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Eddy Break-Up Based Models for Industrial Diffusion Flames with Complex Gas Phase Chemistry

Anders Brink

Academic Dissertation

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Preface

The work presented in this thesis has mainly been carried out at the Combustion Chemistry Research Group at the Åbo Akademi University during the years 1994-1998 within the research programs LIEKKI II and CFD.

Without the aid and support of a number of people, this thesis would never been written. First, I would like to acknowledge my boss, co-author, and supervisor Professor Mikko Hupa, who has at the same time given me a free hand to work with the things I like, and still managed to keep me on the road forward. I am also grateful for the valuable input of the co-authors of the manuscripts and publications that are the basis of this thesis. Dr. Pia Kilpinen, who was the carrying force of the first combustion related project I ever was involved in, has helped me with starting to understand the secrets of combustion chemistry. Dr. Lars Kjäldman at VTT, who honestly has shared his long experience in combustion modeling, is without a doubt the person outside the Combustion Chemistry Research Group who has had the largest impact on my research. Dr. Christian Mueller, from Ruhr-Universität Bochum in Germany and a recently joined colleague at the Åbo Akademi University, who not long ago finalized his thesis on a similar subject, has not only been a co-author, but has also provided the possibility of a continuos discussion on the feasibility of the results and findings. The work of Mr. Teppo Ahremaa, who did his master thesis within the same project, is gratefully acknowledged, and the luxury of not having to do everything oneself has been nice to enjoy. Of the persons acting as co-authors, Mr. Tommy Norström is the last to be acknowledged. This is not because his input is the least, rather the opposite. He joined the Combustion Chemistry Research Group shortly after me, and we have not only been involved in the same projects, and taken part in the same courses, but I have had the great pleasure of sharing office with him, which has lead to very regular contributions from his side. Hopefully he too will find that our discussions have been of benefit to him when he is writing his Ph.D.-thesis.

In order not to make this thesis too thick, I will not try to list the input of my colleagues at the Combustion Chemistry Research Group one by one. Many of these people have contributed by helping me with my questions, but the enormous contribution from all of them to make everyday routines enjoyable and fluent deserves big thanks.
I have also had the opportunity to do part of my research abroad. In 1994, I visited the Ruhr-Universität Bochum for a short stay. It was an educating stay and the opportunity to get a perspective on my own work by seeing how Ph.D. students in another country are working has been important. In 1997, I had the chance to work at the research station of the International Flame Research Foundation in IJmuiden, the Netherlands, for a short while. This stay too, was very educating and inspiring since this gave me the chance to get away from the academic world and into applied research for a while. I would also like to acknowledge the researchers at the Engler-Bunte-Institut der Universität Karlsruhe, Germany, who provided me with experimental data and instructed me in the modeling.

This work would not have been possible to carry out without the financial support from the Finnish National Combustion and Gasification Research Program (LIEKKI II), the Finnish National CFD Technology Program, the Academy of Finland, supplied through the Graduate School in Chemical Engineering and through the project co-sponsored by the Deutscher Akademischer Austauschdienst (DAAD), and the EuroFlam project sponsored by the European Commission. I would also like to thank Foster Weeler Energia Oy, IVO Group, Kvaerner Pulping Oy, and Wärtsilä NSD, companies that have contributed with their funding through the Finnish National Combustion and Gasification Research Program. The sponsors are acknowledged not only for supplying my salary and necessary equipment, but also for giving me the possibility to participate in workshops, conferences, and symposia of relevance to my research.

Finally, there is my family, my loving wife Maria, who has given her continuous support and many times struggled through my manuscripts. Soon, it will no longer be Dr. Brink and husband, but Dr. & Dr. Brink, thank you Maria! My daughter Johanna has not had a chance to contribute to this thesis yet, but I am sure her time will come.

Åbo, October 1998

Anders Brink
Abstract

In this thesis, two types of models used in the CFD modeling of practical combustion devices with a turbulent flow are investigated. The models are applied to a number of test cases, but the goal of the investigations are not to demonstrate the ability of the models to simulate practical devices but to investigate them, as well as to propose improvements. The investigated models are all related to the Eddy Break-Up model, but they differ from each other in that one group utilizes the perfectly stirred reactor in the description, whereas the other group compares the reaction rate given by mixing with a kinetically determined reaction rate. The models in the first group are based on the Eddy Dissipation Concept. These models allow for the use of a comprehensive reaction mechanism. In the studies, it is found that the mixing time used in this model is too short to be consistent with the other assumptions the model is based on. The test cases used in the study of this model could be better described if a longer mixing time was used. It was, however, found that there is a connection between the description of the reaction kinetics and the mixing time giving the best results. Finally, a new version of this reactor based model was proposed, where suggestions reported in the literature on how to estimate the mixing time as well as the reacting fraction in a turbulence-chemistry interaction model for the modeling of non-steady spray combustion have been applied. The second group of models consists of various versions of the Eddy Dissipation Combustion Model. In this study, it is found that these models are as reliable as the Eddy Dissipation Concept for the modeling of the main combustion, although the reaction kinetics must be described with simplified mechanisms. It is further found that basing the calculations of the reaction rates on mean quantities is a reasonable approach in hydrocarbon flames. Last, a modification to the Eddy Dissipation Combustion Model is proposed, where a temperature pdf is used in the estimation of the reaction rate determined by the reaction kinetics.

In most CFD simulations of practical devices, one is forced to use a simplified description of the chemistry, where only a very limited number of global reactions are used to describe the complicated chemistry. To identify to what
Abstract

extent the simplified description of the chemistry restricts the reliability of the modeling, perfectly stirred reactor simulations are used to assess the frequently used simplified mechanisms by comparing the results with those obtained with a comprehensive reaction mechanism consisting of elementary reactions. It is found that the oxidation of the fuel can be described with a four-step mechanism. However, none of the tested simplified mechanisms for the nitrogen chemistry were reliable. The perfectly stirred reactor was also used to study the effect of temperature fluctuations. For this, the transient behavior of the reactor was modeled. Here it was found that apart from the formation of thermal-NO, the conversion of NH$_3$ to N$_2$ at fuel rich conditions was also strongly affected by temperature fluctuations.
Table of contents

Preface ......................................................................................... i
Abstract ...................................................................................... iii
Table of contents ......................................................................... v
Nomenclature .............................................................................. viii
  Latin letters .............................................................................. viii
  Greek letters ............................................................................ ix
1. Introduction ............................................................................ 1
  1.1 Motivation of this thesis ................................................... 1
  1.2 Present contribution ......................................................... 2
  1.3 Outline of this thesis ......................................................... 3
2. The mathematical bases of turbulent combustion modeling .......... 5
  2.1 Basic equations ................................................................. 5
  2.2 Computational procedure ............................................... 8
3. Combustion regimes in turbulent reactive flows ......................... 10
  3.1 Premixed flames .............................................................. 11
  3.2 Diffusion flames ............................................................... 13
4. Review of turbulence-chemistry interaction models .................... 15
  4.1 The probability density function (pdf) method ..................... 15
  4.2 The presumed pdf method ............................................... 22
    4.2.1 Presumed pdf - fast chemistry .................................... 24
    4.2.2 Presumed pdf - simple chemistry ............................... 25
    4.2.3 Presumed pdf - flamelet models ............................... 27
  4.3 Flamelet models with a balance equation for flame surface density .... 28
  4.4 Eddy Break-Up models ..................................................... 29
    4.4.1 The Eddy Break-Up model ........................................ 30
    4.4.2 Multi-Fluid Model of Turbulence .............................. 31
    4.4.3 The Eddy Dissipation Combustion Model ................. 33

v
# Table of contents

4.4.4 The Eddy Dissipation Concept .............................................. 33
4.5 I.E.M. models ........................................................................... 35

5. Reaction mechanisms used in this thesis .................................... 38
  5.1 Detailed kinetic mechanism for hydrocarbon oxidation ......... 38
  5.2 Simplified mechanisms for hydrocarbon oxidation ............ 38
  5.3 Detailed kinetic mechanism for nitrogen chemistry .......... 43
  5.4 Simplified mechanisms for nitrogen chemistry ................. 44

6. Ideal reactor studies ................................................................. 48
  6.1 Adiabatic perfectly stirred reactor studies ....................... 48
  6.2 Critical residence time .......................................................... 53
  6.3 Isothermal perfectly stirred reactor studies ..................... 55
  6.4 perfectly stirred reactor studies with fluctuating temperatures .................. 65
  6.5 Summary of the ideal reactor studies ............................... 77

7. Test cases used in this thesis ..................................................... 80
  7.1 Natural gas combustor A ......................................................... 80
  7.2 Natural gas combustor B ......................................................... 81
  7.3 Natural gas combustor C ......................................................... 82
  7.4 Syngas jet flame ................................................................. 84

8. The Eddy Dissipation Concept .................................................. 87
  8.1 Effect of the description of the chemistry ......................... 90
  8.2 Effect of the characteristic mixing time ............................. 98
  8.3 Effect of the characteristic mixing time and reacting fraction 112
  8.4 Summary of the investigation of the Eddy Dissipation Concept ........ 120

9. The Eddy Dissipation Combustion Model .................................. 123
  9.1 Effect of the description of the chemistry ......................... 124
  9.2 Importance of fluctuations .................................................... 134
  9.3 Outline of an Eddy Dissipation Combustion/ PDF Model .......... 145
  9.4 Summary of the investigation of the Eddy Dissipation Combustion Model ......................................................... 147
Table of contents

10. Discussion .................................................................................................................. 149
10.1 Steady state reactor studies ..................................................................................... 149
10.2 Transient reactor studies ......................................................................................... 150
10.3 Studies of the Eddy Dissipation Concept ................................................................. 151
10.4 Studies of the Eddy Dissipation Combustion Model .............................................. 153
11. Conclusions ............................................................................................................... 156
12. Literature .................................................................................................................. 158
Appendix A: Hydrocarbon chemistry mechanism ......................................................... 168
Appendix B: Nitrogen chemistry mechanism ................................................................. 174
Nomenclature

Latin letters

\( A \)  Constant in the Eddy Dissipation Combustion Model
\( A \)  Pre-exponential factor
\( B \)  Constant in the Eddy Dissipation Combustion Model
\( c \)  Progress variable
\( C \)  Constant in the Eddy Dissipation Combustion/PDF Model
\( C_{EBU} \)  Constant in the Eddy Break-Up model
\( C_\mu \)  Constant in the empirical expression for turbulent viscosity
\( C_\omega \)  Constant in the fast chemistry formulation of the Eddy Dissipation Concept
\( D \)  Diffusion coefficient for mixture fraction (m\(^2\)/s)
\( d \)  Diameter (m)
\( d_i \)  Diffusion coefficient of species \( i \) (m\(^2\)/s)
\( E_A \)  Activation energy (J/mol, cal/mol)
\( e_L \)  Laminar flame thickness (m)
\( f \)  Probability density function
\( F \)  Distribution function
\( f \)  Mass density function
\( F \)  Parameter in model for critical residence time
\( F_\beta \)  External force acting in direction \( x_\alpha \) (kg/m\(^2\) s\(^2\))
\( g \)  General scalar variable
\( g_\alpha \)  Gravitational force in direction \( x_\alpha \) (m/s\(^2\))
\( h \)  Enthalpy (J/kg)
\( I \)  Intermittency factor
\( J_i^\alpha \)  Diffusion flux of species \( i \) in direction \( x_\alpha \) (kg/m\(^2\) s)
\( k \)  Turbulent kinetic energy (m\(^2\)/s\(^2\))
\( k \)  Specific reaction rate constant (1/s)
\( K \)  Equilibrium constant
\( l_i \)  Integral length scale of turbulence (m)
\( m \)  Mass flow rate (kg/s)
\( M_i \)  Molecular weight of species \( i \) (kg/mol)
Nomenclature

N  Number of samples
p  Pressure (Pa)
P  Probability
\dot{Q}  Heat exchange (W)
R  Gas constant (J/mol K)
r  Radius (m)
r_f  Stoichiometric constant expressed on mass basis
r_i  Reaction rate for species \(i\) (kmol/m^3 s, mol/cm^3 s)
S  Swirl number
T  Temperature (K)
t  Time (s)
u  Axial velocity components (m/s)
u_L  Laminar flame velocity (m/s)
u_\alpha  Cartesian velocity component in direction \(x_\alpha\) (m/s)
U  General stochastic variable
V  Sample space of \(U\)
V  Reactor volume (m^3)
w  Velocity of swirl component (m/s)
x  Axial distance (m)
x_\alpha  Cartesian co-ordinate direction (m)
Y_i  Mass fraction of species \(i\)
z_i  Elemental mass fraction of the \(i\)th species

Greek letters

\alpha  Probability of ignition in the M.I.L. model
\alpha  Parameter in the P.E.U.L. model
\chi  Scalar dissipation rate of mixture fraction (1/s)
\chi  Fraction of fluid that is reacting
\varepsilon  Dissipation rate of turbulent energy (m^2/s^3)
\phi  General stochastic variable
\gamma  Fraction of fluid containing fine structures
\gamma^3  Fraction of fluid consisting of fine structures
\eta  Kolmogorov length scale (m)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>Progress variable</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Parameter in the Eddy Dissipation Concept</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Parameter in the fast chemistry formulation of the Eddy Dissipation Concept</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Fraction of the fluid that can react in the model of Karlsson and Chomiak</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Stoichiometric ratio</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>Mass of the $i$th element per unit mass of the $j$th element</td>
</tr>
<tr>
<td>$\mu_t$</td>
<td>Turbulent viscosity (kg/ms)</td>
</tr>
<tr>
<td>$\nu_t$</td>
<td>Turbulent kinematic viscosity ($m^2/s$)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (kg/m$^3$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Schmidt or Prandtl number</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Flame surface density (1/m)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Progress variable</td>
</tr>
<tr>
<td>$\tau_{ch}$</td>
<td>Chemical time scale (s)</td>
</tr>
<tr>
<td>$\tau_{I.E.M.}$</td>
<td>Mixing time in the I.E.M. model (s)</td>
</tr>
<tr>
<td>$\tau_{mix}$</td>
<td>Turbulent mixing time (s)</td>
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<tr>
<td>$\tau_{mix1}$</td>
<td>Turbulent mixing time (s)</td>
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<td>$\tau_{mix2}$</td>
<td>Turbulent mixing time (s)</td>
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<tr>
<td>$\tau_{mix3}$</td>
<td>Turbulent mixing time (s)</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>Turbulent time scale (s)</td>
</tr>
<tr>
<td>$\tau^*$</td>
<td>Mixing time in the Eddy Dissipation Concept (s)</td>
</tr>
<tr>
<td>$\tau_{a\beta}$</td>
<td>Viscous tensor (kg/ms$^2$)</td>
</tr>
<tr>
<td>$\tau_\eta$</td>
<td>Kolmogorov time scale (s)</td>
</tr>
<tr>
<td>$\omega_i$</td>
<td>Reaction rate of species $i$ (1/s)</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Mixture fraction</td>
</tr>
<tr>
<td>$\xi^*$</td>
<td>Mixture fraction variance</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Sample space of $\phi$</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Progress variable</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Scalar dissipation rate (1/s)</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 Motivation of this thesis

Combustion is not only among the oldest technologies of mankind, it is also one of the most important ones. The increase in the standard of living in the developing countries is associated with an increase in the energy consumption. Since much of this energy is produced from coal and other fossil fuels, combustion will continue to be an important technology. Unfortunately, the proportions of this activity are such that it has global effects on the environment through the emission of hazardous emissions and green house gases. To minimize the effects of combustion on the environment, it is important to increase the efficiency of combustion processes. For the local environment though, it is as important to minimize harmful emissions such as NO\textsubscript{x}, SO\textsubscript{x}, unburned hydrocarbons, soot, and particulate matters.

The optimization of combustion processes is not an easy task. Due to the large scale of the combustion devices, experiments are extremely costly. In addition, the environment inside these devices is not a friendly one, which makes them difficult to study. During the last decade the technology has made powerful computers affordable and easily available. This development has led to that computational fluid dynamics (CFD) has established itself as a tool among engineers for design purpose and for gaining understanding of combustion processes. In this way, the need for expensive experimental runs and pilot scale experiments has decreased. CFD can be used to study the effect of modifications to existing boilers. These studies may include the effect of modifications of the burner or rearrangement of the air distribution. The effect of the fuel properties or the effect of co-firing can also be studied. Although the development in the CFD field is fast, the models used by most engineers are those available in the commercial CFD tools. These models are considered as established ones and are not in focus of the research any more. However, these models are frequently used in combination with more complex descriptions of the chemistry, as well as of other physical processes, compared with the descriptions they originally were intended for. This situation calls for a constant evaluation of the models. Traditionally, fluid mechanics and power plant optimization are areas that
mechanical engineers have been dealing with. However, the increasing attention on harmful emissions, which requires understanding of chemistry and reaction kinetics, has made this field interesting to chemical engineers as well.

1.2 Present contribution

This thesis concentrates on assessing and improving two models that are used for accounting for the turbulence-chemistry interaction in the CFD modeling of practical combustion devices. Emphasis is also put on evaluating the simplified reaction mechanisms for hydrocarbon combustion chemistry and nitrogen chemistry that are suited for use in combination with the turbulence-chemistry interaction models in practical CFD studies. The main contributions are:

- Numerical investigation of the simplified reaction mechanisms for the methane and nitrogen chemistry at perfectly stirred reactor conditions.

- Numerical investigation of the effect of temperature fluctuations on the chemistry. In this study, a comprehensive reaction mechanism consisting of elementary reactions was used where both the main chemistry and the nitrogen chemistry were described.

- Investigation of the influence of the way the chemistry is described on the predictions with the Eddy Dissipation Concept.

- Investigation of the time scale associated with the mixing in the reacting part of the Eddy Dissipation Concept.

- A new turbulence-chemistry interaction model combining the structure of the Eddy Dissipation Concept with ideas put forth by Karlsson and Chomiak.

- Identifying why the finite rate chemistry version of the Eddy Dissipation Combustion Model can be used in the modeling of hydrocarbon flames although the kinetic expressions are based on mean quantities. The analysis
Introduction

utilized a mixture fraction and mixture fraction variance based presumed probability density function approach.

- Outlining of a new version of the finite rate Eddy Dissipation Combustion Model that uses a presumed pdf approach in the evaluation of the mean kinetic reaction rate.

