ABSTRACT

GUPTA, KAMLESH GOVINDRAM. Numerical Studies of H\textsubscript{2} and H\textsubscript{2}/CO Autoignition in Turbulent Jets. (Under the direction of Dr. Tarek Echekki.)

The present study is carried out in two parts. In the first part, the autoignition of hydrogen in a turbulent jet with preheated air is studied computationally using the stand-alone one-dimensional turbulence (ODT) model. The simulations are based on varying the jet Reynolds number and the mixture pressure. Also, computations are carried out for homogeneous autoignition at different mixture fractions and the same two pressure conditions considered for the jet simulations. The simulations show that autoignition is delayed in the jet configuration relative to the earliest autoignition events in homogeneous mixtures. This delay is primarily due to the presence of scalar dissipation associated with the scalar mixing layer in the jet configuration as well as with the presence of turbulent stirring. Turbulence plays additional roles in the subsequent stages of the autoignition process. Pressure effects also are present during the autoignition process and the subsequent high-temperature combustion stages. These effects may be attributed primarily to the autoignition delay time sensitivity to the mixture conditions and the role of pressure and air preheating on molecular transport properties. The overall trends are such that turbulence increases autoignition delay times and accordingly the ignition length and pressure further contributes to this delay.

In the second part of this study, similar autoignition study of mixture of hydrogen and carbon monoxide is conducted. Two different mixture compositions are considered. They
correspond to H₂:CO:N₂ ratios by volume of 15:35:50 and 20:30:50. Each composition is simulated for two oxidizer preheat temperatures and two fuel jet Reynolds numbers at atmospheric pressure. Homogeneous autoignition is carried out for same preheat mixture conditions for comparison with the turbulent jet results. The autoignition delay time recorded for jet cases is lower than the homogeneous autoignition delay time. This is attributed to the differential diffusion of hydrogen, which plays an important and enhancing role of the diffusion of hydrogen into the oxidizer.
Numerical Studies of H₂ and H₂/CO Autoignition in Turbulent Jets

by
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A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Mechanical Engineering

Raleigh, North Carolina

2009

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DEDICATION

I would like to dedicate this work to the entire Gupta Family –

Grand Parents: (Late) Hetram and Durgadevi

Parents: Govindram and Kanta

Brothers and their Wives:

Sandeep and Neelam

Rajkumar and Dipti

and my nephew

Akshat

For being my strength and support always
Kamlesh Govindram Gupta was born on 14 August 1983 in Mumbai, the business capital of India. He attended Vidyavardhini’s College of Engineering and Technology in Mumbai for his undergraduate studies, worked with Air India for his senior year project, and earned his Baccalaureate in Mechanical Engineering degree in June 2005.

Kamlesh was employed by Mercantile and Industrial Development Corporation (MIDCO) as an executive engineer in the engineering department from August 2005 to July 2006. This opportunity provided him exposure to the designing and testing of hydraulic pumps and related components.

His passion for education and efforts to pursue a Master’s degree bore fruit, and he enrolled as a graduate student in the Mechanical and Aerospace Engineering Department of North Carolina State University in Fall 2007. He has been awarded teaching assistantships for the Spring 2008, Fall 2008 and Spring 2009 semesters. His research interest led him to Dr. Tarek Echekki, who has been his advisor since Fall 2008.
ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisor, Dr. Tarek Echekki, without whose guidance, support and encouragement, this thesis work would have been impossible.

I would also like to thank Dr. William Roberts and Dr. Tiegang Fang for their valuable insights and suggestions.

A special thanks to Rashmi Vembar, for all her support through thick and thin.
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CHAPTER 1

Introduction

1.1 Motivation

Autoignition is defined as the ignition of a combustible mixture of gases in the absence of any external ignition source. It is a problem of great fundamental importance and practical interest. For the development of improved, efficient and reduced emission combustors, the understanding of autoignition is crucial. The autoignition of a turbulent jet of fuel released into a co-flow of oxidizer is a very common problem encountered in gas-turbines, ramjets, and diesel engines. It is a complex process involving interactions of chemical reactions, molecular diffusion, and turbulent transport over a wide range of length and time scales. Two important parameters related to autoignition are autoignition temperature (AIT), the lowest temperature at which autoignition occurs, and the autoignition delay time, which is the time taken by the gases after mixing and before the autoignition occurs. In non-homogeneous mixture, when the mixing process is slow, autoignition is initiated at the fuel-oxidizer interface resulting in non-premixed combustion mode. This mode of combustion forms the basic model for the Diesel engines. Various effects are found to impact the autoignition delay in Homogeneous Charge Compression Ignition (HCCI) engines. For example, the ignition delay time is controlled by the addition of hydrogen, which extends the operational range of equivalence ratios and engine loads (Shudao & Yamada, 2007). It has been shown in Diesel

Moreover, in many chemical processes, high pressures and temperatures are encountered. In such processes, to ensure safe and optimal execution, the knowledge of AIT can be used to predict the autoignition hazards. Van den Schoor et al. (2008) studied the autoignition limit of ammonia/methane/air mixtures for different concentrations of ammonia and methane and concluded that the autoignition limit of methane/air mixtures is lowered by the addition of ammonia. Also, the role of AIT in autoignition hazards in a urea plant had been studied by Vandbroek et al. (2002) for ammonia/methane/hydrogen/air mixtures and it was found that the AIT of the mixtures inside the urea plant is below the maximum temperature of the plant,
thus ensuring the safe work environment of the plant. Rota & Zanoelo (2003) investigated
the reliability of a procedure based on detailed kinetic modeling to predict the AIT in a urea
production process.

1.2 Turbulence Modeling Approach

The scope of the application of combustion has broadened significantly with the discovery of
new technologies and advancement in computational power. The solution to any combustion
problem depends on the level of detail in statistics needed. The branch of fluid sciences,
which deals with the computation of complex fluid flows application is called as
computational fluid dynamics (CFD). On the basis of cost, accuracy and time required to
attain a particular solution, there are three basic approaches as follows:

1.2.1 Direct Numerical Simulation (DNS)

A method used to solve the Navier-Stokes equations numerically without any turbulence
model is known as Direct Numerical Simulations (DNS) (Echekki & Chen, 2003). In DNS,
all the spatial and temporal scales of turbulence are resolved to fine grids. Since the number
of grid points to be considered increases with the turbulence intensity, the memory storage
requirements for computations in DNS are huge and increases with increasing Reynolds
number. Also, for the accuracy of results, the time step used for the integration of the
solution should be small. The number of computational operations needed is approximately
proportional to the third power of the Reynolds number. This increases the computation cost and hence, is suitable only for low Reynolds number. The largest number of grid points considered in the DNS to date is $4096^3$. This simulation was performed on the Earth Simulator supercomputer at Japan in 2002. Though DNS is expensive, it can provide the physical insight of turbulent chemistry interactions between the fuel and the oxidizer to a very accurate scale.

1.2.2 Reynolds Averaged Navier-Stokes Equations (RANS)

The Reynolds-averaged Navier-Stokes equations provides time averaged governing equations for scalars and momentum of the flow field, which calculates the average value for all the quantities in the flow (Ranganath & Echekki, 2006, 2008, 2009). Due to the averaging, the details about the temporal and spatial resolutions is lost, which is showed by closure terms in the governing equations. When compared with DNS, it is cost effective and is not as expensive as DNS, but since the results are approximated, they are not accurate.

1.2.3 Large Eddy Simulation (LES)

Large eddy simulation is an approach, which is based on the concept of Kolmogorov’s theory of self-similarity (Kolmogorov, 1941). It states that, in a flow large eddies are dependent on the geometry of the flow, whereas the smaller eddies are self-similar and have a common universal characteristic. In this approach, the solution is calculated explicitly for large eddies
and the smaller eddies are taken into account by considering a separate sub grid scale model. LES needs less computational power than DNS and is therefore cheaper than DNS. The cost of LES is more than RANS. The main advantage over RANS is that it can estimate the instantaneous flow characteristics of quantities. This would be helpful in the fuel-oxidizer chemistry, where RANS calculated average quantities would not be enough to initiate an ignition, but LES can capture concentrations in a localized region, which are high enough to initiate a reaction. The Linear Eddy Model (LEM) (Kerstein, 1991) is a mixing model using LES approach, and a recent advancement to this model is the ODT (Kerstein, 1999).

Both LEM and ODT can be implemented as stand-alone models for simple flows, such as the flow illustrated in this work. The ODT model evaluates solutions in 1D domains, while it maintains a DNS-like resolution. Therefore, it is capable of modeling realistic flows and relatively higher Reynolds numbers.

1.3 Overview

The objective of this work is to simulate and study the autoignition process in hydrogen/air (H₂/air) and carbon monoxide/hydrogen/air (CO/H₂/air) mixtures in a turbulent jet configuration. The study is carried out for different inlet conditions, including pressure, preheat temperature for the oxidizer, Reynolds number, and fuel concentration. The results obtained from these simulations are post-processed to obtain statistics for different species,
temperature and measures of transport and combustion mode (dissipation rate and flame index).

This work is organized as follows: First, a brief background of autoignition and turbulence models is provided. Following the background discussion is Chapter 2, which deals with the description, formulation and numerical implementation of One Dimensional Turbulence model (ODT) (Echekki et al., 2001). Chapters 3 and 4 focus on the discussion of chemistry of reaction mechanism and their conditional statistical results for H\textsubscript{2}/air and CO/H\textsubscript{2}/air mixtures respectively.
CHAPTER 2

The One Dimensional Turbulence Model

2.1 Introduction

Turbulence is always characterized as an unsteady process, which does not have any particular pattern. In a turbulent flow, very high velocity fluid mixing and reactions occurs, which is always characterized by wide range of length and time scales. The modeling and simulation of turbulent combustion flows with detailed chemistry has always been a great challenge.

Kerstein developed a turbulence model (LEM) (Kerstein, 1991), which adequately addressed the issue of predicting the mixing-reaction couplings at all scales by resolving the process of turbulent advection, scalar and momentum transport and chemistry, spatially and temporally, on a 1D domain. The main feature of this model is its capability to implement turbulent advection and molecular transport processes separately. Solutions to molecular and reaction processes are determined by solving the unsteady reaction-diffusion equations. To implement the turbulent advection, triplet map (Kerstein, 1991) stirring events are implemented. These maps emulate the compressive strain, rotational folding characteristics of turbulent eddies. The application of this model is for a wide variety of flows involving mixing in shear flows (Kerstein, 1989, 1990, 1992). Conventionally, a homogenous incompressible diffusion flame turbulence-chemistry interactions are being studied by LEM. The ODT model is a further
development of LEM (Kerstein, 1999). In the ODT model, the solution obtained for the components of velocity vector provides a mechanism for implementing turbulent advection. This feature distinguishes ODT as a ‘self-contained turbulence model’, in contrast to LEM, which is known as a ‘mixing model’.

Due to its one-dimensional approach, the cost of implementing this model is lower than the cost of 2D or 3D DNS. The one-dimensional approach also has its own disadvantages, one being the applicability of the model. It cannot be applied to highly complex turbulent flows. To extend the applicability of ODT model, it has to be coupled with multi-dimensional formulations like the RANS or LES.

## 2.2 Numerical Implementation

A detailed description of the ODT model formulation is given by Echekki et al. (2001). The ODT model is based on a deterministic implementation of reaction and diffusion and a stochastic implementation of turbulent advection in a time-resolved simulation on a 1D domain. The 1D domain corresponds to the transverse direction of mean flow. The temporal evolution of the 1D profile for the stream wise momentum, energy and the species equations is interpreted as a downstream evolution of the jet profiles.

