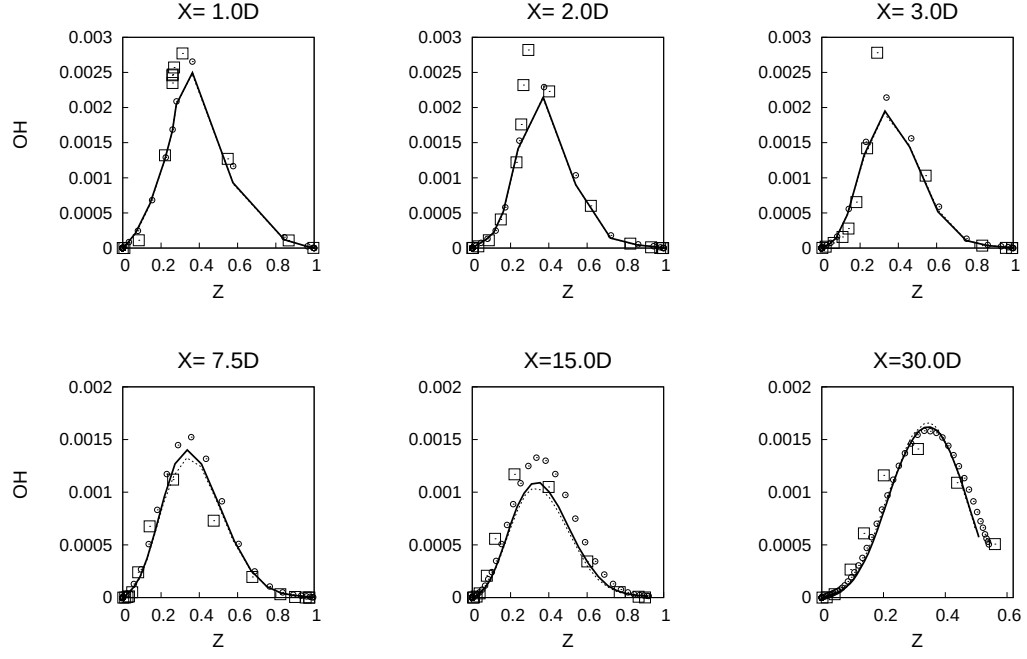


Figure 5.47: Flame E: mean mass fractions of OH in mixture fraction space. Legend as in fig (5.17) caption

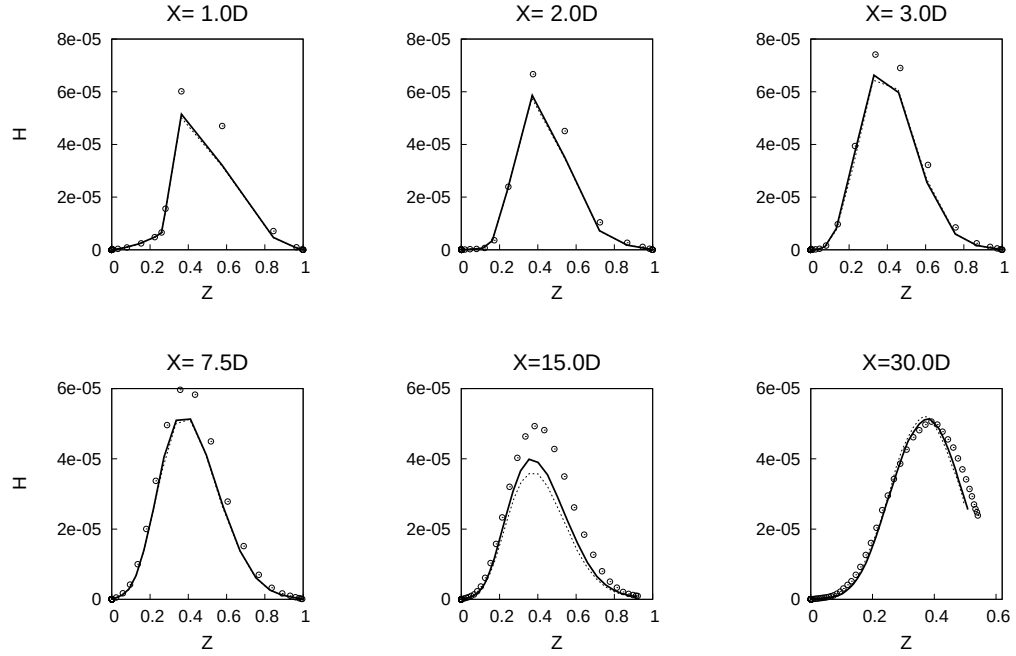


Figure 5.48: Flame E: mean mass fractions of H in mixture fraction space. Legend as in fig (5.17) caption

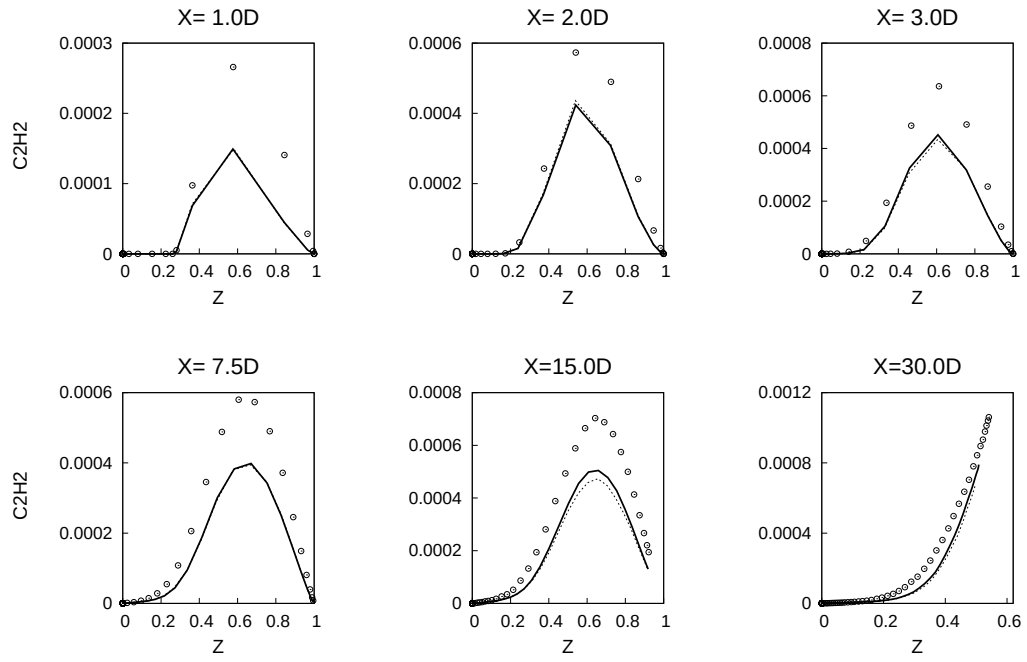


Figure 5.49: Flame E: mean mass fractions of C_2H_2 in mixture fraction space. Legend as in fig (5.17) caption

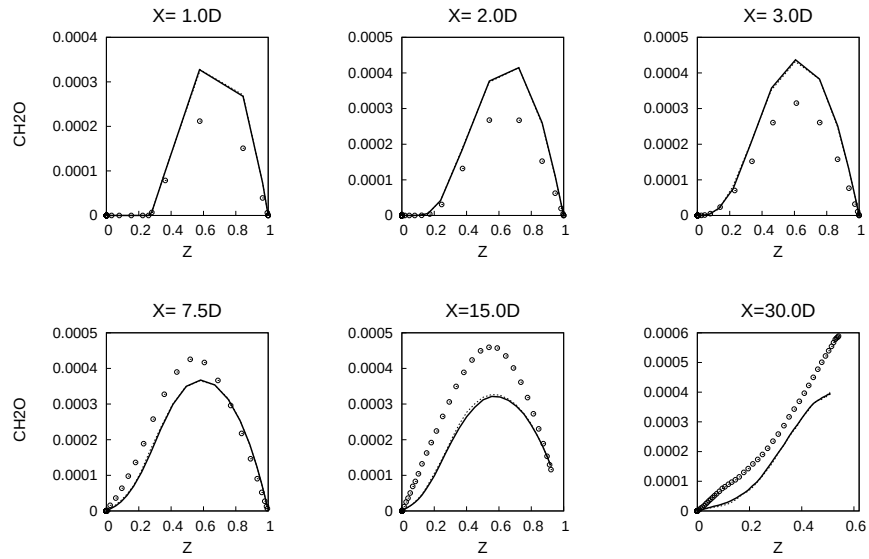


Figure 5.50: Flame E: mean mass fractions of CH_2O in mixture fraction space. Legend as in fig (5.17) caption

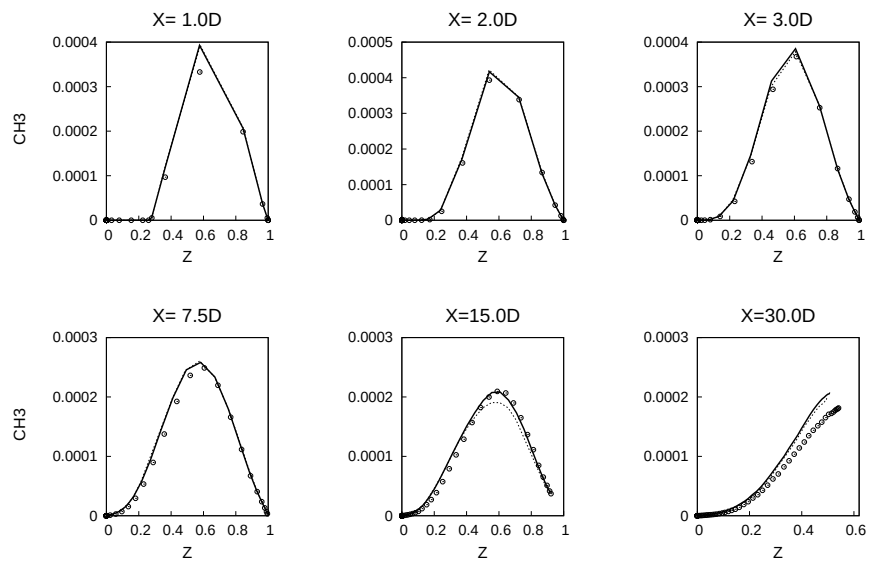


Figure 5.51: Flame E: mean mass fractions of CH_3 in mixture fraction space. Legend as in fig (5.17) caption

5.5.5 Further discussion of results of flame F

The unconditional scalar field results of flame E are shown in the figures (5.52 to 5.69). The mixture fraction predictions in flame F are better than flames D and E in some regions. In particular, the mean mixture fraction profile at $30D$ is well predicted in contrast to the other two flames where the values close to the centreline are considerably underpredicted in this axial location. The peak of mean temperature is overpredicted by approximately 400 K in the $7.5D$ and $15D$ but improved considerably at $30D$. The extinction at $15D$ is not fully captured as has been illustrated in the scatter plots. The calculation of this flame with $C_\phi = 2.0$ (not shown) gave considerable improvement for the mean temperature at $15D$ because more particles were extinguished but this was not followed by subsequent ignition at $30D$. The temperature overprediction is accompanied with overpredicted consumption rates of reactants (O_2 and CH_4) in the flame zone at $x = 7.5D$ and $x = 15D$ and overprediction of the major combustion products which implied that the current PDF calculations were unable to produce enough amount of extinction.

The accuracy of the rms of mixture fraction and temperature are comparable to those in flame E. The rms of mixture fraction is well predicted like in the other two flames. On the other hand, examination of rms of temperature at $x = 7.5D$ and $x = 15D$ in this flame shows considerable overprediction on the fuel-rich side of the flame (closer to the centreline). This is probably attributed to inadequate single-scale mixing modelling and its incapability in reproducing the extinction and ignition mechanisms. On the other hand, comparison of rms of both mixture fraction and temperature at $x = 30D$ shows that significant temperature rms extends radially to the outer fuel-lean side of the flame while mixture fraction rms decays closer to the centreline. In other words observation of significant temperature rms does not always correspond to a large the mixture fraction rms. This is qualitatively captured in the calculations. It indicates that the temperature fluctuation is correlated with statistics of several scalar quantities due to the presence of complicated TCI causing significant amount of extinction and reignition.

Some of the RCCE profiles slightly differentiate from the DI predictions particularly at $x = 30D$. This may imply the severe challenge exerted by the reignition phenomenon in this flame on the current simulations.

5.5.6 Comparison with Previous Studies of Sandia Flames

Here we compare the present results for the three flames which have been discussed in the previous subsections with those from previous studies in the literature. The studies which are compared with the present work differ in one or more elements of the simulation. In terms of chemical kinetics, the comparison between the results of the full GRI-3.0 and the RCCE-reduced mechanisms which were both obtained in the current work gave better and more reliable assessment than the comparison with other studies would provide. Furthermore, differences in other components of the simulation such as turbulence modelling and mixing models do not allow trustworthy comparisons of the influence of chemical mechanisms.

One of the frequent observations in previous studies of Sandia flames is that the mean mixture fraction is overpredicted on the centreline particularly at $30D$ and higher axial locations such as the LES-PDF study of [96] and the RANS-PDF studies [29, 30]. Similar results were only observed in the current methodology when a linear interpolation scheme was employed for particle motion. On the contrary, the Jenny et al. scheme [80] which was exploited in the results presented in this study results in underprediction of the mean mixture fraction on the centreline at axial distances higher than $30D$. The RANS-MMC study of flame E by Wandel and Lindstedt [220] and of flame D by Vogiatzaki et al. [217] predict the flame with some radial overspreading. Similar issue is observed in the current results upto $x = 15D$ only. These are important observations since modifying the mixing field has explicit and implicit effects on the predictions of temperature and chemical species. If we look at the mean temperature on the centreline at $30d$, we find that it is being underpredicted by the studies which predict too high centreline mixture fraction. On the other hand, the present study gives higher temperature at this location because the computed mixture fraction value is closer to stoichiometric value (underpredicted).

In addition, the presence of turbulence and its interaction with chemistry result in deep and indirect modifications to the species profiles when the mixture fraction field is modified.

Another point is that most of the studies (including this study) predicted insufficient amount of extinction in flame F at $15D$ and consequently the peak temperature is around 400 K higher than the measured values. The only study that did not suffer from this overprediction is the simulations of Cao and Pope [29] with the EMST and GRI-3.0 in which radiative effects were not neglected. The overprediction of mean temperature in the extinction zone of flame F demonstrates the challenge of flame F case to simulations in predicting the measured amount of extinction without causing blow-off of the flame.

The profiles of the mixture fraction rms are generally well predicted in the current simulations. For example, the peak mixture fraction rms did not suffer from severe underpredictions as in the results of flame E in [30] with similar mixing (IEM modelling) for the three flames. These underpredictions in [30] resulted from the fact that their PDF simulations adopted large C_ϕ values to ignite the flames (i.e 3.3 with the IEM and 3.8 with the MCD). Here we refer to the results of Coa et al. [30] both in the main paper and their supplementary material which presented detailed predictions of flame E. Their underprediction of the mixture fraction rms with the IEM and MCD was also accompanied with similar underprediction of the rms of temperature particularly at $15D$ and $30D$ axial locations. On the other hand, their simulations with EMST mixing model and GRI-3.0 in [30, 29] produced good profiles for the rms of mixture fraction at those two locations. This gave more evidence for the influence of the mixing coefficient C_ϕ since it was assigned a value of 1.5 with the EMST model. Also, the levels of temperature rms were recovered with EMST at $15D$ but resulted with overprediction at $30D$. Their scatter plots for flame E with IEM and MCD also show that the large values of C_ϕ resulted in minimal amount of scatter in temperature and stoichiometric products. This has an important indication since their computation with the IEM only differs from current

GRI3 computation in the type of PDF and the C_ϕ value.

The trends of the radial profiles of the rms of temperature in the present work (particularly in flame F) are probably more similar to those predicted by the LES-CMC simulations of Garmory and Mastorakos [65]. However, one can notice that the amount of disagreement is not the same at all locations as well. For instance, their temperature rms predictions also exhibited the two-maxima profiles at 7.5D, 15D and 30D locations. Present results show relatively larger amount of overprediction in the fuel-rich side while achieving better agreement closer to stoichiometry and on the fuel-lean side.

Further on the scatter plots, both the LES of [96] and [68] predict more extinction in flame F at 15D than in flame E. Current scatter plots at this extinction location (e.g. fig. 5.12) did not show noticeable difference between the flames E and F even with the full GRI-3.0 mechanism indicating the advantage of the LES-PDF and LES-MMC methods over the RANS-PDF method. There are some similarities between present scatter plots of flame D and those presented by Wang and Chen in [221] including the delay of reignition after $x = 30D$. Their methodology is consistent with the current study in employing the GRI-3.0 mechanism in the context of the joint scalar PDF and RANS modelling. They, however, implemented the EMST mixing model not the IEM model.

On the other hand, this work is distinguished with the level of accuracy of mean CO peak value particularly in the fuel-rich regions of flames E and F. Mean CO profiles of flame E show less overprediction than the LES-PDF simulations of [96], the LES-FPV simulations of [77] and the RANS-MMC simulations of [220]. Furthermore, the amount of overprediction in peak value of CO at the 30D axial location of flame F in [96] is larger than in this study. The reason for this may be related to the effect of adopting the Jenny et al. model [80] for particle motion. This reasoning is supported with the fact that computations of flame D with linear interpolation also showed tendency to overpredict the CO mass fraction with greater amount than with Jenny et al. model [80].