1.3 Outline of this thesis

This thesis is mainly based on reports, conference papers, and manuscripts that have been or are in the process to be submitted to scientific journals. In order to make the thesis more readable the material has been rearranged into a monograph. In this way, it has not only been possible to avoid multiple description of test cases and model assumptions shared by the different pieces, but it has also been possible to ensure that a consistent vocabulary is used throughout the thesis. The material is presented in such an order that helps the reader to finding the “red line” of the research this thesis is based on.

Most of the material in Chapters 2-4 is taken from Brink, A., "Turbulence — Chemistry Interaction Models in Combustion", REPORT 96-2, 1996.

Chapter 5 is a compilation of the reaction kinetics used in this thesis. In Chapter 6, ideal reactor simulations with the reaction mechanisms are presented. The material in these chapters is mainly taken from Brink, A., Kilpinen, P., Hupa, M., and Mueller, C. "An improved description of the hydrocarbon combustion is the key to advanced NOx modeling", 12th IFRF Members Conference, Noordwijkerhout, the Netherlands, May 6-8(1998); Brink, A., Kilpinen, P., Hupa, M., and Kjäldman, L. "Study of Alternative Descriptions of Methane Oxidation for CFD Modeling of Turbulent Combustors", submitted to Combustion Science and Technology; Kjäldman, L., Brink, A., and Hupa, M., "Micro Mixing Time in the Eddy Dissipation Concept", submitted to Combustion Science and Technology; and Brink, A., Norström, T., Kilpinen, P., and Hupa, M. "Predictions of NOx Formation in an NH3-Doped Syngas Flame Using CFD Combined with a Detailed Reaction Mechanism", 4th Colloquium on Process


Chapter 9 is based on material from Brink, A., Ahremaa, T., Mueller, C., and Hupa, M. "Assessing the Applicability of Different Reaction Schemes with the Eddy Break-Up Model Using Presumed PDF", to be submitted; and from Brink, A., Kilpinen P., Hupa, M., and Mueller, C., "An improved description of the hydrocarbon combustion is the key to advanced NOx modeling", 12th IFRF Members Conference, Noordwijkherout, the Netherlands, May 6-8 (1998).
2. The mathematical bases of turbulent combustion modeling

2.1 Basic equations

A turbulent reacting flow can be described by the Navier-Stokes equation together with the continuity equation and the diffusion-reaction equation. This system of differential equations is highly non-linear and sensitive to the boundary conditions. The dimension of the smallest structures that needs to be resolved for a successful modeling is utterly small as compared with the physical dimensions of any practical device. Today, direct numerical simulation, where the set of differential equations is solved in their full time dependent form is only possible for flows of low or moderate Reynolds number and with a chemically simple fuel (Swaminathan and Bilger 1997). Based on this, the conclusion can be made that for the modeling of most technical applications, where mainly the average situation is of interest, a different approach is still needed.

In combustion, where the heat-release gives rise to large density variations, the variable density must be taken into account. Therefore, in flows with variable density, the governing equations are often used in their density-weighted forms. Usually the density-weighted mean with respect to time, sometimes referred to as the “Favre average”, is indicated by a tilde (\( \tilde{\cdot} \)) to separate it from the conventional time mean or “Reynold’s average”, denoted by a bar (\( \bar{\cdot} \)). The density-weighted mean is related to the conventional mean according to

\[
\tilde{g} = \left( \frac{\rho g}{\bar{\rho}} \right)
\]

(1).

In the computational modeling the density-weighted mean is usually used for velocity components (\( u_\alpha \)), mass fractions (\( Y_\alpha \)), enthalpy (\( h \)) and temperature (\( T \)), whereas conventional means are used for pressure (\( \rho \)) and density (\( \rho \)). In conjunction with a statistical modeling approach, the expectation, denoted \( \langle g \rangle \) is often used instead of the mean. In the statistical modeling approach this notation is preferred since it is then easier to indicate other statistical quantities, such as the conditional expectation.
To account for the fluctuating nature of the quantities, the approach that is used is to split them into a mean part and a fluctuating part, where the fluctuating part is given by

\[ g' = g - \bar{g} \]  

(2).

Sometimes the notation \( g'' \) is used to indicate the fluctuation of density-weighted quantities. In particular, this notation is needed in situations where fluctuations of variables that are not density-weighted appear simultaneously.

With the definitions above, the continuity equation can be written,

\[ \frac{\partial \bar{\rho}}{\partial t} + \frac{\partial}{\partial x_\alpha} (\bar{\rho} \bar{u}_\alpha) = 0 \]  

(3).

Similarly, the Navier-Stokes equation becomes

\[ \frac{\partial}{\partial t} \left( \bar{\rho} \bar{u}_\beta \right) + \frac{\partial}{\partial x_\alpha} \left( \bar{\rho} \bar{u}_\alpha \bar{u}_\beta \right) = -\frac{\partial}{\partial x_\alpha} \left( \bar{\tau}_{\alpha\beta} - \bar{\rho} \bar{u}_\alpha \bar{u}_\beta \right) - \frac{\partial \bar{\rho}}{\partial x_\beta} + \bar{F}_\beta \]  

(4)

where \( \tau_{\alpha\beta} \) is the viscous tensor and \( F_\beta \) the external force field. \( \alpha \) and \( \beta \) take the values 1, 2, and 3, i.e., the co-ordinate directions.

The balance equation for the mass fraction of species \( i \) is given by

\[ \frac{\partial}{\partial t} \left( \bar{\rho} \bar{Y}_i \right) + \frac{\partial}{\partial x_\alpha} \left( \bar{\rho} \bar{u}_\alpha \bar{Y}_i \right) = \frac{\partial}{\partial x_\alpha} \left( \bar{J}_i^{(i)} - \bar{\rho} \bar{u}_\alpha \bar{Y}_i^{(i)} \right) + \bar{\rho} \bar{\omega}_i \]  

(5)

where

\[ \bar{J}_i^{(i)} = \rho d_i \frac{\partial \bar{Y}_i}{\partial x_\alpha} \]  

(6).

In the equation above, \( d_i \) is the mass diffusion coefficient of species \( i \). Here, other necessary equations, such as the balance equation for the density-weighted enthalpy and the equations of state, are not presented. These expressions as well as a more detailed introduction to the subject have been extensively covered in
the literature and can, e.g., be found in the paper of Borghi (1988) which this introduction follows.

The diffusion fluxes in the equations above involve correlations between fluctuations and not only mean values. In turbulent flows, these fluxes are often larger than the molecular ones and can thus not be neglected. In the models used for numerical simulation of turbulent flows, the fluxes are usually assumed to be proportional to the gradients according to an analogy with Fick’s law, i.e.,

$$u'_{a}v'_{\beta} = -v_{t} \left( \frac{\partial \bar{u}_{a}}{\partial x_{\beta}} + \frac{\partial \bar{u}_{\beta}}{\partial x_{a}} \right) \quad \alpha \neq \beta$$  \hspace{1cm} (7)

and

$$u'_{a}y'_{i} = -\frac{v_{t}}{\sigma_{i}} \frac{\partial \bar{y}_{i}}{\partial x_{a}}$$  \hspace{1cm} (8)

where $v_{t}$ is the turbulent viscosity. The turbulent viscosity is not a property of the fluid, but a property of the turbulence. The simplest model for the turbulent viscosity is to assume that it depends on the kinetic energy of the turbulence, $k$, and the integral length scale of the turbulence according to

$$v_{t} = C_{\mu} k^{1/2} l_{i}$$  \hspace{1cm} (9)

where $C_{\mu}$ is a constant. Using the quantities known from the k-ε model, a turbulence model frequently used to model turbulence in turbulent reacting flows, the turbulent viscosity is given as

$$v_{t} = C_{\mu} \frac{k^{2}}{\varepsilon}$$  \hspace{1cm} (10)

where $\varepsilon$ is the dissipation rate of turbulent kinetic energy.

Until now, the reaction term in Equation 5 has not been described. It was pointed out above that fluctuations are essential to include in the modeling. When modeling combustion reactions, this is further emphasized. Here, the activation energy is usually large, making the dependence on temperature strong. Another
The mathematical bases of turbulent combustion modeling

problem is that numerous reactions occur in combustion and all of them are highly coupled in a non-linear way. The use of mean quantities can in this case cause very erroneous predictions. Following Borghi (1988), this can be demonstrated using the bimolecular reaction between species \( R \) and \( S \) forming \( P \). For this reaction, the reaction rate given by the chemical kinetics is

\[ -\dot{\omega}_R = -\dot{\omega}_S = \dot{\omega}_P = k Y_R Y_S \]  

(11).

In a constant temperature field, the mean reaction rate is given by

\[ \tilde{\omega}_R = -k \tilde{Y}_R \tilde{Y}_S = -k \tilde{Y}_R \tilde{Y}_S - k Y'_R Y'_S \]  

(12).

In the extreme case when the mass fractions \( Y_R \) and \( Y_S \) are fluctuating in opposite phase so that \( \tilde{Y}_R \tilde{Y}_S = 0 \), the mean reaction rate will be zero although \( \tilde{Y}_R \tilde{Y}_S \) is not zero. Evidently, the correlation of the fluctuating quantities must be modeled correctly before the model has any physical validity. Moreover, the temperature fluctuations should correctly be taken into account.

2.2 Computational procedure

In this thesis, the equations describing the flow have been solved with commercial CFD software. Most calculations have been carried out using FLUENT (Version 4.3) by Fluent Inc. Exceptions are the calculations the results presented in Section 8.2 are based on. These were carried out using PHOENICS (Version 1.6) by CHAM Ltd.

FLUENT and PHOENICS uses a control volume based technique to solve the conservation equations of mass, momentum, energy, species, and turbulence. In short the control volume technique consists of three steps: 1) division of the domain into discrete control volumes, 2) integration of the equations on the individual control volumes in order to transfer the partial differential equations into an algebraic form, and, 3) solving the discretized equations.
The main difference between FLUENT and PHOENICS is that FLUENT uses a non-staggered grid, whereas PHOENICS uses a staggered grid to store the variables. In the non-staggered grid storage scheme the same control volume is employed for integration of all conservation equations and all variables are stored at the control volume cell center. In the staggered grid, used by PHOENICS, the velocity components are stored in the middle of the computational cell wall, whereas the scalar variables are stored at the cell center. Still, both approaches require an interpolation scheme to interpolate face values of the variables needed in the calculations. In FLUENT and PHOENICS the linearized equation set is solved in a sequential way, which imposes the need for an algorithm that described the update of the pressure. Here different versions of the SIMPLE algorithm are used.

Apart from the eddy break-up related models for the reaction term, the submodels used with FLUENT, including turbulence models, radiation model and the mixture fraction/presumed probability density function approach, are in their "off the shelf" versions. In PHOENICS, on the other hand, several submodels have been modified. A closer description of these submodels can be found elsewhere, see Kjälldman (1993).
3. Combustion regimes in turbulent reactive flows

Turbulent flows are characterized by eddy-like motions of various length scales. These eddies, that enhance the mixing necessary for reactions to occur, may be divided into three classes according to their size. The largest eddies have a size that is smaller than the dimensions of the vessel but much larger than the smallest structures of the turbulent field. The local concentration gradients remain unaffected by this mixing process, often referred to as macro-mixing. Superimposed on these large scale eddies are eddies which are responsible for the division of large regions of fixed composition into smaller ones. As the last step in the mixing process, molecular diffusion is responsible for the mixing on the molecular level. Mixing on the molecular level is a prerequisite for reactions to occur, since reactions can only occur as molecules collide.

The characteristics of the turbulence and of the chemistry may be used for classifying flames. Such a classification has been done by Borghi (1988), who identified certain combustion regimes according to the relation between the turbulence scales and the chemical reaction rates. The regimes, in which different physical aspects play the most important role, may be illustrated graphically. This is done in Figures. 3.1 and 3.2. Since different physical aspects play the most important role in the different regimes, this classification can be of great benefit when choosing an appropriate turbulence-chemistry interaction model. However, it should be noted that combustion chemistry is characterized by a huge number of elementary reactions. These reactions have different rates, but many of the elementary reactions are coupled together through common radicals. In many cases, this makes the use of a single chemical time-scale possible. Nevertheless, the NO\textsubscript{x} chemistry is an example of a chemistry that is only partly independent of the hydrocarbon chemistry. For example, prompt-NO formation is closely interconnected with the hydrocarbon chemistry, whereas the thermal-NO formation relies on a high temperature at which the O-radical can exist. Once this temperature is reached, thermal-NO will continue to be formed although the hydrocarbons have already been consumed. As a consequence, the hydrocarbon chemistry and the prompt-NO chemistry in the flame can be related to a certain combustion regime, whereas the thermal-NO chemistry will take place in another “combustion” regime.
3.1 Premixed flames

The first obvious classification of flames that may be done is to divide them into premixed flames and non-premixed or diffusion flames. In Figure 3.1, different combustion regimes are plotted for the premixed case. The x-axis is the ratio of $l_t$, the integral length scale of turbulence, to $e_L$, the laminar flame thickness. The y-axis is the ratio of $k^{1/2}$, the fluctuation velocity, to $u_L$, the flame velocity.

![Figure 3.1. Different combustion regimes of turbulent premixed flames (after Borghi 1988).](image)

In the combustion regime called “wrinkled flames”, the turbulent intensity is so low that all turbulent length scales are larger than $e_L$. This occurs when the smallest scale in turbulence, referred to as the Kolmogorov micro scale, $\eta$, is
larger than the laminar flame thickness. In this case, the turbulent movements only wrinkle the flame front. In this combustion region the flame front modeling is of great importance. If the fluctuations of velocity become larger with respect to \( u_L \), a situation will occur where pockets of fresh and burned gases exist. The limit when these pockets are present continuously, i.e., where the consumption of these pockets by the laminar flame is smaller than their rate of birth due to the interactions of large turbulent movements, is given by \( k^{1/2}/u_L > 1 \). This regime has been called the “wrinkled flame with pockets” regime or the “corrugated flame” regime. In this regime, the flame surface becomes more difficult to model. In Figure 3.1 the “wrinkled flame with pockets” has nor been separated form the “wrinkled flames” regime, but is bounded by \( k^{1/2}/u_L = 1 \) and \( e_L = \eta \).

In the case where \( l_t > e_L \) but \( k^{1/2} \) is further increased, the influence of the turbulence on the flame front becomes more complicated. Now, the flame fronts will start to interact with each other. The velocity gradients in the flow will stretch the flames so that they are locally extinct. This occurs when the Kolmogorov micro scale is equal to the flame thickness, i.e., \( e_L = \eta \), which was the upper limit for the “wrinkled flame with pockets” regime. This limit may also be expressed as the point where \( \tau_{ch} \approx \tau_\eta \), where the Kolmogorov time scale \( \tau_\eta = (k^{3/2}/l_t \nu)^{-1/2} \). In this region, referred to as the “thickened wrinkled flame” region, the flames are thickened due to an enhancement by turbulence of the effective diffusion coefficient.

When the velocity fluctuations become so large that the thickness of the thickened flames, \( e^* \), becomes equal to \( l_t \) a flame front can no longer be distinguished. This line can also be characterized by the turbulent Damköhler number, \( Da_t = \tau_t/\tau_c \), where \( \tau_t = l_t/k^{1/2} \). This regime has been subdivided into two. The first one is called the “thickened flames” region. The other regime, where \( l_t \) is smaller than \( e_L \), is referred to as the “thick flames” region. As mentioned above, the flame front cannot be localized in this region. In this region the modeling problem will approach that of a perfectly stirred reactor.
3.2 Diffusion flames

Diffusion flames can be characterized in a similar way as premixed flames, although in diffusion flames the laminar flame speed and thickness have no equivalence. In diffusion flames, the flame thickness is dependent on the diffusion layers on both sides of the reacting surface. This thickness, on the other hand, will be dependent on time. To overcome this problem, it is necessary to specify a chemical time scale. In a diffusion flame, the chemical time scale must be defined for a certain equivalence ratio. From this time scale and the diffusion coefficient, it is then possible to define $u_L$ and $e_L$, although, they do not have a very precise physical meaning. Figure 3.2 shows the different regimes found in diffusion flames.

![Diagram](image)

Figure 3.2. Different combustion regimes of turbulent diffusion flames (after Borghi 1988).
The first regime, the "wrinkled and stretched flamelets" regime is characterized by stretched diffusion-reaction layers having a one-dimensional structure. The thickness of these flamelets scales with the Kolmogorov microscale. If the turbulence is created by shear, complicated situations can occur in this region since the flamelets will interact in the center of the vortices. When modeling flames in this region, the diffusion-reaction layer is of great importance.

Above the line where the Kolmogorov time scale equals the chemical time scale extinction of the flamelets can occur. Here, the interaction with other flamelets becomes more frequent and important. The local extinction, and the subsequent re-ignition when the stretching decreases, results in a partially premixed flame. Borghi (1988) calls this regime the "perturbed flamelets" regime. Apart from the diffusion-reaction layer, the eddy break-up rate is of importance when modeling this region.

When the chemical time scale is larger than the turbulent mixing time, the diffusion flame will more and more resemble a premixed one. This regime has been referred to as the "thickened flames" regime. As in the "thickened flames" regime and the "thick flames" regimes in the premixed case, the modeling problem will approach that of a perfectly stirred reactor.

As can be seen from Figures 3.1 and 3.2, the different regimes are bound in an almost identical way. The physical explanation for this is that the same phenomena occur both in premixed flames and in diffusion flames. It should be observed that the limits between the combustion regimes are not sharp and that in most practical applications, combustion takes place in more than one regime.
4. Review of turbulence-chemistry interaction models

In this section, a number of approaches for accounting for the influence of turbulence on the effective reaction rate are reviewed. Included in this review are three groups of models: 1) those that mainly can be used in fundamental research applications, 2) those that are suitable for engineering purposes, and 3) those that are included for historical reasons.

4.1 The probability density function (pdf) method

The pdf method relies on a complete statistical description of the flow at each point. In turbulent combustion modeling, three different pdfs that have been used, i.e., composition pdf, $\tilde{f}(\psi)$ (Chen and Kollman 1988), velocity-composition joint pdf, $\tilde{f}(V, \zeta, \psi)$ (Pope and Correa 1986, Correa et al. 1994), and the joint pdf of velocity, dissipation and composition, $\tilde{f}(V, \zeta, \psi)$ (Norris and Pope 1995).