The molecular processes are prescribed by the following unsteady reaction-diffusion equations:
• The stream wise momentum equation:

\[
\frac{\partial u}{\partial t} = \frac{1}{\rho} \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right).
\]  
Eq. (2.1)

• The species equation:

\[
\frac{\partial Y_k}{\partial t} = -\frac{1}{\rho} \frac{\partial}{\partial y} \left( \rho V_k Y_k \right) + \frac{\dot{\omega}_k}{\rho},
\]  
Eq. (2.2)

The energy equation,

\[
\frac{\partial T}{\partial t} = \frac{1}{\rho \bar{c}_p} \sum_{k=1}^{N} c_{p,k} Y_k \frac{\partial T}{\partial y} + \frac{1}{\rho \bar{c}_p} \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) - \frac{1}{\rho \bar{c}_p} \sum_{k=1}^{N} h_k \dot{\omega}_k.
\]  
Eq. (2.3)

In the above equations, \( u \) is the mixture stream wise velocity; \( \rho \) is the mixture density; \( Y_k, V_k, h_k, c_{p,k} \) and \( \dot{\omega}_k \) are, respectively, the mass fraction, the diffusion velocity, the total enthalpy (chemical and sensible), the heat capacity and the mass production rate per unit volume per unit time of the \( k \)th species; \( T \) is the mixture temperature; \( \lambda \) is the mixture heat conductivity; \( \bar{c}_p \) is the mixture heat capacity. The thermodynamic pressure, \( p \), is assumed to be spatially uniform, and the equation of state:

\[
p = \rho R T \sum_{k=1}^{N} \frac{Y_k}{W_k},
\]  
Eq. (2.4)

is used to compute the mixture density, \( \rho \). In the above equation, \( R \) is the universal gas constant and \( W_k \) is the \( k \)th species molecular weight.
Eqs. (2.1)-(2.4) represent a temporal solution of a turbulent jet flame. The temporal evolution of the solution represents a downstream evolution of the spatial profiles of the solution vector. The temporal evolution is converted to a downstream distance, \( x \), on the vertical axis using the following equations (Echekki et al., 2001):

\[
\overline{u} - u_\infty = \frac{\int_{-\infty}^{+\infty} \rho \left( u - u_\infty \right)^2 dy}{\int_{-\infty}^{+\infty} \rho \left( u - u_\infty \right) dy} \quad \text{and} \quad x(t) = \int_0^t \overline{u}(t') dt'.
\]

Eq. (2.5)

where \( \overline{u} \) and \( u_\infty \) correspond, respectively, to a bulk velocity and the co-flow velocity.

Turbulent advection is implemented stochastically using stirring events, each involving the application of a ‘triplet map’ (Kerstein, 1989) to a randomly selected segment (eddy) of size \( \hat{l} \) and left boundary location, \( \hat{y} \), so that the triplet map is applied to the eddy of span range of \( [\hat{y}, \hat{y} + \hat{l}] \) in the computed 1D scalar field.

Figure 2.1: Application of the triplet map to an initially linear profile.
In fig. 2.1, the rearrangement event consists of the replacement of the 1D profile on a segment, \( l \), by three identical copies compressed to one-third of their original size. The middle copy is then inverted to obtain continuity of the values on the new profile. However, derivatives at the interfaces of the three sub-intervals are not continuous.

The frequency of stirring events is governed by an eddy rate distribution, which is determined by associating a time scale with every possible event at a given instant. The model has two adjustable parameters of order unity (Echekki et al., 2001). The first parameter, \( A \), relates an eddy characteristic time to the inverse of the rate of shear applied at the eddy. The second parameter, \( \beta \), relates the eddy characteristic time to the elapsed temporal evolution of the jet. This parameter is used to exclude triplet maps that are associated with characteristic times that are longer than the elapsed time and is responsible for the progressive growth of eddy sizes involved in the stirring events as a function of downstream distance. Number of flames has used parameters \( A \) and \( \beta \), to predict the finite rate chemistry effects with reasonable success (Echekki et al., 2001; Hewson & Kerstein, 2001, 2002; Zhang & Echekki, 2008).

The temporal discretization of the governing equations is based on full splitting of diffusion and reaction in which diffusion is advanced using the first-order Euler method, while the source term is integrated using a stiff-integrator, DVODE (Brown et al., 1989). Transport properties for heat and mass are based on a mixture-averaged formulation and computed using transport libraries (Kee et al., 1983) within the Chemkin II suite (Kee et al., 1983). The
boundaries of the ODT computational domain are maintained at free-stream conditions throughout the jet. In the present implementation, dilatation is accompanied by an expansion of the computational cells on the 1D domain proportional to the density decrease (Echekki et al., 2001).
CHAPTER 3

Autoignition in Hydrogen/Air Mixtures

3.1 Introduction

Autoignition in non-premixed mixtures in a jet configuration is relevant to a number of practical applications, including diesel engines. In this configuration, turbulent mixing may play an important role in delaying the onset of ignition. The same mechanism can increase the volumetric rate of combustion following the ignition stage. Both experimental and numerical studies have been carried out in recent years to elucidate the mechanisms and conditions of ignition in fuel jets issuing into co-flowing preheated air. Markides and Mastorakos (2005) studied experimentally the autoignition behavior of hydrogen in a turbulent co-flow of heated air at atmospheric pressures. These authors observed statistically steady conditions of randomly occurring autoignition kernels for a wide range of air preheat temperatures and fuel jet velocities. They determined minimum autoignition lengths and showed that these lengths increase with the air velocity and decrease with the air temperature. They also showed that turbulence has a delaying effect on autoignition. Similar experiments in non-premixed flame configurations were implemented for acetylene (Markides, 2005) and \textit{n}-heptane (Markides \textit{et al.}, 2007).
Numerical studies with detailed chemistry were carried out for hydrogen-air mixtures using the LES approach (Jones & Navarro-Martinez, 2008), the joint scalar PDF method (Lee & Mastorakos, 2008) and the conditional moment closure (CMC) model (Patwardhan & Lakshmisha, 2008). A principal scope of these papers was the determination of the ignition length as a function of inlet conditions. The study of the role of turbulent mixing and entrainment has been studied in similar flow configurations, but to a much lower extent in jet flows. Similar work has been carried out in counter-flow jet configurations (Blouch & Law, 2003; Sadanandan et al., 2007), random non-homogeneous mixtures (Cao & Echekki, 2007; Echekki, 2008; Echekki & Chen, 2002, 2003), and scalar mixing layers (Hilbert & Thevenin, 2002; Im et al., 1998; Mastorakos et al., 1997). The work by Echekki (2008) is based on the use of the linear-eddy model (LEM) in a stratified mixture (Kerstein, 1989). The LEM model is based on 1D solution in which boundary layer equations with reaction and diffusion are solved deterministically, while turbulent transport is implemented stochastically. The turbulent mixing rules are prescribed by global parameters that specify the turbulence conditions. An extension of the LEM model is the one-dimensional turbulence (ODT) model (Kerstein, 1999). The ODT model has been successfully implemented as stand-alone in a number of jet configurations (Echekki et al., 2001; Hewson & Kerstein, 2001, 2002; Ranganath & Echekki, 2006, 2008, 2009; Zhang & Echekki, 2008) and as part of a hybrid scheme with LES by Cao & Echekki (2008).
In the present study, the autoignition of non-homogeneous mixture of hydrogen-nitrogen jet in heated air is studied computationally using the ODT model. The emphasis is placed on the role of finite-rate chemistry effect on this transient problem with evolving interaction between chemistry and molecular and turbulent transport. At the same time the effect of pressure and turbulent intensity on non-homogeneous autoignition delay time and temperature and mixture fraction on ignition kernels locations and propagation are investigated as well. For the present problem, nine species are included: \( \text{H}_2, \text{O}_2, \text{OH}, \text{H}, \text{O}, \text{HO}_2, \text{H}_2\text{O}_2, \text{H}_2\text{O}, \) and \( \text{N}_2 \) (Yetter et al., 1991b). Table 3.1 shows the detailed mechanism for this chemistry.
Table 3.1: H₂/Air mechanism rate constants are in the form $k_f = AT^\beta \exp \left( -\frac{E_a}{R \cdot T} \right)$; units are moles, cm, sec, K and kcal/mol. Third body coefficients in reactions 5, 6, 7, 8, 9 and 15 enhancement factors are 12 for H₂O and 25 for H₂.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$A$</th>
<th>$\beta$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + O₂ ⇌ O + OH</td>
<td>$1.92 \times 10^{14}$</td>
<td>0.0</td>
<td>16.44</td>
</tr>
<tr>
<td>2</td>
<td>O + H₂ ⇌ H + OH</td>
<td>$5.08 \times 10^{4}$</td>
<td>2.67</td>
<td>6.29</td>
</tr>
<tr>
<td>3</td>
<td>OH + H₂ ⇌ H + H₂O</td>
<td>$2.16 \times 10^{8}$</td>
<td>1.51</td>
<td>3.43</td>
</tr>
<tr>
<td>4</td>
<td>OH + OH ⇌ O + H₂O</td>
<td>$1.23 \times 10^{4}$</td>
<td>2.62</td>
<td>-1.88</td>
</tr>
<tr>
<td>5</td>
<td>H₂ + M ⇌ H + H + M</td>
<td>$4.57 \times 10^{19}$</td>
<td>-1.4</td>
<td>104.4</td>
</tr>
<tr>
<td>6</td>
<td>O + O + M ⇌ O₂ + M</td>
<td>$6.17 \times 10^{15}$</td>
<td>-0.50</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>O + H + M ⇌ OH + M</td>
<td>$4.72 \times 10^{18}$</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>H + OH + M ⇌ H₂O + M</td>
<td>$2.25 \times 10^{22}$</td>
<td>-2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>H + O₂ + M ⇌ HO₂ + M</td>
<td>$6.17 \times 10^{19}$</td>
<td>-1.42</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>HO₂ + H ⇌ H₂ + O₂</td>
<td>$6.63 \times 10^{13}$</td>
<td>0.0</td>
<td>2.13</td>
</tr>
<tr>
<td>11</td>
<td>HO₂ + H ⇌ OH + OH</td>
<td>$1.69 \times 10^{14}$</td>
<td>0.0</td>
<td>0.87</td>
</tr>
<tr>
<td>12</td>
<td>HO₂ + O ⇌ OH + O₂</td>
<td>$1.81 \times 10^{13}$</td>
<td>0.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>13</td>
<td>HO₂ + OH ⇌ H₂O + O₂</td>
<td>$1.45 \times 10^{16}$</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>HO₂ + HO₂ ⇌ H₂O₂ + O₂</td>
<td>$3.02 \times 10^{12}$</td>
<td>0.0</td>
<td>1.39</td>
</tr>
<tr>
<td>15</td>
<td>H₂O₂ + M ⇌ 2 OH + M</td>
<td>$1.20 \times 10^{17}$</td>
<td>0.0</td>
<td>45.5</td>
</tr>
<tr>
<td>16</td>
<td>H₂O₂ + H ⇌ H₂O + OH</td>
<td>$1.00 \times 10^{13}$</td>
<td>0.0</td>
<td>3.59</td>
</tr>
<tr>
<td>17</td>
<td>H₂O₂ + H ⇌ H₂ + HO₂</td>
<td>$4.82 \times 10^{15}$</td>
<td>0.0</td>
<td>7.95</td>
</tr>
<tr>
<td>18</td>
<td>H₂O₂ + O ⇌ OH + HO₂</td>
<td>$9.55 \times 10^{6}$</td>
<td>2.0</td>
<td>3.97</td>
</tr>
<tr>
<td>19</td>
<td>H₂O₂ + OH ⇌ H₂O + HO₂</td>
<td>$7.00 \times 10^{12}$</td>
<td>0.0</td>
<td>1.43</td>
</tr>
</tbody>
</table>
3.2 Run Conditions

To study autoignition in a turbulent jet configuration, two sets of computations are carried out. The first computations correspond to homogeneous ignition over a range of equivalence ratios/mixture fractions spanning from fuel-lean to fuel-rich conditions. The homogeneous ignition computations will serve as a basis of comparison with the jet configuration. The second set of computations corresponds to a room temperature fuel jet surrounded by a preheated air co-flow. The two sets of computations are carried out at two different pressures, which remain uniform throughout the computations. Pressure affects both the chemical mechanism of autoignition as well as molecular transport, through its effect on transport coefficients for heat, mass and momentum. As demonstrated below, the choice of fuel dilution with nitrogen and the choice of the air preheat temperature yields stoichiometric mixture fractions of approximately 0.5 and similar minimum autoignition times for most reactive mixture fraction conditions. Moreover, another parameter is varied for the jet simulations, which corresponds to the fuel inlet Reynolds number.