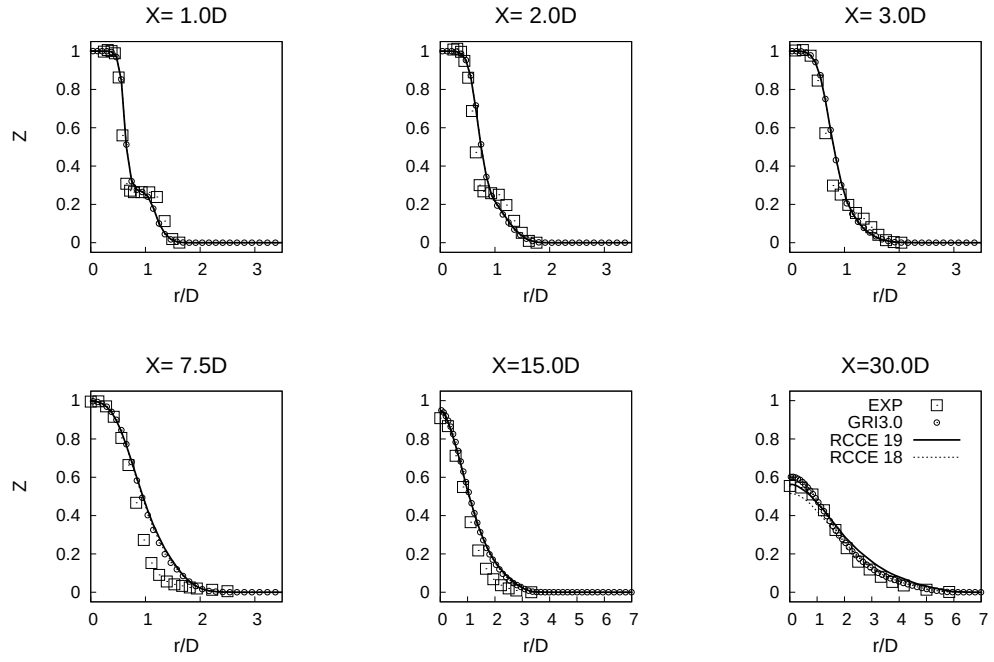


Figure 5.52: flame F: mean mixture fraction. Legend as in fig (5.17) caption

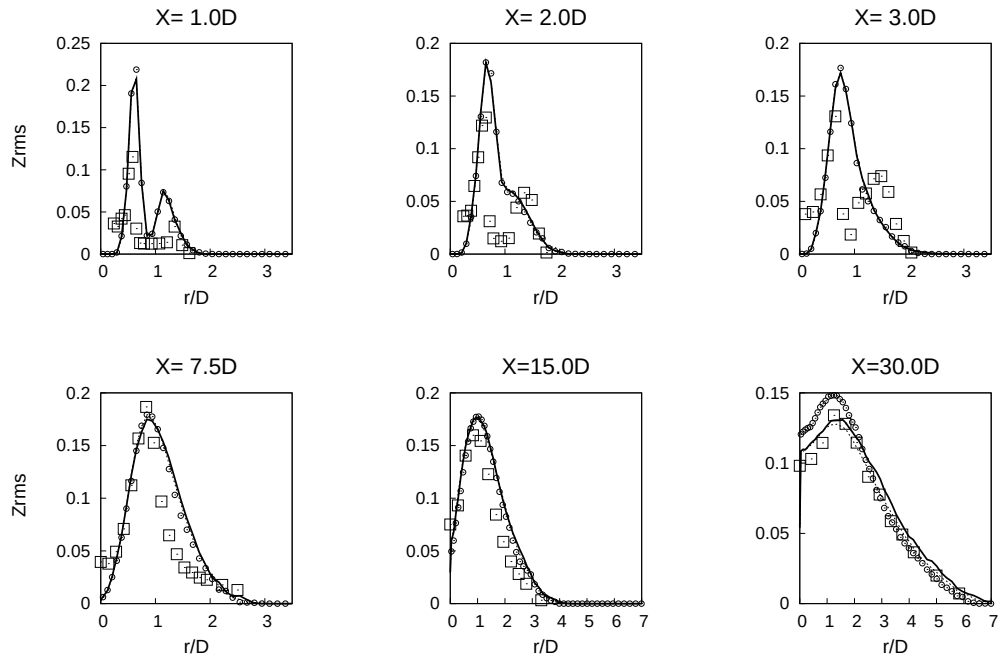


Figure 5.53: flame F: rms of mixture fraction. Legend as in fig (5.17) caption

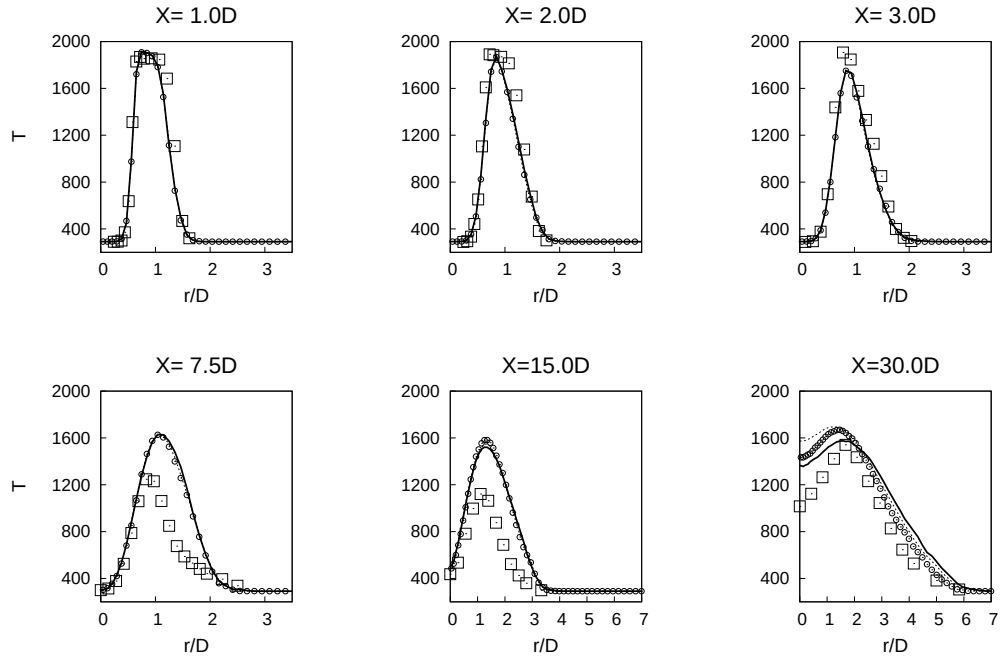


Figure 5.54: Flame F: mean temperature. Legend as in fig (5.17) caption

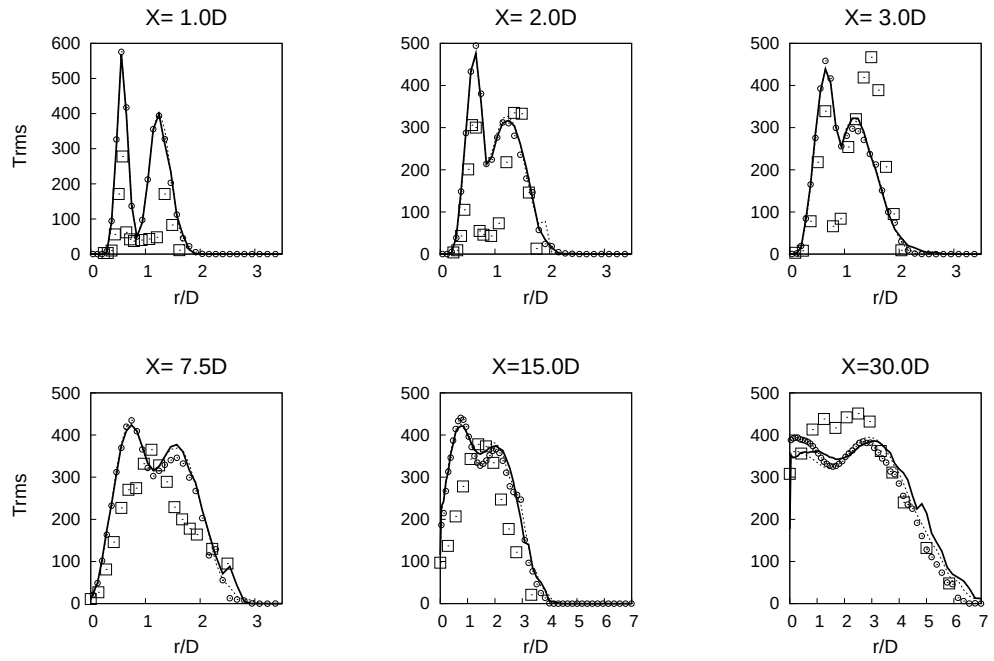


Figure 5.55: Flame F: rms of temperature. Legend as in fig (5.17) caption

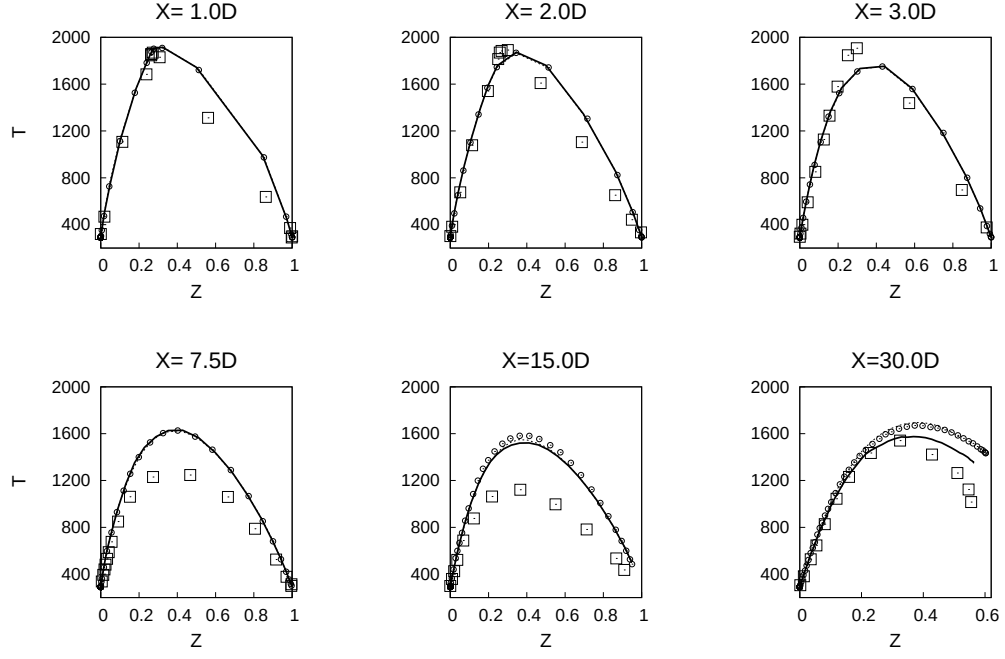


Figure 5.56: Flame F: mean and rms of temperature in mixture fraction space. Legend as in fig (5.17) caption

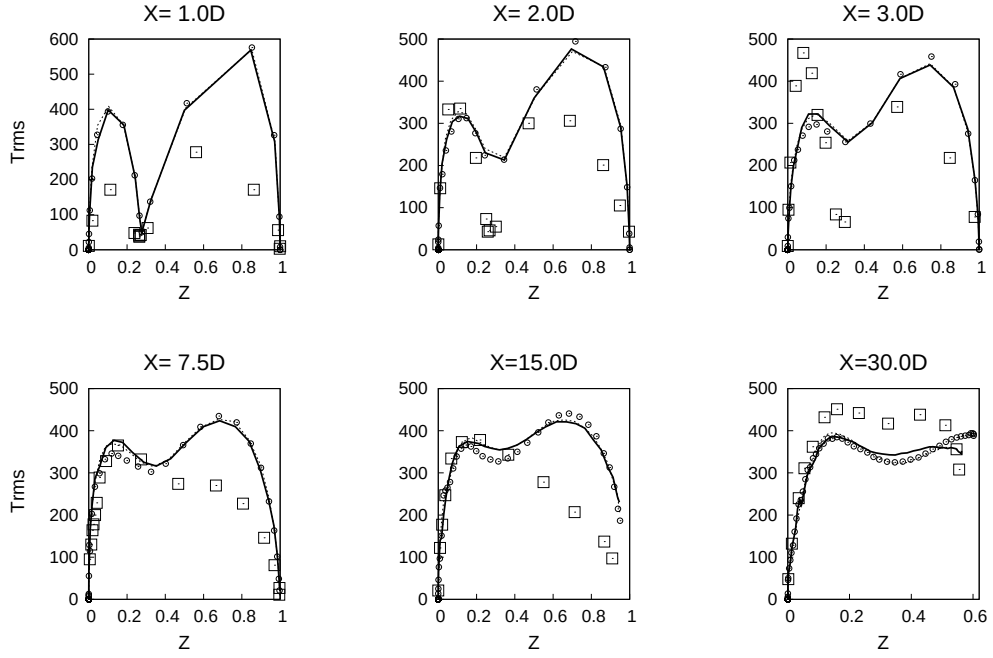


Figure 5.57: Flame F: rms of temperature in mixture fraction space. Legend as in fig (5.17) caption

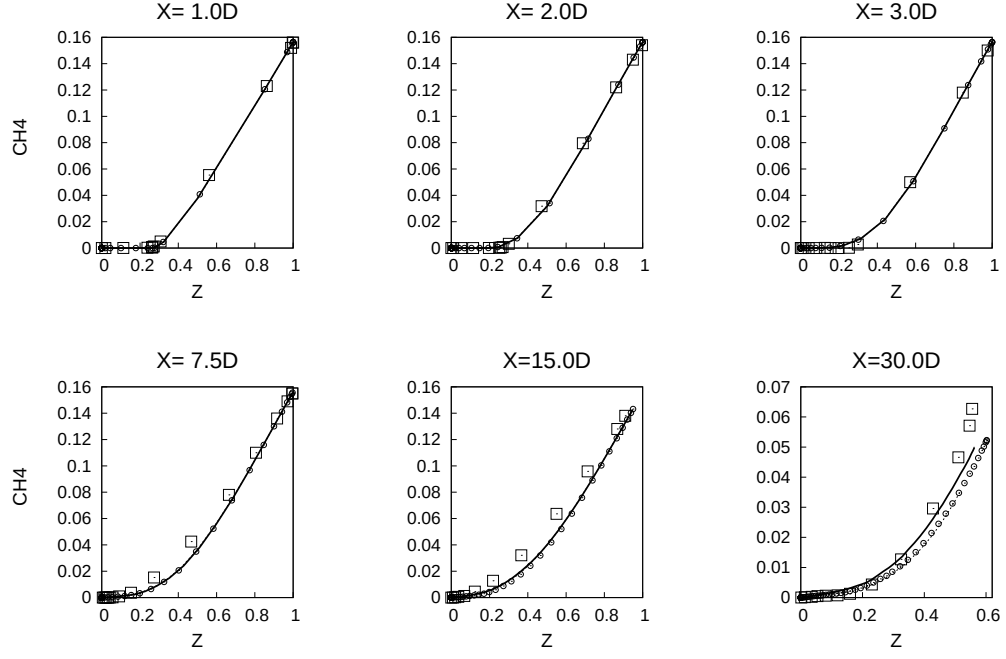


Figure 5.58: Flame F: mean mass fractions of CH_4 in mixture fraction space. Legend as in fig (5.17) caption

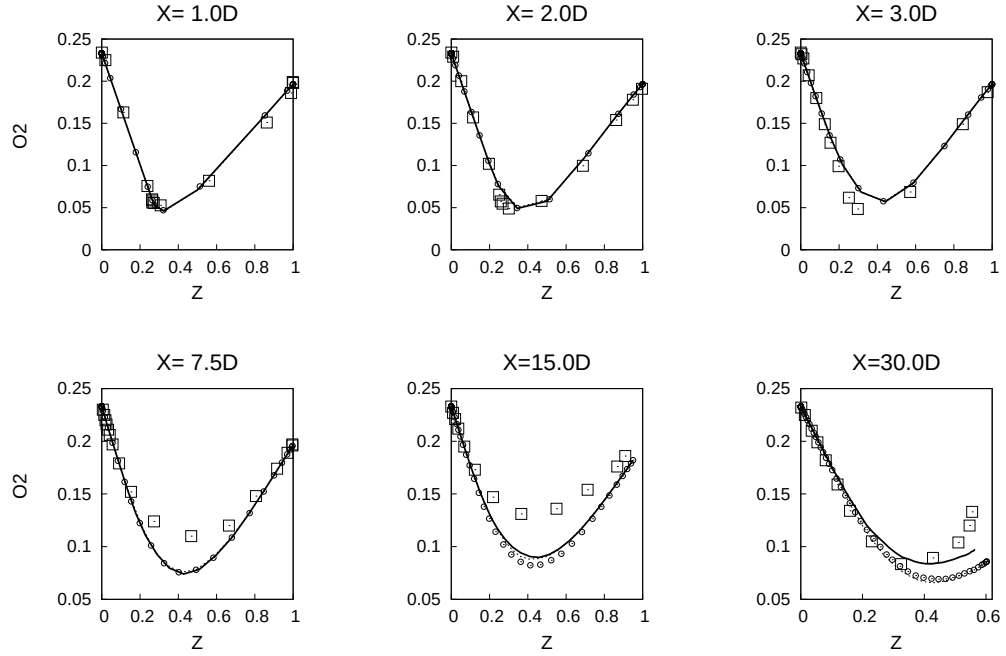


Figure 5.59: Flame F: mean mass fractions of O_2 in mixture fraction space. Legend as in fig (5.17) caption

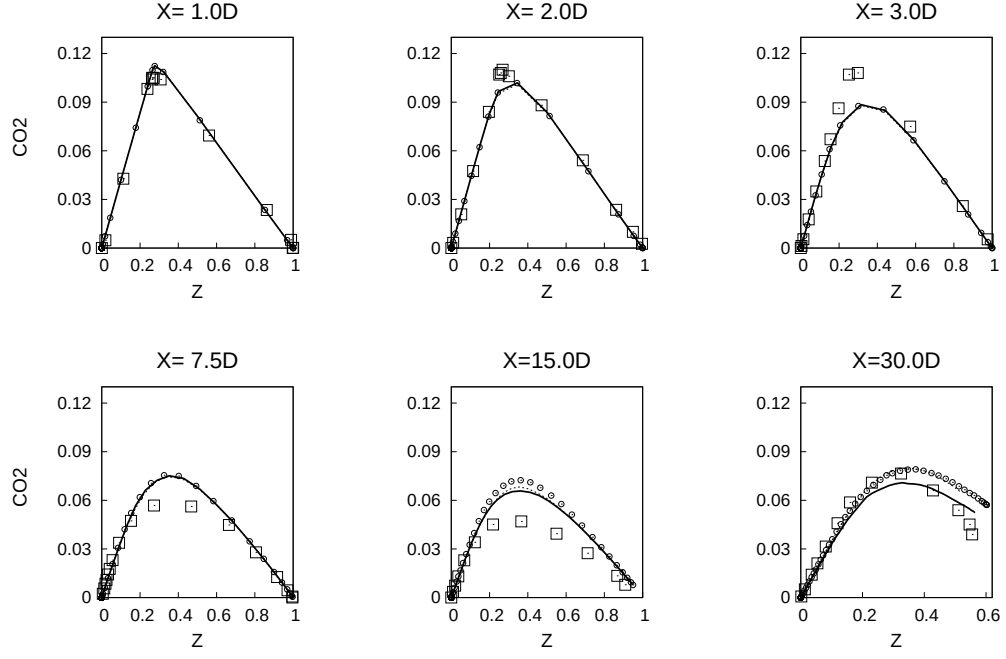


Figure 5.60: Flame F: mean mass fractions of CO_2 in mixture fraction space. Legend as in fig (5.17) caption

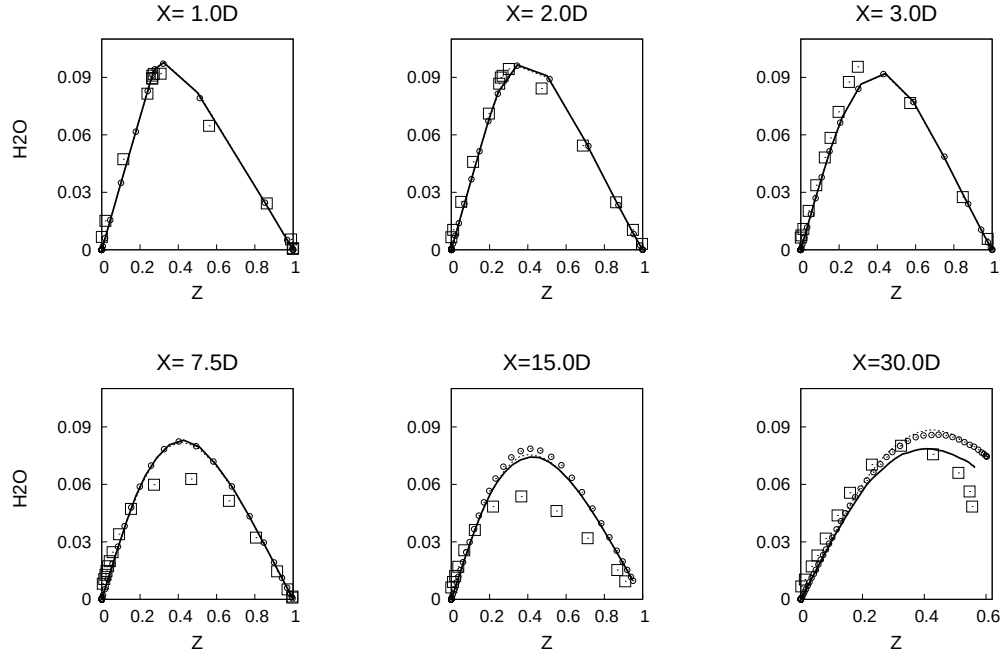


Figure 5.61: Flame F: mean mass fractions of H_2O in mixture fraction space. Legend as in fig (5.17) caption