For a random variable $\phi$, the pdf $f_\phi(\psi)$ is defined as the derivative of the distribution function $F_\phi(\phi)$:

$$ f_\phi(\psi) = \frac{d}{d\psi} F_\phi(\psi) $$

Here, the subscript $\phi$ indicates that the stochastic variable $\phi$ is considered. $\psi$ is referred to as the sample space of $\phi$. The distribution function $F_\phi(\psi)$ gives $P(\phi < \psi)$, i.e., the probability that $\phi$ is smaller than $\psi$. Some fundamental properties of the distribution function are that $F_\phi(-\infty) = 1$ and $F_\phi(\infty) = 1$. The distribution function is a non-decreasing function.

Integrating the probability density function between $\psi_A$ and $\psi_B$ ($\psi_A < \psi_B$) gives

$$ \int_{\psi_A}^{\psi_B} f_\phi(\psi) d\psi = F_\phi(\psi_B) - F_\phi(\psi_A) $$

$$ = P(\psi_A \leq \phi \leq \psi_B) $$

15
i.e., the probability of $\phi$ lying in a region is equal to the integral of the pdf over that region. Since the expression $-\infty \leq \phi \leq \infty$ must always be true the equality

$$\int_{-\infty}^{\infty} f_\phi (\psi) \, d\psi = 1 \quad (15)$$

should hold.

When statistically stationary flows are studied, the mean values of the various variables are of interest. If the pdf is known, the mathematical expectation is easy to calculate. The mathematical expectation of $\phi$, $\langle \phi \rangle$, is related to the pdf as follows:

$$\langle \phi \rangle = \int_{-\infty}^{\infty} \psi f_\phi (\psi) \, d\psi \quad (16).$$

Further, the mathematical expectation of a variable $Q$, being a function of $\phi$, is obtained as

$$\langle Q(\phi) \rangle = \int_{-\infty}^{\infty} Q(\psi) f_\phi (\psi) \, d\psi \quad (17).$$

Apart from the mean, another important statistical property is the variance. When the described decomposition of a stochastic variable into a mean part and a fluctuating part is made, the variance is the mean of the square of the fluctuations. The variance is related to the pdf by

$$\langle \phi'^2 \rangle = \int_{-\infty}^{\infty} (\psi - \langle \phi \rangle)^2 f_\phi (\psi) \, d\psi \quad (18).$$

Another closely related statistical property is the standard deviation, which is the square root of the variance. The standard deviation can be viewed as a measure of the width of the pdf.

Most systems involve more than one independent stochastic variable. To describe such a system, the joint pdf of the independent variables is needed. The pdf $f_\phi (\psi)$ contains all the information about $\phi$. If a second independent stochastic variable
is needed to describe the system, e.g., \( U \) that can be represented in the \( V \)-space, a pdf \( f_u(V) \) will contain all information about this variable. However, \( f_\psi(\psi) \) and \( f_u(V) \) do not contain information about the probability that two events occur simultaneously. A joint pdf \( f_{u\psi}(V, \psi) \) is then needed. Now, the integral

\[
\int_{\psi_A}^{\psi_B} \int_{V_A}^{V_B} f_{u\psi}(V, \psi) dV d\psi
\]

(19)

will give the probability that \( U \) is greater than \( V_A \) but smaller than \( V_B \) when \( \psi_A < \phi < \psi_B \). Here too, the event that \(-\infty \leq U \leq \infty \) when \(-\infty \leq \phi \leq \infty \) is certain, which mathematically is expressed

\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_{u\psi}(V, \psi) dV d\psi = 1
\]

(20).

In a similar way that \( \langle Q(\phi) \rangle \) can be calculated when the pdf \( f_\phi(\psi) \) is known the mathematical expectation of a variable that is a function of both \( U \) and \( \phi \) is given by

\[
\langle Q(U, \phi) \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} Q(V, \phi) f_{u\psi}(V, \psi) dV d\psi
\]

(21).

An important characteristic of the joint pdf is the covariance

\[
\langle U' \phi' \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (V - \langle U \rangle)(\psi - \langle \phi \rangle) f_{u\psi}(V, \psi) dV d\psi
\]

(22)

which is a measure of the correlation between the variables. For two independent variables the covariance will be zero. In this case, the joint pdf, \( f_{u\phi}(V, \psi) \), can be written as the products of the two marginal pdfs, i.e.,

\[
f_{u\phi}(V, \psi) = f_u(V) f_\phi(\psi)
\]

(23).
However, a lack of correlation does not necessarily imply that the two variables are independent. The joint pdf can be constructed from the marginal pdfs only if the variables are independent. For a closer introduction to probability density functions, see e.g., the review of Pope (1985).

Using the pdf approach, the chemical reaction term appears in closed form. The transport equation for the composition pdf can be written (Pope 1985, Lau 1995)

\[
\frac{\partial (\rho) \tilde{u}_a \tilde{f}}{\partial x_a} + \frac{\partial}{\partial \psi} \left[ (\rho) \tilde{\omega}_i (\psi) \tilde{f} \right] = -\frac{\partial}{\partial x_a} \left[ (\rho) \langle u'_a \mid \psi \rangle \tilde{f} \right] + \frac{\partial}{\partial \psi} \left[ \left( \frac{\partial J_{\psi}}{\partial x_a} \right) \psi \tilde{f} \right]
\]  

(24).

Although this approach appears straightforward, the computational effort needed for calculating the pdf in each point is notable. The transport due to velocity fluctuations is often modeled using the gradient diffusion model

\[
\langle \rho \rangle \langle u'_a \mid \psi \rangle \tilde{f} = -\mu_i \frac{\partial \tilde{f}}{\partial x_a}
\]  

(25).

Once the pdf is known the mean of any quantity being a function of the other variables in the turbulent field can be calculated according to the principle given in Equation 21. There are, however, certain other terms that present a problem. A serious weakness of the pdf method is in the treatment of molecular diffusion (Pope 1990). To account for diffusion, a mixing model can be applied. Usually, it is assumed that the fluid particles mix with each other at a rate inversely proportional to the turbulent time scale \(k/\epsilon\). This assumption is valid only when turbulent straining causes the steepest concentration gradients, which is the case when the laminar flame thickness is much larger than the Kolmogorov scale. In the flamelet region, the mixing model must be modified in order to be realistic.

In flows with variable density, instead of the density-weighted pdf \( \tilde{f} \), it is more convenient to use the mass density function \( \varphi \) (Pope 1985). The mass density function is the product of the density and the pdf, i.e.,

\[
\varphi (\psi) = \rho(\psi) f(\psi) = \langle \rho \rangle \tilde{f}(\psi)
\]  

(26).
Most methods suitable for solving the Eulerian approach are intractable when applied to joint pdfs of large dimensionality (Pope 1990). Instead, a Lagrangian approach is beneficial to use, since then Monte Carlo methods can be used to solve the pdf equations. The benefit of using Monte Carlo methods is that the computational effort only increases linearly with the number of composition variables. The pdf is now indirectly represented by a large number of computational fluid particles. The mean value of a variable, e.g., the density, in each cell given by

$$\langle \rho \rangle = \left[ \int \frac{1}{\rho(\psi)} f(\psi) d\psi \right]^{-1}$$

(27)

can, using the Lagrangian approach, be estimated from the ensemble average, i.e.,

$$\langle \rho \rangle_N = \left[ \frac{1}{N} \sum_{n=1}^{N} \frac{1}{\rho(\psi^n)} \right]^{-1}$$

(28).

The same processes that have to be modeled in the Eulerian approach must also be modeled in the Lagrangian approach. The set of equations describing the behavior of the individual fluid particles is given by (Pope 1990):

$$\frac{dx^*_a}{dt} = u^*_a$$

(29)

$$\frac{du^*_a}{dt} = g_a - \frac{1}{\rho(\psi^*_a)} \frac{\partial \langle \rho \rangle}{\partial x_a} + \left\{ \frac{1}{\rho} \frac{\partial \tau_{a\beta}}{\partial x_\beta} - \frac{1}{\rho} \frac{\partial p'}{\partial x_a} \right\}^*$$

(30)

$$\frac{d\phi^*_i}{dt} = \omega_i(\psi^*_a) - \left\{ \frac{1}{\rho} \frac{\partial J^*_i}{\partial x_a} \right\}$$

(31)

and

$$\frac{de^*_i}{dt} = \{\dot{\phi}^*_i\}^*$$

(32).
Review of turbulence-chemistry interaction models

The superscript + indicates that the value of the property refers to the fluid particle. In the equations above, the terms within braces are not known in terms of particle properties and must be modeled separately. The first equation describes the trajectory of the particle. The right hand side is known, i.e., no gradient diffusion assumptions must be made to describe the convective transport. The velocity-equation takes the effect of gravity and average pressure gradient exactly into account, whereas the molecular stresses and the effect of fluctuating pressure must be modeled. In the composition equation, the reaction rate appears in closed form. This is one of the most important arguments for this approach. Nevertheless, in the same equation, the molecular diffusion must be modeled. The instantaneous dissipation rate cannot be expressed in terms of particle properties and must be modeled.

When reactions are introduced, the situation becomes more complex, even though the linear dependence with respect to the number of variables still holds for the needed computational effort in the estimation of the joint pdf. To describe the oxidation process of a complex fuel, numerous species have to be considered. In the equations describing the evolution of the fluid particle, i.e., Equation 31, then represents a large number of differential equations. The problem is now that this set of differential equations is stiff and requires advanced methods to be solved. When taking into account that this set of equations has to be solved separately for each computational fluid particle, it is realized that the use of a detailed chemistry description is computationally prohibited. The method used today to incorporate a more complex description of the reaction kinetics is to use reduced kinetic schemes, typically with five or fewer reactions (Pope 1990). The reduced kinetic scheme is then used to generate a look-up table from which the change in composition can be obtained as a function of reaction time and initial composition.

In the current mixing models, diffusion and reaction are often assumed not to occur simultaneously. If the modeling is improved in such a way that the combustion regimes where this is important also can be modeled, including the flamelet regime, the look-up table approach becomes less attractive. The reason for this is that the diffusion rate depends not only on the fluid particle
composition but also on the composition of the surroundings. An alternative approach to the mixing model is to replace the velocity-dissipation-composition joint pdf by the velocity-dissipation-composition-composition gradient joint pdf, \( \tilde{f}(V, \xi, \Psi, \nabla \Psi) \). This is mainly a formal solution to the problem, since models taking the effects of straining and diffusion into account are still needed. It can be noted that the joint pdf of the mixture fraction and the scalar dissipation used in the flamelet model contain the same information as the joint pdf of composition and composition gradient.

If the velocity-dissipation-composition joint pdf \( \tilde{f}(V, \xi, \Psi) \) is used, the model is closed. No turbulence model is needed to account for the mean velocity field and the turbulence field. However, the information on time scales and length scales that the joint pdf contains refers to the velocity field. Therefore, the assumption that the scales of the composition field are proportional to the scales of the velocity field must be made (Pope 1990). If less complete pdfs are used, i.e., \( \tilde{f}(\Psi) \) and \( \tilde{f}(V, \Psi) \), additional information about the turbulent field is needed. If the velocity-composition joint pdf is used, the joint pdf provides information about mean velocities and the Reynolds stresses, and thus also the turbulent kinetic energy \( k \). However, when modeling processes dependent on the turbulent length or time scales, a model for the dissipation is needed. Here, the standard description used in the \( k-\epsilon \) model can be used. The composition pdf does not contain any information about the turbulent quantities.

The pdf method has been applied to problems of simple geometry, mainly to demonstrate the capability of the method. For the premixed case, only few calculations have been done using the Lagrangian approach. The main reason for this is that premixed combustion often occurs in the flamelet region, where alternative closure strategies are preferable (Pope 1990). On diffusion flames, more work has been done. Pope and Correa (1986) studied a CO/H\(_2\)/N\(_2\)-air diffusion flame using the velocity-composition joint pdf approach. Despite the success to predict the flame, Pope (1990) pointed out that this is not enough to judge the validity of the model, since similar agreement has been obtained using the presumed pdf approach and the flamelet model. Chen and Kollman (1988) have calculated a propane/air jet diffusion flame using a composition joint pdf
description. The conclusion made from their work is that the reduced kinetic scheme they used was insufficient to describe the chemistry. More complicated pdfs, such as the velocity-dissipation-composition joint pdf have also been used. For example, Norris and Pope (1995) have used this approach to model extinction in diffusion flames. A more complete review of applications can be found in Pope (1990). From the comparisons between calculations and experiments reviewed by Pope it can be noted that the assumption of equal diffusivity breaks down.

4.2 The presumed pdf method

The presumed pdf method (conserved scalar approach) tries to combine the advantages of the full pdf approach and the moment’s approach. The basic principle is to use an approximate, but hopefully realistic, shape of the composition pdf, which can be described using only a few parameters and which can be computed from the balance equations of its first and second moments (Pope 1990).

The two parameters most frequently used to find an approximate pdf are the mixture fraction, \( \xi \), and the variance of the mixture fraction, \( \xi'' \). The mixture fraction can be defined from the starting point that, during chemical reactions, the chemical elements are conserved (Correa and Shyy 1987). The elemental mass fraction, \( z_i \), of a certain element \( i \) can be calculated from

\[
z_i = \sum_{j=1}^{n} \mu_{ij} Y_j
\]

where \( \mu_{ij} \) is the mass of the \( i \)th element per unit mass of the \( j \)th species. In the case of two separate inlets, one for the fuel and the other for the air, the mixture fraction can be defined as

\[
\xi = \frac{z_i - z_i^1}{z_i^2 - z_i^1}
\]

where \( z_i^1 \) refers to stream 1, and \( z_i^2 \) to stream 2, respectively. The elemental mass fraction of the chemical elements, \( z_{ni} \), can be retrieved from the equation
\[ z^*_i = z^*_i' + \left( z^*_i - z^*_i' \right) \xi \]  \hspace{1cm} (35)

Finding a realistic shape of the pdf can be difficult. Usually it is assumed that the different variables are statistically independent. This restricts the use of these models to cases where the statistical fluctuations are small, namely to premixed flames and to diffusion flames with infinitely fast chemistry (Bilger 1988). Borghi (1988) has discussed what would be a realistic shape of the presumed pdf and whether the ratios between the relevant time scales that can be used to describe the flame type influences on the shape of the pdf. Each type of flames gives rise to a different pdf. This is also reflected in the existing models. Consequently, the pdf may be approximated either by a Gaussian curve, a \( \beta \)-function, a rectangle, or two delta-functions.

A popular function for describing the pdf is to use a \( \beta \)-function i.e.,

\[ \tilde{f}(\xi) = \frac{\xi^{a-1}(1-\xi)^{b-1}}{\int_0^1 \xi^{a-1}(1-\xi)^{b-1} d\xi} \]  \hspace{1cm} (36)

When \( \xi \) and \( \xi^* \) are known from their transport equations, the values of parameter \( a \) and \( b \) that satisfy the definitions

\[ \tilde{\xi} = \int \xi \tilde{f}(\xi) d\xi \]  \hspace{1cm} (37)

and

\[ \tilde{\xi}^* = \int (\xi - \tilde{\xi}) \tilde{f}(\xi) d\xi \]  \hspace{1cm} (38)

can be calculated.

Another alternative is to assume that the fluctuations in the mixture fraction consist of a turbulent part as well as of a non-turbulent part (Kent and Bilger 1976). The pdf for the mixture fraction, \( \xi \), can then be approximated as

\[ \tilde{f}(\xi) = \tilde{f}_t(\xi) + (1 - \tilde{T}) \delta(\xi) \]  \hspace{1cm} (39)
where the intermittency $\tilde{T}$ defines the relative contributions from the two parts of the flow.

If the flame is non-adiabatic, a separate balance equation is needed for enthalpy. In order to avoid the complications associated with the solving of a joint pdf of mixture fraction and enthalpy, it is often assumed that the enthalpy fluctuations are independent of the enthalpy level.

The presumed pdf only provides information about the statistical distribution of the mixture fraction. In order to calculate the mean reaction rate, information about the reaction kinetics is also required. In the next three sections, different approaches to include chemistry are described. Of these approaches, the fast chemistry approach is the simplest, and probably the most frequently applied one, whereas the flamelet approach has the greatest potential to include multi-step reaction schemes.

4.2.1 Presumed pdf - fast chemistry

If it is assumed that the chemical reactions occur at an infinite rate, the instantaneous composition is given by the equilibrium composition. Solving the transport equation for the mixture fraction, the local mass fractions of the chemical elements can be calculated. Once the mass fractions of the chemical elements are known the composition is obtained from the equilibrium composition. The pdf of the mixture fraction is then used as a weighting function to calculate the mean values.

The presumed pdf approach can be used in the calculations of industrial-scale processes and is incorporated in many commercial CFD softwares. The presumed pdf–fast chemistry approach can be used in the modeling of diffusion flames as well as in the modeling of premixed flames. In the modeling of premixed flames he probably best known approach is the Bray-Moss-Libby (BML) model (Bray et al. 1985).
4.2.2 Presumed pdf - simple chemistry

In many cases, equilibrium assumptions lead to higher predicted values of CO than can be measured. In order to improve the predictions, it is necessary to include reaction kinetics in the modeling. In the presumed pdf approach, it is difficult to incorporate a complex description of the chemistry, since the solution of joint pdfs of higher dimensionality than two or three becomes time consuming. The true shape of these pdfs are neither easy to work out (Borghi 1988). One way to incorporate reaction kinetics, without having to consider joint pdfs of high dimensionality, is to discriminate between fast shuffle reactions such as

\[ \text{H}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H} \]

and rather slow three body recombination reactions such as

\[ \text{H} + \text{OH} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M} \]

Then, one or more combined variables are introduced by linear combination of concentrations. These variables are defined in such a way that their formation rates are independent of the fast shuffle reactions. A two variable approach has been applied to the H\(_2\)/air system (Janicka and Kollman 1979) and the H\(_2\)/CO/air system (Correa et al. 1984, Correa and Gulati 1992). In these systems the combined variable is \( Y_{H_2}^* \). This variable can vary between its unburned value, \( Y_{H_2}^{*u} \) and its equilibrium value, \( Y_{H_2}^{*e} \) which makes it possible to define a progress variable \( \eta \):

\[ \eta = \frac{Y_{H_2}^{*e} - Y_{H_2}^{*u}}{Y_{H_2}^{*e} - Y_{H_2}^{*u}} \] (40).