Table 3.2 and 3.3 shows the mixture conditions corresponding to the homogeneous and jet autoignition runs, respectively. The fuel is 30% hydrogen and 70% nitrogen by volume at 300 K. Two pressures are considered corresponding to 1 and 3 atmospheres. For each pressure, a preheat air temperature is prescribed as given in Table 3.2, corresponding to 980 K and 1030 K for 1 and 3 atmospheres, respectively.
### Table 3.2: Run conditions for homogeneous autoignition.

<table>
<thead>
<tr>
<th>Range of mixture fractions</th>
<th>Pressure (atm)</th>
<th>Fuel temperature (K)</th>
<th>Air temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01-0.22</td>
<td>1</td>
<td>300</td>
<td>980</td>
</tr>
<tr>
<td>0.01-0.22</td>
<td>3</td>
<td>300</td>
<td>1030</td>
</tr>
</tbody>
</table>

### Table 3.3: Run conditions summary for the jet cases A, B, C and D.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>5000</td>
<td>10000</td>
<td>5000</td>
<td>10000</td>
</tr>
<tr>
<td>Air temperature (K)</td>
<td>980</td>
<td>980</td>
<td>1030</td>
<td>1030</td>
</tr>
</tbody>
</table>

### 3.2.1 Homogeneous Autoignition

Homogeneous ignition is implemented by solution of the species equations under adiabatic conditions:

- The species equation,

\[
\frac{\partial Y_k}{\partial t} = \frac{\dot{\omega}_k}{\rho}, \quad \text{Eq. (3.1)}
\]
The energy equation,

$$\frac{\partial T}{\partial t} = -\frac{1}{\rho c_p} \sum_{k=1}^{N} h_k \dot{\omega}_k.$$  \hspace{1cm} \text{Eq. (3.2)}

describes the energy transfer for two different fixed pressures and preheat temperatures for air. Again, these equations are integrated using the stiff-integrator DVODE (Brown & Byrne, 1989), and thermodynamic properties are determined using Chemkin libraries for the same reaction mechanism and species used in the jet autoignition studies. The autoignition delay is, then, studied for a range of mixture fractions extending from an all oxidizer mixture to an all fuel mixture. The initial mixture composition is prescribed in terms of a mixture fraction, $Z$, which may be expressed as:

$$Z = \frac{Y_{H_2} - Y_{H_2,0}}{Y_{H_2,F} - Y_{H_2,0}} = \frac{Y_{O_2} - Y_{O_2,0}}{Y_{O_2,F} - Y_{O_2,0}} = \frac{Y_{N_2} - Y_{N_2,0}}{Y_{N_2,F} - Y_{N_2,0}}.$$  \hspace{1cm} \text{Eq. (3.3)}

In this expression, the subscript O and F correspond to the reference mixtures of either pure oxidizer (air) or pure fuel (H$_2$ and N$_2$). For the present level of dilution, the reference mass fractions for H$_2$, O$_2$ and N$_2$ in the oxidizer stream are 0, 0.2329 and 0.7670, respectively, and in the fuel stream 0.0299, 0 and 0.9700, respectively. Based on the level of dilution of the fuel, the mixture fraction at stoichiometric conditions corresponds to 0.5. The mixture preheat temperature is determined from adiabatic mixing of the fuel and air mixtures at the prescribed mixture fraction. It is noteworthy to mention that a second, and more general, definition of the mixture fraction is used at a later section of this study. This second
definition (see Eq. (3.5)) considers reactants, products and intermediate species. The present definition in Eq. (3.3) considers only a fuel and air mixture and is implemented primarily for the homogeneous ignition studies.

3.2.2 Jet Autoignition

Fig. 3.1 shows the computational setup for the jet simulations. The initial configuration consists of 2D segregated fuel jet with heated air in the co-flow. The fuel and oxidizer compositions correspond to the same conditions used in the homogeneous ignition studies (30/70 for hydrogen and nitrogen in the fuel, 21/79 for oxygen and nitrogen in the oxidizer). The fuel jet has an inlet width of \( d = 1.5 \) cm; the remaining sections of the inlet extending 4 cm around the fuel jet centerline represent the co-flow oxidizer inlet. The mixture pressure, which is considered constant throughout the runs, and corresponding initial air temperature are different for four cases. The initial air temperature is set high enough to result in autoignition within the second ignition limit. Two different sets of oxidizer temperatures and corresponding pressures result in comparable shortest ignition delay times for homogeneous mixtures. Different Reynolds numbers based on the fuel jet width for identical pressures are used to investigate turbulent transport effects on the autoignition process. The Reynolds numbers are expressed as \( \text{Re}_d = \frac{Ud}{\nu} \), where \( U \) is the fuel jet bulk velocity, \( d \) is the fuel jet width, and \( \nu \) is the kinematic viscosity of the fuel at the inlet conditions. The co-flow air
velocity is 1.0 m/s for all the cases. The results presented below correspond to approximately 100 realizations per case.

**Figure 3.1:** Computational configuration and initial run condition.

### 3.3 Results and Discussion

#### 3.3.1 Homogeneous Autoignition

To demonstrate the importance of unsteady dissipation on autoignition, it is necessary to examine the homogeneous mixture autoignition process. The particular relevance to this study is the consideration of the dependence of ignition delay and chemistry on mixture composition and temperature. Figs. 3.2(a) and 3.2(b) show the homogeneous autoignition
delay time as a function of the mixture fraction at 1 atm and 3 atm pressure, respectively. Similar plots can also be found in Zhang’s thesis. The ignition delay times are determined as the times when the temperature increases by 5% of the final temperature rise during the autoignition process. As shown in Fig. 3.2(a) and 3.2(b) the shortest ignition delay time for these two homogeneous cases are similar.

As shown in Fig. 3.2(a) for the atmospheric case, the shortest ignition delay time is less than 1 ms. A broad range of mixture fraction from 0.03 to 0.1 is observed corresponding to short ignition delay time less than 1 ms for the 1 atm case. Fig. 3.2(a) shows that the first ignition appears at $Z = 0.06$. Although the ignition delay time varies very little when mixture fraction is in the range of 0.02 to 0.13, the delay time changes by 4 orders of magnitude in the remaining range. Below $Z = 0.02$ autoignition is delayed by the lack of chemical reaction activities and at $Z$ is greater than 0.12, the autoignition delay time is increased primarily because of reduced mixture temperature.

Fig. 3.2(b) shows the ignition delay time as the function of mixture fraction at the higher pressure (3 atm) of homogeneous ignition case, which is also governed by second explosion limit, corresponding to a higher crossover temperature. An air preheat temperature of 1030 K is used for the case of 3 atm to obtain similar minimum ignition delay times to the atmospheric case. The shortest ignition delay time is less than 1 ms and occurs at $Z = 0.03$. The adiabatic pure mixing temperature as a function of the mixture fraction is also included in both homogeneous ignition delay plots for reference.
Therefore, in both the atmospheric cases and the higher pressure cases, the most preferred mixture for autoignition occurs at mixture conditions, which are much leaner than stoichiometric conditions because of the strong dependence of autoignition chemistry on temperature.
Figure 3.2: Autoignition delay time and mixture temperature vs. mixture fraction at a) $p = 1$ atm, b) $p = 3$ atm. Solid lines: ignition delay, $\tau_{\text{ign}}$; dashed lines: preheat temperature.
3.3.2 Jet Autoignition

In this section, results on the jet autoignition are presented. First, a general structure of the combustion process from induction, to the formation of ignition kernels to the eventual propagation of this ignition, is presented in terms of 2D renderings of the unsteady ODT solutions. These renderings illustrate the coupling between chemistry and turbulent transport in the jet configuration. Then, details of these profiles as a function of time are presented to further elucidate the ignition delay to the presence of mixing and entrainment and identify the modes of combustion present during the ignition and the following high-temperature combustion stage. Finally, statistics of the autoignition process will be presented based on conditional profiles of reactive scalars and the scalar dissipation rate. In the present study, we adopt two viewpoints for presenting results. The first viewpoint is based on scalar profiles at different times of the solution (starting from the imposed initial conditions). These temporal profiles may be used to provide direct comparisons with the autoignition process in homogeneous mixtures. The second viewpoint is based on statistics at different downstream distances from the jet inlet. To obtain these statistics, an interpretation of the temporal evolution of the 1D ODT solutions to spatial evolution downstream of the jet inlet is carried out; this interpretation is discussed below. Statistics at distances downstream of the inlet are relevant to comparisons with experimental data trends and to study the evolution of the ignition length as a function of flow and fluid properties (e.g. Reynolds number, pressure). Fig. 3.3 shows 2D renderings of OH mass fractions corresponding to a single realization for
cases A, B, C and D. The 1D domain corresponds to the horizontal axis. The temporal evolution is converted to a downstream distance according to Eq. (2.5). The 2D rendering of stirring events shown in Fig. 3.3 also show that stirring events are initiated at the interfaces between the fuel jet and co-flow air, and that the size of eddies progressively increases as a function of downstream distance, emulating the progressive growth of the shear layers. Evidence of the existence of an ‘energy cascade’ is also demonstrated by the presence of smaller eddies that trail larger eddies, with regions of spatial intermittency, as these smaller eddies dissipate. It is important to note that different realizations of the ODT solutions for all cases exhibit differences in the downstream distance corresponding to the onset of autoignition, the placement of the stirring events and the contours of OH mass fractions. Nonetheless, the renderings provide important insight on the role of turbulent transport on the onset of autoignition and the subsequent high-temperature combustion stages.

From Fig. 3.3, two zones may be identified, which correspond to an induction stage near the jet inlet and a high-temperature combustion stage further downstream. Different parameters, primarily the jet Reynolds number and the pressure determine the ignition height and the concentration of OH downstream of the ignition point. The figure shows that for the higher Reynolds cases, B and D, stirring events start nearer to the jet inlet, also signifying higher turbulence intensity in these jets. Stirring events result in increased scalar interfaces, including the number of autoignition kernels. Therefore, they emulate two fundamental effects in turbulent flames (Echekki et al., 2001).
The first is associated with the effects of curvature and flame-flame interactions, which are exhibited by relatively small-size eddies. These effects appear to be dominant in the near-field where eddy size ranges are narrow. The second is associated with wrinkling resulting in the multiplication of flame kernels as shown further downstream where the range of eddy sizes is larger.