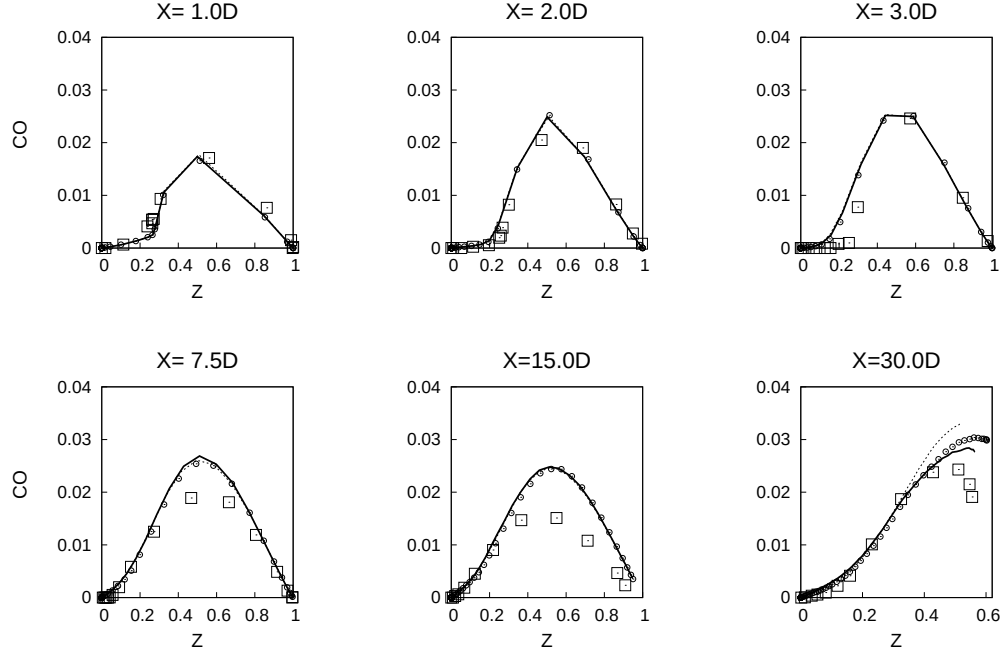


Figure 5.62: Flame F: mean mass fractions of CO in mixture fraction space. Legend as in fig (5.17) caption

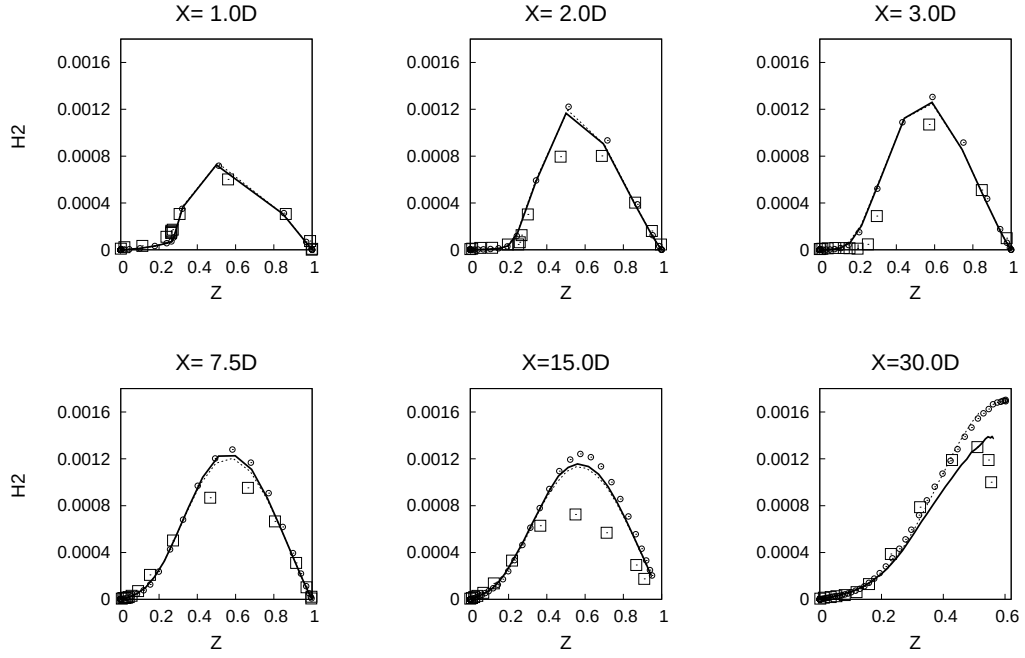


Figure 5.63: Flame F: mean mass fractions of H_2 in mixture fraction space. Legend as in fig (5.17) caption

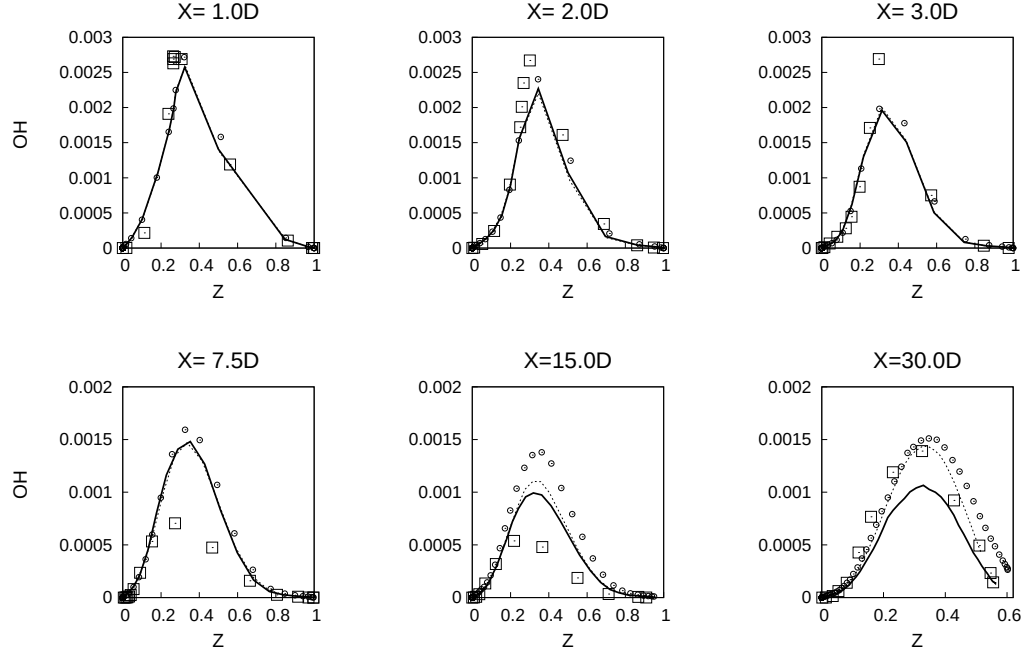


Figure 5.64: Flame F: mean mass fractions of OH in mixture fraction space. Legend as in fig (5.17) caption

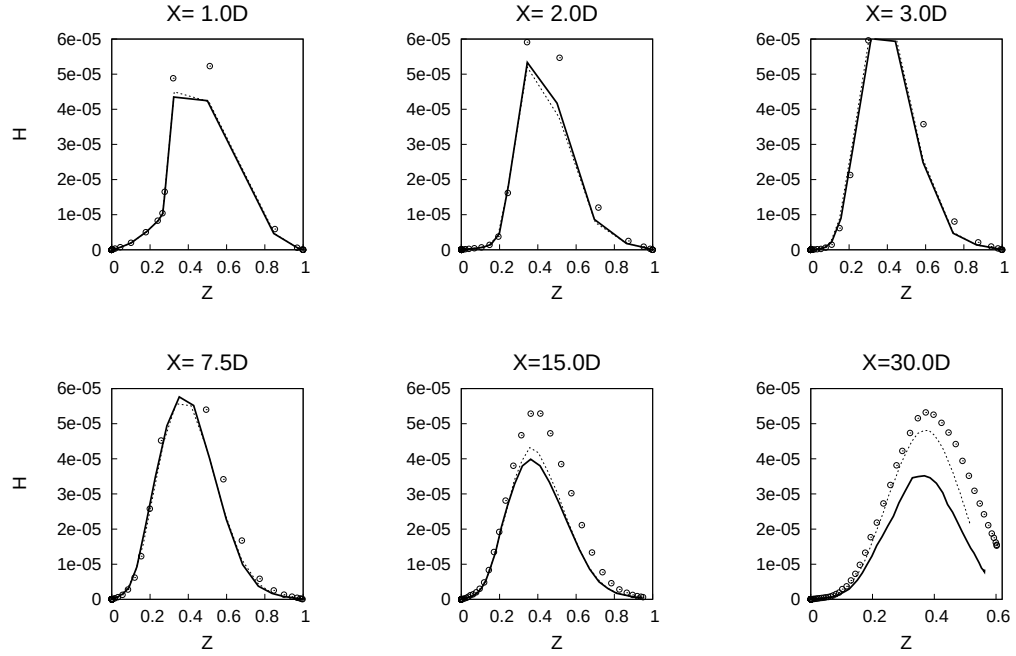


Figure 5.65: Flame F: mean mass fractions of H in mixture fraction space. Legend as in fig (5.17) caption

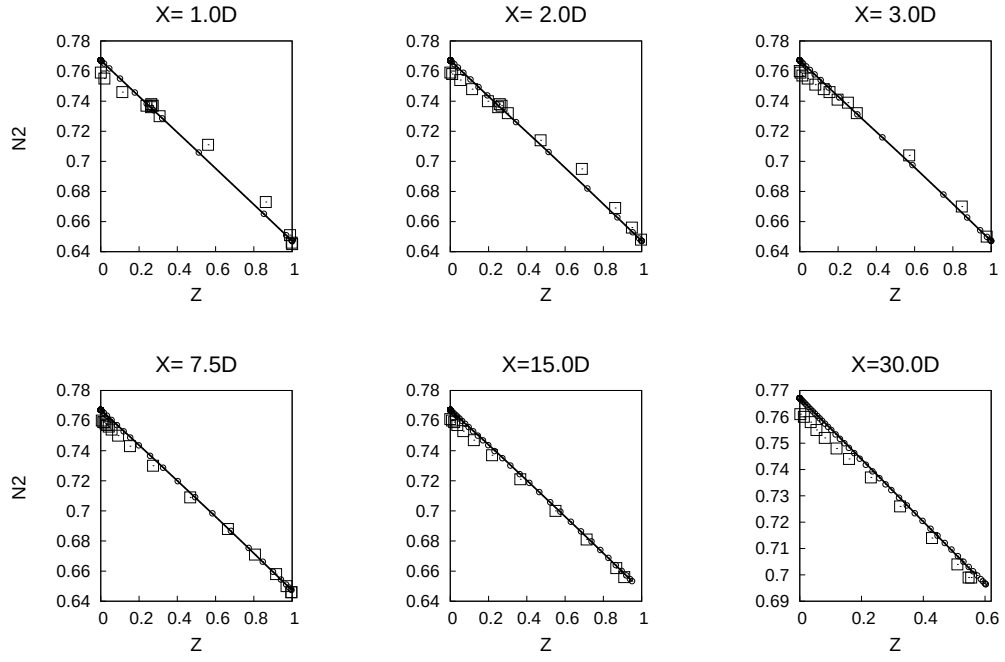


Figure 5.66: Flame F: N_2 in mixture fraction space. Legend as in fig (5.17) caption

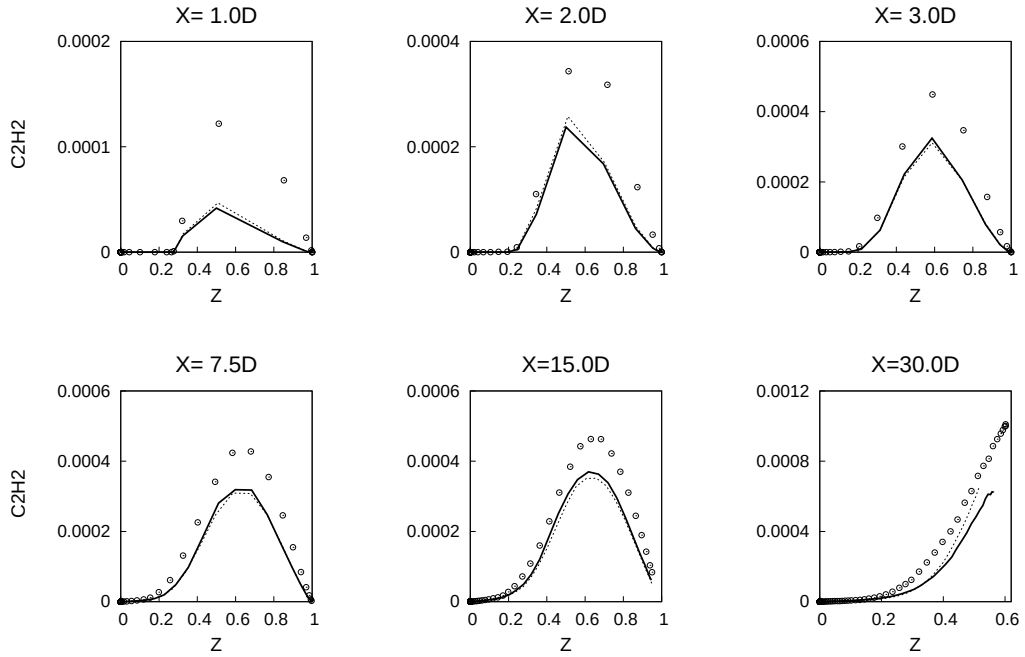


Figure 5.67: Flame F: mean mass fractions of C_2H_2 in mixture fraction space. Legend as in fig (5.17) caption

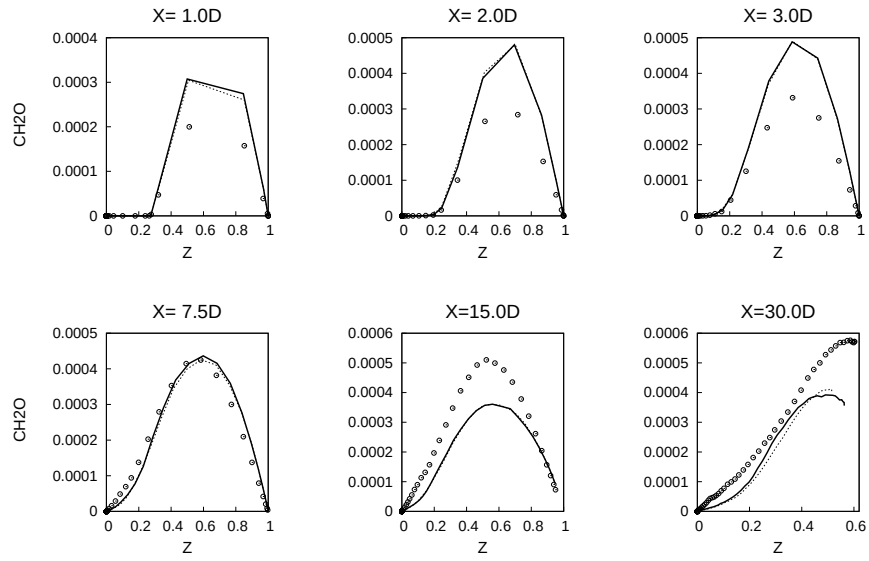


Figure 5.68: Flame F: mean mass fractions of CH_2O in mixture fraction space. Legend as in fig (5.17) caption

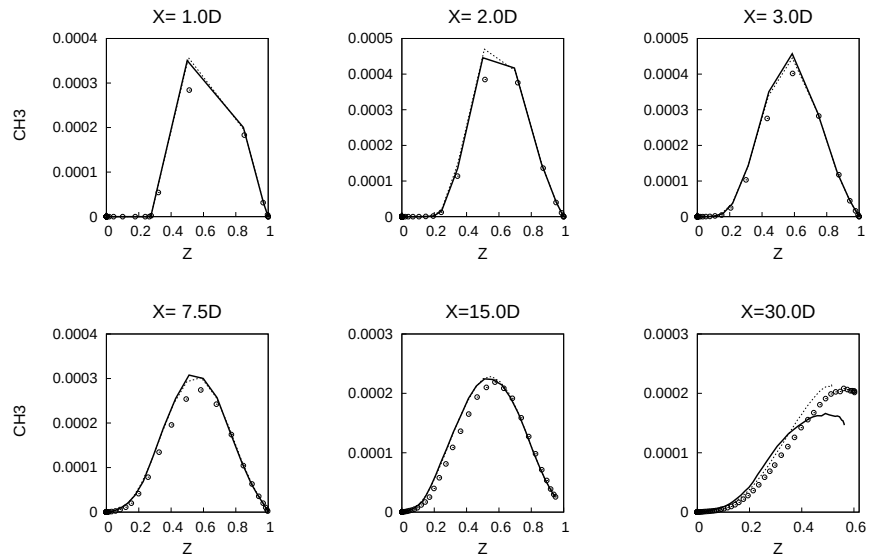


Figure 5.69: Flame F: mean mass fractions of CH_3 in mixture fraction space. Legend as in fig (5.17) caption

Chapter 6

Simulation of Soot Flames with the PDF-RCCE Method

6.1 Introduction

In this study, the combined PDF-RCCE methodology is employed to compute flames with soot formation and thermal radiation. It has been shown that PDF methods provide closure for the interaction between turbulence and gas-phase chemistry. Detailed and reduced chemical kinetic mechanisms can be coupled with the transported PDF method. This is achieved by performing the chemistry integrations directly on the compositions of Lagrangian particles in a sub-step which is separate from other processes like turbulent transport and micromixing. The methodology can be extended to incorporate the interaction with soot formation and radiative heat transfer. Models for the mechanisms of soot formation and thermal radiation need to be coupled with the PDF model to compute the source and sink terms of soot variables and enthalpy. The independent variables in the joint scalar PDF equation include gas composition, enthalpy and soot variables. In Lagrangian Monte Carlo methods, enthalpy and soot variables are assigned to notional particles in addition to gaseous composition. Gas-phase chemistry, radiation model and soot formation model compute the dynamic evolution of notional particles in the scalar space. Soot properties are subjected to the same micromixing rate as gaseous species and enthalpy. This implies that soot is assumed to have a diffusivity that is equal to the

diffusivity of gaseous species which may have considerable consequences on the prediction of soot formation.

6.2 Test Cases Configuration

In this study, experimental test cases under consideration are three turbulent jet diffusion flames. The first two flames correspond to the methane-air experiments studied by Brookes and Moss [26] which have the similar configuration and same mass flow rates but differ in the pressure. The third flame is one of the propane-air flames measured by Nishida and Mukohara [162].