The formation rate of the combined variable is dependent on the contributions from the slower reactions. The contributions from these reactions are combined to a reaction rate \( \phi_{H_2}^* \). Temperature, density, and concentrations of the species that are considered, in this case nine species, are now dependent on only two variables, i.e., the mixture fraction and the progress variable. From the joint pdf of these two variables it is possible to calculate the necessary mean values. Here
too, it must be assumed that the joint pdf can be written as the product of the marginal pdfs, i.e., the pdf of the mixture fraction $\tilde{f}(\xi)$, and the pdf of the progress variable $\tilde{f}(\eta)$. The pdf of the mixture fraction can be described with the presumed pdf approach, i.e., it is also necessary to know the mixture fraction variance. For the pdf of the progress variable, Janicka and Kollman (1979) have proposed a three Dirac-delta function,

$$\tilde{f}(\eta) = c_1 \delta(\eta) + c_2 \delta(\eta - \bar{\eta}) + c_3 \delta(1 - \eta)$$  \hspace{1cm} (41).

The parameters $c_1$, $c_2$, and $c_3$ are assumed to be functions of the variance of the progress variable which results in that an equation for the variance of the progress variable is also needed. In contrast to the transport equation for the mixture fraction, the transport equations of the progress variable and the variance of the progress variable will include a term accounting for the reaction kinetics.

The model described so far assumes that CO is in partial equilibrium, assuming that the reaction

$$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$$

is fast. To account for the CO kinetics, a second progress variable, $\psi$, must be introduced. This progress variable is defined as

$$\psi = \frac{Y_{CO} - Y_{CO}^{pe}}{Y_{CO}^u - Y_{CO}^{pe}}$$  \hspace{1cm} (42)

where $Y_{CO}^u$ is the mass fraction CO in the unburned mixture and $Y_{CO}^{pe}$ the mass fraction CO assuming partial-equilibrium. A brief description of results obtained with a model including this additional progress variable can be found in Correa and Shyy (1987). From the description of the relatively simple cases above, it can be seen that the approach relies on several assumptions with respect to the shape of the joint pdfs and that the extension to hydrocarbon flames is not straightforward.
4.2.3 Presumed pdf - flamelet models

An alternative approach to describe the reactions is based on the flamelet concept (Peters 1984). The flamelet concept assumes that the reactions take place in asymptotically thin layers embedded in the turbulent flow field. This is the case when the chemical time scale is short compared with the time scales of convection and diffusion. It is further assumed that these flamelets are identical to those found in laminar flames. Usually the flamelets are modeled as the mixing-layer type found in the counter-flow geometry or stagnant-point flow setup. The choice of this type of flame has the advantage that these flames have been studied experimentally and theoretically more in recent years as compared with other diffusion flames. The flamelet idea is presented in Figure 4.1.

![Diagram of Turbulent Premixed and Nonpremixed Flames](image)

**Figure 4.1. Schematic illustration of the flamelet concept (Candel et al. 1994). The reactions in a real flame are assumed to occur in structures identical to those found in laminar strained flames.**

Using the flamelet concept, it is possible to de-couple complex chemistry and molecular transport problems from the calculations of the turbulent flow field. The advantage of de-coupling the chemistry calculations from the turbulent flow
Review of turbulence-chemistry interaction models

field calculations is that the flamelet calculations can be made a priori and the results stored in a flamelet library. Usually, a presumed pdf is used to couple the flamelet to the flow description. This type of model has been formulated both for the premixed and the non-premixed case. The flamelet concept has been developed further to include partly premixing and extinction of the flame. Under these conditions, however, the combustion is taking place outside the flamelet region.

In the model used for the non-premixed case, the flow is divided into two parts, a reaction zone, and a non-reacting part. In the reaction zone, the reaction rates depend on the mixture fraction and the scalar dissipation. In the non-reacting or inert part, only mixing occurs. The mixture fraction and its scalar dissipation, $\chi$, defined as $\chi = 2D(\partial \xi / \partial x_a)^2$, are the two parameters accounting for the effects of stoichiometry and flame stretch in linking the turbulent flame structure to that of a laminar flame. Usually, it is assumed that the mixture fraction and its dissipation are independent stochastic variables, which allows their joint probability density function $\tilde{f}(\xi, \chi)$ to be written as the product of the two marginal pdfs, i.e., $\tilde{f}(\xi, \chi) = f_1(\xi)f_2(\chi)$. The shapes of the two probability density functions are presumed. This model can take local extinction into account. This is accomplished by comparing the rate of the scalar dissipation with a critical one at which extinction occurs. However, at these conditions the assumptions behind the flamelet concept are no longer valid, as was pointed out above.

4.3 Flamelet models with a balance equation for flame surface density

Another approach using the flamelet concept to describe the chemistry is to use a balance equation to calculate the flame surface density, $\Sigma$. The flame surface density describes the flame surface per unit volume. The flame surface density concept is used in a model in which terms such as turbulent diffusion, production, and destruction of the flame surface area due to various physical phenomena are accounted for. The transport equation for the flame surface density is
\[
\frac{\partial \Sigma}{\partial t} + \frac{\partial}{\partial x_a}(\bar{u} \Sigma) = \frac{\partial}{\partial x_a} \left( \frac{\nu}{\sigma_x} \frac{\partial \Sigma}{\partial x_a} \right) + S_1 + S_2 + D \tag{43}
\]

In the equation above, \(\sigma_x\) is a turbulent Schmidt number and \(\nu\) the turbulent kinematic viscosity. \(S_1\) gives the flame surface created due to the stretch of the flame surface by the mean flow. \(S_2\) gives the flame surface created due to stretch induced by the turbulent eddies. \(D\) gives the consumption of flame surface due to consumption of the reactants, by interactions of the flame front but also by other chemical effects, i.e., quenching. For further references to this type of models, see Candel et al. (1994).

The flame surface density concept was first developed for premixed combustion but has later been extended to the non-premixed case. For the premixed case, various flame surface density models have been compared by Duclos and co-workers (1993). Under the assumption of local equilibrium between the production and dissipation of flame surface density, the reaction rate in several of the models becomes proportional to the eddy break-up rate.

There are also a few other models based on the flamelet concept. One such model uses the flamelet passage frequency to evaluate the reaction terms. Here, the reaction rates are calculated as a product of the flame crossing frequency and the mean reaction rate per flame crossing. A brief description of this model too can be found in Candel et al. (1994), where further references can be found.

4.4 Eddy Break-Up models

The models described in this section assume that the reaction rate is dependent on the rate of the eddy break-up process. This dependence holds if it is assumed that the mixing time needed for the fluid to mix, on a level where heat conduction and chemical reactions are significant, is much slower than the purely chemical reaction rate. Later, certain modifications have been made that also the chemical reaction rate to be taken into account. The Eddy Dissipation Combustion Model
Review of turbulence-chemistry interaction models

(Magnussen and Hjertager 1976) is at the moment one of the most frequently used models. Unfortunately, the nomenclature when referring to the models in this group is not very clear. Today, when the term EBU, the acronym for Eddy Break-Up (Spalding 1971), is used, the Eddy Dissipation Combustion Model is usually in mind. To make the situation even more puzzling, this model is often shortened EDC, as is the more complex Eddy Dissipation Concept (Magnussen 1981 and 1989). The Eddy Dissipation Combustion Model and the Eddy Dissipation Concept, two models belonging to this family of models, are treated in more detail in Chapters 8 and 9.

4.4.1 The Eddy Break-Up model

The first person to realize that the eddy break-up process in many cases is the rate determining process in turbulent combustion was Spalding (1971). In the model proposed by him in 1971, this was taken as the dominant mechanism, in fact so dominant that the chemical reaction rate could be ignored.

Originally, the model was developed for premixed conditions. It was assumed that the fluid consisted of fully burned gas, having the temperature of the burned gas \( T_b \), and of unburned gas, having the temperature of the unburned gas \( T_u \). The observed local average temperature is then considered to represent the relative passing frequency of the hot and cold fragments. A progress variable, \( \tau \), given by

\[
\tau = \frac{Y_{f_{b}} - Y_{f_{u}}}{Y_{f_{b}} - Y_{f_{u}}} \tag{44}
\]

and describing the reactedness, is defined to qualitatively account for the reaction rate as a function of the local state of the fluid. This model stems from the early days of computational fluid dynamics, so the turbulence was modeled using a simpler approach than today. Therefore, the rate of the eddy break-up was assumed proportional to the local velocity gradient and in its original form of the Eddy Break-Up model, the mean reaction rate was written proportional to the local velocity gradient and to \((1 - \tau)\), i.e.,

30
\[ \tilde{\omega} = -C_{EBU} (1 - \tau) \left| \frac{\partial u}{\partial x} \right| \] (45)

where \( C_{EBU} \) is an empirically determined constant. In his paper, Spalding points out that when the chemical kinetics and the eddy break-up rate both influence the reaction rate, the rate can be calculated from a combination of the two terms as follows:

\[ \tilde{\omega} = \left( \tilde{\omega}_{\text{chem}}^{-1} + \tilde{\omega}_{\text{EBU}}^{-1} \right)^{-1} \] (46).

The Eddy Break-Up model has been developed further by Mason and Spalding (1973). In their version, the strain rate is assumed proportional to \( \varepsilon / k \), and the chemical reaction rate proportional to the root mean square of the oxygen fluctuations, i.e.,

\[ \tilde{\omega} = -C_{EBU} \frac{\tilde{\varepsilon}}{k} \left( \nabla \rho \right)^{1/2} \] (47).

As mentioned above, the EBU model has mainly been used to study premixed turbulent combustion. A shortcoming of the Eddy Break-Up models is lack of concentration dependence on the reaction rate. Reactions only occur when oxygen and fuel are mixed, which is not accounted for in the models.

### 4.4.2 Multi-Fluid Model of Turbulence

The Eddy Break-Up model has later been modified by Spalding (Spalding 1984 and 1995). In the Two-Fluid Model of Turbulence (Spalding 1984), the two states of the fluid, in the premixed case the hot and the cold fragments, are treated as two separate fluids, and the conservation equations are solved for both fluids. As in the Eddy Break-Up model, the reactions are assumed to take place at the interface between the fluids. There is no rigorous treatment of the chemical kinetics in this model, but the qualitative behavior of the reaction rate for premixed combustion is included through the assumption that the increase of reactedness, \( \tau \), is proportional to \( \tau^n (1 - \tau) \), where \( n \) is a constant.
More recently, the ideas of the Two-Fluid Model of Turbulence (Spalding 1984) have been generalized, making it possible to take chemical kinetics into account. This model is referred to as the Multi-Fluid Turbulence Model (Spalding 1995). For the premixed case, it seems that a minimum of four different fluids would be needed in order to incorporate the reaction term more rigorously. The four fluids are: 1) cold unburned gas, 2) a mixture of unburned gas and product gas, but too cold to react, 3) a mixture of unburned gas and product gas sufficiently heated to react, and 4) hot product gas.

For the diffusion flame case, the situation becomes more complicated, and notably more fluids are needed to represent the flow. Spalding suggests a minimum of seventeen fluids for this case. In the Multi-Fluid Turbulence Model, the different fluids are allowed to couple with any other indiscriminately at a rate depending on their availability. In the subsequent splitting process, the resulting states will possess the characteristics of either parent state, in any proportion. In the multi-dimensional concentration space, the offspring will lie on or close to the diagonal joining the parents. The values of the constants needed in the model are still preliminary and have been taken from the precursors of the multi-fluid model.

From the information each fluid states carry, it is possible to find various probability density functions. In this way, the Multi-Fluid Turbulence Model is related to the pdf approach. In the section where the pdf approach was discussed, it was mentioned that the Eulerian approach has been abandoned because of the difficulties of evaluating the multi-dimensional pdf. In the Multi-Fluid Turbulence Model, the description of the physics is somewhat simplified, which makes this approach computationally less demanding. The coupling and splitting process has been modeled according to ideas shown to give reasonable results in earlier Eddy Break-Up models. As in the Two-Fluid Model of Turbulence, a complete set of conservation equations must be solved for each fluid. In this more general model, the physical phenomena that can be considered for pre-mixed flames with the Two-Fluid Model of Turbulence can also be considered for diffusion flames.
4.4.3 The Eddy Dissipation Combustion Model

The Eddy Break-Up model (Spalding 1971) was set up for premixed conditions without any place for chemical kinetics. Magnussen and Hjertager (1976) suggested a solution to this problem in a model they presented as an Eddy Dissipation Combustion Model. If it is assumed that chemical reactions are fast, the rate of combustion will be determined by the rate of mixing of the reactants on a molecular scale. Moreover, the rate will be limited either by the availability of the fuel or of the oxidizer. They also included a term in which the products occur. This term stems from the fact that without hot combustion products present, the temperature of the mixture is such that probably no reactions are able to proceed. In a more compact way, the model can be written

\[ \bar{\omega}_f = \frac{A}{k} \min \left[ \frac{\bar{Y}_f}{r_f}, \frac{\bar{Y}_{O_2}}{r_f}, B \frac{\bar{Y}_p}{1 + r_f} \right] \]  

(48).

This model also differs from the Eddy Break-Up model in that it relates the dissipation of eddies to the mean concentration of the intermittent quantities, i.e., oxidizer and fuel, instead of to the concentration fluctuations which make the model easy to use. The model is widely used both for diffusion and premixed cases and is probably the most popular model for modeling practical devices. The Eddy Dissipation Combustion Model was constructed assuming that the chemical kinetics can be described with a single-step, infinitely fast, irreversible reaction. Later, this model has been extended to permit for the inclusion of reaction kinetics. This model is discussed and investigated in greater detail in Chapter 9.

4.4.4 The Eddy Dissipation Concept

The Eddy Dissipation Concept (Magnussen 1981 and 1989) is a further development of Eddy Dissipation Combustion Model (Magnussen and Hjertager 1976). This model takes into account that the reactions only occur in a fraction of the fluid, which in the model is referred to as fine structures. The reacting part of the fine structure is treated as an adiabatic perfectly stirred reactor. Denoting the
mass fraction of species $i$ in the non-reacting surroundings by $Y_i^0$, the mass fraction of the species in the burning fine structures, $Y_i^*$, can be found from

$$Y_i^* = Y_i^0 + \frac{\omega_i^* M_i}{\rho^* \tau^*} \tag{49}$$

where $\tau^*$ is the mixing time and $M_i$ the molecular weight of species $i$. The mean mass fraction is made up by a contribution from the surrounding fluid and from the reacting fine structures according to

$$\bar{Y}_i = (1 - \gamma^3) Y_i^0 + \gamma^3 Y_i^* \tag{50}$$

where $\gamma^3$ is the fraction of fluid consisting of fine structures and $\gamma$ is the fraction of the fine structures that is reacting. The mean reaction rate for a species $i$ can then be expressed as

$$\bar{\omega}_i = \frac{\gamma^3 \chi}{\tau^*} (Y_i^0 - Y_i^*) \tag{51}.$$ 

It is also possible to account for reactions in the surrounding fluid. In this case, the overall reaction rate will be

$$\bar{\omega}_i = (1 - \gamma^3 \chi) \bar{\omega}_i^0 \frac{\rho}{\bar{\rho}} + \gamma^3 \chi \bar{\omega}_i^* \frac{\bar{\rho}}{\rho} \tag{52}.$$ 

In premixed flames, in particular, the predicted reaction rate in the tail of the flame has been found too low. To improve the predictions, an additional factor, $\eta$, has been introduced to account for the fact that the reactant concentration in the non-reacted fragments may be much higher than the average concentrations. This model is investigated in greater detail in Chapter 8, where also certain modifications to the model are discussed.
4.5 I.E.M. models

The Exchange by Interaction with the Mean (I.E.M.) model (see Borghi 1988) is a model describing the “thickened wrinkled” or “thickened” flame region, cf. Figure 3.1. The model relies on a Lagrangian representation. The diffusion fluxes or the small-scale mixing between the fluid particle and the surroundings are represented with a term where the exchange with the mean occurs. The species conservation equation then becomes

\[
\frac{\partial Y_i}{\partial t} + u_a \frac{\partial Y_i}{\partial x_a} = \frac{\bar{Y}_i - Y_i}{\tau_{I,E,M}} + \dot{\omega}_i
\]  

(53).

In the I.E.M. model, the pdf of an fictitious inert tracer, e.g., the mixture fraction, $\xi$, is used to construct a “skeleton” of the multidimensional pdf $\tilde{f}(Y)$, enabling the evaluation of the mean reaction rate. This pdf-“skeleton” can be constructed using the Eulerian equations for the mean mass fractions combined with Equation 55. The pdf of the inert tracer can be calculated using the presumed pdf approach. As earlier pointed out, this requires the solution of two additional transport equations. However, the model relies on the additional assumption that the fluid particles are suddenly transferred to the present location, where they spend most of their lives. In this way, the particle trajectory in the physical domain does not need to be solved; it is sufficient to integrate Equation 53, considering the properties $\bar{Y}$ and $\tau_{I,E,M}$ of this point but with the initial conditions of the inlets. In common with the Monte Carlo based methods, the computational demand increases only linearly with the number of species and offers thus a way to include complex chemistry.

In the case of fast chemistry, certain interesting features can be observed. In diffusion flames, the instantaneous composition will be given by the equilibrium composition, i.e.,

\[
Y_i = Y_i^{eq}(\xi)
\]  

(54)

and is independent of the mean composition or the exchange time, $\tau_{I,E,M}$. In this case, the mean mass fraction of species $i$ can be found from
\[ \tilde{Y}_i = \frac{1}{0} y_{i,eq}(\xi) \tilde{f}(\xi) \, d\xi \]  
(55).

In case of premixed flames, under the assumption that the chemistry can be described by a single reaction whose equilibrium is given by the absence of the fuel, the equation for the mean reaction rate will be of the eddy break-up type. It can be noted that the mixing time in the I.E.M. model is assumed to be proportional to \( kl/\varepsilon \).