While case A has a similar inlet jet Reynolds number as case C, and similarly for cases B and D, the two pressures exhibit different autoignition delay times as shown by the higher ignition lengths in the high pressure jets. The trends may be interpreted based on the role of chemistry and molecular transport at the different pressure conditions:

(1) As demonstrated in Figs. 3.2(a) and 3.2(b), the higher pressure mixtures exhibit a much narrower range of the mixture fractions exhibiting the shortest ignition times. For example, homogeneous mixtures that ignite with an induction time lower than 1 ms are from values of the mixture fraction between approximately 0.03 and 0.11 for 1 atmosphere and 0.02 to 0.045 for 3 atmospheres. In the non-homogeneous case exhibited by the jet configuration, the narrow range of the mixture fraction corresponding to the shortest ignition times for the high pressure translate into a narrow spatial extent of the mixture that will ignite at below 1 ms; while, this range extent is broader for the 1 atmosphere cases. The different trends also explain the narrow peaks of OH obtained for cases C and D in contrast with cases A and B.
Moreover, at higher pressures and considering the higher air preheat temperature for the higher pressure cases, the molecular transport coefficients for heat, mass and momentum are also higher. Therefore, any gradients in the mixture fraction translate into much higher rates of the dissipation of heat and mass and momentum, resulting in higher induction times. While the higher rates of heat and mass dissipation contribute to increasing the autoignition delay time, they may also play an enhancing role of the propagation of the autoignition kernels once they are generated.
Figure 3.3: Two-dimensional rendering of OH mass fraction based on a single realization of cases A, B, C and D.
Figs. 3.4 to 3.7 shows the spatial 1D profiles of the temperature at different times of the evolution of the jet autoignition process for cases A, B, C and D. The position, $y = 0$, corresponds to the centerline of the jet. At $t = 0$ ms, there is no reaction between the oxidizer and the fuel and the temperature profiles indicate two distinct values corresponding to the preheated air at 980 K (for cases A and B) or 1030 K (for cases C and D) and the cold fuel at 300 K. At later times, the profiles are different for the different cases considered. We start first with case A. In this case, the profiles corresponding to 1 ms already show the formation of a local peak, albeit barely noticeable, indicating the onset of autoignition. In the homogeneous case, the autoignition starts sooner than 1 ms, and therefore, the temperature profiles already exhibit a further delay in the autoignition. The temperature profiles at 1 ms also indicate that no stirring events have already occurred at that time, in contrast to the profiles shown for 3.5 ms and later. Therefore, the delay is associated primarily with the presence of a scalar mixing layer and non-zero dissipation in contrast to the homogeneous runs already discussed.

At higher fuel jet Reynolds numbers (case B), stirring events have already started by 1 ms; and where stirring events occur, the local peak of temperature at the interface between fuel and oxidizer is not present (here only the left interface indicates the implementation of a stirring event). A contrast between the left and right interfaces at 1.5 ms also shows the role of stirring on increasing the ignition delay. In the absence of stirring, the peak temperature at the interface between the fuel and the oxidizer is higher by a few hundred degrees.
However, while turbulent stirring may delay the onset of autoignition or inhibit the formation of ignition kernels, it plays a different role at later stages, resulting in a faster completion of the combustion processes as illustrated by the temperature profiles at 10 and 20 ms between cases A and B.

In contrast to cases A and B or the homogeneous ignition cases, the higher pressure cases, C and D, exhibit more delay in their autoignition process. This delay may be attributed to the presence of scalar dissipation and the enhancement of this dissipation rate by the strong sensitivity of mass and heat diffusion coefficients to pressure and, to a lower extent, the air preheat temperature. Also, despite similarities between the Reynolds numbers between cases A and C and between cases B and D, stirring events are delayed as well because of the higher viscosities at the higher pressure conditions. Case C remains “laminar” (i.e. no stirring events) even after 20 ms from the evolution of the temperature profiles from the jet, while the turbulence intensity at the higher Reynolds number case D is even lower than that of the lower jet Reynolds number at 1 atmosphere, case A. Therefore, the higher viscosity conditions at high pressure contribute to the laminarization of the jet flow. Despite the absence of stirring events in case C, the ignition kernel grows in time, albeit at a different rate than the growth enhanced by stirring. As shown for $t = 20$ ms and for cases C and D, turbulence, again, contributes to a higher rate of completion of the high-temperature combustion process.
Figure 3.4: 1D spatial profiles of temperature for case A.
Figure 3.5: 1D spatial profiles of temperature for case B.
Figure 3.6: 1D spatial profiles of temperature for case C.
**Figure 3.7**: 1D spatial profiles of temperature for case D.
From Figs. 3.4 to 3.7, we can summarize the approximate autoignition delay time, $\tau_{ig}$, of the four different cases with their dominant properties in Table 3.4. The numbers are approximate and do not exhibit the small variations of the ignition delay times between different Reynolds number conditions.

**Table 3.4:** Summary of ignition delay times for the jet flame cases A, B, C and D.

<table>
<thead>
<tr>
<th>Parameter $\tau_{ig}$ (ms)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 3.4 shows that among the conditions at the same pressure, the ignition delay time are nearly the same. However, the present results show that the ignition delay time is increased with the pressure due to the sensitivity of the ignition delay time to the mixture fraction as demonstrated for homogeneous ignition. Moreover, there appears to be little effect of the fuel jet Reynolds number, and accordingly turbulence intensity, on ignition delay, except when the rates turbulent mixing are competitive with the short delay times. In the ODT solution, this translates into conditions when the first stirring events occur earlier than the ignition delay time. Therefore, compared with the role of transport properties and chemistry, turbulence has a relatively small effect on the ignition delay time, as already suggested by Mastorakos *et al.* (1997). However, the jet Reynolds number, and accordingly the turbulence intensity has an important effect on the eventual evolution of the ignition kernels. Stronger
turbulence intensity increases the mixing process by increasing scalar interfaces and ignition kernels as seen in Fig. 3.5 resulting in either interacting kernels, which may potentially annihilate each other, or higher volumetric rates of fuel consumption.

At this point, it is useful to identify the combustion modes that contribute to the propagation of ignition in jet flows once it is started. In non-homogeneous random mixtures (Cao & Echekki, 2007; Echekki & Chen, 2002), the autoignition process is characterized by the formation of ignition kernels near the most reactive mixture (i.e. lean conditions for hydrogen in preheated air) and then propagation into other mixtures (i.e. richer conditions for hydrogen in preheated air). As the premixed fronts cross the stoichiometric lines, non-premixed flames may form. Given the inherent two-stream nature of the jet, the autoignition transition from induction to high-temperature combustion may be subject to the following stages:

- An induction stage, where a build-up of radicals occur with insignificant heat release.
- An ignition and transition to high-temperature combustion phase
- The formation of non-premixed flames downstream.

The different modes of the growth of autoignition kernels are illustrated using the flame index $FI$ (Lock et al., 2005), which is expressed in 1D as:
\[ F I = \frac{Z - Z_s}{|Z - Z_s|} \left[ \frac{1}{2} \left( \frac{dY_{H_2}}{dy} \frac{dY_{O_2}}{dy} \right) \right], \] 

Eq. (3.4)

where \( Z_s = 0.5 \) is the stoichiometric mixture fraction. Beyond identifying whether the mode of combustion is premixed or non-premixed, the expression also identifies whether a premixed flame is rich or lean. The term in the brackets "[ ]" represents the standard normalized form for the flame index (Yamashita et al., 1996); it takes the value of unity for a premixed flame and 0 for a non-premixed flame. The ratio, \((Z - Z_s)/|Z - Z_s|\), yields additional information about whether the premixed flame is rich or lean. If the premixed flame is rich, this ratio is +1; when it is lean, this ratio is -1. In this expression, we adopt a different definition of the mixture fraction to allow for species originating in the fuel to be represented. Therefore, we use the Bilger mixture fraction (Bilger, 1990):

\[ Z = \frac{(Y_{H} - Y_{H,O})/(2W_H) - (Y_{O} - Y_{O,O})/W_O}{(Y_{H,F} - Y_{H,O})/(2W_H) - (Y_{O,F} - Y_{O,O})/W_O} \]  

Eq. (3.5)

where \( W_H \) and \( W_O \) refer to the hydrogen atom and the oxygen atom atomic weights with values of 1 and 16.

Figs. 3.8 to 3.11 shows correlation of the reaction rate of \( H_2O, \dot{\omega}_{H_2O} \), vs. the flame index, \( FI \), at different times as in Figs. 3.4 to 3.7 for cases A, B, C and D. The water reaction rate serves as an indicator of the presence of a flame. Correlations of this reaction rate with the flame
index identify which combustion mode (non-premixed, lean premixed and rich premixed) is dominant at the different stages of the ignition process. Initially, at time $t = 0$ ms, for all the cases, chemistry has not started between the fuel and oxidizer and the H$_2$O reaction rate profiles have zero values and the profiles indicate zero reaction rates for water.

At subsequent times, the evolution of the dominant modes of combustion at different times may or may not be captured entirely with the limited number of times shown. For examples, in both cases A and B, the correlation of $\dot{\omega}_{\text{H}_2\text{O}}$ vs. $FI$ indicates that at 1 ms, the dominant combustion mode is a non-premixed flame; although, at 1.5 ms and 3.5 ms for case A, combustion in rich premixed mode is also present. The expected scenario is that for all cases, ignition starts at relatively lean conditions (with the ignition delay time is shortest), then evolves through propagation of the ignition kernel to richer conditions passing through stoichiometric conditions. The combustion eventually evolves to a non-premixed flame mode, as suggested by subsequent times past 3.5 ms.

In cases C and D, no indication of chemical activity is found for the three initial times shown, 0, 1 and 1.5 ms, indicating the ignition delay associated with the high-pressure cases. However, at 3.5 ms, combustion at stoichiometric non-premixed and lean premixed conditions is seen. At subsequent times, the dominant mode of combustion is the non-premixed flame mode. Therefore, elements of the transition from lean premixed, to rich premixed and non-premixed combustion modes can be found in the different snapshots for cases A, B, C and D yielding eventually to combustion in a non-premixed flame.
Figure 3.8: Reaction rate of H$_2$O vs. flame index for case A.
Figure 3.9: Reaction rate of H$_2$O vs. flame index for case B.
Figure 3.10: Reaction rate of H$_2$O vs. flame index for case C.
Figure 3.11: Reaction rate of H$_2$O vs. flame index for case D.
Next, we present conditional statistics of the scalar dissipation rate and two reactive scalars: the mixture temperature and the OH mass fraction. Means of these quantities are conditionally-averaged based on the Bilger mixture fraction defined in Eq. (3.5). The results are presented for different downstream distances, \( x/d = 1, 2, 3, 4, 5, \) and 6. Figs. 3.12 to 3.15 shows the scalar dissipation rate, \( \chi \), conditional means for cases A, B, C and D. The dissipation rate is based on the 1D profiles and is expressed as:

\[
\chi = 2 \alpha \left( \frac{dZ}{dy} \right)^2. \tag{3.6}
\]

In this expression, \( \alpha \) is the mixture thermal diffusivity. As expected, the conditional means for the scalar dissipation rate exhibit higher values for the higher Reynolds number cases at least in the near-field. The higher dissipation rates decreases rapidly as a function of downstream distance. The role of stirring contributes to increasing the rate of dissipation initially, and the rate of mixing, which eventually decreases the rate of dissipation. Moreover, the higher pressure conditions also exhibit higher rates of dissipation in the near-field. These higher values may not be attributed to higher turbulence intensity and higher rates of stirring (which act primarily on the mixture fraction gradients in Eq. (3.6)); instead, they are associated with the higher rates of thermal diffusivities associated with the higher pressures.