6.2.1 Configuration of the methane-air flame

Two flames have been measured by Brookes and Moss and are computed here. One was carried out at atmospheric pressure and the other was operated by elevating the pressure to 3 atmospheres. The diameter of the fuel jet nozzle in the Brookes and Moss experiment is 4.07 mm. Pure methane was jetted through this nozzle into a chamber which is 155 mm in diameter and 980 mm in height. the two flames have similar fuel and air mass flow rates and thus have the same jet exit Reynolds number ($Re = 5000$). The atmospheric pressure flame ($p = 1$ atm) has an inlet bulk velocity of 20.3 m/s while the elevated-pressure flame ($p = 3$ atm) has a bulk velocity around 6.7 m/s. Fuel and air inlet temperatures are set to room temperature. The pilot is a burned fuel-rich methane-oxygen mixture with methane flow rate less than 2% of main jet flow rate and has an annular width of 0.16 mm.

6.2.2 Configuration of the propane-air flame

The propane flame configuration comprises a nozzle with 2-mm diameter through which gaseous propane was jetted into the atmospheric-pressure combustion chamber. The combustion chamber has an inner diameter of 115 mm and is 1000 mm in height. The propane flame case studied here is one of four cases studied in [162].

The four flames operated at similar overall equivalence ratio. Every two of the four flames have the same inlet mass flow rates but differed in the inlet coflowing air temperature. In this study, calculations were performed for the flame which has bulk fuel jet velocity of 30 m/s (i.e. $Re = 13000$) and air preheated to 500°C. The average coflowing air velocity is 0.96 m/s which gives the same mass air flow rate of the lower-air-temperature (50°C) flame whose air velocity is 0.4 m/s. The overall equivalence ratio Φ equals 0.6, which implies that although initial combustion reactions start in fuel-rich conditions, the flow exiting the long combustion chamber is a fully burned fuel-lean mixture. The flow at the outlet consists mainly of CO_2 , H_2O and excess air. The air preheating makes the initial fuel pyrolysis and formation of soot precursors more rapid in the fuel-rich regions (i.e. closer to the nozzle than the lower air temperature flame). Actually, it is observed that the overall rates of global combustion reactions are enhanced in the higher-air-temperature including soot formation and oxidation. Soot reaches a higher peak value at lower axial distance from the nozzle in this higher air temperature and this is followed by a rapid decay of soot and intermediate products.

6.3 Numerical Implementation

The same hybrid RANS-PDF-RCCE algorithm which has been described in section 4.5 and applied to compute Sandia flames has been employed to compute these sooting turbulent diffusion flames. RCCE reduced chemistry models were established to compute the chemical kinetics of both methane-air and propane-air flames. For methane-air flames, the RCCE models obtained from the GRI-3.0 detailed mechanism while propane RCCE models are based on the detailed natural gas mechanism of Petersen et al[171]. Brookes and Moss methane flames were computed with both the Jenny et al. [80] scheme for mean velocity interpolation and by the linear interpolation scheme while the propane flame was only computed with the scheme of Jenny et al. [80] only.

Thus the implementation is similar to the procedure for adiabatic non-sooting

flame simulations in the previous chapter. However, the number of scalars that are carried by the notional particle in the PDF-RCCE simulations of non-adiabatic sooting flame is $N_{sc} = M_c + 4$. These scalars evolve by mixing and chemical reaction and they include the ordinary $M_c + 1$ scalars transported in the adiabatic non-sooting case. Mixture fraction is a conserved scalar while the M_c chemical constraints evolve due to combustion according to the chemical kinetic mechanism. The last three scalar quantities which are added in the current simulation of sooting flames with thermal radiation are specific enthalpy h , soot mass fraction Y_{st} and soot particle number density $N_{p_{st}}$. The source term of h is computed from the radiation model (RADCAL) with an added radiation contribution for soot.

6.3.1 Generation of the grids

The grids employed here are axisymmetric with orthogonal non-uniform cells in the x-r plane of the physical cylindrical geometry of the round jet. The solution domain of the atmospheric methane flame ($p = 1$ atm) extends 600 mm axially using 80×40 grid nodes in the axial and radial direction respectively. The pressurised flame ($p = 3$ atm) extends to 370 mm only using 60×40 grid nodes in the axial and radial direction respectively. Both methane flames are simulated radially to the cylinder walls (radius = 77.5 mm). The propane flame is simulated with a solution domain that extends axially to 600 mm and radially also to the cylinder walls (radius = 57.5 mm) using 80×40 grid nodes in the axial and radial direction respectively. Fine resolution is ensured close to the nozzle and in the shear layer region and the discretisation is let to expand weakly as it progresses outwardly in the radial and axial directions. The expansion ratios are set to 1.03 and 1.06 in the axial direction and radial directions respectively.

6.3.2 Setting of the boundary conditions

For all the sooting flames studied here, the inlet axial velocity profiles were obtained from the bulk velocity using the one-seventh empirical power law. k at the inlet boundary is computed assuming 5% turbulence intensity. The scalar field at the inlet boundary is specified using mixture fraction, temperature and pressure for the

fuel and oxidiser streams. Scalar fluctuations are set to zero at the inlet. All the flames are reported to have small pilots but there is lack of information on these pilots. Methane flame experiments were stabilised using very small and fuel-rich methane-oxygen pilots. However, for consistency issues and applicability of mixture fraction formalism, the composition assigned to the pilot is a fuel-lean methane-air mixture burned to full equilibrium. The bulk velocity of the pilot is computed so that its fuel content does not reach or exceed the above limit. Despite that the size of the annular numerical pilot is relatively small, it could not be confined to the size of the actual methane-oxygen annulus since some pilot premixing with air is assumed. Similarly, the propane flame was simulated with a small pilot which burns fuel-lean propane-air mixture with fuel content that makes less than 1% of the main jet.

At the walls, an adiabatic no-slip condition is applied. Notional particles that are able to penetrate the wall boundary are reflected into the domain in a similar way to the symmetry boundary. Other boundary conditions are similar to those settings in the Sandia flames study.

6.3.3 Selection of Constraints for methane flames

The selection of optimal sets of constraints for the sooting methane flames is similar to the procedure which has been followed for Sandia flames. However, the flamelet profiles for flames with pure-methane fuel are different from Sandia flames whose fuel is partially premixed with air. No major difference was noticed in the ordering of significance of individual species between the two flamelet compositions. In addition, it has been noticed that several sets of constraints behaved similarly in the two cases. However, it is found that pure methane flamelets extinguish at strain rates that are roughly half of the extinction strain rate of Sandia composition flamelets when both are computed by the same chemistry. Brookes and Moss reported that no stable flame could be experimentally established at atmospheric pressure with Re number higher than that of the measured flame even in the presence of the pilot. Despite that the atmospheric methane flame exhibits a lower level of mean velocity

and turbulence energy than the Sandia flames, the latter burn mainly in fuel-lean situations which makes them stabilise at higher Re . This is in agreement with what has just been stated that extinction strain rates of the flamelets scale approximately by 2 between the two compositions.

The main point that one makes regarding these flames is that it is crucial for the RCCE reduced mechanism to burn at high strain rates similar to the detailed mechanism. The PDF calculations do not invoke additional assumption on the chemistry. However, it might be required that the chemical mechanism burns at higher strain rates or ignites slightly more easily to overcome the inadequacies of the transport and mixing modelling. RCCE mechanisms incorporating CH_3 as a constraint like those adopted in the previous chapter for Sandia flames did not burn in PDF simulations of these pure methane flames. Likewise, the RCCE flamelets of these sets are found to extinguish at strain rates lower than the DI flamelets. The constraint-removing feature used in Sandia flames calculations has not been applied here. Alternative sets of constraints which do not include CH_3 were tested.

The testing of RCCE sets for methane flamelets was performed by adding one or few constraints to the primary 15-constraint set. This set uses the following 15 species as constraints: CH_4 , O_2 , CO_2 , CO , H_2O , N_2 , H_2 , H , OH , O , CH_2O , C_2H_2 , C_2H_4 , C_2H_6 and CH_3OH . Additional species were used as constraints and the following three RCCE sets were chosen:

- RCCE-16: constructed from the above 15 plus HCO only.
- RCCE-18 : constructed from the above 15 plus CH_2CO , CH_2 and $\text{CH}_2(\text{s})$
- RCCE-19 : constructed from the above 15 plus CH_2CO , CH_2 , $\text{CH}_2(\text{s})$ and HCO

Figures (6.1 to 6.3) show some flamelet profiles for these RCCE models and DI of the full GRI-3.0 mechanism. The flamelet with RCCE-16 produced reasonable predictions for temperature and major species only in comparison with DI flamelets. However, it suffers from some CO discrepancy at high strain rates and it tends

to underpredict OH mass fraction. Despite of this, it has been tested with PDF simulation of the pressurised flame for comparison with the other RCCE sets. It was remarked that the RCCE-18 set showed some contrasting performance in the flamelet and PDF calculations. This set has been applied to both the atmospheric and pressurised flames. Results with the last set with 19 constraints (RCCE-19) have been obtained for the pressurised flame only. This RCCE set may give some information of the effect of adding CH_2CO , CH_2 or $\text{CH}_2(\text{s})$ to the RCCE-16 set or the effect of adding HCO to the RCCE-18 set.

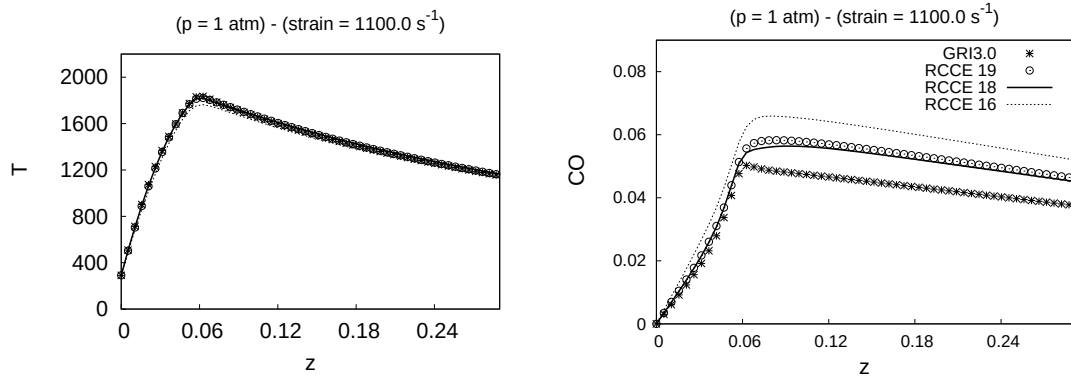


Figure 6.1: Temperature and CO mass fraction in pure methane flamelets at $p = 1 \text{ atm}$ and strain rate $= 1100 \text{ s}^{-1}$

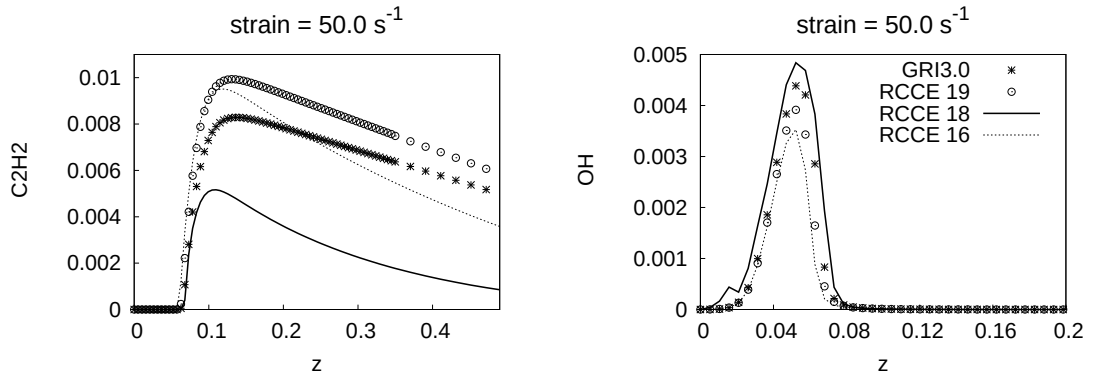


Figure 6.2: Acetylene (C_2H_2) and hydroxyl (OH) mass fractions in pure methane flamelets at $p = 1 \text{ atm}$ and strain rate $= 50 \text{ s}^{-1}$

6.3.4 Selection of Constraints for propane flames

The set of constraints for the propane flame is selected manually by a similar procedure to methane flames although the investigation was less exhaustive. From

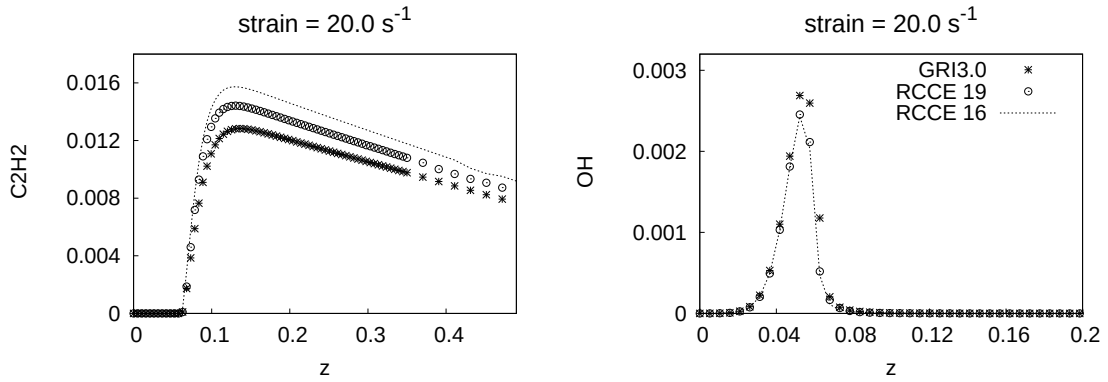


Figure 6.3: Acetylene (C_2H_2) and hydroxyl (OH) mass fractions in pure methane flamelets at $p = 3$ atm and strain rate $= 20 \text{ s}^{-1}$

flamelet direct integration (DI) of the mechanism of Petersen et al. [171], the following 35 species are identified to be the most dominant:

H, H_2 , O_2 , H_2O , OH, O, CO, CO_2 , C_3H_8 , C_2H_4 , C_2H_2 , CH_4 , C_3H_6 , C_2H_6 , CH_2CO , $C_3H_4 - p$, $C_3H_4 - a$, CH_3 , CH_2O , C_3H_3 , CH_3CHO , $C_3H_5 - a$, $HCCO$, $C_2H_4O1 - 2$, CH_3CHCO , CH_3OH , C_2H_3 , C_2H_5 , $HCCOH$, CH_2 , C_3H_2 , C_2H_3CHO , $HOCHO$, HO_2 and H_2O_2 . This set developed difficulties with PDF-RCCE methodology while a 32-constraint set which excludes HO_2 and H_2O_2 burned the flame but with high CPU time. N_2 is an inert species in this mechanism. It is not included in the constraints but the N element composition is one of the constraints. Further reduction was applied to the above list and an alternative RCCE set with 22 constraints was found to work well without experiencing considerable number of failures. The CPU time for this RCCE system was around 12 particles per second with one CPU on the College HPC cluster. The 22 constraints are: H, H_2 , O_2 , H_2O , OH, O, CO, CO_2 , C_3H_8 , C_2H_4 , C_2H_2 , CH_4 , C_3H_6 , C_2H_6 , CH_2CO , CH_2O , CH_3CHO , CH_3OH , C_2H_5 , C_2H_3 , CH_3 , $HOCHO$

6.4 Results of Brookes and Moss methane soot flame

The atmospheric flame ($p = 1$ atm) was simulated only with one RCCE set (RCCE-18) while the pressurised flame ($p = 3$ atm) was simulated with the three RCCE sets.

The structures of the flames were generally well predicted when linear interpolation scheme is applied to compute notional particle transport in physical space. The Jenny et al. interpolation scheme has the typical outcome of underpredicting the flame length. There are considerable differences in the radial profiles of the two schemes although predictions of peak values soot and temperature were comparable in the two cases. On the other hand, the Jenny et al. scheme appears to be able to reproduce the flames at $C_\phi = 2.3$ while the linear interpolation required that C_ϕ is increased to 2.5 to stabilise the flames numerically. Mean mixture fraction is not affected by changing C_ϕ unless the calculations show that the flame is completely quenched in which case a short jet is predicted. On the other hand, it is important to note that the scalar field and in particular soot are affected by the change of this coefficient due to the dominant role of mixing. The predictions with linear interpolation agree better with measurements and are presented here.

6.4.1 Results of the atmospheric methane flame ($p = 1$ atm)

The predictions of the atmospheric pressure flame are shown in the figures (6.4 - 6.10). The centreline profiles in figure 6.4 and radial profiles of mean mixture fraction in figure 6.5 and mean temperature in figure 6.6 imply that the structure of the flame is reasonably reproduced.

Profiles of mean mixture fraction (figure 6.5) show reasonable prediction of the jet flame spreading. The flame length is accurately predicted. This also agrees with the statement of Brookes and Moss [26] that the visible length of the flame is about 600 mm since the present results show that centreline mean mixture fraction drops to 0.02 at this location. The radial profile at 150 mm show overprediction of mean mixture fraction on the centreline but this improves significantly at higher distances from the nozzle. The location of stoichiometric composition on the centreline is well captured. On the other hand, radial profiles of mean mixture fraction and all other variables show underprediction of the radial spread rate of the flame. This appears to be opposite of what the LES-CMC calculations in [159] suffered from which seem to overpredict the flame length while capturing the radius of the flame well. The prediction of flame spreading in the axial and radial directions are strongly depen-

dent on the implementation of the particle motion model and its inputs from flow field calculations. Chemistry can also have an effect on this but this is limited to how much the density field can be modified by the chemistry change.

Good predictions of mean temperature are shown in figure 6.6. This implies that the radiation model gives reasonable estimation of radiative heat emissions. At low axial distances (less than 250 mm), values of mean temperature are slightly under-predicted on the centreline while good agreement is achieved in the reaction zone and in the fuel-lean side. This is probably due to overpredictions of mean mixture fraction on the centreline.

In general, RADCAL model for thermal radiation loss appears to be appropriate in this flame which exhibits an optically-thin character. The radiative loss term by soot also leads to a reasonable temperature reduction. However, the underprediction of mean temperature observed in the 425-mm profile may be attributed to the peak soot values in this region which may result in radiation loss rate higher than the practical rate.

The soot volume fraction predictions of this flame are reasonable. In conformity with measurements, very negligible soot values have been predicted in the lower region of the flame (i.e. $x < 300$ mm). It appears that soot is mainly predicted later but in the fuel-rich regions. The centreline value is well predicted in the middle profile ($x = 350$ mm), underpredicted in the lower location ($x = 300$ mm) and overpredicted in the higher location ($x = 425$ mm). In addition, present soot profiles extend radially to a considerably lower radius than the measurements. The latter observation in the present soot predictions has also appeared in other predictions such as [111] where similar RANS and soot models were used.