In the I.E.M. model it is assumed that all fluid particles suddenly move to the vicinity of the point of interest. A correct description requires that particle trajectories in the physical domain, starting from the inlet, are calculated. In order to avoid computations of particle trajectories but still obtain mean mass fractions corresponding to those that would be obtained by calculating particle trajectories, a method referred to as P.E.U.L. (Programme Eulerien Lagrangien) (see Borghi 1988) has been suggested. In this method, some additional starting points are considered. If \( n \) new points are considered, it is possible to determine \( n \) weights \( w_j \), such that the mean mass fraction obtained solving

\[ \tilde{Y}_i = \sum_{j=1}^{n} w_j \int_{0}^{\xi} y_{i,(j)}(\tilde{Y}_i, \xi) \tilde{f}(\xi) \, d\xi \]  
(56)

equals the mean mass fraction obtained in the case particle trajectories were considered. The choice of the additional starting points is not straightforward but should as a rule be distributed equally throughout the domain.

The M.I.L. (Modèle Intermittent Lagrangien) (Borghi 1988, Obounou et al. 1994), another extension to the I.E.M. model, has been developed recognizing that many chemical processes are so sudden that fluctuations in the exchange time can result in dramatic changes. In combustion, this jump can physically be interpreted as ignition. Now, the knowledge of the pdf of the tracer species is no longer sufficient to calculate the mean reaction rate, the jump must also be
properly modeled. The probability that a jump, i.e., ignition, occurs, can be calculated from

\[ \alpha = \int_{\tau_{ign}}^{\infty} f_{\tau}(\tau_{I.E.M.}) d\tau_{I.E.M.} \]  

(57)

where \( \alpha \) is the probability of a jump, and \( f_{\tau}(\tau_{I.E.M.}) \) a pdf describing the distribution of exchange time. The unique feature of the M.I.L. is the assumption that the mixing time follows a turbulent time scale distribution and cannot be represented by a single mixing time. The lower boundary of the integral in Equation 57 shows that only when the exchange time is greater than the ignition time, a jump can occur. The mean reaction rate can be calculated as

\[ \bar{\omega}_F = \int_0^{\infty} f_{\tau}(\xi) \int_{\tau_{ign}}^{\infty} \bar{\omega}_F(\tau_{I.E.M.}) f_{\tau}(\tau_{I.E.M.}) d\tau_{I.E.M.} d\xi \]  

(58).

Subscript \( F \) (for fuel) implies that, with the M.I.L. model, intermediate species cannot be taken into account. However, calculation of \( \tau_{ign} \) requires the use of a complex chemistry description.
5. Reaction mechanisms used in this thesis

5.1 Detailed kinetic mechanism for hydrocarbon oxidation

In this work, a detailed chemical reaction mechanism for methane combustion has been used in ideal reactor calculations as a reference to which simplified mechanisms have been compared. The results of the computations with the detailed mechanism have also been used when setting up a model for extinction. In the CFD calculations, the detailed mechanism has been used together with a modified version of the Eddy Dissipation Concept to model a CO/H₂/N₂–air jet flame. This mechanism, compiled and evaluated by Kilpinen and co-workers (Kilpinen et al. 1994, Aho et al. 1995, Mueller et al. 1998), is given in Appendix A. In the mechanism, the C₁-C₂ reactions mainly stem from Glarborg and Hadvig (1991), while the CO oxidation reactions are taken from Glarborg et al. (1993).

5.2 Simplified mechanisms for hydrocarbon oxidation

In many cases, the use of a detailed mechanism is prohibited due to the large computational effort it implies. Many practical fuels also include hydrocarbons for which a comprehensive mechanism is not available, and comprehensive mechanism cannot be used with many of the turbulence-chemistry interaction. In these cases, a simplified reaction mechanism has to be used. For engineering purposes, necessary information can in many cases be obtained with a less complete description of the chemistry. A benefit of the simplified mechanisms is that they easily handle more complex fuels too.

The simplest description of the fuel oxidation is that with an irreversible single-step reaction,

\[ C_nH_m + (n + \frac{m}{4})O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O \]

Empirically determined reaction rates for a number of hydrocarbons are available in the literature and are often expressed using a modified Arrhenius formulation,
The constants $A, n, E_a, a,$ and $b$ are used to tune the reaction rate to reproduce the laminar burning velocity for a wide range of conditions, including the rich and lean flammability limits. Constants for the single-step formulation for various fuels can be found in the literature, e.g., Westbrook and Dryer (1984) have listed them for a number of fuels. Since intermediate products are not included in this formulation, the extent of reaction is overestimated. Still, this formulation is very popular in computational fluid dynamics. Many of the turbulence-chemistry interaction models used today have been developed assuming that the chemistry can be described with a single irreversible reaction. It is often even assumed that the reaction is infinitely fast. The assumption of infinitely fast chemistry has in this thesis been used for comparison. A variant of the fast chemistry approach was also used when the influence of the description of the chemistry was investigated with the Eddy Dissipation Concept. In this case, it was assumed that the thermodynamic equilibrium was approached instantaneously. This description of the reaction kinetics as well, or lack of description of reaction kinetics, is often used together with the presumed pdf approach.

Hydrocarbon fuels burn in a somewhat sequential manner, i.e., the fuel is partially oxidized to CO and H$_2$, which are subsequently oxidized to CO$_2$ and H$_2$O. The explanation can be found in the comprehensive schemes. The elementary reaction

$$H + O_2 \rightleftharpoons O + OH$$

is the most important chain branching reaction. However, the reaction rate for the H-radical with O$_2$ is smaller than for most hydrocarbons, suppressing the production of O and OH-radicals until the hydrocarbons have been consumed. In hydrocarbon combustion, most of the CO oxidation occurs through the elementary reaction

$$CO + OH \rightleftharpoons CO_2 + H$$
Dryer and Glassman (1972) used this observation to construct a two-step formulation for the oxidation of methane. If this formulation is extended to other hydrocarbons, the reactions can be written

\[
C_nH_m + \left( \frac{n}{2} + \frac{m}{4} \right) O_2 \rightarrow nCO + \frac{m}{2} H_2O \\
CO + \frac{1}{2} O_2 \rightarrow CO_2
\]

In this thesis, this description has been extended to a three-step simplified mechanism with fast irreversible global reaction steps describing the oxidation of CH\(_4\) and H\(_2\), and the empirical rate given by Howard and co-workers (1972) describing the irreversible oxidation step of CO:

\[
CH_4 + O_2 \rightarrow CO + H_2 + H_2O \\
H_2 + \frac{1}{2} O_2 \rightarrow H_2O \\
CO + \frac{1}{2} O_2 \rightarrow CO_2
\]

The reaction rate for the CO oxidation determined by Howard and co-workers is

\[
r_{CO} = -1.3 \cdot 10^{13} \exp(-30,000/R T)[CO][O_2]^3[H_2O]^5
\]

This reaction rate is expressed in mol/cm\(^3\)s. The concentrations should be given in mol/cm\(^3\), the temperature in Kelvin, and the activation energy in calories. This description has been used in the investigation of the influence of the reaction kinetics with the Eddy Dissipation Concept.

Another, similar description is also utilized in this work. This description was developed in an earlier study (Brink et al. 1995) where it was found that the two-step simplified mechanism satisfactorily describes the overall reaction rates of methane at fuel lean conditions. However, it was also found that at fuel rich
Reaction mechanisms used in this thesis

conditions, the omission of H₂ as an intermediate combustion product gives rise to an overestimation of the CO concentration. This results in that the CO₂ concentration was underestimated, whereas the H₂O concentration was overestimated. To improve the description, a mechanism including the intermediate products CO and H₂, and where the water-shift equilibrium is taken into account, was developed. The mechanism is similar to a simplified mechanism put forth by Abdalla and co-workers (1983) but is tailor-made for perfectly stirred reactor calculations with the Eddy Dissipation Concept. The first step in the calculations with this mechanism is to check whether locally lean or fuel rich conditions are prevailing. Due to its optimized character, the mechanism can only be written in the conventional way for the fuel lean case. In this case, the mechanism can be presented by three global reactions:

\[ C_nH_m + \left(\frac{n}{2} + \frac{m}{4}\right)O_2 \rightarrow nCO + \frac{m}{2} H_2O \]

\[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \]

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]

The step describing the break-down of the hydrocarbon and the H₂ oxidation step is assumed to be infinitely fast, whereas the kinetics of the CO oxidation are described by the expression proposed by Howard and co-workers (1972). The H₂ oxidation step is at fuel lean conditions only needed for description of the oxidation of the H₂ formed in fuel rich regions upstream.

In the fuel rich case, the water-shift reaction is used to calculate the equilibrium composition. Then the amounts of H₂ and H₂O are frozen at the values given by this equilibrium calculation. The CO₂ formed in the reactions is then reconverted to CO and O₂. This state is then used as the starting condition in the perfectly stirred reactor calculations. Now, the only active reaction is the one describing the oxidation of CO. In the fuel rich case too, the CO oxidation is described by the expression of Howard and co-workers (1972).
Jones and Lindstedt (1988) have proposed a four-step simplified mechanism for hydrocarbon oxidation. For methane their global reactions are:

\[
\begin{align*}
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow & \text{CO} + 2\text{H}_2 \\
\text{CH}_4 + \text{H}_2\text{O} \rightarrow & \text{CO} + 3\text{H}_2 \\
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons & \text{H}_2\text{O} \\
\text{CO} + \text{H}_2\text{O} \rightleftharpoons & \text{CO}_2 + \text{H}_2
\end{align*}
\]

The first two global reaction steps, numbered as reactions 10 and 9 by Jones and Lindstedt, describe the break-down of the hydrocarbon fuel. The first one, i.e., reaction 10, is dominant in fuel lean conditions whereas the second one, i.e., reaction 9, is important in fuel rich conditions. The third global reaction step, referred to as reaction 7 by Jones and Lindstedt, describes the oxidation of H\(_2\), and the last one the water-shift reaction. In the publication of Jones and Lindstedt this reaction was referred to as reaction 8.

The rate expression for the forward reactions in the four-step mechanism of Jones and Lindstedt (1988), using the numbering of Jones and Lindstedt, are

\[
\begin{align*}
\dot{r}_{10} &= 0.44 \cdot 10^{12} \exp(-30,000/RT)\text{CH}_4^{0.5}\text{O}_2^{0.25} \\
\dot{r}_9 &= 0.31 \cdot 10^9 \exp(-30,000/RT)\text{CH}_4\text{H}_2\text{O} \\
\dot{r}_7 &= 0.25 \cdot 10^{17}T^{-1} \exp(-40,000/RT)\text{H}_2^{1}\text{O}_2^{0.25}\text{H}_2\text{O}^{-1} \\
\dot{r}_8 &= 0.275 \cdot 10^{10} \exp(-20,000/RT)\text{CO}\text{H}_2\text{O}^{-1}
\end{align*}
\]

The units of the reaction rates are kmol/m\(^3\)s, the species concentrations are given in kmol/m\(^3\), the temperature in Kelvin, and the activation energy in calories. In the calculations, the rate for the H\(_2\) oxidation may cause numerical problems since it goes to infinity as the concentration of H\(_2\)\text{O} approaches zero. Although the calculations of the backward rates follow the usual principles, especially the rate expression for the backward rate of the H\(_2\) oxidation reaction may need a few additional lines. At equilibrium, the forward and the backward rate should be equal. Knowing the equilibrium constant and the forward rate for the reaction, it
should be possible to calculate the backward rate. For the H₂ oxidation reaction, the backward rate then becomes

\[ r_7^b = 0.25 \cdot 10^{17} T^{-1} \exp(-40,000/RT)K_7^{eq^{-1}}[H_2]^{0.5}[O_2]^{0.75} \]

As the expression for the forward rate for this reaction, the expression for the backward rate may cause numerical problems. Here too, the reaction rate can go towards infinite values. In addition, care must be taken since the dissociation of H₂O is according to the expression above independent of the presence of H₂O. In this work, the backward rate has been neglected in many of the computations, since it is not important at fuel rich conditions and at low temperatures. Other four step mechanisms have also been proposed. Hautman and co-workers (1981) proposed a mechanism with C₂H₄ incorporated, representing the olefinic intermediates from the aliphatic hydrocarbon break-down, allowing the same reaction rates to be used for a number of hydrocarbons. In this thesis, only the four-step mechanism put forth by Jones and Lindstedt (1988) has been applied in the calculations.

5.3 Detailed kinetic mechanism for nitrogen chemistry

Comprehensive detailed reaction mechanisms are not only available for hydrocarbon oxidation; also the elementary reactions describing the nitrogen chemistry have been compiled into detailed mechanisms. In the compilation of a detailed mechanism for the nitrogen chemistry, it must be ensured that elementary reactions shared with the hydrocarbon chemistry are compatible with the mechanism for the hydrocarbon oxidation. It is not safe to combine a detailed reaction mechanism for nitrogen chemistry with that for the hydrocarbon oxidation without an extensive evaluation of the combined scheme. In this work, a detailed reaction mechanism for the nitrogen chemistry, compiled by Kilpinen and co-workers (Kilpinen et al. 1994, Aho et al. 1995) has been used. The mechanism has been evaluated together with the hydrocarbon oxidation mechanism given in Appendix A.
5.4 Simplified mechanisms for nitrogen chemistry

As mentioned in the previous section, the simplified hydrocarbon mechanisms can in many cases be used for obtaining sufficient information about temperature and flow field. In the nitrogen chemistry case, the situation is more complex than in the hydrocarbon chemistry case. It is well known that the thermal-NO formation is extremely temperature sensitive, and thus sensitive to an accurate prediction of the temperature. Unfortunately, this means that the thermal-NO formation is also sensitive to the description of the temperature fluctuations. The nitrogen chemistry is also very complicated compared with the hydrocarbon chemistry in that the nitrogen present in the fuel can be converted into a number of different species, all of importance when emissions are of concern. The formation of the thermal-NO, on the other hand, is not dependent on nitrogen from the fuel but on a sufficiently high temperature. If a simplified reaction mechanism has been used when modeling the flow field and temperature distribution it is difficult to apply a detailed mechanism for the nitrogen chemistry part, since the radicals are mainly produced in the hydrocarbon oxidation.

The fact that it is not possible to use a comprehensive reaction mechanism with most turbulence-chemistry interaction models, results in that there is still a large need for simplified nitrogen mechanisms. In this work, three different simplified nitrogen mechanisms have been used. The first one is that of de Soete (1974). He determined the reaction rates for oxidation of HCN and NH₃ with O₂ as well as the reaction rates for the formation of N₂ from HCN and NH₃ with NO. He also determined an overall reaction rate for the formation of prompt-NO, i.e., NO formed when hydrocarbon radicals attack N₂ in the combustion air. In this work, only the reactions with NH₃ have been used since only gas mixtures containing NH₃ have been studied. The reaction rate for the NH₃-O₂ reaction, referred to as reaction A by de Soete, is

\[
r_A = 4.0 \times 10^6 \exp(-32,000 / RT) [\text{NH}_3] [\text{O}_2 \left( \frac{P}{RT} \right)^{-a}]^b
\]
where the exponent \( b \) is a function of the \( \text{O}_2 \) mole fraction. For \( \text{O}_2 \) mole fractions less than approximately 0.004, the value of \( b \) is 1, whereas the reaction becomes zero with respect to \( \text{O}_2 \) when the \( \text{O}_2 \) mole fraction exceeds approximately 0.02. The rate expression for the \( \text{NH}_3 \)-\( \text{NO} \) reaction, referred to as reaction \( B \) by de Soete, is

\[
r_B = 1.8 \cdot 10^8 \exp(-27,000 / RT) [\text{NH}_3][\text{NO} \left( \frac{P}{RT} \right)]^{-1}
\]

In the expressions above, the reaction rates are given in mol/cm\(^3\)/s. The concentrations are in mol/cm\(^3\), the activation energy in calories, and the temperature in Kelvin. In his paper, de Soete only gives the reaction rate without writing out the formal reactions. In this work, the formal reactions used by Mitchell and Tarbell (1982) have been used, i.e.,

\[
\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2
\]

\[
\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2
\]

Mitchell and Tarbell developed an empirical mechanism consisting of 12 global reactions for the formation of \( \text{NO} \) in pulverized coal combustion. The scheme includes both homogeneous and heterogeneous reactions as well as reactions needed to describe the combustion of the fuel. Often, the nitrogen species reactions are used separately, although Mitchell and Tarbell, using a regression technique determined the values of the parameters in the rate expressions for the reactions describing the nitrogen chemistry. If a main chemistry is used that behaves drastically different from that used during their parameter fitting procedure, there is a great risk that the reaction rates associated with the nitrogen chemistry do not behave as intended. In their global mechanism describing the nitrogen chemistry, i.e.,

\[
\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2
\]

\[
\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2
\]

\[
\text{HCN} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}
\]

45
Reaction mechanisms used in this thesis

\[ \text{NO} + \text{CH}_4 \rightarrow \text{HCN} + \text{H}_2\text{O} + \frac{1}{2}\text{H}_2 \]

\[ \text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \]

NH\textsubscript{3} is included as an intermediate species in the conversion of HCN to NO or N\textsubscript{2}. In the calculations presented in this thesis, where the nitrogen chemistry mechanism of Mitchell and Tarbell has been used, the reaction that describes the thermal-NO formation has not been included.