Finally, another common feature of the dissipation rate profiles is associated with their shapes. Most dissipation rate profiles exhibit a dip at or near stoichiometric conditions for intermediate \( x/d \)'s of 2 and 3. We speculate that these dips follow the same trend discussed
above: higher dissipation rates conditions, which at stoichiometric conditions, are a result of higher temperatures, eventually beget lower dissipation rates, as dissipation tends to homogenize the mixture.
Figure 3.12: Scalar dissipation rate conditional means for case A.
Figure 3.13: Scalar dissipation rate conditional means for case B.
Figure 3.14: Scalar dissipation rate conditional means for case C.
Figure 3.15: Scalar dissipation rate conditional means for case D.
Figs. 3.16 to 3.19 shows the conditional means of OH for cases A, B, C and D at the different downstream distances listed above. The principal observation is that higher Reynolds number conditions result in higher ignition lengths as displayed by the reacting and non-reacting, respectively, profiles for OH for lower and higher, respectively, Reynolds number. Given that temporal profiles do not exhibit significant differences in autoignition delay times, the difference in autoignition lengths may be attributed primarily to the higher inlet flow velocities in the higher Reynolds number cases.

A comparison between peak values of the profiles of OH between the low jet Reynolds cases (A and C) and the high jet Reynolds cases (B and D) show that the lower jet Reynolds cases exhibit higher peaks. These higher values reflect conditions of lower rates of scalar dissipation for cases A and C in contrast to cases B and D, respectively. Some of the profiles exhibit double peaks indicating the predominance of two combustion modes, a premixed (e.g. lean premixed for case D at \( x/d = 2 \) and 3) and a non-premixed mode. Further downstream, the OH profiles start to decay, primarily because of increased rates of scalar dissipation associated with turbulent mixing.
Figure 3.16: OH mass fraction conditional means for case A.
Figure 3.17: OH mass fraction conditional means for case B.
Figure 3.18: OH mass fraction conditional means for case C.
Figure 3.19: OH mass fraction conditional means for case D.
Figs. 3.20 to 3.23 shows the conditional means of temperature for cases A, B, C and D at the different downstream distances listed above. Comparing profiles at $x/d = 1$, for low Reynolds number case A and C with high Reynolds number case B and D, show that ignition is delayed in space for the higher Reynolds number cases, resulting in higher autoignition lengths for the higher Reynolds number cases. For case C, the temperature rise is the highest due to increased pressure and low Reynolds number. For case A and B the highest temperature attained is below 2000 K, whereas for case C and D, the maximum temperature is well above 2000 K.
Figure 3.20: Temperature conditional means for case A.
Figure 3.21: Temperature conditional means for case B.
Figure 3.22: Temperature conditional means for case C.
Figure 3.23: Temperature conditional means for case D.
3.4 Conclusions

The autoignition of a segregated mixture of diluted hydrogen and preheated air in a jet configuration is studied numerically using the ODT model. The simulations are carried out using a detailed mechanism and mixture averaged transport properties. Comparisons of the jet autoignition simulations are carried out with homogeneous autoignition at a broad range of mixture fractions. The simulations are implemented at two fuel jet Reynolds numbers and two pressure conditions. The principal observations of the present results are as follows:

(1) Autoignition in the jet configuration undergo more delay compared to homogeneous autoignition due to the presence of scalar dissipation in the scalar mixing layer where ignition is initiated.

(2) The autoignition in the jet configuration, while subject to dissipation rates, exhibits comparable induction times as a function of the fuel jet Reynolds number. However, spatial profiles will exhibit higher autoignition lengths for higher inlet Reynolds numbers. This trend may be attributed primarily to the higher travel distance over a given induction time incurred by an ignition kernel at higher inlet velocities.

(3) Turbulence is found to have an effect on autoignition delay only when turbulent time scales are shorter that the induction time for chemistry. However, turbulence plays a more important role in the subsequent stages of high-temperature combustion where more complete burning is achieved with higher turbulent stirring.
(4) The mixture sensitivity to autoignition delay also plays an important role in the onset of autoignition in the jet configuration. For the higher pressure simulations, although, the shortest induction time is similar to the lower pressure simulations, a narrow range for the most reactive mixture results in further coupling with scalar dissipation and further delay in the autoignition process. This delay is enhanced by the enhancement of molecular transport properties by temperature.

(5) In the jet configuration, different combustion modes can be found during the autoignition process, including a quick transition within the scalar mixing layer from lean premixed combustion, through richer mixtures and a final transition to a non-premixed flame mode further downstream from the inlet.
CHAPTER 4

Autoignition in Carbon Monoxide/Hydrogen/Air Mixtures

4.1 Introduction

Autoignition of carbon monoxide/hydrogen/air mixtures has always been a subject of great interest (Yetter et al., 1991a; Dean et al., 1978; Dixon-Lewis, 1955; Warnatz, 1985). Since the ignition of pure carbon monoxide is difficult, previous studies carried out for pure CO systems were better described, considering the presence of a small amount of water vapor or wet CO oxidation (Brokaw, 1970) as well as the addition of hydrogen, resulting in syngas. It has been shown in (Semenov, 1934; Kondrat’ev, 1944; Enikolopyan, 1950) that homogeneous oxidation of carbon monoxide can occur only in the presence of hydrogen containing compounds, which promote an increasing and essential role for OH or H radicals. The mechanism for CO/H\textsubscript{2}/O\textsubscript{2} systems, like H\textsubscript{2}/O\textsubscript{2} mechanism, forms an integral part of all hydrocarbon (oxidation) mechanisms. It falls between simpler H\textsubscript{2}/O\textsubscript{2} systems and more complex formaldehyde systems, in the hierarchical system of complex hydrocarbons. Studies (Kondrat’ev, 1944; Enikolopyan, 1950) show that addition of small amounts of hydrogen accelerates the oxidation of carbon monoxide and expands the region of ignition of a mixture of CO and O\textsubscript{2}. The sensitivity of CO systems is very high even to the presence of small amounts of hydrogenous species, and hence for the study of pure CO systems, the removal of
these system contaminations was an experimentally challenging task. However, all practical combustion systems contain some amount of hydrogenous species, and therefore, recent studies have focused on CO and H$_2$ chemistry instead of pure CO systems.

A number of studies have been carried out for the homogeneous combustion (Dean et al., 1978; Dixon & Lewis, 1955; Yetter et al., 1991; Warnatz, 1985) of CO/H$_2$. Comparatively, fewer studies are available, which focus on the combined effect of chemical kinetics and molecular transport (Cherian et al., 1981; Olson & Olson, 1992; Mishra et al., 1994; Maas and Waranatz, 1988). Trujillo et al. (1997) studied ignition in non-premixed counter-flowing CO/H$_2$ versus heated air and identified three ignition regimes based on the concentration of hydrogen. Yetter et al. (1991b) validated a comprehensive reaction mechanism for CO/H$_2$/O$_2$ kinetics with the reproduction of experimental results over a wide range of parameters, including equivalence ratios, C/H ratios, pressures and temperatures. The work done by Hewson & Kerstein (2001) involves the application of ODT model to study the turbulent jet flames in CO/H$_2$/N$_2$ systems.

In the present study, the ODT model is implemented to investigate the turbulent autoignition process in a jet configuration of CO/H$_2$ in preheated co-flow of air. The study attempts to identify the role of molecular and turbulent transport in CO/H$_2$ ignition in a turbulent jet configuration. The effect of H$_2$ concentration on ignition characteristics is also discussed. For the present simulations, the comprehensive reaction mechanism from Yetter et al. (1991b) is used. The mechanism has 28 reversible reactions and 13 species: H$_2$, O$_2$, OH, H, O, HO$_2$, ...
H$_2$O$_2$, H$_2$O, CO, CO$_2$, HCO, N$_2$, Ar. Table 4.1 shows the complete mechanism with the reaction rate coefficients. The first 19 reversible reactions correspond to the H$_2$/O$_2$ system already discussed in Chapter 3.

**Table 4.1:** CO/H$_2$/Air mechanism rate constants are in the form $k_f = AT^\beta \exp\left(-\frac{E_a}{RT}\right)$; units are moles, cm, sec, K and kcal/mol. Third body coefficients in reactions 5, 6, 7, 8, 9, 15, 20 and 24 enhancement factors are 12 for H$_2$O, 2.5 for H$_2$, 1.9 for CO and 1.8 for CO$_2$.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$A$</th>
<th>$\beta$</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+O$_2$ ⇔ O + OH</td>
<td>1.92 x 10^{14}</td>
<td>0.0</td>
<td>16.44</td>
</tr>
<tr>
<td>2</td>
<td>O+H$_2$ ⇔ H + OH</td>
<td>5.08 x 10^{4}</td>
<td>2.67</td>
<td>6.29</td>
</tr>
<tr>
<td>3</td>
<td>OH+H$_2$ ⇔ H + H$_2$O</td>
<td>2.16 x 10^{8}</td>
<td>1.51</td>
<td>3.43</td>
</tr>
<tr>
<td>4</td>
<td>OH + OH ⇔ O + H$_2$O</td>
<td>1.23 x 10^{4}</td>
<td>2.62</td>
<td>-1.88</td>
</tr>
<tr>
<td>5</td>
<td>H$_2$ + M ⇔ H + H + M</td>
<td>4.57 x 10^{19}</td>
<td>-1.4</td>
<td>104.4</td>
</tr>
<tr>
<td>6</td>
<td>O + O + M ⇔ O$_2$ + M</td>
<td>6.17 x 10^{15}</td>
<td>-0.50</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>O + H + M ⇔ OH + M</td>
<td>4.72 x 10^{18}</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>H + OH + M ⇔ H$_2$O + M</td>
<td>2.25 x 10^{22}</td>
<td>-2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>H + O$_2$ + M ⇔ HO$_2$ + M</td>
<td>6.17 x 10^{19}</td>
<td>-1.42</td>
<td>0.0</td>
</tr>
<tr>
<td>10</td>
<td>HO$_2$ + H ⇔ H$_2$ + O$_2$</td>
<td>6.63 x 10^{13}</td>
<td>0.0</td>
<td>2.13</td>
</tr>
<tr>
<td>11</td>
<td>HO$_2$ + H ⇔ OH + OH</td>
<td>1.69 x 10^{14}</td>
<td>0.0</td>
<td>0.87</td>
</tr>
<tr>
<td>12</td>
<td>HO$_2$ + O ⇔ OH + O$_2$</td>
<td>1.81 x 10^{13}</td>
<td>0.0</td>
<td>-0.4</td>
</tr>
<tr>
<td>13</td>
<td>HO$_2$ + OH ⇔ H$_2$O + O$_2$</td>
<td>1.45 x 10^{16}</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>HO$_2$ + HO$_2$ ⇔ H$_2$O$_2$ + O$_2$</td>
<td>3.02 x 10^{12}</td>
<td>0.0</td>
<td>1.39</td>
</tr>
<tr>
<td>15</td>
<td>H$_2$O$_2$ + M ⇔ 2 OH + M</td>
<td>1.20 x 10^{17}</td>
<td>0.0</td>
<td>45.5</td>
</tr>
<tr>
<td>16</td>
<td>H$_2$O$_2$ + H ⇔ H$_3$O + OH</td>
<td>1.00 x 10^{15}</td>
<td>0.0</td>
<td>3.59</td>
</tr>
<tr>
<td>17</td>
<td>H$_2$O$_2$ + H ⇔ H + HO$_2$</td>
<td>4.82 x 10^{13}</td>
<td>0.0</td>
<td>7.95</td>
</tr>
</tbody>
</table>
Table 4.1 (continued)