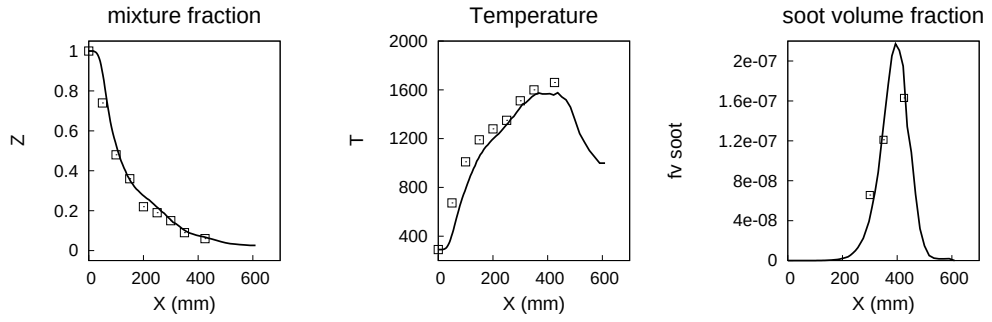


Figure 6.4: centreline profiles of mean mixture fraction, mean temperature and mean soot volume fraction for the flame with ($p = 1$ atm). Legend: squares :measurements, line: RCCE-18

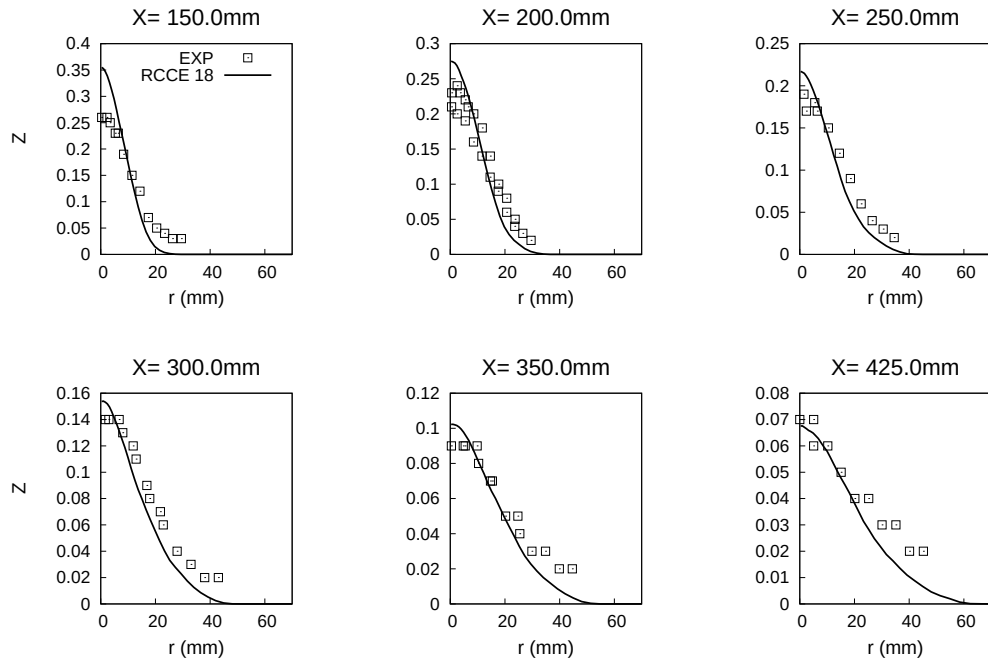


Figure 6.5: mean mixture fraction for the flame with ($p = 1$ atm). Legend is on the (150-mm) plot and as in caption of figure (6.4)

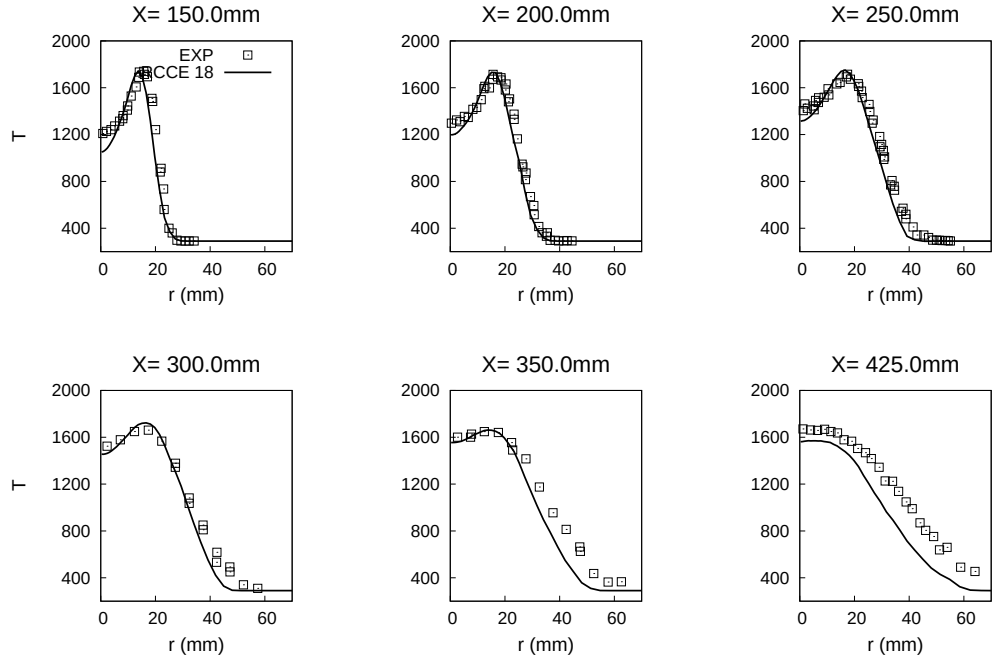


Figure 6.6: mean temperature for the flame with ($p = 1$ atm). Legend is on the (150-mm) plot and as in caption of figure (6.4)

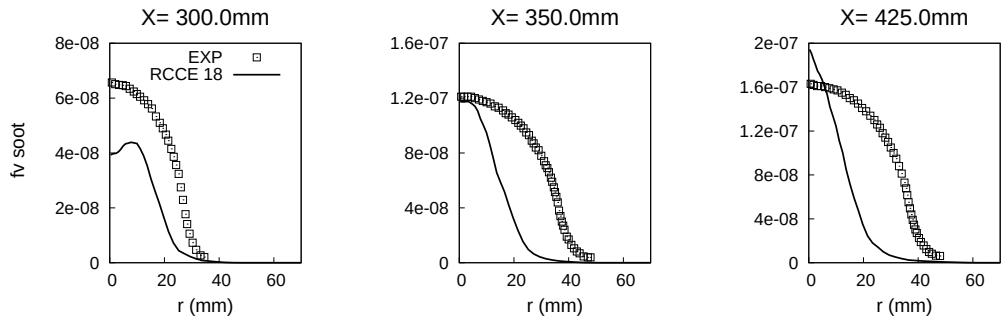


Figure 6.7: Radial profiles of soot volume fraction for the flame with ($p = 1$ atm). Legend is on the (150-mm) plot and as in caption of figure (6.4)

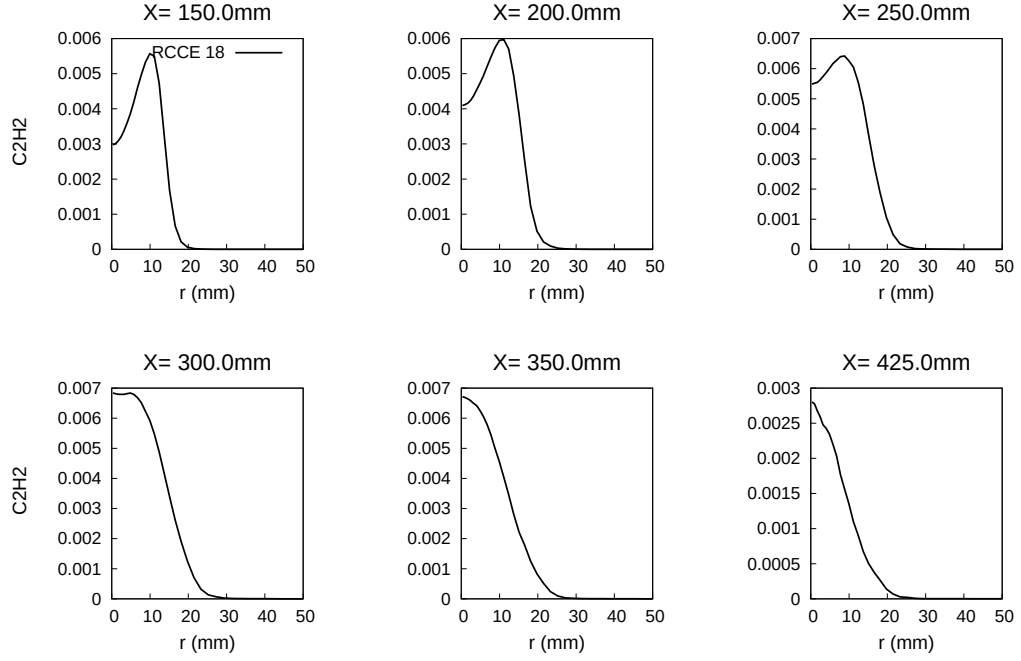


Figure 6.8: mean C_2H_2 mass fraction with RCCE-18 for the flame with ($p = 1$ atm)

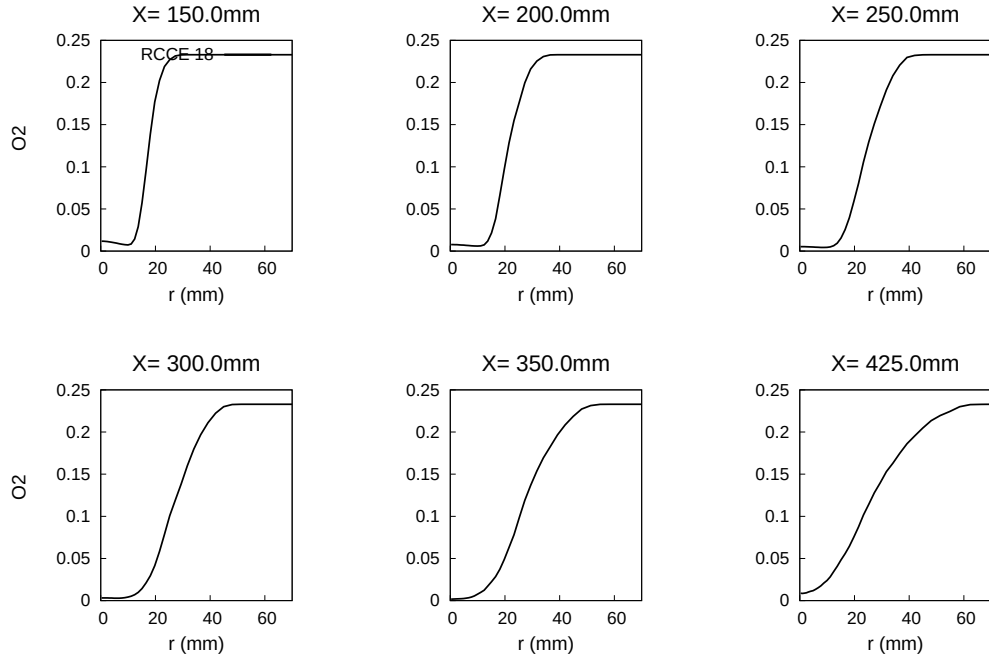


Figure 6.9: mean O_2 mass fraction with RCCE-18 for the flame with ($p = 1$ atm)

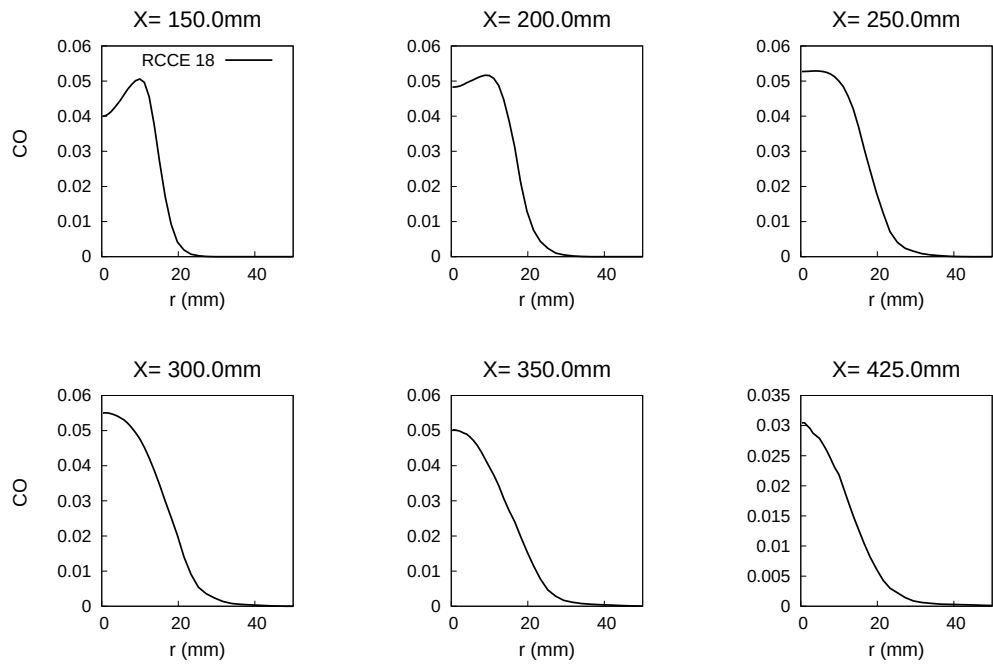


Figure 6.10: mean CO mass fraction with RCCE-18 for the flame with ($p = 1$ atm)

6.4.2 Results of the pressurised methane flame ($p = 3$ atm)

This flame has been simulated with the three RCCE mechanisms which have been listed in Section 6.3.3. The structure of this jet flame is reproduced with good agreement with experimental results. Brookes and Moss [26] reported that this flame has a visible length about 400 mm. The results show that mean mixture fraction on the centreline reaches stoichiometry (i.e. $z = 0.055$) at approximately 300 mm and drops to 0.03 at approximately 350 mm. Temperature profiles also support that the flame length is well predicted. The three RCCE models produce similar temperature profiles which are in good quantitative consistency with measurements.

As the usual observation, high levels of soot are predicted in the fuel-rich side of the reaction zone where temperature is high. The peak measured value is well predicted by some of the RCCE models. The early burning region closer to the nozzle do not show large amount of soot as they are just initial nucleation regions of soot. Similar to the atmospheric flame, soot volume fraction profiles show that measured soot forms earlier and extends to the stoichiometric regions while the calculations indicate faster depletion of soot at lower radial distances. For example, the predicted soot drops to 2×10^{-7} at radii 10 to 20 mm while in the measurements this soot level corresponds to radii 20 to 30 mm depending on the axial location. Despite that some soot is predicted close to stoichiometric axial locations (i.e. 300 mm to 350 mm), there is considerable underpredictions in these locations.

To assist in the interpretation of these soot predictions, it is important to recollect that soot formation interacts with turbulence, gaseous chemistry and radiation. The dependence of soot on gaseous species (precursors and oxidisers) and temperature is explicitly incorporated in the soot model. The interaction between soot and turbulence is incorporated by the PDF model. Fluctuations of temperature and gaseous species influence the dynamics of soot formation process. Coupling between soot and temperature is more complicated since temperature appears in both soot production and oxidation models and it is the most affected quantity by radiative emission. Thus, while more soot is produced at higher temperatures, oxidation rates

are also enhanced if temperature is increased. On the other hand, high soot levels leads to considerable temperature reductions from the adiabatic values.

There are no measurements of gaseous species and no direct integration calculations have been performed for these flames. Therefore, the accuracy of the RCCE chemistry and its consequent effects on soot predictions can not be confidently assessed. However, qualitative analysis can be done on the whole set of results. First, the soot model employed here is a simplified model and the level of accuracy achieved here is reasonable with respect to the details incorporated in this model. Particle number density can be predicted by this model but no information is contained in it on the particle size distribution.

The observed faster depletion of predicted soot might be attributed to higher soot oxidation rates in these high temperature regions. However, the possibility that lack of acetylene in these regions leads to underprediction of surface growth rate can not be excluded as well. For instance, although the RCCE-18 predicts higher C_2H_2 at 150 mm axial distance, its soot volume fraction profile is thinner and has lower peak than in the RCCE-16. Since the two temperature profiles are indistinguishable from each other, it must be the higher OH levels in RCCE-18 which is causing stronger soot oxidation rate. The actual correct concentrations of C_2H_2 and OH are not known to verify the performance of either of the RCCE models. It appears to be typical behaviour for RCCE mechanisms which use HCO as a constraint to produce lower levels of OH as the RCCE-18 which does not include (HCO constraint which predicts the highest OH among the PDF calculations).

The PDF predictions of major species like O_2 and CO show strong agreement between the RCCE-18 and RCCE-19 mechanisms while there is some discrepancy in the RCCE-16 mechanism. The discrepancies in other averaged species between the predictions of the PDF-RCCE calculations and RCCE-flamelet calculations differ from a species to another. For instance, the peak mass fraction of C_2H_2 is also higher in flamelets but CO levels are comparable.