In the CFD calculations where the mechanism of Mitchell and Tarbell are used only the two first reactions, referred to as reactions 7 and 6 in the paper of Mitchell and Tarbell (1982), are used. The reaction rates for these reactions are:

\[ r_7 = 6.22 \cdot 10^{-6} \exp\left(-\frac{55,000}{RT}\right) \left[\text{NH}_3\right] \left[\text{NO}\right] \left(\frac{P}{RT}\right)^{-1} \]

\[ r_6 = \frac{3.48 \cdot 10^{20} \exp\left(-\frac{100,000}{RT}\right) \left[\text{NH}_3\right] \left[\text{O}_2\right]}{1 + 6.9 \cdot 10^{-6} \left[\text{O}_2\right] \left(\frac{P}{RT}\right)^{-1}} \]

The use of only the two first reactions are justified by the findings of the ideal reactor studies described in the next chapter. In the reactor studies also the reactions including HCN have been included. The rate expressions for the reactions, referred to as reaction 9 and 10 by Mitchell and Tarbell are given by the following expressions:

\[ r_9 = 1.94 \cdot 10^{15} \exp\left(-\frac{78,400}{RT}\right) \left[\text{HCN}\right] \left[\text{O}_2\right] \left(\frac{P}{RT}\right)^{-1} \]

\[ r_{10} = 1.00 \cdot 10^{4} \left[\text{NO}\right] \left[\text{CH}_4\right] \left(\frac{P}{RT}\right)^{-1} \]

The reaction rates are given in mol/cm\textsuperscript{3}s, the temperature in Kelvin, and the activation energy in calories. The reaction describing thermal-NO has not been taken into account in the calculations.
Brouwer and co-workers (1996) more recently developed a simplified nitrogen chemistry mechanism. They used a regression procedure to determine rate expressions. A detailed mechanism was used to produce the data needed for the regression. Their mechanism is developed for CFD simulations of selective non-catalytic reduction (SNCR). The mechanism consists of seven irreversible, finite-rate reactions. In this work, their mechanism has been applied to the oxidation of NH₃. Since the SNCR process can be realized with several reacting agents, only two of their seven reactions are of interest in this case. These reactions, referred to as reaction 1 and 2 in the scheme of Brouwer and co-workers (1996), are

\[
\begin{align*}
\text{NH}_3 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{H} \\
\text{NH}_3 + \text{O}_2 & \rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}
\end{align*}
\]

In their study, Brouwer and co-workers found that the influence of CO was that important that the rate expressions needed to be modified in order to take it into account. The suggested rate expressions are

\[
\begin{align*}
r_1 &= 4.24 \times 10^8 \left[ T + 17.5 \cdot \ln([\text{CO}]) - 68 \right]^3 \exp \left\{ \frac{-83,600}{T + 17.5 \cdot \ln([\text{CO}]) - 68} \right\} [\text{NH}_3][\text{NO}] \\
r_2 &= 3.5 \times 10^5 \left[ T + 17.5 \cdot \ln([\text{CO}]) - 68 \right]^3 \exp \left\{ \frac{-125,300}{T + 17.5 \cdot \ln([\text{CO}]) - 68} \right\} [\text{NH}_3][\text{O}_2]
\end{align*}
\]

In the expressions above, the rates are given in mol/cm³s, and the temperatures in Kelvin. The concentrations of NH₃, NO and O₂ are given in mol/cm³, whereas CO should be given in ppm. As already mentioned, this mechanism was developed for SNCR conditions. The relevant temperature window for the SNCR process is 850-1100°C. Brouwer and co-workers also tested their mechanism for slightly higher temperatures. In this thesis this mechanism is evaluated against the comprehensive mechanism in a broader temperature range using perfectly stirred reactor assumptions. This mechanism was then applied to model an NH₃-doped swirling natural gas combusitor.

47
6. Ideal reactor studies

6.1 Adiabatic perfectly stirred reactor studies

A successful CFD study relies on a number of models. The most preferable way to test such a model, including a chemical reaction scheme, would be to test it together with the other models required for the CFD modeling. Unfortunately, it is difficult in such a case to judge to what extent an inadequate chemical scheme contributes to the quality of the prediction compared with the contribution of other, perhaps inadequate, models of other important physical phenomena. Usually, this process is further complicated by the fact that there are often uncertainties in the boundary conditions required for the CFD modeling. In particular, it is difficult to obtain boundary conditions for the turbulence models, since the required quantities are normally not possible to measure inside burners. A solution to this is to include the burner into the computational domain, but in many applications the complexity of the burner and the small size of the details of the burner compared with the size of the furnace itself makes this approach less tractable. Apart from problems with boundary conditions for the turbulence models, in many industrial applications the fuel and material properties are not known well enough. This problem is probably more severe when modeling solid fuels. Probably the best way to overcome this problem is to use an ideal reactor model in the assessment of the chemical reaction scheme. In this work, the perfectly stirred reactor was chosen. One strong argument for choosing the perfectly stirred reactor and not a plug flow reactor is that the perfectly stirred reactor is an integral part of the Eddy Dissipation Concept which is also investigated in this work. In the investigation presented here, three different schemes for hydrocarbon combustion have been tested. They are the comprehensive reaction mechanism consisting of elementary reactions, the three-step simplified mechanism, which is an extension of the two-step mechanism, and the four-step mechanism of Jones and Lindstedt (1988). A closer description of the mechanisms was given in Chapter 5.

In the perfectly stirred reactor calculations, the PSR code (Glarborg et al. 1986) from the CHEMKIN library (Kee et al. 1991) was used. The equations describing the perfectly stirred reactor are the species conservation equation
Ideal reactor studies

\[ \dot{m}(Y_{i}^{\text{out}} - Y_{i}^{\text{in}}) - r_{i}M_{i}V = 0 \]  

(59)

and the energy conservation equation

\[ \dot{m} \sum_{i=1}^{K} \left( Y_{i}^{\text{out}} h_{i}^{\text{out}} - Y_{i}^{\text{in}} h_{i}^{\text{in}} \right) + \dot{Q} = 0 \]  

(60).

In the equations above, \( \dot{m} \) is the mass flow rate through the reactor, \( Y_{i}^{\text{out}} \) and \( Y_{i}^{\text{in}} \) the mass fraction of the species \( i \) in the reactor and the inlet, respectively, \( \dot{W}_{i} \) the chemical reaction rate, \( M_{i} \) the molecular weight, \( h_{i} \) the specific enthalpy, \( V \) the reactor volume, and \( \dot{Q} \) the heat exchanged with the surrounding. For isothermal reactor calculations only the species conservation equations need to be considered.

The set of \( K+1 \) equations, where \( K \) is the total number of species, is a set of non-linear algebraic equations. In many cases, it is difficult to find the solution to this set of equations. It is then possible to integrate a corresponding set of time dependent differential equations to determine the steady state solution. The PSR code (Glarborg et al. 1986) used in this study is written for reaction mechanisms consisting of elementary reactions. In order to be able to use the same code with the simplified reaction mechanisms consisting of global reaction steps described by empirical rate expressions, the subroutine CKWYP had to be modified.

In Figures 6.1 and 6.2, the results from adiabatic perfectly stirred reactor calculations with methane-air mixtures are shown. Both the detailed mechanism and the four-step simplified mechanism are able to predict a critical residence time below which no reactions occur.
Figure 6.1. Mole fractions of the main components and the temperature versus residence time in a fuel lean perfectly stirred reactor. Adiabatic conditions have been assumed in the calculations. The stoichiometric ratio, $\lambda$, was 1.5 and the inlet temperature of the fresh methane-air mixture was 300 K. a) Result obtained with the three-step simplified mechanism, b) results with the four-step simplified mechanism of Jones and Lindstedt (1988), and c) results with the comprehensive mechanism. The results from a thermodynamic equilibrium analysis are also indicated.
Figure 6.2. Mole fractions of the main components and the temperature as a function of residence time in a fuel rich perfectly stirred reactor at adiabatic conditions. The stoichiometric ratio, $\lambda$, was 0.5 and the inlet temperature of the fresh methane-air mixture was 300 K. a) Result obtained with the three-step mechanism, b) results with the four-step mechanism of Jones and Lindstedt (1988), and c) results with the comprehensive mechanism. The results from a thermodynamic equilibrium analysis are also shown.
Ideal reactor studies

In the fuel lean case, shown in Figure 6.1, the stoichiometric ratio, $\lambda$, was 1.5. At this condition, the agreement between the two simplified mechanisms and the comprehensive mechanism is excellent if the residence time is longer than approximately 0.5 ms. The three-step simplified mechanism has not the capability to predict a critical residence time, but the prediction of the CO oxidation rate is in agreement with the predictions obtained with the more complex mechanisms. There is a slight difference in the predictions of the critical residence time obtained using the four-step simplified mechanism compared with that obtained using the comprehensive mechanism. Close to the critical residence time, the four-step simplified mechanism predicts a higher CO concentration and it relaxes towards equilibrium faster than for the comprehensive mechanism.

In the fuel rich case, shown in Figure 6.2, the stoichiometric air to fuel ratio, $\lambda$, was 0.5. Such conditions are likely to exist locally also in diffusion flames with an overall excess of air. At fuel rich conditions, the difference in the predictions is much more evident. The three-step simplified mechanism completely fails to reproduce the predictions obtained by the comprehensive mechanism. The thermodynamic equilibrium is not approached with the three-step mechanism. Already for short residence times the three-step mechanism predicts a high temperature in the perfectly stirred reactor which is due to the assumption of an infinitely fast break-down of methane. At fuel rich conditions, the agreement between the prediction obtained with the four-step simplified mechanism and with the comprehensive mechanism is less satisfactory as compared with the fuel lean case. Both the four-step simplified mechanism and the comprehensive mechanism predict a critical residence time, but there is an order of magnitude difference in its value. The difference in the predicted compositions is also notable. The four-step simplified mechanism relaxes towards equilibrium significantly faster than the comprehensive mechanism. Jones and Lindstedt (1988) pointed out that equilibrium was approached too rapidly in their calculations when compared with available measurements. In their paper, they did neither test their mechanism for very fuel rich or fuel lean conditions nor for preheated flames. With the comprehensive mechanism, equilibrium was not reached even after 1 s residence time.
Although the four-step mechanism cannot predict the chemistry as accurate at fuel rich conditions as at fuel lean conditions, the four-step simplified mechanism of Jones and Lindstedt (1988) seems to be a good compromise between accuracy and required computational effort. With this approach, the equilibrium-state is reached both in the fuel rich case and in the fuel lean case if the residence time is sufficiently long. However, at very fuel rich situations it will not be able to predict the equilibrium since the hydrocarbon break-down reactions are assumed to be irreversible reactions. Away from stoichiometric conditions and for preheated fuel-air mixtures, the four-step mechanism was faster than the comprehensive mechanism.

6.2 Critical residence time

In the modeling of turbulent combustion, it is important to be able to correctly account for the effect of enhanced micro mixing on the combustion. If this micro mixing is sufficiently high, the flow may locally extinct. In the adiabatic perfectly stirred reactor studies reported in the previous section, it was found that the four-step mechanism (Jones and Lindstedt 1988) was capable of predicting a critical residence time at which the heat release from the reactions is just sufficient for the reactions to proceed. Thus, if the residence time is further decreased, reactions will no longer occur. In the previous section, it was also found that the four-step mechanism is a good compromise between the required computational effort and the accuracy of the predictions. Still, in many applications, the effect of local extinction of the flow has a more drastic effect on the quality of the predictions than a slightly wrong prediction of the concentrations in the flue gas. To further investigate the four-step mechanism, this critical residence time was mapped in the range from very fuel rich mixtures, $\lambda = 0.1$, to very fuel lean mixtures, $\lambda = 10.0$. In addition, the effect of the temperature of the fresh fuel-air mixture was investigated. In the mapping of the critical residence time, the fuel was assumed to consist of pure methane. The result of the calculations is shown in Figure 6.3. For the case where the inlet temperature of the reactants was 300 K, the agreement between the four-step mechanism and the comprehensive mechanism is satisfactory. In particular, this applies to stoichiometric and near-stoichiometric conditions. However, further away from stoichiometric conditions,
the four-step mechanism generally underestimates the minimum residence time needed to sustain the combustion. For the higher inlet temperature case, where the inlet temperature was set to 700 K, the four-step mechanism is significantly faster than the comprehensive mechanism and the agreement is less satisfying. Nevertheless, this additional study contributes to the finding that for many practical applications, the four-step mechanism provides an adequate description of the chemistry at reasonable costs.

Figure 6.3. Critical residence time in a perfectly stirred reactor obtained through the comprehensive detailed elementary reaction mechanism (continuous line) and through the four-step mechanism of Jones and Lindstedt (1988) (broken line) versus the stoichiometric ratio. Two temperatures of the fresh methane-air mixture have been studied in the calculations. The results for the 300 K cases are plotted with thin lines whereas the 700 K cases are plotted with bold lines.
6.3 Isothermal perfectly stirred reactor studies

The main purpose for carrying out the isothermal perfectly stirred reactor studies was to investigate the reliability of the simplified nitrogen reaction schemes. In the mathematical modeling of flames where the modeling of the nitrogen chemistry relies on a simplified mechanism, the main chemistry too will be modeled by a simplified mechanism. In the previous sections, it was found that the four-step mechanism of Jones and Lindstedt provides an adequate description in a wide range of stoichiometry although the critical residence time generally was shorter with the four-step mechanism than it was with the detailed mechanism. Compared with the adiabatic perfectly stirred reactor problem the isothermal perfectly stirred reactor problem is simpler. However, the good agreement between the four-step reaction mechanism and the detailed mechanism does not necessary hold at isothermal conditions.

Figure 6.4 presents the results of the calculations of a perfectly stirred reactor as a function of temperature. The nominal residence time was 1 ms. The fresh mixture consisted of CH₄, NH₃, and air. The NH₃ content of the fresh fuel-air mixture was 1000 ppm. The stoichiometric ratio, λ, of the CH₄-NH₃-air mixture was 1.5, i.e., the mixture was fuel lean. For temperatures above 1300 K, the agreement between the predictions obtained with the four-step mechanism and those obtained with the detailed mechanism is excellent. However, below this temperature the detailed mechanism predicts that almost no reactions occur, whereas the four-step mechanism predicts that almost all CH₄ is oxidized at 1000 K too. In the adiabatic perfectly stirred reactor calculations, it was found that the four-step mechanism behaves similarly to the detailed mechanism. Both mechanisms were able to predict a critical residence time. In isothermal perfectly stirred reactor calculations there will be no critical residence time at which the heat release from the reactions are just large enough to sustain the combustion. Still, the detailed mechanism shows a behavior very similar to that in the adiabatic calculations. This time, however, the sudden drop in the oxidation rate of CH₄ is probably due to that the reaction rates of the elementary reactions become too low for sustaining the radical level that is needed for the CH₄ oxidation. In the four-step mechanism no information about the radicals are included. At fuel lean
conditions, the oxidation of CH₄ mainly proceeds through the reaction with O₂ and the predicted oxidation rate is a function of temperature only. As a consequence, the four-step mechanism does not show the same temperature sensitivity as the detailed mechanism.

Figure 6.4. Mole fractions of the main components and the temperature as a function of temperature in a fuel lean perfectly stirred reactor at isothermal conditions and a nominal residence time of 1 ms. In the calculations the stoichiometric ratio, λ, was 1.5. a) Results obtained with the four-step mechanism of Jones and Lindstedt and b) results obtained with the comprehensive mechanism.
Figure 6.5. NH$_3$ oxidation calculations as a function of temperature during methane combustion with air in a perfectly stirred reactor with a 1 ms residence time operated at fuel lean conditions. a) Results obtained with the mechanism of de Soete (1974), b) the result obtained with the mechanism of Brouwer and co-workers (1996), c) the results obtained with the mechanism of Mitchell and Tarbell (1982), and d) results obtained with the detailed mechanism.

Figure 6.5 shows the predicted mole fractions of NH$_3$, HCN and NO calculated with the mechanism of de Soete (1974), the mechanism of Mitchell and Tarbell (1982), the mechanism of Brouwer and co-workers (1996), and the detailed mechanism. Of the simplified mechanisms, only the mechanism of Mitchell and
Tarbell includes HCN. At fuel lean conditions, the comprehensive mechanism predicts that HCN mainly appears in the temperature range from 1300 K to 1500 K. For temperatures below 1300 K, the difference in the prediction of the main components obstructs the evaluation of the nitrogen chemistry. However, it can be noted that all simplified mechanisms predict a slower oxidation of NH$_3$ than the four-step mechanism predicted for CH$_4$. This behavior is not surprising since the simplified nitrogen mechanisms were not developed together with the four-step mechanism for the methane combustion. However, it suggests that in flame calculations the O$_2$ availability for NH$_3$ oxidation is restricted since the CH$_4$ oxidation will start consuming the O$_2$ before NH$_3$ starts reacting. The simplified reaction mechanism of de Soete predicts the lowest reaction rate for NH$_3$. With this mechanism not even a temperature of 2000 K is enough for consuming more than 60% of the NH$_3$ at the present conditions. According to the mechanism of Mitchell and Tarbell, most of the NH$_3$ is consumed at 1500 K. The mechanism of Brouwer and co-workers predicts the fastest consumption of NH$_3$. In the temperature interval, where the main chemistry is correctly predicted, the predicted NH$_3$ concentration agree well with those obtained with the detailed mechanism.

Although the NH$_3$ level predicted with the mechanism of Brouwer and co-workers agreed well with that obtained with the detailed mechanism, the quality of the NO predictions were not that good. In the temperature range from 1300 K to 1600 K this mechanism overestimates the importance of the reaction path leading to N$_2$. The situation is similar with the mechanism of Mitchell and Tarbell, although the discrepancy is not as large. At higher temperatures, on the other hand, the mechanism of Mitchell and Tarbell overestimates the importance of the path leading to NO. In this temperature range, the quality of the predictions obtained with the mechanism of Brouwer and co-workers is satisfactory. As already mentioned, the mechanism of de Soete is much too slow and does not provide predictions that agree as well with those obtained with the detailed mechanism as the other two simplified mechanisms do.
The situation is similar if the residence time of the perfectly stirred reactor is increased to 100 ms. Now, the agreement between the four-step mechanism of Jones and Lindstedt (1988) and the detailed mechanism becomes even better. Only at temperatures lower than 1100 K, the disagreement is striking as it was below 1300 K in the 1 ms case. However, only at temperatures higher than 1200 K, the agreement can be described as excellent. The trends found for the nitrogen chemistry in the 1 ms case can also be found in the 100 ms case. Here, the importance of the path leading to N₂ according to the mechanisms of Mitchell and Tarbell and of Brouwer and co-workers is in better agreement with that found using the detailed mechanism. At this residence time too, the mechanism of de Soete is too slow and the NH₃ is completely consumed first at a temperature of 2000 K. With the mechanism of de Soete, approximately 80% of the NH₃ that has reacted is converted to NO in a large temperature range. However, the other mechanisms predicted that the NO yield increases with temperature and is almost 100% at 2000 K.