<table>
<thead>
<tr>
<th></th>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponential</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>( \text{H}_2\text{O}_2 + \text{O} \rightleftharpoons \text{OH} + \text{HO}_2 )</td>
<td>( 9.55 \times 10^6 )</td>
<td>2.0</td>
<td>3.97</td>
</tr>
<tr>
<td>19</td>
<td>( \text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{HO}_2 )</td>
<td>( 7.00 \times 10^{12} )</td>
<td>0.0</td>
<td>1.43</td>
</tr>
<tr>
<td>20</td>
<td>( \text{CO} + \text{O} + \text{M} \rightleftharpoons \text{CO}_2 + \text{M} )</td>
<td>( 2.51 \times 10^{13} )</td>
<td>0.0</td>
<td>-4.54</td>
</tr>
<tr>
<td>21</td>
<td>( \text{CO} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{O} )</td>
<td>( 2.53 \times 10^{12} )</td>
<td>0.0</td>
<td>47.7</td>
</tr>
<tr>
<td>22</td>
<td>( \text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H} )</td>
<td>( 1.50 \times 10^7 )</td>
<td>1.3</td>
<td>-0.765</td>
</tr>
<tr>
<td>23</td>
<td>( \text{CO} + \text{HO}_2 \rightleftharpoons \text{CO}_2 + \text{OH} )</td>
<td>( 6.02 \times 10^{13} )</td>
<td>0.0</td>
<td>23.0</td>
</tr>
<tr>
<td>24</td>
<td>( \text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M} )</td>
<td>( 1.86 \times 10^{17} )</td>
<td>-1.0</td>
<td>17.0</td>
</tr>
<tr>
<td>25</td>
<td>( \text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2 )</td>
<td>( 7.58 \times 10^{12} )</td>
<td>0.0</td>
<td>0.41</td>
</tr>
<tr>
<td>26</td>
<td>( \text{HCO} + \text{OH} \rightleftharpoons \text{CO} + \text{H}_2\text{O} )</td>
<td>( 3.02 \times 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>27</td>
<td>( \text{HCO} + \text{H} \rightleftharpoons \text{CO} + \text{H}_2 )</td>
<td>( 7.23 \times 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>28</td>
<td>( \text{HCO} + \text{O} \rightleftharpoons \text{CO} + \text{OH} )</td>
<td>( 3.02 \times 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

4.2 Run Conditions

The run conditions for this turbulent jet configuration are similar to those described in Chapter 3, with the exception of the addition of carbon monoxide to the fuel jet. The computations are carried out for homogeneous ignition and for a turbulent jet configuration. For the homogenous ignition, a wide range of equivalence ratios/mixture fractions is considered spanning from fuel-lean to fuel-rich conditions. The scope of the homogeneous ignition study is to identify the most favorable mixture conditions for ignition and to provide a baseline reference case for comparison with the jet autoignition configuration.
For the jet configuration, two sets of computations are carried out with 50% dilution by nitrogen and varying CO and H₂ concentrations. The choice of preheat temperatures and dilution yields a stoichiometric mixture fraction of 0.5 and 0.53 for the two sets of composition, respectively. Moreover, the effect of changing fuel jet velocities is also studied. All the statistics shown of jet autoignition below are based on more than 50 ODT realizations. The resolution used is 401 with 1D domain extending from -4 to 4. The time taken for the computation of 1 realization, on the NCSU High-Performance Computing IBM clusters with Portland group compilers, pgf90, varied from 1 to 2 hours. The simulations are carried out to downstream distances in which a non-premixed flame is established; but, they are not necessarily carried out to the flame heights or beyond.

Table 4.2 and 4.3 shows the mixture conditions corresponding to the homogeneous and jet autoignition runs, respectively. Fuel jet temperature and pressure is uniform at 300 K and 1 atmosphere. The two sets of fuel composition are 15% H₂, 35% CO, 50% N₂, and 20% H₂, 30% CO, 50% N₂, respectively as shown in Table 4.4. For each composition, a preheat temperature is prescribed as given in the Table 4.3, corresponding to 980 K and 950 K, respectively. Also, for each preheat temperature, two jet Reynolds numbers, based on the fuel inlet bulk velocity and diameter, are examined. The mixture and inlet conditions are given in Table 4.3, corresponding to 5000 and 10000, respectively.
Table 4.2: Run conditions for homogeneous autoignition.

<table>
<thead>
<tr>
<th>Range of mixture fractions</th>
<th>Pressure (atm)</th>
<th>Fuel temperature (K)</th>
<th>Air temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001-0.15</td>
<td>1</td>
<td>300</td>
<td>980</td>
</tr>
<tr>
<td>0.001-0.15</td>
<td>1</td>
<td>300</td>
<td>950</td>
</tr>
</tbody>
</table>

Table 4.3: Run conditions summary for the jet cases A, B, C and D.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reynolds number</td>
<td>5000</td>
<td>10000</td>
<td>5000</td>
<td>10000</td>
</tr>
<tr>
<td>Air temperature (K)</td>
<td>980</td>
<td>980</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td>Pressure (atm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.4: Fuel composition.

<table>
<thead>
<tr>
<th>Composition</th>
<th>H₂ (%)</th>
<th>CO (%)</th>
<th>N₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>35</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>
4.2.1 Homogeneous Autoignition

The homogeneous autoignition is implemented in a similar manner as explained earlier in chapter 3. The solution to the species equation, (Eq. (3.1)) is determined under adiabatic conditions for two different preheat temperatures for air. The mixture fraction $Z$, (Eq. (3.3)), is modified, as follows:

$$Z = \frac{Y_{H_2} - Y_{H_2,O}}{Y_{H_2,F} - Y_{H_2,O}} = \frac{Y_{CO} - Y_{CO,O}}{Y_{CO,F} - Y_{CO,O}} = \frac{Y_{O_2} - Y_{O_2,O}}{Y_{O_2,F} - Y_{O_2,O}} = \frac{Y_{N_2} - Y_{N_2,O}}{Y_{N_2,F} - Y_{N_2,O}}$$  

Eq. (4.1)

For both compositions considered, the reference mass fractions for $H_2$, $O_2$, CO and $N_2$ in the oxidizer stream are 0, 0.2329, 0 and 0.7670, respectively, while, in the fuel stream, they are 0.0125, 0, 0.4065 and 0.5808 for composition 1, and 0.0176, 0, 0.3683 and 0.6139 for composition 2, respectively. The dilution of the fuel results in a stoichiometric mixture fraction to 0.5 for composition 1 and 0.53 for composition 2.

4.2.2 Jet Autoignition

The initial computational setup and geometry of the flow is identical to $H_2$-air mechanism as described in chapter 3. The two sets of fuel and oxidizer compositions correspond to the same conditions used in the homogeneous ignition studies. For each composition, four cases are considered using a combination of one of two values of preheat temperatures and Reynolds number each. Also, the co-flow air velocity is 1.0 m/s for all cases considered. The statistical results presented below correspond to approximately 50 realizations per case.
4.3 Results and Discussion

4.3.1 Homogeneous Autoignition

As stated earlier, homogeneous ignition serves as an important baseline case to understand the role of diffusive and turbulent transport in autoignition delay. Another important role of the homogeneous ignition study is to investigate the favorable conditions for autoignition and their extent in composition space. In the hydrogen simulations, it was found that that the lower pressure conditions result in a broad range (in composition or mixture fraction space) of favorable early ignition conditions. A similar investigation is carried out by looking at the role of oxidizer preheat temperature and H\textsubscript{2}/CO ratio in the fuel. Fig. 4.1 shows the homogeneous autoignition delay time as a function of the mixture fraction at the two (H\textsubscript{2}/CO) compositions and preheat temperatures considered in this study. The combination of composition and preheat temperatures yields four different plots as shown in Fig. 4.1. The ignition delay times are determined as the times when the temperature increases by 5% of the final temperature rise during the autoignition process. As shown in Fig. 4.1, there are qualitative similarities and differences between the 4 mixture conditions considered. The shorted ignition times correspond to very fuel-lean conditions. At the same oxidizer preheat temperature, a higher H\textsubscript{2}/CO ratio (i.e. composition 2) results in a shorter ignition delay time.
A higher oxidizer preheat temperature results in a broader range of minimum ignition delay times. Beyond this range, the ignition delay time increases significantly at leaner or rich conditions away from this range. Moreover, a higher preheat temperature shifts the conditions of minimum ignition delay time to slightly more richer conditions. Nonetheless, the ignition delay times are comparable in magnitude and correspond to values of the order of 2 ms (i.e. no major disparities between the different composition and preheat temperature results). Table 4.5 shows a summary of ignition delay times for the four homogeneous cases.

<table>
<thead>
<tr>
<th>Compositions</th>
<th>$T_{\text{oxidizer}}$ (K)</th>
<th>$\tau_{\text{ignition}}$ (ms)</th>
<th>Most Reactive Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:35:50 H$_2$:CO:N$_2$</td>
<td>980</td>
<td>2.1</td>
<td>0.04 or 0.05</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>6.8</td>
<td>0.03</td>
</tr>
<tr>
<td>20:30:50 H$_2$:CO:N$_2$</td>
<td>980</td>
<td>1.5</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>4.8</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Figure 4.1: Autoignition delay time and mixture temperature vs. mixture fraction. Solid lines: ignition delay, $\tau_{\text{ign}}$; dashed lines: preheat temperature.
As already discussed for the H$_2$/O$_2$ system, the extent to which the range of early autoignition delay is broad may play an important role in the competition between chemistry and (molecular and turbulent) transport and their effects of autoignition delay in the jet configuration.