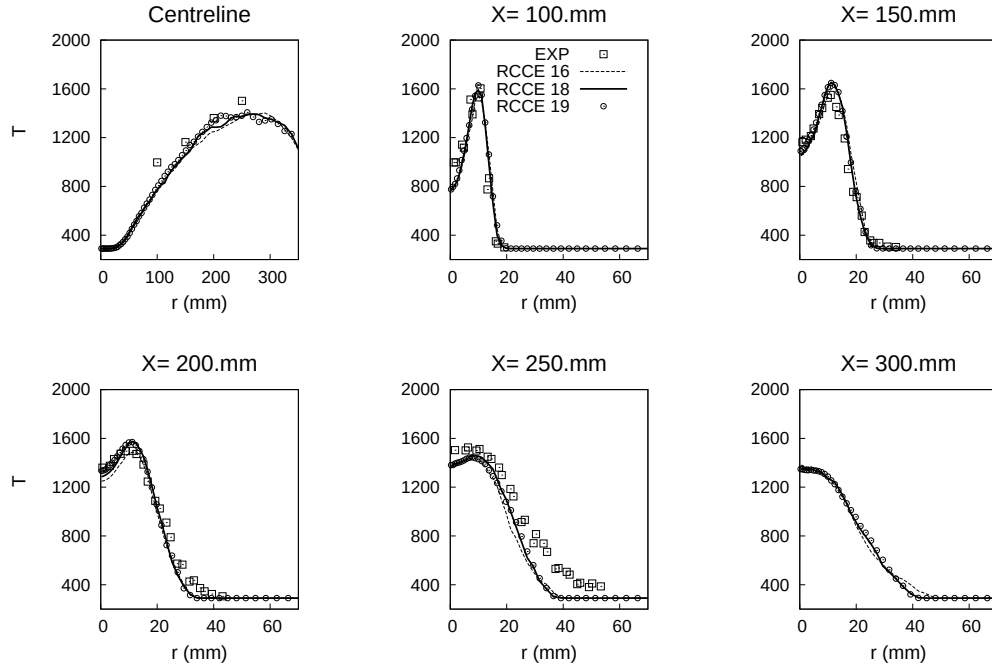


Figure 6.11: radial profiles of mean temperature for the flame with ($p = 3$ atm). Legend: dashed line: RCCE-16 , solid line: RCCE-18, small circles : RCCE-19, squares :measurements

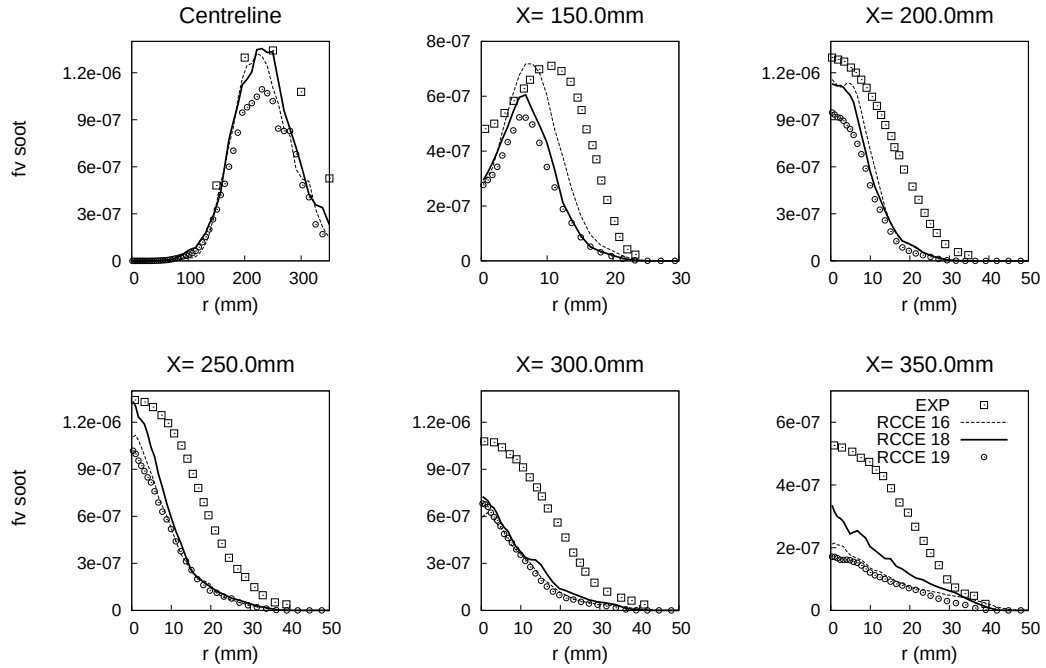


Figure 6.12: radial profiles of soot volume fraction for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11)

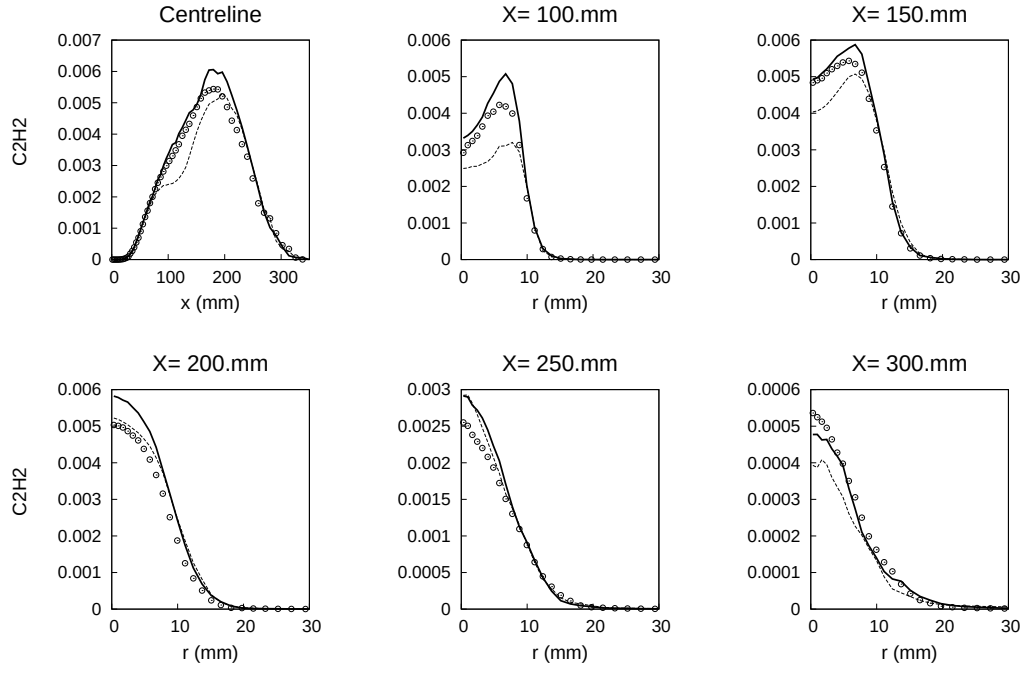


Figure 6.13: C_2H_2 mass fraction for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11)

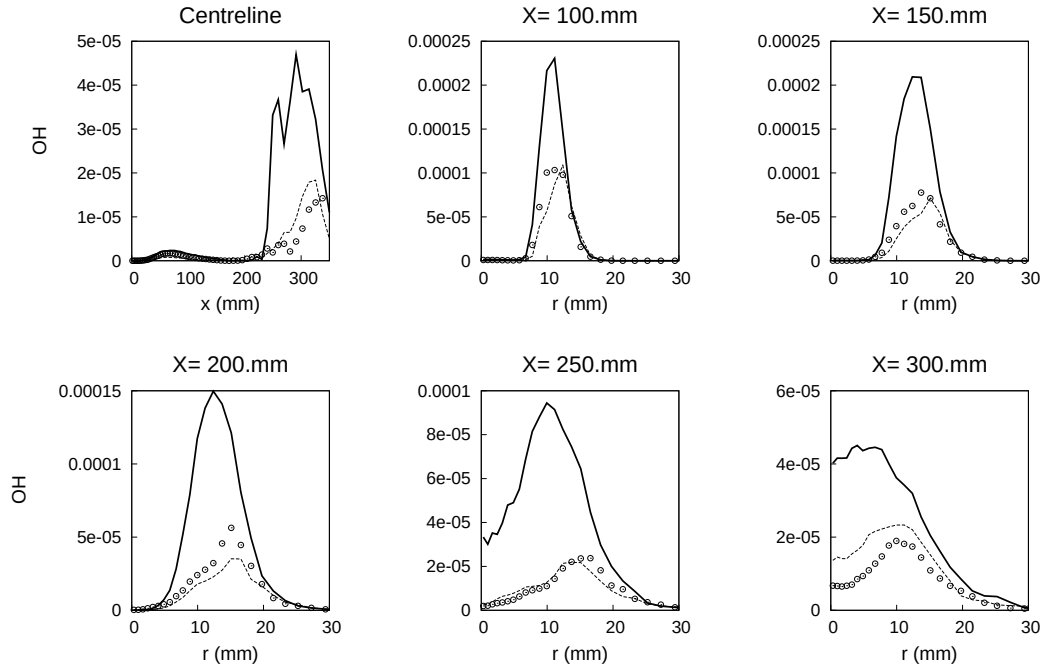


Figure 6.14: OH mass fraction for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11) caption

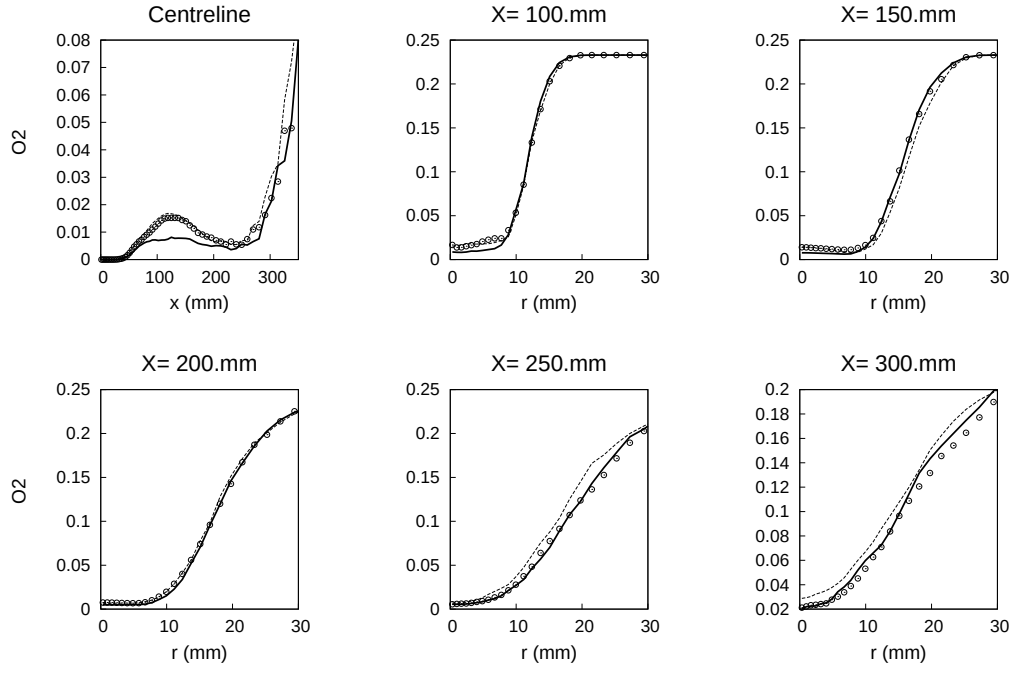


Figure 6.15: O_2 mass fraction for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11)

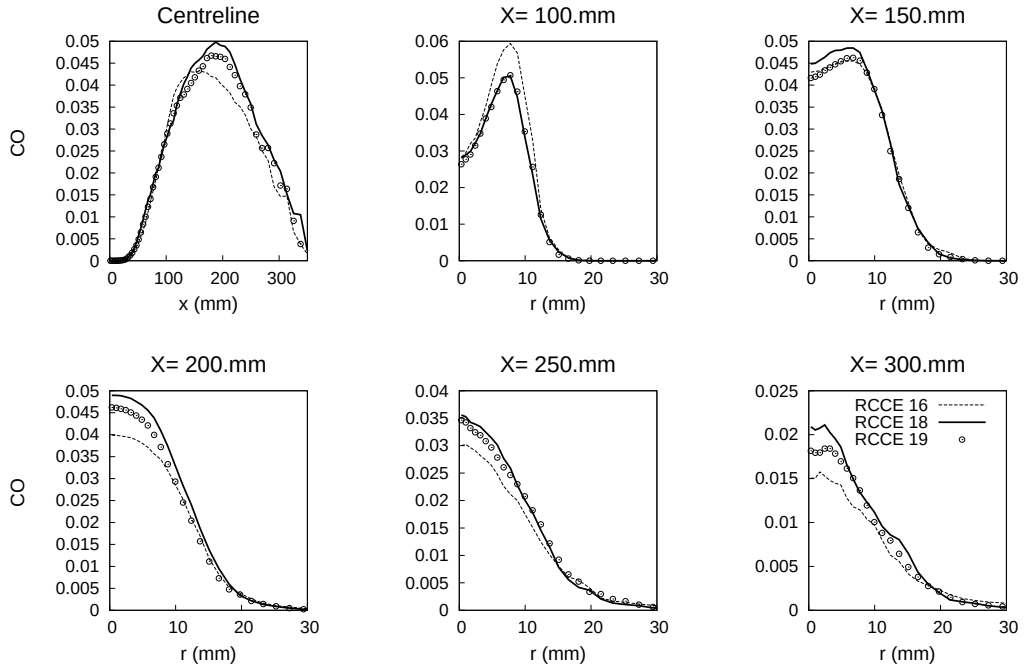


Figure 6.16: CO mass fraction for the flame with ($p = 3$ atm). Legend is on 300-mm profile here and as in caption of figure (6.11)

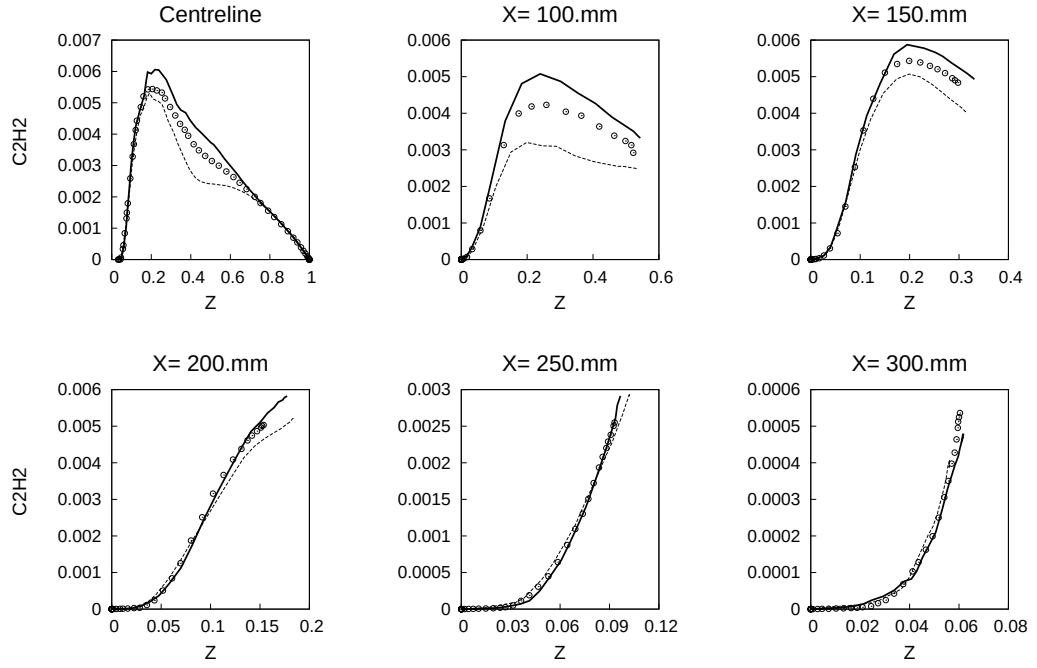


Figure 6.17: C_2H_2 mass fraction in mixture fraction space for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11)

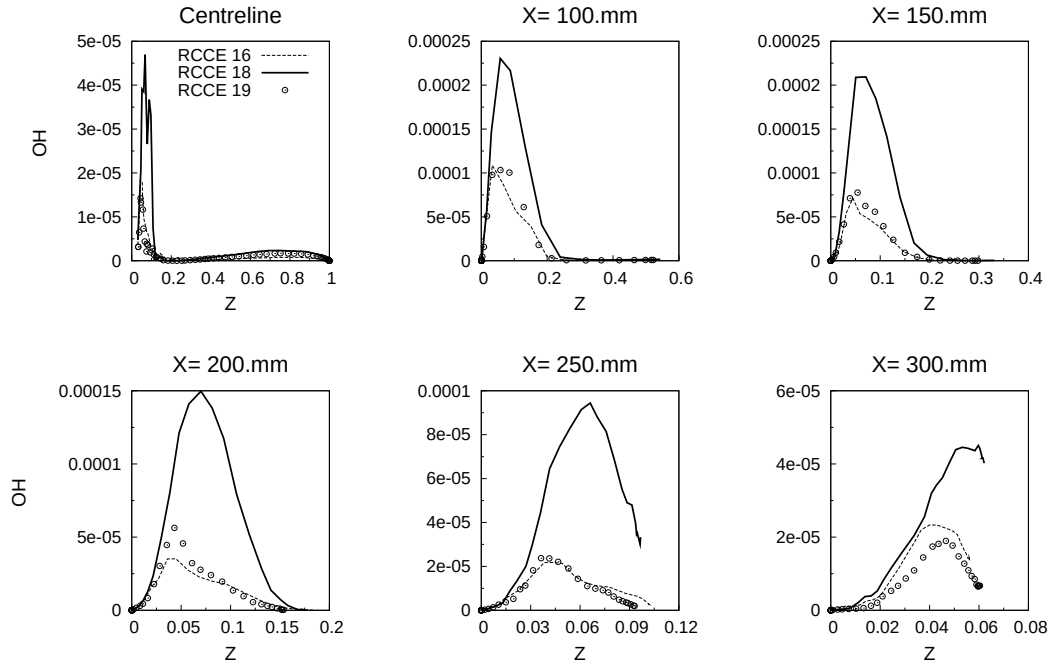


Figure 6.18: OH mass fraction in mixture fraction space for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11)

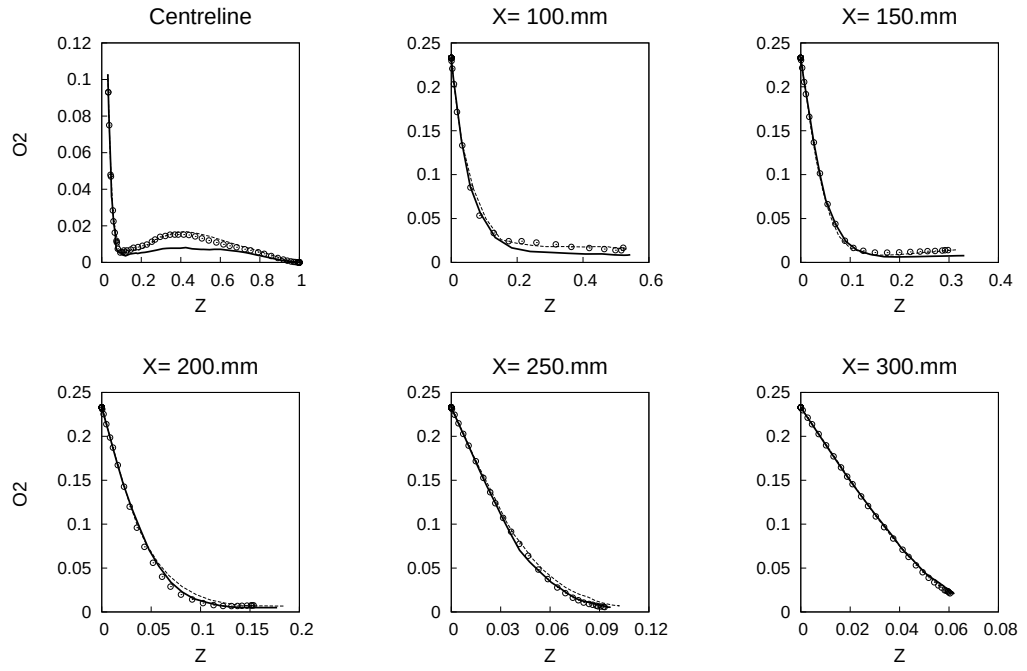


Figure 6.19: O₂ mass fraction in mixture fraction space for the flame with ($p = 3$ atm). Legend as in caption of figure (6.11)

6.4.3 Comparison with previous studies

The atmospheric flame has been computed in more studies than the pressurised flame. Examples of studies which presented soot predictions of the first flame are the RANS computations in [203, 111, 229, 234] and the LES computations in [159]. From these studies, only three RANS studies [203, 111, 229] presented soot results for the pressurised flame. Most of these results employed the CMC combustion model but the scalar PDF model was used in [203]. In general, the results presented for these flames are reasonable. However, like other studies, they still need considerable improvements in soot predictions.

Most of the computations of these methane flames share the fact that mean mixture fraction and mean temperature are in better agreement with measurements than soot predictions. In particular, flame length, location of stoichiometric mixture and peak temperature are well predicted in these simulations. The linear interpolation of notional particle velocity in the PDF algorithm produced the correct lengths of these methane soot flames. On the other hand, the centreline value of the mean mixture fraction at $x = 150mm$ in the atmospheric flame was relatively overpredicted in comparison with other studies of this flame. In spite of the early overprediction of mean mixture fraction, the profile improves at higher distances while several other studies overpredict the flame length.

The study of Stoellinger and Roekaerts [203] used the RANS-PDF method for these two flames. However, their methodology differs largely with this RANS-PDF study. In particular, they employed the Reynolds stress model for the flow field. Their scalar PDF model included only five independent variables which include the mixture fraction, progress variable, enthalpy and the two soot variables. Gaseous chemical composition was obtained from tabulated flamelet chemistry which are parametrised by the first three mentioned independent variables. Heat loss effects were included in their tabulated flamelet library to ensure that effects of radiation losses on chemical composition are accounted for. In terms of the results, radial profiles were not included and their axial profiles showed comparable level of accuracy

to the results of the present study and some CMC results which are cited here.