Assuming isothermal conditions, the agreement between the results obtained with the four-step mechanism of Jones and Lindstedt (1988) and those obtained with the detailed mechanism was fair for fuel lean conditions. Assuming fuel rich conditions, the situation is not as satisfying anymore. Figure 6.6 shows the calculated species concentrations as a function of temperature in a perfectly stirred reactor having a 1 ms residence time. The stoichiometric ratio, \( \lambda \), is 0.5, i.e., the mixture is fuel rich. Here too, the NH₃ content of the fresh fuel-air mixture was 1000 ppm. With the detailed mechanism a temperature below which almost no reactions occur can be found, although there is a smooth transition between temperatures where reactions proceed and temperatures where they do not. Once again, the four-step mechanism does not show this behavior. However, in contrast to the fuel lean situation, here the agreement between the predictions in the high temperature region is not satisfying. Only at the very highest temperatures the species concentrations predicted with the four-step mechanism are similar to those predicted with the detailed mechanism. Still, the difference in the H₂O, H₂, but also CO concentrations is notable.
Figure 6.6. Mole fractions of the main components as a function of temperature in a fuel rich perfectly stirred reactor at isothermal conditions and a nominal residence time of 1 ms. The stoichiometric ratio, \( \lambda \), was 0.5. a) Results obtained with the four-step mechanism of Jones and Lindstedt (1988) and b) results obtained with the comprehensive reaction mechanism.

The poor agreement between the main species predictions using the four-step mechanism of Jones and Lindstedt (1988) and the detailed mechanism at fuel rich conditions complicates the evaluation of the simplified nitrogen chemistry schemes. However, the combination of a simplified description of both the main chemistry and of the nitrogen chemistry is representative for the chemical schemes used in CFD modeling, and is for this reason alone of great interest.
Figure 6.7. Calculated NH₃ oxidation as a function of temperature in a perfectly stirred reactor with a 1 ms residence time operated at fuel rich conditions. a) Results obtained with the mechanism of de Soete (1974), b) result obtained with the mechanism of Brouwer and co-workers (1996), c) results obtained with the mechanism of Mitchell and Tarbell (1982), and d) results obtained with the detailed mechanism.
Figure 6.7 shows the mole fractions of NH₃, HCN, and NO calculated with the mechanism of de Soete, the mechanism of Mitchell and Tarbell, the mechanism of Brouwer and co-workers, and the detailed mechanism as a function of the temperature in the fuel rich case. The figure shows that none of the simplified mechanisms provides an acceptable description at this condition. It is especially worth noting that at high temperatures the detailed chemistry predicts that most of the NH₃ is converted to HCN. At the highest temperature used in this study, i.e., 2000 K, the HCN mole fraction is approximately 700 ppm. The schemes of Brouwer and co-workers and de Soete do not contain the reactions needed to describe this conversion, but it is more remarkable to find that the scheme of Mitchell and Tarbell does not produce a significant amount of HCN. One reason for this might be that Mitchell and Tarbell used another set of overall reactions to describe the main chemistry. However, a more plausible explanation for the poor conversion of NH₃ to HCN is that in the mechanism of Mitchell and Tarbell, the path from NH₃ leading to HCN goes via NO. The formation of NO from NH₃ requires oxidizing conditions, whereas the formation of HCN from NO requires reducing conditions. It is also interesting to notice that the simplified mechanisms predict almost identical species levels as in the fuel lean case, although the conversion to NO is slightly less complete. The extensive conversion to NO predicted with the simplified mechanisms is probably due to the fact that the 1 ms residence time is too short for consuming all O₂. Even at a temperature of 2000 K there is a surplus of O₂ compared with the amount of O₂ needed for the oxidation of the NH₃.

Increasing the residence time to 100 ms does not change the situation radically, although the change is more pronounced than in the fuel lean case. Figure 6.8 shows the calculated mole fractions of the main species as a function of the temperature for the fuel rich case.
Figure 6.8. Mole fractions of the main components as a function of temperature in a fuel rich perfectly stirred reactor at isothermal conditions and a nominal residence time of 100 ms. The stoichiometric ratio $\lambda$ was 0.5. a) Results obtained with the four-step mechanism of Jones and Lindstedt (1988) and b) results obtained with the comprehensive reaction mechanism.

Compared to the 1 ms case, the agreement between the predictions with the four-step mechanism of Jones and Lindstedt (1988) and the detailed mechanism in the high temperature region is better, although it becomes very poor for temperatures below 1400 K. In contrast to the 1 ms case, the $O_2$ is almost completely consumed at high temperatures in the 100 ms case. Although the predictions with the four-step mechanism of Jones and Lindstedt (1988) are in slightly better agreement for the 100 ms case compared with the 1 ms case, the description of the nitrogen chemistry is still not satisfying.
Figure 6.9. $NH_3$ oxidation calculations as a function of temperature in a perfectly stirred reactor with a 100 ms residence time operated at fuel rich conditions. a) Results obtained with the mechanism of de Soete (1974), b) result obtained with the mechanism of Brouwer et al. (1996), c) results obtained with the mechanism of Mitchell and Tarbell (1982), and d) results obtained with the detailed mechanism.
Figure 6.9 shows the predicted mole fractions of NH₃, HCN, and NO for the fuel rich 100 ms case. Compared with the 1 ms case, the trends in the predictions with the detailed mechanism are very different. In the 1 ms case, the decrease in the total amount of nitrogen found as NH₃, HCN, and NO was only about 10%, whereas in this case, the decrease was even 75%. The trends in the predictions with the simplified mechanism are similar to those obtained in the fuel lean case, although the importance of the path leading to N₂ increases substantially for the mechanisms of Mitchell and Tarbell and of Brouwer and co-workers. At 2000 K, the mechanism of Mitchell and Tarbell predicted that approximately 40% of the nitrogen is converted to N₂. Neither at these conditions does their mechanism predict any substantial amounts of HCN. With the mechanism of Brouwer and co-workers, it was predicted that the path leading to N₂ should be even more important. Here, more than 50% of the nitrogen in the NH₃ was converted to N₂. With the mechanism of de Soete, approximately 35% of the nitrogen in the NH₃ were converted to N₂ compared with approximately 20% in the fuel lean case. Once again, the conversion is much less temperature sensitive than for the other two mechanisms.

6.4 perfectly stirred reactor studies with fluctuating temperatures

In the previous sections, the results obtained from perfectly stirred reactor calculations using simplified reaction mechanisms were compared with the results obtained using a detailed mechanism. In this section, the perfectly stirred reactor is used to study the influence of temperature fluctuations on the chemistry. Although this study does not directly relate to any practical applications, e.g., only fluctuations in the temperature is accounted for, and the fluctuations are regular, it is still believed that it illuminates the problems the turbulent fluctuations impose in combustion modeling.

In contrast to the previous calculations, the study of the effect of fluctuations requires that the transient behavior of the perfectly stirred reactor is modeled. In order to keep the study as simple as possible, the temperature fluctuations were described with a square wave, i.e., the temperature alternates between a maximum and a minimum temperature with a constant periodicity. In this way, the
temperature is known and the problem reduces to the modeling of a transient perfectly stirred reactor with a volume fluctuating in phase with the temperature fluctuations. The expression describing the transient species equation is

$$\rho V \frac{dY_i^{\text{out}}}{dt} = -\dot{m}(Y_i^{\text{out}} - Y_i^{\text{in}}) + r_i M_i V$$

(61).

To study the influence of temperature fluctuations, a 100 ms perfectly stirred reactor was chosen. According to Flagan and Seinfeld (1988), the mixing time of industrial burners, such as the ones used in utility boilers, is in the range of 30 to 300 ms. Consequently, the residence time chosen here is of the same order of magnitude as the mixing time in a large industrial burner.

The temperature varied ±500 K around the average temperature. The size of the fluctuations corresponds approximately to the maximum size of the temperature fluctuations reported by Stapf and Leuckel (1993) in a 350 kW swirling natural gas diffusion flame, although the root mean square of the temperature fluctuations in a real flame is smaller than that used in this study. In most of the calculations presented here, the duration at each temperature level was set to 1 ms. The distribution of the temperature fluctuations is artificial, but their periodicity is supported by measurements by Stapf and Leuckel. They found that the characteristic turbulent time scale was in the range 0.45 to 0.71 ms in the flame stabilization zone in their burner.

In the study of the influence of the temperature fluctuations, all calculations rely on the use of the detailed reaction mechanism. As the main purpose of this study was to investigate the influence of the temperature fluctuations on the nitrogen chemistry, this chemistry too was described with the detailed scheme. The PSR code (Glarborg et al. 1986) from the CHEMKIN library (Kee et al. 1991) was used in the calculations, but as in the case with calculations with the simplified mechanism, certain changes had to be made to the code. In this case, only some additional code handling the output from the routines used in the calculation of the transient perfectly stirred reactor had to be written.
As a starting point, the influence of the mean temperature on the main components and on the radicals occurring in largest amounts, i.e., O, OH, and H, was investigated. A stoichiometric CH₄-air mixture was used for this purpose. Four different mean temperature levels were chosen: 1400, 1600, 1800, and 2000 K. It was found that the influence of the temperature fluctuations on the main species concentrations was small. Figure 6.10 shows the species fluctuations in the 2000 K case, where the thermal dissociation of H₂O and CO₂ was most pronounced.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mole_fraction_plot}
\caption{Mole fractions of the main components and the temperature as a function of time in a perfectly stirred reactor with a nominal residence time of 100 ms. The stoichiometric ratio, \(\lambda\), was 1.0. The figure shows the transient history the first 10 ms after the temperature fluctuations were started.}
\end{figure}

As shown in Figure 6.10, the periodicity of the fluctuations in the main species becomes regular almost immediately. Since the magnitude of the fluctuation was ±500 K, the temperature during the high temperature stage was 2500 K, which is a considerably high temperature. In the calculations with lower mean
temperatures, the fluctuations were much less pronounced, e.g., in the 1400 K case, the fluctuations were almost negligible.

Although the effect of the fluctuations on the concentrations of the main species was not strong, their influence on the radicals with the highest concentrations was remarkable. Figure 6.11 shows the fluctuations of the O, OH, and H radicals in the 2000 K case. The figure shows that the reaction rates of the reactions influencing the levels of the O, OH, and H radicals are extremely fast. As the temperature changes, there is an almost immediate reconfiguration of the radicals. This reconfiguration is followed by a slower change in the radical concentrations, which is strongly connected with the change in the main species concentrations. The situation is very similar in the 1400 K case although the mole fraction of the OH radical only reached 1800 ppm, compared with more than 6000 ppm in the 2000 K case.

![Figure 6.11. Mole fractions of O, OH, and H and the temperature as a function of time in a perfectly stirred reactor with a nominal residence time of 100 ms. The stoichiometric ratio, λ, was 1.0. The figure shows the transient history the first 10 ms after the temperature fluctuations were started.](image)

68
So far the transient perfectly stirred reactor study has shown that the fluctuations in the main species as well as in the radicals with the highest concentration quickly become regular. Figure 6.12 shows the effect of the temperature fluctuations the NO mole fraction.

![Graph showing NO mole fraction and temperature as a function of time.](image)

*Figure 6.12. Mole fraction NO and the temperature as a function of time in a perfectly stirred reactor with a nominal residence time of 100 ms. The stoichiometric ratio, $\lambda$, was 1.0. The figure shows the transient history of the first 10 ms after the temperature fluctuations were started.*

The figure shows that NO, in contrast to the previously investigated species, does not quickly reach a regularly fluctuating state. In fact, the nitrogen chemistry required approximately 100 ms before the species fluctuations become periodical. This time is not only depending on the rate of the reactions involved in the nitrogen chemistry, but depends on the residence time of the perfectly stirred reactor as well. In the 2000 K case, the initial NO concentration was approximately 210 ppm and most total fixed nitrogen (TFN), which is the sum of the concentration of all nitrogen containing species except N$_2$, was found as NO. Since these calculations were obtained with a detailed mechanism, all paths
leading to NO were included. In the present case the vast majority of the NO was formed through the thermal-NO path, but also some NO was formed through other reaction paths. The NO mole fraction varied between 1620 ppm and 1690 ppm when the NO fluctuations become periodical. In the case of a fluctuating temperature too, most of the TFN was found as NO although approximately 5 ppm HCN was formed during the low temperature periods.

![Graph showing the relationship between mean temperature and mole fraction.](image)

**Figure 6.13.** Total fixed nitrogen as a function of mean temperature for a steady state perfectly stirred reactor and for a perfectly stirred reactor with a fluctuating temperature. The amounts of methane and air in the inlet corresponded to a stoichiometric mixture. The fresh mixture did not include any \( \text{NH}_3 \). The stoichiometric ratio, \( \lambda \), was 1.0. The larger squares show the calculated results with temperature fluctuations, and the bold broken line shows the trend fitted with an exponential expression. The smaller squares and the thinner broken line show the same results for the steady state perfectly stirred reactor.

In Figure 6.13, the TFN is plotted as a function of temperature, both for a steady state perfectly stirred reactor as well as for a perfectly stirred reactor with a fluctuating temperature. The figure shows that in both cases, with and without temperature fluctuations, the TFN increases with temperature. This increase is due to more NO being formed through the thermal-NO path. In the non-
fluctuating case, the increase is exponential whereas it is the even stronger in the fluctuating case. As can be seen from the curve showing the TFN for the non-fluctuating case, the increase in TFN due to formation of thermal-NO becomes important, only at temperatures higher than approximately 1800 K.

The main purpose of this investigation was to study the influence of temperature fluctuations on the nitrogen chemistry. The importance of the temperature on thermal-NO formation is well known and is here of little interest. To obtain a more complicated system with respect to the nitrogen chemistry, the CH₄-air mixture was doped with 1000 ppm NH₃.

![Graph showing mole fraction vs mean temperature](image)

**Figure 6.14.** Total fixed nitrogen as a function of mean temperature for a steady state perfectly stirred reactor and for a perfectly stirred reactor with a fluctuating temperature. The fresh stoichiometric methane-air mixture was doped with 1000 ppm NH₃. The stoichiometric ratio, $\lambda$, was 1.0. The larger squares show the calculated results with temperature fluctuations, and the bold broken line shows the trend fitted with an exponential expression. The smaller squares and the thinner broken line show the same results for the steady state perfectly stirred reactor.
Figure 6.14 shows the evolution of the nitrogen chemistry as a function of mean temperature in this case. The results from the steady state perfectly stirred reactor calculations are also shown. In this case, the fluctuations in the temperate appear not to influence the nitrogen chemistry until the temperature exceeds 1800 K, where the influence suddenly becomes very drastic. However, this insensitivity with respect to fluctuation is only an artifact due to the amount of NH$_3$ in the fresh fuel-air mixture.

![Graph showing mole fraction of NH$_3$ at inlet (ppm) vs. mole fraction of NH$_3$ (ppm) showing different trends for TFN and TFN.]

*Figure 6.15. Total fixed nitrogen as a function of the amount of NH$_3$ present in the fresh fuel-air mixture for a steady state perfectly stirred reactor and for a perfectly stirred reactor with a fluctuating temperature. The stoichiometric ratio, $\lambda$, was 1.0. The larger squares shows the calculated results with temperature fluctuations, and the bold broken line shows the trend fitted with an exponential expression. The smaller squares and the thinner broken line show the same results for the steady state perfectly stirred reactor.*

Figure 6.15 shows the situation for the 1800 K case when the amount of NH$_3$ in the inlet varies from 0 to 1000 ppm. It can be noted that when no NH$_3$ is added to the mixture, there is significant difference in the TFN between the steady state perfectly stirred reactor and the one with a fluctuating temperature. As the amount of added NH$_3$ increases, the difference becomes smaller.
So far, all calculations have been carried out for a stoichiometric fuel-air mixture. In the cases where also NH$_3$ has been added, this has been taken into account so that the stoichiometry has remained unaltered. Next, the influence of the stoichiometry was investigated. In the calculations, a mean temperature of 1800 K was used. Figure 6.16 shows the evolution of the nitrogen chemistry as a function of stoichiometry when no NH$_3$ was added to the CH$_4$-air mixture.

![Graph showing mole fraction of TFN and TFN as a function of stoichiometric ratio (λ).]

*Figure 6.16. Total fixed nitrogen as a function of stoichiometry for the steady state perfectly stirred reactor and for a perfectly stirred reactor with a fluctuating temperature. The mean temperature of the reactor was 1800 K. Only methane and air were present at the inlet. The larger squares show the calculated results with temperature fluctuations, and the bold broken line shows the trend fitted with an exponential expression. The smaller squares and the thinner broken line show the same results for the steady state perfectly stirred reactor.*

As shown in Figure 6.16, the influence of the stoichiometry on the TFN is small for a steady state perfectly stirred reactor having a temperature of 1800 K and a residence time of 100 ms. At first, the trend that the TFN obtains its highest value for the stoichiometric mixture is surprising. It is well known that the thermal-NO
formation increases with increasing $O_2$ partial pressure. In this case, one would thus expect to find the highest TFN at $\lambda = 1.5$ as is the case when fluctuations in the temperature are considered. However, at a temperature of 1800 K the prompt-NO path is dominating one and the importance of this path decreases as the $O_2$ concentration increases. At more fuel rich conditions, there are probably also other reactions being important. This is surely the case when the temperatures are fluctuating. At $\lambda = 0.5$ the contribution of HCN to TFN is approximately 25%. When 1000 ppm $NH_3$ is present in the fuel-air mixture the situation becomes much more interesting. Figure 6.17 shows the TFN as a function of temperature in this case.

**Figure 6.17.** Total fixed nitrogen as a function of stoichiometry for the steady state perfectly stirred reactor and for a perfectly stirred reactor with a fluctuating temperature. The mean temperature of the reactor was 1800 K. The fresh fuel-air mixture contained 1000 ppm $NH_3$. The larger square symbols shows the calculated results with temperature fluctuations, and the bold broken line shows the trend fitted with an exponential expression. The smaller square symbols and the thinner broken line shows the same results for the steady state perfectly stirred reactor.
Ideal reactor studies

Figure 6.17 shows that in the steady state case, the TFN increases only slowly with the partial pressure of O\textsubscript{2} at fuel lean conditions. Here most of the NH\textsubscript{3} is oxidized to NO, but slightly more than 30% of the nitrogen in the NH\textsubscript{3} is converted to N\textsubscript{2}. In the case when the temperature is fluctuating, the NO increases as expected with increasing partial pressure of O\textsubscript{2}. On the fuel rich side, some remarkable trends can be found. At $\lambda = 0.75$, there is no apparent effect on the TFN from the fluctuations, while a $\lambda = 0.5$ the TFN in the steady state case is suddenly five times as high as in the case when the temperature is fluctuating. In the steady state case, the concentration of NH\textsubscript{3} is 400 ppm and the concentration of HCN is 320 ppm, whereas the concentration of NO is less than 10 ppm. When the temperature is fluctuating, the concentration of TFN is less than 150 ppm of which 100 ppm is NO. This is to be compared with a concentration of more than 2000 ppm NO in the case when $\lambda = 1.5$. In Figure 6.18 the distribution of nitrogen in the most important nitrogen containing species is shown.