### 4.3.2 Jet Autoignition

**Overall Autoignition Region Structure: 2D Rendering of OH Mass Fraction**

Fig. 4.2 shows the 2D rendering of OH mass fractions for case A, B, C and D of composition 1. Comparing cases B and D with cases A and C, it is seen that the stirring events start nearer to fuel jet inlet for the higher Reynolds number jets, cases B and D. The effect of early stirring events due to increased turbulence intensity causes the onset of autoignition to be delayed further downstream. Also, the lower Reynolds number cases A and C show the presence of more ignition kernels due to lower dissipation of heat. These ignition kernels merge and propagate through the mixture resulting in broader spatial profiles. A curious observation in case B is of a separated flame, which occurs at the centre of the fuel jet. It occurs in between the induction and propagation mode of combustion with many small eddies forming around it.
Fig. 4.3 shows the 2D rendering of OH mass fractions for case A, B, C and D of composition 2. The OH profiles show an increase in concentration due to the higher $\text{H}_2/\text{CO}$ ratio in the fuel. Case B shows some early stirring events, which not only enhance the mixing rate but also initiate the onset of autoignition, earlier than in case A. This may be attributed to the differential diffusion of hydrogen, which is amplified by this increased mixing rate. The lower oxidizer preheat temperature cases C and D shows similar development of flames with increased OH concentrations. The onset of autoignition is shifted further downstream due to the lower oxidizer preheat temperature.
**Figure 4.2:** Two-dimensional rendering of OH mass fraction based on a single realization of cases A, B, C and D for composition 1.
Figure 4.3: Two-dimensional rendering of OH mass fraction based on a single realization of cases A, B, C and D for composition 2.
**1D Temperature Profiles**

Figs. 4.4 to 4.7 shows the spatial 1D profiles of the temperature at different times of the evolution of the jet autoignition process for cases A, B, C and D for composition 1. The time steps shown, \( t=0, 1, 2.3, 2.8, 5 \) and 10 ms, capture the start of ignition for the different cases. The temporal profiles are convenient to identify the onset of autoignition and the comparison of the autoignition delay time compared to homogeneous ignition. The profiles are used prior to the temporal-to-spatial conversion of profiles as is done in Fig. 4.2. In case A, which corresponds to \( \text{Re} = 5000 \) and an oxidizer preheat temperature of 980 K, the temperature profile for time \( t=1 \) ms, shows a formation of a local peak, which indicates the onset of autoignition in the mixture. The first stirring event is shown at time \( t=2.8 \) ms; therefore, autoignition occurs before the onset of turbulence effects represented by the stirring events. When compared with the higher fuel jet Reynolds number cases (case B), stirring events have already started by 1 ms; therefore, in case B, turbulent transport is in direct competition with the chemical processes leading to autoignition. For the same time of 1 ms, the two interfaces of the fuel and oxidizer mixtures show different outcomes; on the left, there is an onset of autoignition indicated by a temperature rise; while on the right, there is no local temperature peak present. It is noteworthy that the delay time of 1 ms is shorter than the shortest ignition delay time in the homogeneous ignition cases. This trend may be interpreted from the mechanism of differential diffusion of the fuel species, given the disparate rates of diffusion between \( \text{H}_2 \) and \( \text{CO} \). In fact, the ratio of the \( \text{H}_2 \) to \( \text{CO} \) mass fractions at first site of
ignition in cases A and B is 0.33 and 0.076, respectively; while, the prescribed ratio in the fuel jet is only 0.03. Therefore, the autoignition is enhanced by increased dilution of the fuel with H₂. The trends observed highlight the effects of molecular transport in dual-fuel mixtures, as is the case of H₂/CO. Table 4.6 shows the H₂/CO ratio for different compositions and cases.

Table 4.6: H₂/CO ratio for different compositions and cases.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Homogeneous autoignition</th>
<th>Case A</th>
<th>Case B</th>
<th>Case C</th>
<th>Case D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition 1</td>
<td>0.030</td>
<td>0.33</td>
<td>0.076</td>
<td>0.36</td>
<td>0.165</td>
</tr>
<tr>
<td>Composition 2</td>
<td>0.048</td>
<td>0.148</td>
<td>0.10</td>
<td>0.516</td>
<td>0.273</td>
</tr>
</tbody>
</table>

Once autoignition is established at both interfaces (see for example, \( t = 2.8 \) ms) the temperature profiles indicate a higher degree of broadening for the earlier (left) ignition interface. This process of broadening continues at later times indicating the merger of combustion zones.

Considering their lower oxidizer preheat temperature, cases C and D exhibit increased ignition delay in comparison to cases A and B. Because of this increased delay time, stirring events are in direct competition with autoignition chemistry even for the lower Reynolds
Case C shows small ignition kernels at 2.3 ms, while the higher Reynolds number case D shows the onset of ignition at 2.8 ms, indicating higher ignition delay.

Figs. 4.8 to 4.11 shows the spatial 1D profiles of the temperature at different time steps for composition 2 corresponding to $t=0, 0.9, 1.9, 2.2, 5, 10$ ms. Again, this composition is characterized by a higher $\text{H}_2/\text{CO}$ ratio, and therefore, a shorter ignition delay time. The ignition delay time is reduced for all the 4 cases with similar trends noted above for composition 1. Table 4.7 shows a summary of ignition delay times for the four cases of composition 1 and 2.

**Table 4.7:** Summary of ignition delay times for the jet flame cases A, B, C and D.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Composition</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{ig}$ (ms)</td>
<td>Composition 1</td>
<td>1</td>
<td>1</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Composition 2</td>
<td>0.9</td>
<td>0.9</td>
<td>1.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Figure 4.4: 1D spatial profiles of temperature for case A for composition 1.
Figure 4.5: 1D spatial profiles of temperature for case B for composition 1.
Figure 4.6: 1D spatial profiles of temperature for case C for composition 1.
Figure 4.7: 1D spatial profiles of temperature for case D for composition 1.
Figure 4.8: 1D spatial profiles of temperature for case A for composition 2.
Figure 4.9: 1D spatial profiles of temperature for case B for composition 2.
Figure 4.10: 1D spatial profiles of temperature for case C for composition 2.
Figure 4.11: 1D spatial profiles of temperature for case D for composition 2.
Combustion Modes: The Flame Index

As discussed earlier for the hydrogen chemistry cases, an understanding of the modes governing the combustion from autoignition to flame formation is very important. The combustion modes again are identified using the flame index. Equations 3.4 and 3.5 are modified to include the presence of CO as a fuel and carbon as an additional element. The flame index and the mixture fraction are expressed as follows:

\[ FI = \frac{Z - Z_s}{|Z - Z_s|} \left[ \frac{1}{2} \left( 1 + \frac{d}{dy} \left( Y_{H_2} + Y_{CO} \right) \frac{dY_{O_2}}{dy} \right) \right] \]

Eq. (4.2)

where

\[ Z = \frac{2\left( Y_C - Y_{C,O,0} \right)/W_C + \left( Y_H - Y_{H,O,0} \right)/(2W_H) - \left( Y_O - Y_{O,O,0} \right)/W_O}{2\left( Y_{C,F} - Y_{C,O,0} \right)/W_C + \left( Y_{H,F} - Y_{H,O,0} \right)/(2W_H) - \left( Y_{O,F} - Y_{O,O,0} \right)/W_O} \]

Eq. (4.3)

As previously interpreted, values of -1, 0, and 1 for the flame index, indicate burning at lean premixed, diffusion and rich premixed flame conditions. Figs. 4.12 to 4.15 shows scatter plots of the reaction rate of water, \( \dot{\omega}_{H_2O} \), versus the flame index for the cases A, B, C and D of composition 1. The time steps shown are the same as those considered for figs. 4.4 to 4.7. All the cases show combustion occurring in lean premixed mode after the establishment of ignition fronts.
Starting from non-premixed mode with zero reaction rates for water at initial times, ignition propagates to lean premixed conditions with first increasing and then decreasing reaction rates for water. Even at a later time step of \( t=10 \) ms, the ignition continues to propagate into the lean premixed flame conditions, unlike H\(_2\)/air flames, which propagated to rich premixed mode for larger downstream distances. All the cases are in agreement with the results reported above for the ignition delay times in Table 4.7, and do not show any chemical activity until the onset of ignition.

Figs. 4.16 to 4.19 shows the reaction rate of water, \( \dot{\omega}_{\text{H}_2\text{O}} \), versus the flame index for composition 2, for the same time steps shown in figs. 4.8 to 4.11. Results similar to composition 1, are observed for composition 2. For composition 2, increased reaction rate for water is found for all the four cases when compared to the four cases of composition 1.
Figure 4.12: Reaction rate of H₂O vs. flame index for case A for composition 1.
Figure 4.13: Reaction rate of $\text{H}_2\text{O}$ vs. flame index for case B for composition 1.
Figure 4.14: Reaction rate of H$_2$O vs. flame index for case C for composition 1.
Figure 4.15: Reaction rate of H$_2$O vs. flame index for case D for composition 1.
Figure 4.16: Reaction rate of H$_2$O vs. flame index for case A for composition 2.
Figure 4.17: Reaction rate of H$_2$O vs. flame index for case B for composition 2.
Figure 4.18: Reaction rate of H₂O vs. flame index for case C for composition 2.
Figure 4.19: Reaction rate of $\text{H}_2\text{O}$ vs. flame index for case D for composition 2.
Temperature and CO$_2$ Mass Fraction Conditional Means

Fig. 4.20 shows the temperature conditional means of all the cases for composition 1 at different locations of $x/d=0.5$, 0.7, 1.1, 1.2, 2.3, 4, 6 and 10. Initially, at $x/d=0.5$, the profiles are almost linear indicating a pure mixing profile with no chemistry or local peaks. At ignition conditions, shown here starting at $x/d=0.7$, case A shows a departure from the pure mixing profiles and depicts the formation of a small peak indicating the onset of ignition. This peak continues to “propagate” towards the stoichiometric conditions as a function of downstream distance. Similarly, peaks are evident for cases B, C and D at $x/d=1.1$, 1.2 and 2.3 respectively. The role of the preheat oxidizer temperature in delaying the onset of ignition could be seen from cases A and C, which have the same Reynolds number, but lower oxidizer preheat temperature. Higher Reynolds number cases, B and D, exhibit a delayed peak formation for higher downstream distances. The oxidizer preheating in the system causes the onset of ignition for a lean mixture fraction range, and as the combustion proceeds the peak shifts towards right and settles down at $Z=0.4$. It can be noted from later downstream locations of $x/d=6$ and 10, that the different Reynolds numbers and the different oxidizer preheat temperatures do not ultimately change the far downstream temperature profiles.
Fig 4.21 shows the temperature conditional means for composition 2 at different locations of $x/d=0.5, 0.6, 1, 1.1, 2, 4, 6$ and 10. Due to the increased hydrogen content in the mixture, all the cases, marks the onset of autoignition at lower values of $x/d$, when compared to the four cases of composition 1. Table 4.8 shows the summary of downstream locations $x/d$ at which the autoignition starts for the four cases of composition 1 and 2.

**Table 4.8:** Summary of $x/d$ locations for the jet flame cases A, B, C and D.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Composition</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x/d$</td>
<td>Composition 1</td>
<td>0.7</td>
<td>1.1</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>Composition 2</td>
<td>0.6</td>
<td>1</td>
<td>1.1</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 4.20: Temperature conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.21: Temperature conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
Fig 4.22 shows the conditional means for CO$_2$ mass fraction of all the cases for composition 1. CO$_2$ is a major product of CO oxidation, and hence the CO$_2$ profile does not show any value before the ignition occurs for all the cases. Ignition for case A starts at $x/d=0.7$ and a small amount of CO$_2$ gets produced, which is showed by magnifying the view by a factor of 10. As the combustion progresses towards completion, the amount of CO$_2$ increases as can be seen from the profiles. Considering case B, which has a higher ignition delay than case A, occurrence of CO$_2$ starts at a higher downstream distance. Similar results are seen for cases C and D, which have even higher ignition delays.

Fig. 4.23 shows the conditional means for CO$_2$ mass fractions for composition 2. With the decreased concentration of CO, the concentration of CO$_2$ produced is lower and hence lower peaks are obtained for composition 2 profiles.
Figure 4.22: CO$_2$ mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.23: CO\textsubscript{2} mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
**OH Mass Fraction Conditional Means**

Fig. 4.24 shows the conditional means of OH mass fraction for cases A, B, C and D for compositions 1 at different downstream locations as shown for fig. 4.20. As seen in case A, the ignition starts at a lean mixture fraction and the peak shifts towards richer mixture conditions at increasing downstream locations. The shifting of the peak finally settles at \( Z=0.4 \) for \( x/d=10 \). This trend is common in all the cases. In fig. 4.20, the ignition delay is captured by the profiles at \( x/d=0.7, 1.1, 1.2 \) and 2.3 for the cases A, B, C and D, respectively. This ignition delay is evident from the plots where the concentration of OH is zero. Hence, cases C and D, which have longer ignition delay times, exhibit very small concentrations of OH for larger downstream distances than cases A and B. Also, due to low oxidizer temperature, a shift from OH to O and H takes place, which further reduces the peak concentration of OH in cases C and D than in cases A and B.