Despite the discrepancies in the 1 – atm flame predictions, the profiles are better than predictions with equal-diffusivities CMC calculations in [111, 229, 159]. The CMC simulations in [111, 229] as well as [234] employed similar level of turbulence closure (i.e. RANS $k - \varepsilon$ model) to the current study, though with more comprehensive chemical mechanisms. The present RCCE chemistry model is comparable to the RCCE model employed in the LES-CMC calculations reported in [159] although their RCCE reduction was applied to a different detailed mechanism involving 63 species. The soot and radiation models used here are similar to the models used in these CMC studies apart from the fact that benzene was used in [229, 234] as an additional nucleation species. This indicates the merits and advantage of the transported PDF model over the CMC model. CMC computations with no differential diffusion commonly gave severe underpredictions of soot levels while including differential diffusion [111, 229, 234, 159] resulted in restoring higher levels of soot which are in better agreement with measurements. Thus, it is often concluded that these improvements are merited because of the consideration of differential diffusion. However, the amount of disagreement in the current PDF computation is comparable to those CMC computations with differential diffusion. It is noted that good soot levels are only produced near the centreline which vanish at lower radial distances both in the current PDF study and most CMC predictions cited above. The study of Yunardi et al. [234] indicated strong sensitivity of soot formation to temperature predictions and the inclusion of benzene in the soot mechanism. All of the mechanisms in the later study were detailed and comprehensive but some of them like the GRI-3.0 do not include the mechanism of benzene formation which cancels the step of soot nucleation by this species.

Discrepancies are also observed in the present and other soot predictions of the pressurised flame. However, it might be seen that the two CMC calculations with differential diffusions provided better soot predictions over the present PDF computations at some locations. On the other hand, profiles of mean temperature in

the current study and the said CMC computations of this flame are all in good agreement with measurements.

6.5 Results of Propane soot flame

The propane flame described in Section 6.2.2 is calculated using the same RANS-PDF-RCCE methodology which has been used for methane flames. The RCCE model has 22 constraints. The same soot and thermal radiation models employed for methane flames have been used for this propane flame with a modification to the radiation model. This modification is to extend the radiation model to account for the contribution of C_3H_8 to radiative emissions which is taken from [218] and has a similar polynomial form of the emissions from other gaseous species in the RADCAL model [72]. Discussion of results with the RCCE chemistry reduction are presented and discussed in the following subsection and then a comparison with other calculations of the flame follows in another subsection.

6.5.1 Discussion of results

The results of this flame are plotted against the measurements of Nishida and Mukohara [162] in the figures (6.20) to (6.28). The length of the flame can be deduced from the mean mixture fraction or equivalence ratio on the centreline in figure (6.20). The data shown as the experimental mixture fraction are computed from the centreline Φ data in [162] which is also shown on the right. Despite the fact that N_2 is inert and conserved in the chemical reaction, mean mixture fraction can not be computed from its mole fraction. The reason for this is the appearance of the total number of moles in the relation which is strongly modified by chemical reaction. The flame length defined by the location of the stoichiometric composition (i.e $\Phi = 1$ or $z = 0.0604$) which is approximately 360 mm is well predicted by the calculations. However, more downstream of this location, the calculations predict the flame tip to vanish steeply compared to the measurements. As a result, the model does not

predict the flame to reach the end of the solution domain (i.e $x = 600\text{mm}$) while the measured flame showed combustion products reaching the end of the chamber. This is a typical outcome of the Jenny et al. scheme for velocity interpolation employed in the current calculations. When this scheme was replaced with the linear interpolation scheme in the study of methane flames, the flame length predictions was reproduced very well. Luckily the region where dominant combustion reactions and soot formations take place (i.e. $100 < x < 400 \text{ mm}$) has good mixture fraction predictions on the centreline.

The predictions of major species (CO_2 , H_2O , O_2 , N_2 and CO) are in qualitative agreement with the measurements. The reasons of the discrepancies are known in some locations and not known in other locations. An estimations of the error in the species measurements was not provided. The predicted mole fractions of all gaseous species are computed from their respective specific mole numbers using equation (2.8). Part of the error in the computed species mole fraction could come from the estimation of the total number of moles. The mole fraction of CO_2 is well predicted upto the stoichiometric location after which there is a jump up and steep drop to zero in the calculations. The composition downstream of stoichiometry where the combustion is complete is mainly a mixture of CO_2 , H_2O and N_2 and there are very small concentrations of other species like O_2 , CO and H_2 . The downstream steep drop is the result of predicting shorter flame as seen by the steep decay of mean mixture fraction. Similar issue in the centreline H_2O profile is also noticed. There is a further issue in the centreline profile of H_2O which is predicting lower value for the mole fraction in the upstream fuel-rich region. The measured high H_2O mole fraction close to the jet nozzle could be due to tendency of the flame to burn back to these close locations. However, it is acknowledged that z and Φ show a delay in the entrainment of the oxidant into the jet axis. This is also evident form the centreline profiles of O_2 and N_2 . The radial profiles of these major species are in reasonable quantitative agreement. They show good radial spread rate of the flame at 100 mm. The predicted profiles at 300 mm show that mole fraction are in better agreement on the centreline than in the outer fuel-lean side of the flame. Downstream of this

location, the calculations show a relatively sharp edge of the flame and underpredict the flame spreading towards the side walls and outlet of the chamber.

The agreement in the CO axial and radial profiles (figure 6.25) are quite encouraging and gives indication of reasonable success of this RCCE mechanism. Now we look into the predictions of some minor intermediate species. Acetylene is the most dominant intermediate hydrocarbon species formed during the combustion of this flame. It is the only soot precursor in the soot model employed in this study. The predictions of acetylene C_2H_2 mole fraction (figure 6.26) are also reasonable although the centreline profile and the radial profile at 100 mm show considerable underpredictions of C_2H_2 in these regions where strong soot growth rates are supposed to occur. The mole fraction of C_2H_2 is overpredicted at 300 mm possibly as consequence of a slight overprediction of mixture fraction. The H_2 mole fraction (figure 6.27) is overpredicted by 50% to 100% on the centreline between 100 and 300 mm downstream of the nozzle. This coincides with less significant overprediction of CO mole fraction and underprediction of C_2H_2 .

Soot predictions are not in good agreement with the measurements. The peak predicted value of soot mass per unit volume of the gaseous mixture is about 40% of the measured peak. Despite the severe discrepancy, both the predicted and measured profiles follow similar trends. Soot is formed in the heated fuel-rich regions and soot levels extend radially and axially to the burning zone. The major underprediction of soot at 100 mm imply that a delay has occurred in the formation of soot which may result from C_2H_2 underprediction at this location or at upstream locations. If C_2H_2 is not produced early enough or underpredicted in the near-field regions of the flame, low nucleation rates would result in underestimation of soot surface area available for growth reactions later. The OH concentration is not measured and its influence in this region can not be quantified. Small growth of soot is also predicted on the 200-mm profile. On the other hand, strong growth rates are predicted in the 200 to 300 mm particularly in the near-centreline region as we can see that soot levels has increased nearly 3 times. Measurements, show slight decrease in soot peak in this region indicating that soot growth reactions are actually accompanied

by competing oxidation rates. In the stoichiometric region (300-400)mm from the nozzle, a decay in soot is observed in both measurements and predictions since oxidation of soot occurs predominantly in this region. Oxidation is enhanced by the high temperature and high OH concentrations in the burning zone and by the bulk amounts of O_2 in the fuel lean regions.

The profiles of mean temperature are generally overpredicted. Discrepancies in major species are known to affect the calculation of temperature. However, it looks here that the underprediction of soot levels is the main reason for the significant temperature overprediction. This is because radiation by soot constitutes the major source for heat losses and the decrease of combustion temperature.

6.5.2 Comparison with previous calculations

The results presented in the previous subsection for the propane flame with air preheat to 773° K are assessed against results of previous studies. The studies used in the comparison include the RANS-CMC computations of Woolley et al. [229] (with and without differential diffusion), the LES-CMC of the Navarro-Martinez et al. [160], LES-flamelet of Paul et al. [167, 168] and the early RANS-flamelet of Fairweather et al. [55]. With regard to gas-phase chemistry, detailed chemical schemes for propane were employed in [229, 167, 168] while several RCCE reduced chemical schemes were employed in [160]. Soot is computed with semi-empirical modelling in all these studies but there are some differences in the rates of reaction steps. For instance, the soot model coupled with the LES-flamelet in [168, 167] as well the RANS-flamelet [55] calculations expressed the surface growth term to be proportional to the square root of surface area and did not account for OH oxidation. The RANS-CMC [229] study, on the other hand, added benzene as a nucleation species in addition to acetylene.

Overall, it can be realised that discrepancies with measurements in all of the computations of the propane flame are larger than in Methane flames even in mean temperature. Flame shape is reasonably predicted here and in most other studies as can be deduced from centreline profiles of $\tilde{z}$ and Φ as well as from centreline and radial profiles of $\tilde{T}$. Other computations did not show sudden vanishing of the flame

at $500mm$ height (at least not as severely) as observed in the present computations with the Jenny et al. scheme for particle velocity. This would be probably avoided if a different interpolation scheme is used. Despite the disagreement with measured temperature in several profiles in most of the studies, only present computations showed considerable overpredictions of peak temperature.

Among the above cited studies, soot predictions have been presented in [55, 168, 229]. As it has been mentioned that discrepancies are large in some locations. The RANS-CMC calculations with differential diffusion appear to offer improved predictions over their equal-diffusivities counterparts and present RANS-PDF calculations. There appears to be shifting in the soot formation region in the RANS-CMC computations that the downstream profile (at $x = 400mm$) show considerable overprediction with differential diffusion.

The profiles of gaseous species have been presented previously in the LES studies [167, 160] but O_2 and C_2H_2 profiles were presented by Fairweather et al. [55] who employed a second-moment closure for turbulence. The RANS-flamelet [55] and the LES-flamelet [168] showed considerable disagreement in gaseous species profiles as well. The weakness in soot predictions in [168, 167] were linked to those in C_2H_2 and O_2 profiles but their simulations are encouraging as they might be improved with a stronger TCI model and a better soot model as well as with the recent advancement in LES implementations.

On the whole, the comparison between the present results and those of previous studies of the propane flame indicated some strengths and weaknesses in the methodology. Overall, present predictions are in a comparable level of accuracy with other studies which employ better turbulence closure like LES or more detailed chemistry. This, from one hand, implies the significance and advantage of the strong TCI attained by the PDF method. On the other hand, more investigations are needed for the chemical model by more successful selection of the list of constraints for the RCCE method.

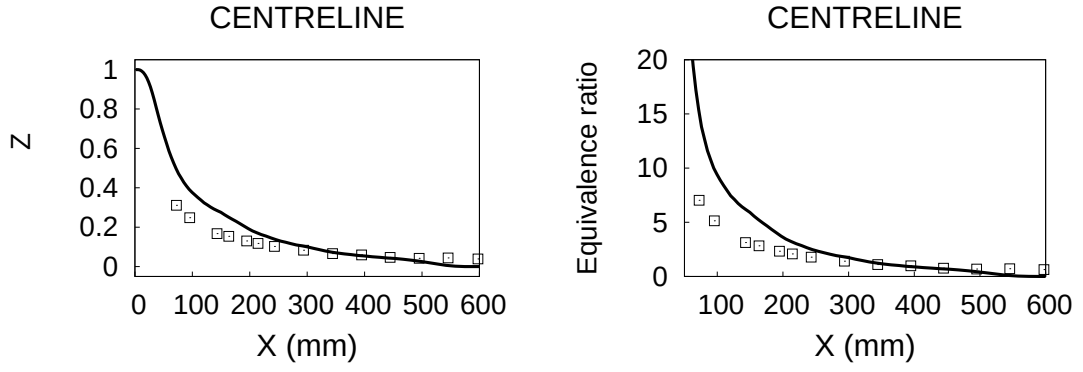


Figure 6.20: Mixture fraction and equivalence ratio on the centreline for the 773-K preheated-air propane flame. Legend: square symbols: measurements [162]. solid line: calculations by RCCE-22 mechanism

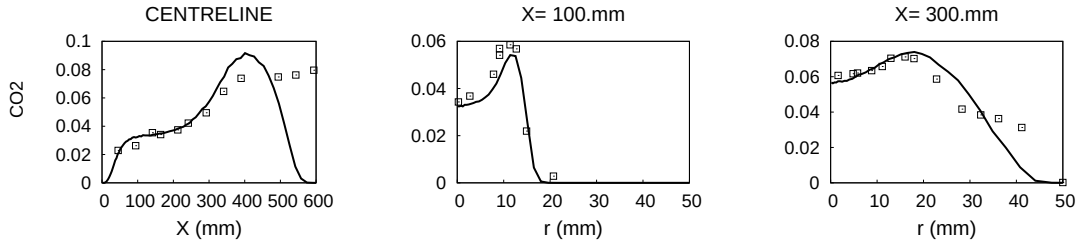


Figure 6.21: CO_2 mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

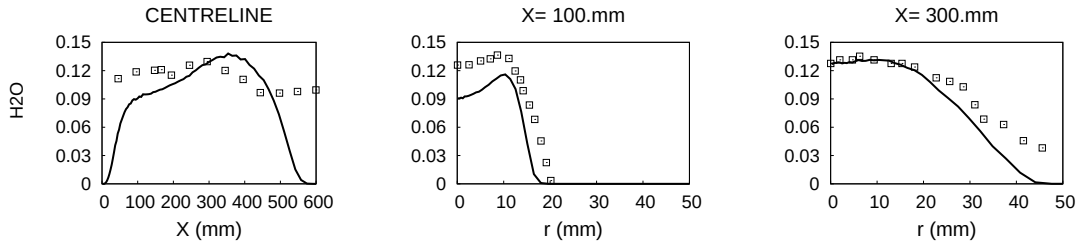


Figure 6.22: H_2O mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

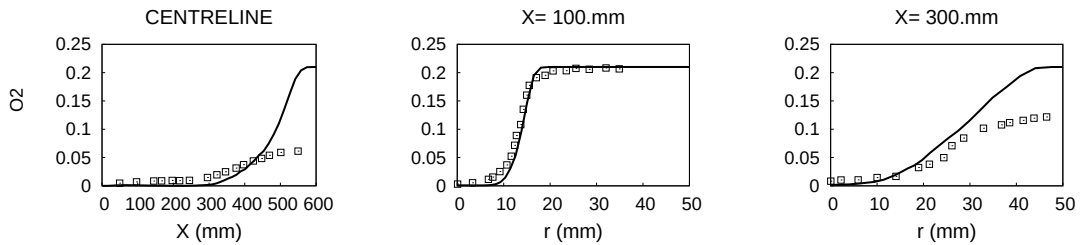


Figure 6.23: O_2 mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

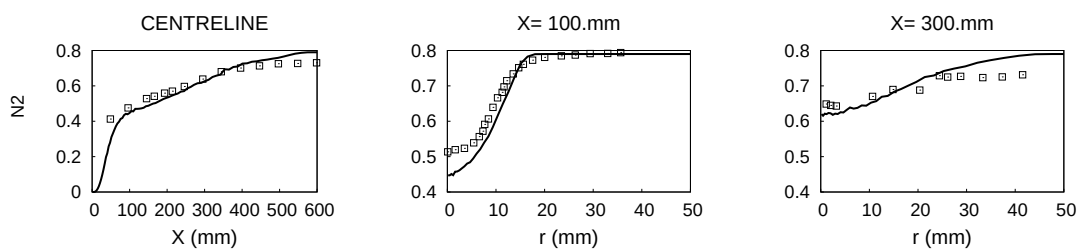


Figure 6.24: N_2 mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

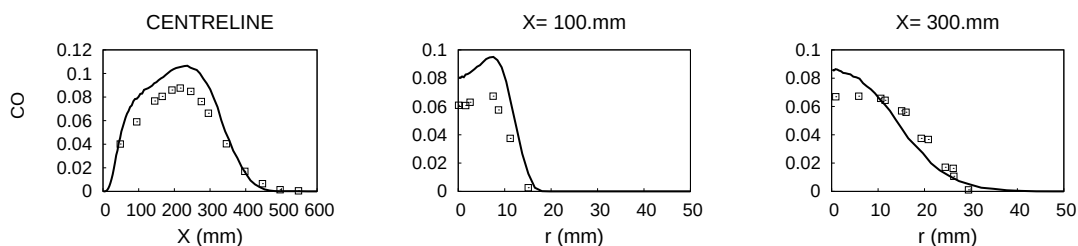


Figure 6.25: CO mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

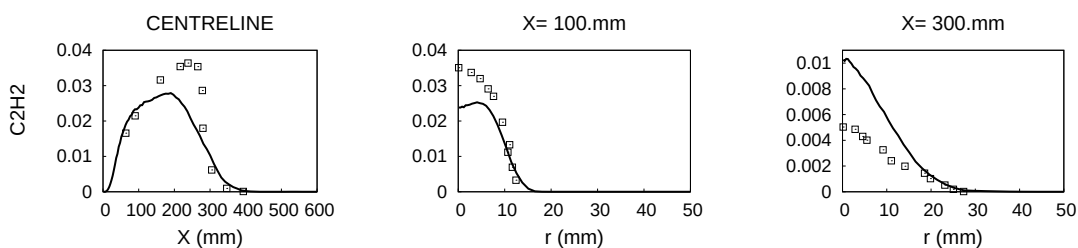


Figure 6.26: C_2H_2 mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

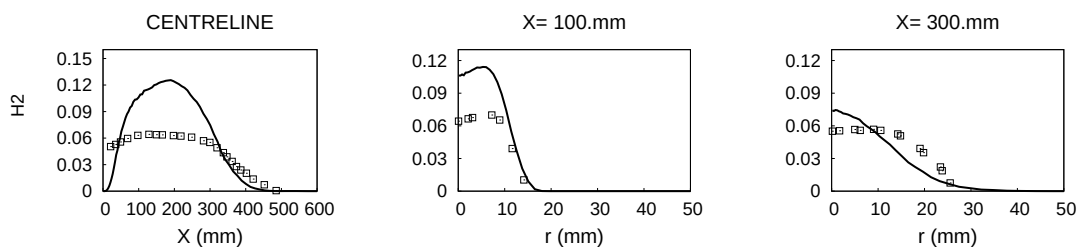


Figure 6.27: H_2 mole fraction for the 773-K preheated-air propane flame. Legend as in fig 6.20