Fig. 4.25 shows the conditional means of OH mass fraction for cases A, B, C and D for compositions 2 at different downstream locations as shown for fig. 4.21. With increasing \( \text{H}_2 \) concentration, the radical concentration of all the four profiles for composition 2 shows higher peaks compared to those of composition 1. The peak concentration occurs in a range of lean mixture fraction of \( Z=0.32-0.37 \), whereas the stoichiometric mixture fraction for composition 2 is 0.53.
Figure 4.24: OH mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.25: OH mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
**CO and H₂ Mass Fraction Conditional Means**

Fig 4.26 shows the conditional means for the CO mass fraction for cases A, B, C and D for composition 1 at similar $x/d$ locations as shown in fig 4.20. At $x/d=0.5$, all cases show a linear profile corresponding to a pure mixing conditions. Case A, which ignites the earliest, shows a departure from the linear profile at $x/d=1.1$. Other cases show a similar departure at later $x/d$ locations. This departure is an indication of the onset of consumption of CO during ignition. As ignition kernels propagate and form a flame, the amount of CO in the mixture decreases and approaches zero at the stoichiometric conditions and lower mixture fraction values.

Fig 4.27 shows the conditional means for the CO mass fraction for cases A, B, C and D for composition 2 at similar $x/d$ locations as shown in fig 4.21. Due to the decreased concentration of CO in the mixture, the value of mass fraction CO is 0 at $Z=0$ and 0.36 at $Z=1$. 
Figure 4.26: CO mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.27: CO mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
Fig 4.28 shows the conditional means for the H\textsubscript{2} mass fraction for cases A, B, C and D for composition 1. At x/d=0.5, all cases show similar but not linear profiles in mixture fraction space compared to the inlet (x/d = 0) conditions. These profiles again correspond to pure mixing and differential diffusion, which tend to shift more H\textsubscript{2} towards fuel-lean conditions. Pure mixing alone yields a linear profile as observed in the CO early profiles of Fig. 4.26. The onset of ignition is characterized by a depletion of H\textsubscript{2} at fuel-lean conditions since H\textsubscript{2} is a deficient reactant at those conditions. The final profiles at x/d = 6 and 10 correspond to a diffusion flame profile once the autoignition process is established. Fig 4.29 shows the conditional means for H\textsubscript{2} mass fraction for cases A, B, C and D for composition 2. Similar trends and results to composition 1 are obtained for composition 2. Due to the increased hydrogen content in composition 2, the mass fraction is 0.017 at Z=1.

Fig. 4.30 shows CO and H\textsubscript{2} mass fraction conditional means for case A for composition 1. It is evident from the profile at x/d=0.5, that the CO and H\textsubscript{2} “pure mixing” profiles exhibit different shapes as a function of mixture fraction. The different shapes are attributed to the difference in mass diffusivities of the two species, which results in a higher rate of depletion of H\textsubscript{2} at fuel-rich conditions (the H\textsubscript{2} profiles dip below the linear initial profiles of “pure mixing”) and enhancement of H\textsubscript{2} at fuel-lean conditions (the H\textsubscript{2} profiles are above the linear initial profiles of “pure mixing”).
Figure 4.28: \( \text{H}_2 \) mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.29: H₂ mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
Figure 4.30: CO and H$_2$ mass fraction conditional means for case A for composition 1 at $x/d = 0.5$ (Solid-CO; Dashed-H$_2$)
HO₂ and H₂O₂ Mass Fraction Conditional Means

Fig. 4.31 shows the conditional means of the HO₂ mass fractions for cases A, B, C and D, for composition 1. The onset of autoignition for case A occurs at x/d=0.7. However, at x/d=0.5, case A already shows the formation of some HO₂. This early formation demarcates the early stages of the autoignition process. As the ignition starts at x/d=0.7, the concentration of HO₂ increases and reaches a maximum value in the mixture fraction range of 0.35-0.45. The HO₂ species is sometime known as the ‘sink’ species due to the fact that its initial formation may serve initially as a mechanism for the depletion of the radical pool; while, it may serve at later stages as a mechanism for the build-up of this radical pool. As the ignition kernels propagate and develop into a flame, the concentration of HO₂ decreases significantly and reaches its minimum value where the temperature is highest. Similar observations are made for case B, C and D. Also, a comparison of case A with case B, and case C with case D, shows the role of turbulence intensity on the formation of HO₂. A decrease in the concentration of HO₂ is observed with the increasing Reynolds number.

Fig 4.32 shows the conditional means of HO₂ mass fractions for the cases A, B, C, and D for composition 2 with similar observations to results of composition 1.
Figure 4.31: HO₂ mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.32: HO\(_2\) mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
Fig. 4.33 shows the conditional means of H$_2$O$_2$ mass fractions for the cases A, B, C and D, for composition 1. For all the cases considered, H$_2$O$_2$ appears at the onset of ignition and peaks at later downstream locations at fuel-rich mixture conditions. The maximum concentration of H$_2$O$_2$ occurs during the induction/ignition stages.

Fig. 4.34 shows the conditional means of H$_2$O$_2$ mass fractions for the cases for composition 2. The increased hydrogen content in the mixture decreases the concentration of H$_2$O$_2$ in the mixture. The maximum concentration of H$_2$O$_2$ is produced for case A, which has a lower turbulence intensity and higher preheat oxidizer temperature. Other observations are similar to those of composition 1.
Figure 4.33: H$_2$O$_2$ mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 1.
Figure 4.34: H$_2$O$_2$ mass fraction conditional means for cases A (black), B (red), C (green) and D (blue) for composition 2.
4.4 Conclusions

For the homogeneous autoignition simulations of the CO/H₂/O₂/N₂ system, the following conclusion can be stated;

1) A higher ratio of H₂/CO will lower the autoignition delay time of the system. Therefore, composition 2 with higher H₂/CO ratio has lower autoignition delay time than composition 1.

2) A higher preheat oxidizer temperature will broaden the range of minimum autoignition delay time in the mixture fraction space. Also, it tends to shift the condition of minimum autoignition delay time to richer mixture fraction.

Autoignition simulations using a jet flow configuration of CO/H₂/N₂ fuel mixtures at two H₂/CO compositions, two Reynolds numbers and two oxidizer preheat temperatures are carried out using the ODT model. The following are the main conclusions;

1) Similar to the homogeneous autoignition, a higher ratio of H₂/CO and a higher preheat oxidizer temperature lower the autoignition delay time.

2) The molecular and turbulent transport in the jet configuration plays an important role in the autoignition process as follows;
• The pure mixing profiles in the mixture fraction space evolve differently for the two fuel components, CO and H$_2$ prior to the autoignition process. The diffusion of H$_2$ is more towards leaner mixture conditions, which results in the differential diffusion effects.

• This differential diffusion plays a crucial role in increasing the H$_2$/CO ratio at the ignition sites, resulting in further reduction in the autoignition delay time.

3) Turbulent transport also plays an important role during the ignition process, especially at higher Reynolds number and when the autoignition is delayed due to lower H$_2$/CO ratio and lower oxidizer preheat temperature.

4) However, turbulent transport plays a key role in enhancing the high-temperature combustion stage part of ignition, as shown by the broader spatial profiles of species and temperature at distances downstream of ignition.
REFERENCES


APPENDIX
APPENDIX

Chemkin Code Mechanism and Details

Chemkin is a software package developed by Sandia National Laboratories. It finds main application in the field of micro-scale combustion processes and in chemical manufacturing and processing companies. Chemkin is a set of well written subroutine codes and libraries, which can simulate any chemical reaction or mechanism in to a reacting flow. Its range varies from highly complex mechanism to simple, one or two order reactions. Chemkin software is built in such a way that by making minor modifications in the build files; it can be used in any environment. In this work, the first set of simulations for H$_2$/air reactions are performed on the IBM’s Power5 machines with xlf compilers at the High Performance Computing center at NC State. Due to hardware maintenance issues, the next set of simulations for CO/H$_2$/air chemistry has been performed on IBM’s henry2 clusters with Portland group compilers pgf90. The procedure for implementing and simulating the reaction mechanism chemistry using Chemkin-II, Version 1.9, is explained below. The very first step towards the simulation of code was to compile it successfully using the correct input files required by the Chemkin interpreter. The three basic user supplied input files includes a chemistry file, a thermodynamic data file and a transport data file.
Chemistry File (chem.inp)

This is the file, which supplies the critical information about the chemical reaction to the software. The file has three parts in fixed order, which cannot be changed. The first part of the file lists all the elements of all the species taking part in the reaction. This helps the interpreter to identify and link the atomic weights of each element correctly. The second part of the file gives the name of all the species involved in the reactions. The name of species specified in this part of file should exactly match everywhere else they have been referenced in chemistry, thermodynamic and transport file. These names will be used to calculate the weight and to gather the thermodynamic and transport data of all the species. The third and the largest part of the file can be called as the heart of the mechanism description. All the reactions involved in the mechanism are listed in this section. Each reaction has a reaction rate constant; calculations for which are based on the modified Arrhenius equation. The parameters for Arrhenius equation, $A$, $b$ and $E_a$ are specified in this order only. Some of the reaction contains a third body reactant or product, which is designated as M. It represents all the species taking part in the mechanism. Also, a few of the reactions are pressure dependent and will not occur when the pressure is high or low but when is in between somewhere. These reactions are called as fall-off reactions. For these reactions, Arrhenius equations parameters are supplied for both the pressure limits. The reaction rate constant for this type of reaction is calculated based on any of the formulation provided by Troe et al. (1983), Stewart et al.(1989) or by Lindemann(1922).
**Thermodynamic File (therm.dat)**

This file has the thermodynamic data for all the species listed in the chemistry file’s species part. The data consists of the 14 temperature coefficients calculated for two temperature ranges. Usually, the temperature ranges considered are 300-1000 K and 1000-5000 K.

The first seven coefficients correspond to the high temperature range and the next seven to the low temperature range respectively. The first line in this file gives the information about the name and chemical formula of the species, number of atoms of each element in the species, the phase of the species and the temperature range considered for the reaction.

**Transport File (tran.dat)**

For all the species, the transport properties like diffusivity, characteristic lengths, bond energies thermal conductivity, shear viscosity are given in this file. The values in this file are generally based on the experimental results. This file is directly used by the transport property fitting code.

**Relationship of Different Input/Output Files**

The above three input files when compiled together with other subroutine library files produces three application files named as chem.e, tran.e and driv.e. The executable chem.e requires chem.inp and therm.dat for its execution and produces two files, chem.out and chem.bin.
Chem.out is a output file, which shows all the elements and species with proper atomic weights and with all the reactions with proper Arrhenius rate coefficients. Chem.bin is a binary file, used in addition to tran.dat for the execution of tran.e to produce two files, tran.out and tran.bin. The tran.out file contains coefficients for species conductivities, viscosities, diffusion etc. Now, the third application file, driv.e, requires the data from tran.bin, a binary file again, chem.bin, along with one user defined input file to produce the desired postprocessing files.

Figure A1: Relationship of different input-output files
Input File (input.dat):

In order to look at the micro-scale combustion process, this input file is used by the executable, driv.e to produce results. This file has some of the crucial information about the reaction input variables. The first line states the number of realizations, which indicates the code where to stop. Also, the temperature, pressure and composition of fuel and oxidizer are specified here. The domain of the problem in this sample file is specified as -4 to 4 with a resolution of 401. The turbulence intensity of fuel is given by Reynolds number, which is given as Re=5000.