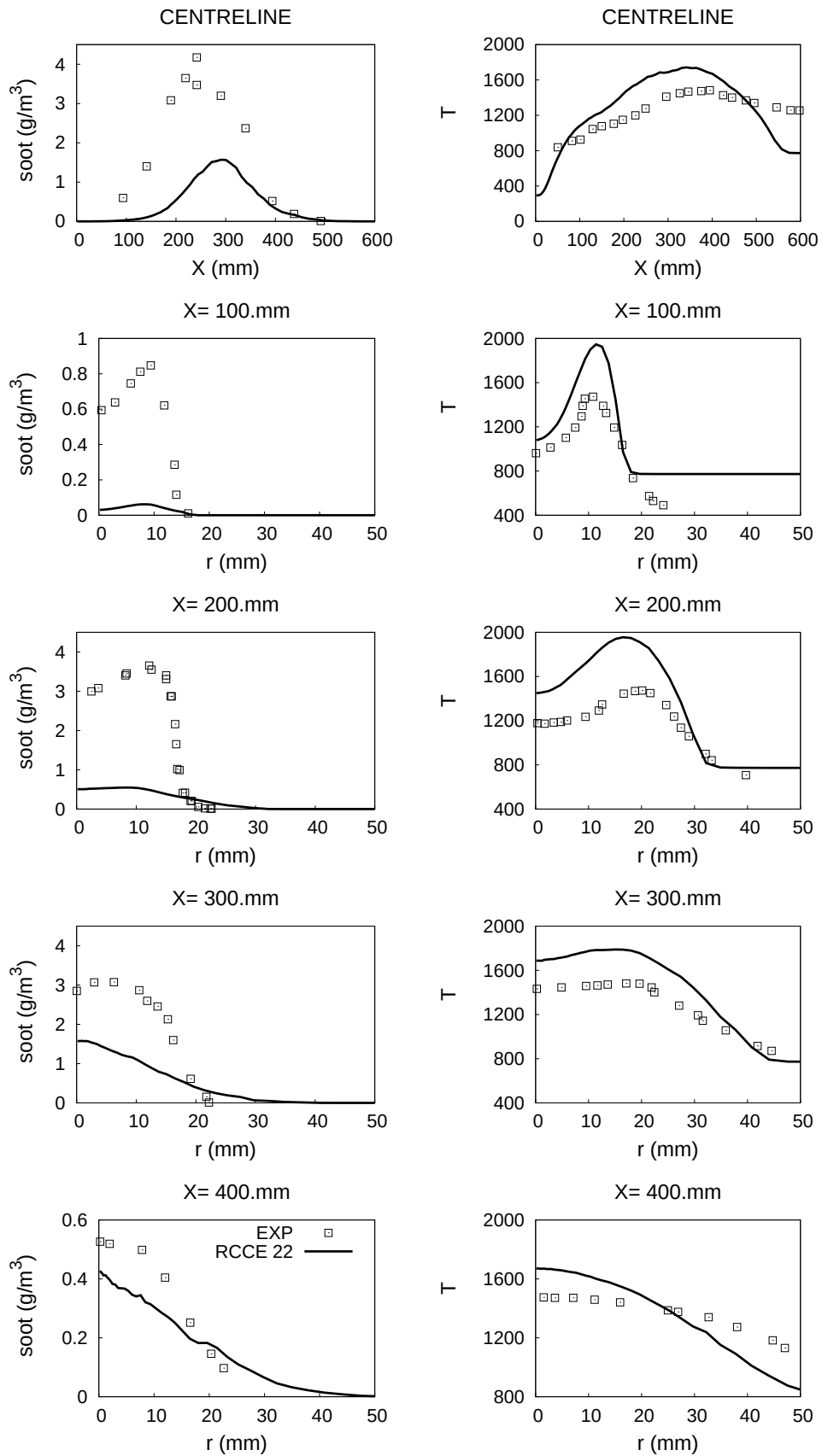


Figure 6.28: Soot (left) and Temperature (right) for 773-K preheated-air propane flame. Legend in bottom soot plot in this figure

Chapter 7

Summary, Conclusions and Recommendations

7.1 Summary and Conclusions

This study combined the transported probability density function (PDF) method and the rate-controlled constrained equilibrium (RCCE) method with RANS turbulence modelling. The combined RANS- scalar PDF-RCCE methodology was applied to several turbulent jet diffusion flames with different fuel compositions. These flames exhibit various complicated phenomena like extinction and reignition, soot formation and thermal radiation. The strengths and weaknesses of submodels of the PDF and the employed RCCE schemes in capturing these phenomena were investigated and assessed. The RANS algorithm employed the eddy-diffusivity $k-\varepsilon$ model. The scalar PDF method was solved with a Lagrangian Monte Carlo method. Tests with a 1-D flamelet code using detailed and RCCE-reduced chemistry at different strain rates were performed to aid the selection of kinetic constraints.

The first set of flames studied in this thesis were the three Sandia piloted turbulent flames D, E and F. The transported PDF method proved to be an advantageous and convenient tool to model the different degrees of turbulence chemistry interaction (TCI) in these three flames. The methodology accounts efficiently for deep turbulence-chemistry interaction (TCI) relative to other models which invoke time-

scale separation such as the steady laminar flamelet model. The present study has shown that the transported PDF method is able to reproduce the extinction and re-ignition phenomena in these flames with reasonable accuracy. This has been proven by obtaining solutions of the three flames with the detailed mechanism. These results showed that the amount of extinction predicted in flame D is less than the amount of extinction predicted in flames E and F if an accurate chemical scheme like the full GRI-3.0 is used. However, the present work demonstrated that the accuracy of the PDF method is constrained by some uncertainties and limitations arising from the simplified mixing submodel, particles transport submodel and the inputs from the flow field calculations.

By relating the scatter plots in this study to other RANS-PDF studies, it can be deduced that the need to employ too high values for the mixing coefficient C_ϕ to ignite the flame represents a significant weakness. The reason for this is because enforcing high mixing rates leads to rapid burning which does not allow the correct amount of extinction to be predicted. On the other hand, the scatter plots of temperature and species of flame E could not be distinguished from those of flame F. This indicated that the amount of extinction was captured only qualitatively in these two flames. Despite the important role of chemical kinetics in these predictions, the mixing field also appears to have a strong contribution.

The Sandia Flames were then computed with the PDF-RCCE methodology. Mixing was treated by the IEM model in both the DI and RCCE cases. The RCCE reduced mechanisms were extracted from the same detailed mechanism (i.e. GRI-3.0 [2]) to establish whether the RCCE method can preserve the capability of the original mechanism. The results demonstrated that if a successful selection of constraints was achieved, the resultant reduced mechanism by RCCE can attain the accuracy of the original detailed mechanism. The RCCE mechanisms which have been applied to the three Sandia flames produced results which are quite comparable to the detailed mechanism. It appears that capturing the reignition phenomenon which follows local extinction in these flames is a more difficult task when a single-

time-scale mixing model is used. The scatter plots with IEM showed some irregular and patchy patterns that reveal how extinction and reignition are captured by this model. It is thought that the reignition of a considerable portion of the extinguished particles is delayed by the mixing process to the extent that a large number of fuel-rich particles do not ignite until their compositions become fuel-lean by mixing with air. The issue of reignition is remedied by slightly increasing C_ϕ so that mixing is enhanced and reignition becomes easier.

The performance of the RCCE mechanism depends on the selection of the constraints. The steady flamelet model does not produce the same accuracy as the PDF model but it can aid the selection of the set of constraints. This can be done by ordering the constraints according to their dominance in the original mechanism. Potential RCCE mechanisms can then be compared with the DI chemistry using the flamelet model. This procedure is quite exhaustive and becomes quite difficult in complex mechanisms. The gain in computational time from applying RCCE to these methane flames is less than expected since the number of kinetic species has been reduced to almost one-third. The reasons for this has not been investigated.

The methodology was then extended to simulate flames with radiative heat losses and soot formation. Despite that coupling between the models in PDF methods is straightforward, there is a complicated interaction between the following four processes: turbulence, chemistry, soot and radiation. All the simulations were performed with simplified models for soot and radiation. The structure of methane soot flames were captured with good accuracy. The good temperature profiles predicted for these flames conclude that applying the RADCAL optically-thin radiation model [72] with a model for soot radiation is sufficient for modelling radiation in these flames. Soot predictions showed alternating accuracy but generally encouraging. In particular, the pressurised methane flame has been simulated with 3 RCCE mechanisms to compare and investigate the effect of gaseous chemistry. The predictions showed that small differences in the gas-phase chemistry lead to a considerable disagreement in soot levels.

An important remark is that predictions of radiative heat transfer and soot formation are dependent on the gaseous composition and temperature since they appear in the source and sink terms of the radiative heat and soot. Accurate predictions of soot precursors and oxidation species are crucial prerequisites for successful computations of soot. In addition, the dependence of soot processes on temperature and the contribution of soot to thermal radiation imply complex interaction between soot formation and radiative heat transfer. The modelling of the interaction between these processes with the scalar PDF method showed to be successful. Soot volume fraction appears to depend largely on the competition between surface growth reactions and the oxidation reactions. The effect of processes controlling the particle number density on soot levels is represented in the present semi-empirical soot mechanism by changes in the soot surface area.

7.2 Recommendations for Future Work

The present study indicated that the scalar PDF method is strongly recommended for modelling of turbulent combustion flows. The continuous advancements in computer resources encourages the use of the PDF method with RCCE-reduced chemistry for the computations of turbulent flames of heavy fuels and flames in real applications. On the other hand, further exploration of the joint scalar PDF implementation and better choices for its submodels are needed to make the methodology more efficient and more robust. For instance, it is crucial to improve the mixing field predictions by employing better and advanced models such as the Multiple Mapping Conditioning (MMC) and by accounting for variations in diffusivities of transported scalars. There is possibility that more accurate implementation and predictions of turbulent transport and mixing fields will result in better understanding of the position of chemical kinetics in turbulent combustion.

Chemistry reduction methods like RCCE are strongly needed in order for PDF simulations of realistic combustors to become tractable. Further, soot formation is

usually more important in heavy fuels and fuel surrogates where reduction of the detailed mechanisms is also essential to make computations of the chemical kinetics less prohibitive. At this stage, further research is still needed even for propane flames to get optimum selections for the constraints of the RCCE. The RCCE method has the capability of reducing the formidable size of these mechanisms and making them easier to handle. In addition, refinement of complicated mechanisms can be facilitated if they are reduced systematically. More CPU time savings can be achieved using tabulation methods such as the ANN which are better applied to reduced chemical schemes.

Inclusion of benzene or other aromatic rings as a nucleation species in soot computations of these flames is important step for better soot modelling. The PDF method with RCCE reduction can still be employed if the detailed mechanism contains gas-chemistry for these nucleation species.

It is recommended that the methodology is extended to study the effect of particle size distribution in turbulent reacting flows. A formulation for the Population Balance Equation (PBE) has been coupled with the transported PDF method [212]. The combined PBE-PDF method can be applied to compute particle size distribution in soot flames and other particulate problems such as nano-particles, aerosols, sprays and precipitation in turbulent flows.

The coupling of RCCE with LES-PDF methods may be regarded as a better choice in some flows as opposed to the RANS-PDF methods since LES capture the structure of turbulent flows more accurately. Even though the LES-PDF method would entail extra computational cost that may become unaffordable with detailed chemistry, it is likely to become more favourable in future with reduced chemistry models.

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Appendices

Appendix A

Derivation of the (index-zero) ODE-RCCE formulation

As have been stated, the pure differential formulation of RCCE system of equations is achieved using the so-called index reduction technique. This RCCE formulation has been previously named as the constraint-potential formulation. The method starts with expanding the total time derivative into partial derivatives of the elements and constraints potentials (λ_β^c , λ_α^c) as well as temperature (T) and density (ρ):

$$\frac{d}{dt}n_s(\rho, T, \underline{\lambda}^e, \underline{\lambda}^c) = \frac{\partial n_s}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial n_s}{\partial T} \frac{dT}{dt} + \sum_{\beta=1}^{M_e} \left(\frac{\partial n_s}{\partial \lambda_\beta^e} \frac{d\lambda_\beta^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(\frac{\partial n_s}{\partial \lambda_\alpha^c} \frac{d\lambda_\alpha^c}{dt} \right) \quad (\text{A.1})$$

Therefore, the following partial derivatives of n_s are first needed which can be obtained by performing partial differentiation on Eq. (4.22):

$$\frac{\partial n_s}{\partial \lambda_\beta^e} = a_{\beta s}^e n_s \quad (\text{A.2})$$

$$\frac{\partial n_s}{\partial \lambda_\alpha^c} = a_{\alpha s}^c n_s \quad (\text{A.3})$$

$$\frac{\partial n_s}{\partial T} = \frac{1}{T} \left(\frac{H_s^o}{RT} - 1 \right) n_s \quad (\text{A.4})$$

$$\frac{\partial n_s}{\partial \rho} = -\frac{1}{\rho} n_s \quad (\text{A.5})$$

The constraints equation

Starting with equation Eq. (4.23)

$$\frac{dC_{\alpha^*}}{dt} = \sum_{s=1}^{N_s} \left[a_{\alpha^*s}^c \left(\frac{\sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k)}{\rho} \right) \right] \quad (\alpha^* = 1, \dots, M_c) \quad (\text{A.6})$$

$$\begin{aligned} \sum_{s=1}^{N_s} a_{\alpha^*s}^c \left[\frac{\partial n_s}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial n_s}{\partial T} \frac{dT}{dt} + \sum_{\beta=1}^{M_e} \left(\frac{\partial n_s}{\partial \lambda_\beta^e} \frac{d\lambda_\beta^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(\frac{\partial n_s}{\partial \lambda_\alpha^c} \frac{d\lambda_\alpha^c}{dt} \right) \right] \\ = \sum_{s=1}^{N_s} \left[a_{\alpha^*s}^c \left(\frac{\sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k)}{\rho} \right) \right] \quad (\alpha^* = 1, \dots, M_c) \end{aligned}$$

$$\begin{aligned} - \sum_{s=1}^{N_s} (a_{\alpha^*s}^c n_s) \frac{1}{\rho} \frac{d\rho}{dt} + \sum_{s=1}^{N_s} \left[(a_{\alpha^*s}^c n_s) \frac{1}{T} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\ + \sum_{s=1}^{N_s} \left[(a_{\alpha^*s}^c n_s) \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_\beta^e}{dt} \right) \right] + \sum_{s=1}^{N_s} \left[(a_{\alpha^*s}^c n_s) \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_\alpha^c}{dt} \right) \right] \quad (\text{A.7}) \\ = \sum_{s=1}^{N_s} \left[a_{\alpha^*s}^c \left(\frac{\sum_{k=1}^{N_R} (\nu_{sk} \hat{\omega}_k)}{\rho} \right) \right] \quad (\alpha^* = 1, \dots, M_c) \end{aligned}$$

Elements equation

$$\frac{d}{dt} \left[\sum_{s=1}^{N_s} (a_{\beta^*s}^e n_s) \right] = 0 \quad (\beta^* = 1, \dots, M_e) \quad (\text{A.8})$$

$$\begin{aligned} \sum_{s=1}^{N_s} a_{\beta^*s}^e \left[\frac{\partial n_s}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial n_s}{\partial T} \frac{dT}{dt} + \sum_{\beta=1}^{M_e} \left(\frac{\partial n_s}{\partial \lambda_\beta^e} \frac{d\lambda_\beta^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(\frac{\partial n_s}{\partial \lambda_\alpha^c} \frac{d\lambda_\alpha^c}{dt} \right) \right] = 0 \\ (\beta^* = 1, \dots, M_e) \end{aligned}$$

$$\begin{aligned} - \sum_{s=1}^{N_s} (a_{\beta^*s}^e n_s) \frac{1}{\rho} \frac{d\rho}{dt} + \sum_{s=1}^{N_s} \left[(a_{\beta^*s}^e n_s) \frac{1}{T} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\ + \sum_{s=1}^{N_s} \left[(a_{\beta^*s}^e n_s) \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_\beta^e}{dt} \right) \right] \quad (\text{A.9}) \\ + \sum_{s=1}^{N_s} \left[(a_{\beta^*s}^e n_s) \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_\alpha^c}{dt} \right) \right] = 0 \quad (\beta^* = 1, \dots, M_e) \end{aligned}$$

Enthalpy equation

$$\frac{d}{dt} \left[\sum_{s=1}^{N_s} (n_s H_s^o) \right] = 0 \quad (\text{A.10})$$

$$\begin{aligned} & \sum_{s=1}^{N_s} \left[H_s^o \frac{\partial n_s}{\partial \rho} \frac{d\rho}{dt} \right] + \sum_{s=1}^{N_s} \left[n_s \frac{\partial H_s^o}{\partial T} + H_s^o \frac{\partial n_s}{\partial T} \right] \frac{dT}{dt} + \\ & \sum_{s=1}^{N_s} \left[H_s^o \sum_{\beta=1}^{M_e} \left(\frac{\partial n_s}{\partial \lambda_\beta^e} \frac{d\lambda_\beta^e}{dt} \right) \right] + \sum_{s=1}^{N_s} \left[H_s^o \sum_{\alpha=1}^{M_c} \left(\frac{\partial n_s}{\partial \lambda_\alpha^c} \frac{d\lambda_\alpha^c}{dt} \right) \right] = 0 \\ & - \sum_{s=1}^{N_s} \left(\frac{H_s^o n_s}{\rho} \right) \frac{d\rho}{dt} + \sum_{s=1}^{N_s} \left[n_s \frac{\partial H_s^o}{\partial T} + \left(\frac{H_s^o n_s}{T} \right) \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} + \\ & + \sum_{s=1}^{N_s} \left[(H_s^o n_s) \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_\beta^e}{dt} \right) \right] + \sum_{s=1}^{N_s} \left[(H_s^o n_s) \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_\alpha^c}{dt} \right) \right] = 0 \end{aligned} \quad (\text{A.11})$$

Equation of state

$$\begin{aligned} \frac{dP}{dt} &= 0 \\ \frac{d}{dt} (n\rho RT) &= 0 \\ nRT \frac{d\rho}{dt} + n\rho R \frac{dT}{dt} + \rho RT \frac{dn}{dt} &= 0 \end{aligned} \quad (\text{A.12})$$

The time derivative of the total mole number $\left(\frac{dn}{dt} \right)$ is expanded just like $\left(\frac{dn_s}{dt} \right)$ in Eq. (A.1):

$$\begin{aligned} & nRT \frac{d\rho}{dt} + n\rho R \frac{dT}{dt} + \rho RT \left[\frac{\partial n}{\partial \rho} \frac{d\rho}{dt} + \frac{\partial n}{\partial T} \frac{dT}{dt} \right] \\ & + \rho RT \left[\sum_{\beta=1}^{M_e} \left(\frac{\partial n}{\partial \lambda_\beta^e} \frac{d\lambda_\beta^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(\frac{\partial n}{\partial \lambda_\alpha^c} \frac{d\lambda_\alpha^c}{dt} \right) \right] = 0 \\ & nRT \frac{d\rho}{dt} + n\rho R \frac{dT}{dt} + \rho RT \left(\frac{-n}{\rho} \right) \frac{d\rho}{dt} + \rho RT \sum_{s=1}^{N_s} \left[\frac{n_s}{T} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\ & + \rho RT \sum_{s=1}^{N_s} \left[\sum_{\beta=1}^{M_e} \left(a_{\beta s}^e n_s \frac{d\lambda_\beta^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c n_s \frac{d\lambda_\alpha^c}{dt} \right) \right] = 0 \end{aligned}$$

$$\begin{aligned}
& \frac{P}{T} \sum_{s=1}^{N_s} \left[1 + \frac{n_s}{n} \left(\frac{H_s^o}{RT} - 1 \right) \right] \frac{dT}{dt} \\
& + \frac{P}{n} \sum_{s=1}^{N_s} \left[n_s \sum_{\beta=1}^{M_e} \left(a_{\beta s}^e \frac{d\lambda_{\beta}^e}{dt} \right) + \sum_{\alpha=1}^{M_c} \left(a_{\alpha s}^c \frac{d\lambda_{\alpha}^c}{dt} \right) \right] = 0
\end{aligned} \tag{A.13}$$

The Eqs. (A.7), (A.9), (A.11), (A.13) are similar to zero-index RCCE formulation represented by Eqs. (4.24) - (4.27)