![Diagram](image)

Figure 6.18. Distribution of nitrogen in the species contributing most to the TFN.

To this point, the temperature has been changed every millisecond in the studies of the temperature fluctuations. Last, the effect of the frequency of the temperature fluctuations was investigated. These calculations were done for a stoichiometric CH\textsubscript{4}-air mixture without any addition of NH\textsubscript{3}. The mean
temperature was set to 1800 K. Apart from the 1 ms case, cases where the temperature was changed every 2, 5, and 10 ms were also investigated. Figure 6.19 shows the result from this study.

![Graph showing mole fraction vs duration of temperature level](image)

**Figure 6.19.** TFN as a function of the frequency of the temperature fluctuation for a perfectly stirred reactor with a fluctuating temperature. The mean temperature of the reactor was 1800 K. The fresh fuel-air mixture contained no NH₃. The larger squares show the calculated results with temperature fluctuations, and the bold broken line shows the trend fitted with an exponential expression. The smaller squares and the thinner broken line show the same results for a steady state perfectly stirred reactor.

From the figure it can be seen that the way the temperature changes will have an effect on the TFN level. It was found that the less frequently the temperature was changed the higher was the TFN. The TFN increased from approximately 300 ppm in the 1 ms case to more than 500 ppm in the 10 ms case. Simultaneously the HCN mole fraction increased from 1 ppm to 16 ppm, although this increase is not as drastic as the increase in NO.
Ideal reactor studies

The investigation of the influence of the temperature fluctuations on the chemistry, and in particular on the nitrogen chemistry, shows that under certain conditions the temperature fluctuations can even change the trends of the nitrogen chemistry compared with the steady state case. For the thermal-NO case, the temperature fluctuations resulted in a dependence on mean temperature that was much stronger than in the non-fluctuating perfectly stirred reactor case. When NH$_3$ was added to the CH$_4$-air mixture, particularly the dependency on the stoichiometry was unexpected. Perhaps more severe, with respect to the frequently used presumed pdf for thermal-NO calculation, was the finding that the nitrogen chemistry was dependent on the transient history of the temperature fluctuations. This result can be explained by considering the two extreme cases: very fast and very slow fluctuations. In the case of very fast fluctuations, the fluctuations will be filtered away since the chemistry will no be able to respond to them. In this case, there is no influence of the fluctuations. In the other extreme case, where the fluctuations are very slow, the mean values will be composed of the steady state values of the lower temperature and the steady state values obtained at the higher temperature.

Although a number of variables were taken into account in the study of the effect of fluctuations, the situation is much more complicated in a turbulent flame. In a flame, the temperature fluctuations are accompanied by fluctuations not only in the composition, but also in the turbulent mixing time scale. Still, this simplified study confirms the fact that the fluctuations are of great importance. This study also shows that it might be impossible to predict trends occurring in technical combustion devices using simplified reactor calculations combined with a detailed description of the reaction kinetics.

6.5 Summary of the ideal reactor studies

The perfectly stirred reactor calculation studies show that, although most turbulence-chemistry interaction models require that a simplified description of the chemistry is used, the situation is satisfactorily with respect to description of the main chemistry. The predictions obtained with the four-step mechanism of Jones and Lindstedt (1988) agreed reasonably well for a broad range of
conditions. Nevertheless, fuel rich conditions still possess a problem. For the nitrogen-chemistry, the situation is less satisfactory. Here too, the most severe shortcomings were encountered when modeling fuel rich conditions: none of the simplified nitrogen chemistry mechanisms that were tested could provide a satisfying description at fuel rich condition. The isothermal perfectly stirred reactor calculations show that the NH$_3$ chemistry is closely coupled with the main chemistry. This coupling has to be taken into account when using a simplified mechanism to describe the nitrogen chemistry, since then usually also the description of the main chemistry relies on a simplified mechanism. The present calculations showed that particularly fuel rich conditions possess a problem. This is partly due to the fact that the main chemistry is poorly described, but also due to the fact that the nitrogen chemistry is even closer coupled with the main chemistry at fuel rich conditions since the hydrocarbon radicals then play a more important role. The calculations also revealed that the frequently used mechanism of de Soete (1974) is much too insensitive to the temperature, but also considerably slower than the predictions with the detailed mechanism. The mechanism of Mitchell and Tarbell (1982) and that of Brouwer and co-workers (1996) behaves similarly, although at fuel rich conditions, in particular, the predictions of the reduction of NH$_3$ with the mechanism of Brouwer and co-workers are in better agreement with those obtained with the detailed mechanism. More important, the calculations showed that the mechanism of Brouwer and co-workers can be used outside the SNCR temperature window with as large a confidence, as the other, more frequently used NO$_x$ schemes. The calculations also showed that when NH$_3$ is the dominating form the fuel-N appears in, there is not much use in including the reactions of Mitchell and Tarbell where HCN is occurring. Without these reactions, the possibility to model reburning of NO is lost, but the modeler is at least aware of that the applied mechanism is not capable of modeling reburning.

The perfectly stirred reactor study with a fluctuating temperature showed that the main chemistry is less sensitive to temperature fluctuations than the nitrogen chemistry. At fuel rich conditions, the temperature fluctuations had a remarkable influence on the nitrogen chemistry. The transient perfectly stirred reactor calculations showed that the nitrogen chemistry is very sensitive to temperature
fluctuations also at such conditions where the thermal-NO is not of great importance. The perfectly stirred reactor study with the fluctuating temperatures also showed that the way the fluctuations occur is of considerable importance.
7. Test cases used in this thesis

7.1 Natural gas combustor A

Lewis and Smoot (1981) have investigated an axisymmetric combustor with a non-swirling coaxial feed of fuel and air. This combustor, shown in Figure 7.1, was used as a test problem in the study of the influence of the description of the main chemistry. This test case was also used in the study of the micro mixing time scale in the Eddy Dissipation Concept.

The combustor had an inside diameter of 203.2 mm and a length of 1524 mm. The fuel tube had a radius of 8 mm and a wall thickness of 3.2 mm. The secondary annulus, i.e., the one for the air inlet, had an outside radius of 28.6 mm. A schematic picture of the burner is also shown in Figure 7.1. The cylindrical combustor was vertically oriented to minimize three-dimensional effects. The molar composition of the natural gas was 88.53% CH\(_4\), 7.44% C\(_2\)H\(_6\), 2.55% N\(_2\), 1.39% CO\(_2\), and 0.09% H\(_2\). The H\(_2\)O content in the fuel was less than 0.01%. Argon was added as a tracer. Approximately 5% of the natural gas stream consisted of argon, whereas the air stream contained 0.93% argon. The mass flow of the natural gas was 2.84 g/s, whereas the mass flow of the air was 36.3 g/s. The mass flow of natural gas corresponded to an inlet velocity of 21.3 m/s, whereas the mass flow of the air corresponded to a flow velocity of 24.3 m/s. The temperature of the fuel stream was 300 K. The air was preheated to 589 K. The combustor walls, insulated with a ceramic insulator, were preheated to 1140 K before the measurements were started.

During their experiments, Lewis and Smoot collected gas samples at several points with water quenched probes or with a traversing water-cooled probe. They used thermocouples to measure the temperature in the combustor. No information on turbulence is available.
Figure 7.1. Schematic drawing of the combustor investigated by Lewis and Smoot (1981).

7.2 Natural gas combustor B

In the study of the Eddy Dissipation Combustion Model, another turbulent diffusion flame fired in a cylindrical furnace was used. The thermal input of this flame was 400 kW. This case is documented in greater detail by Garréton and Simonin (1994). The overall stoichiometry in the furnace was slightly fuel rich ($\lambda = 0.96$). The diameter and the length of the chamber were 500 mm and 1700 mm, respectively. The fuel and the air were fed through coaxial pipes of 60 mm and 100 mm in diameter, respectively. The furnace was fired with natural gas, which according to Garréton and Simonin can be modeled as 90 vol-% methane and 10 vol-% $N_2$. The relative humidity of the air was 80%. The mass flow of the
natural gas was 0.0125 kg/s, whereas the mass flow of the air was 0.186 kg/s. The temperature of the side-walls of the combustor were approximately 120°C. The temperature of the natural gas entering the reactor was 40°C and the temperature of the air 50°C. A schematic drawing of the combustor is shown in Figure 7.2.

![Schematic drawing of the combustor](image)

*Figure 7.2. Schematic drawing of the combustor investigated by Garréton and Simonin (1994).*

The velocity field and the Reynolds stress components were measured using a two-component Laser Doppler Velocimeter. The temperature inside the combustion chamber was measured using a suction pyrometer equipped with shields for protection from radiation. The concentrations of CO₂, CO, O₂, and NOₓ were measured on-line in a stream extracted with a suction pyrometer. The concentration of CH₄ was measured off-line with a gas chromatograph.

### 7.3 Natural gas combustor C

Another test case used in the work presented in this thesis was a swirling natural gas flame measured by Stapf and Leuckel (1993). This test case was used in the
assessment of the importance of an adequate description of the chemistry of the main components for the quality of mathematical modeling. A detailed description of the experiment can be obtained from Stapf (1998). The combustor was operated with a slight excess of air ($\lambda = 1.05$). The theoretical swirl number for the air was 1.0. The theoretical swirl number is given by the following expression

$$S_{0,\text{theo}} = \frac{\int_0^R \rho u w r^2 \, dr}{\int_0^R \rho u^2 r \, dr}$$

(62)

where $u$ is the axial velocity component, $w$ the swirl component, and $R$ the outer radius of the air inlet. The thermal load was approximately 350 kW. Of the test cases used in this work, this case has the most complex flow field. Burners with swirling air are frequently used in industrial applications, due to their stable behavior. Compared to most industrial burners, the present one is less complex. The combustor, schematically shown in Figure 7.3, is vertically oriented with the swirl burner located at the top of the water-cooled cylindrical combustion chamber. The diameter of the combustion chamber was 600 mm. The total length of the chamber was approximately 3000 mm. The diameter of the annular air nozzle in the swirl burner was 90 mm. The inner diameter of the central natural gas pipe was 45 mm. The natural gas was injected through 8 holes having a diameter of 5 mm. The injection angle was 45°. The length of the diffusor was 60 mm, and the diffusor angle was 15°.

The molar composition of the natural gas was 85.1% CH$_4$, 5.73% C$_2$H$_6$, 1.36% C$_3$H$_8$, 0.39% higher hydrocarbons, 1.0% NH$_3$, 1.78% CO$_2$, and 4.64% N$_2$. The volumetric flow of the gas was 35 m$^3$/h and the flow of air was 350 m$^3$/h. The temperature of the upper front wall of the combustion chamber was approximately 1300°C whereas the temperature of the cylindrical wall was approximately 1440°C. The temperature of the fuel and the air streams entering the combustor was approximately 40°C.
Stapf and Leuckel (1993) used a five-hole pressure probe to measure the velocity components in the near burner region. They used compensated thermocouples to measure temperatures and temperature fluctuations, and water-cooled stainless steel probes for gas sampling. Conventional gas analyzers were used for CH₄, CO₂, CO, O₂, H₂, NO, and NOₓ, and an FTIR analyzer for C₂H₄, C₂H₂, NH₃, HCN, N₂O, and NO₂.

### 7.4 Syngas jet flame

In the study of alternative expressions for the mixing time and the reacting fraction of the Eddy-Dissipation Concept an NH₃-doped CO/H₂/N₂–air jet flame was used. This well-characterized, co-flowing jet diffusion flame has been measured by Drake and co-workers (1984). This flame was also used as a test
case together with the flame reported by Garréton and Simonin (1994) in the study of the Eddy Dissipation Combustion Model.

The fuel mixture emerged from a constant-area nozzle with an inner diameter of 3.2 mm. The fuel pipe was located in a 150 mm by 150 mm square duct. A schematic picture of the device is shown in Figure 7.4. The velocity of the co-flowing air was 2.4 m/s, flat to within ±2%. The average flow velocity of the fuel mixture was 54.6 m/s. The fuel mixture consisted of 39.7 ± 0.5, 29.9 ± 0.5, 29.7 ± 0.5, and 0.7 ± 0.01 mol-% of CO, H₂, N₂, and CH₄, respectively. In most of the runs, the fuel mixture was doped with 0.5-1.6 mol-% NH₃. The combustion air was taken directly from the laboratory. Both streams entered the device at room temperature.

![Figure 7.4. Schematic drawing of the experimental device of Drake and co-workers (1984). To the left in the picture a front view of the duct, to the right a close-up of the fuel pipe.](image)

Drake and co-workers used non-perturbing optical diagnostics with a high temporal and spatial resolution. The axial velocity was measured with laser velocimetry. Pulsed Raman scattering was used in order to simultaneously determine the temperature, the concentration of the major species, i.e., N₂, O₂, H₂, CO, and H₂O, the density, and the Favre mixture fraction. They assumed that the atomic ratios of carbon and hydrogen were invariant throughout the flame when determining the CO₂ concentration. NO and NO₂ concentrations were measured at x/d=100, where x is the axial distance and d the inner diameter of the
fuel pipe, using a probing technique combined with chemiluminescent detection. Various probes were used. Drake and co-workers reported no significant difference in the results obtained with a water-cooled stainless steel probe compared with the results obtained with various uncooled quartz probes.

The measurements of Drake and co-workers also provide certain data that can be used to specify the boundary conditions for the flow. They reported that the centerline velocity was 68 m/s, which according to them is consistent with pipe flow theory. They also measured the root mean square of the axial velocity and found that it was approximately 5 m/s. For the co-flowing air they reported a turbulence intensity of 1.3%.
8. The Eddy Dissipation Concept

The Eddy Dissipation Concept (Magnussen 1981 and 1989) was already briefly presented in the literature review section. In this section, the Eddy Dissipation Concept is presented in greater detail. Some of the model parameters are critically reviewed, in particular those describing the characteristic mixing time of the reacting structures. Last, a new version of the Eddy Dissipation Concept is presented. This version combines the structure of the Eddy Dissipation Concept model with ideas put forth by Karlsson and Chomiak.

The Eddy Dissipation Concept (Magnussen 1981 and 1989) is a model related to the Eddy Break-Up model of Spalding (1971) and the Eddy Dissipation Combustion Model of Magnussen and Hjertager (1976), but it is derived following a detailed description of the dissipative process in the flow. In the Eddy Dissipation Concept, the fluctuations are described in a simplified way, but the model has the advantage of being general. It can be used to model flames with both a complex chemistry and with local extinction effects, and it can be used in the modeling of premixed and diffusion flames as well.

A starting point of the Eddy Dissipation Concept is that the fluid can be divided into a reacting and a non-reacting part. Another basic assumption of the model is that the reactions occur where the dissipation of turbulence energy takes place. The part of the fluid where the dissipation of the turbulence energy occurs is referred to as “fine structures”. The characteristic dimensions of the fine structures are those of the Kolmogorov scale in one or two directions but not in the third one. It is further assumed that these fine structures are concentrated in “fine structure regions” occupying a mass fraction \( \gamma \) given by

\[
\gamma = 2.14 \left( \frac{\nu \epsilon}{k^2} \right)^{1/4}
\]

where \( \nu \) is the kinematic viscosity, \( \epsilon \) the dissipation rate of kinetic energy per unit mass, and \( k \) the kinetic energy per unit mass. According to the model, the mass fraction of the flow occupied by fine structures is given by \( \gamma^3 \).
The Eddy Dissipation Concept

Since the fine structures are turbulent ones where the final dissipation occurs, it is argued that in the fine structures the components are mixed on a molecular level. This assumption allows the reactions to be modeled using the perfectly stirred reactor concept. The residence time in the reactor, \( \tau^* \), is given by the expression

\[
\tau^* = 0.4 \left( \frac{V}{\varepsilon} \right)^{1/2}
\]

(64).

It can be noted that the Kolmogorov time scale, which is the shortest time scale of the time spectrum of turbulence, is given by \((V\sqrt{\varepsilon})^{1/2}\).

Further, a factor \( \chi \) has been introduced to describe the fraction of the fine structures where reactions can occur. This parameter expresses the probability of coexistence of reactants, the degree of heating, and the availability of reactants. Gran (1994) pointed out that this parameter mimics the effects of finite rate chemistry and suggested that it could be set to unity if the reaction rates are properly modeled. There is also another parameter, \( \eta \), that has been suggested. This parameter is needed in the modeling of premixed flames where it accounts for the fact that the reactant concentration in the non-reacted fragments may be much higher than the average concentrations.

To obtain an expression for the average reaction rate, an expression for the mass transfer between the fine structures and the surrounding flow is needed. Two different expressions are here suggested. The expression \( \gamma^3/\tau^* \) was originally used (Magnussen 1981 and 1989). Using this expression, the mean reaction rate for a species \( i \) can then be expressed as

\[
\tilde{\omega}_i = \frac{\gamma^3 \chi}{\tau^*} (Y_i^\circ - Y_i^*)
\]

(65)

where \( Y_i^\circ \) denotes the mass fraction of the species in the surrounding and \( Y_i^* \) the mass fraction in the fine structures. In some recent papers (Gran 1994, Magel et al. 1996) the expression \( \gamma^2/\tau^* \) has been used. The expression is based on the assumption that the fine structures mainly exchanges mass with the fine structure
regions they are located in and not with the whole surrounding flow. The mean reaction rate for a species $i$ can then be expressed as

$$\tilde{\omega}_i = \frac{\gamma_i^2}{\tau_i} \left( Y_i^o - Y_i^\ast \right)$$ \hspace{1cm} (66).$$

In this thesis, the latter expression has been used in the investigation of the effect of the description of the hydrocarbon chemistry, whereas the former expression has been used in the study of the mixing time.

The relation between the mean, the surrounding and fine structure value of the mass fraction of a species $i$ can be expressed as

$$\bar{Y}_i = \gamma^3 \chi Y_i^\ast + \left( 1 - \gamma^3 \chi \right) Y_i^o.$$ \hspace{1cm} (67).$$

Magnussen has also suggested that reactions in the surrounding can be taken into account. In this case, the total mean reaction rate will be given by

$$\tilde{\omega}_i = \gamma^3 \chi \tilde{\omega}_i^\ast + \left( 1 - \gamma^3 \chi \right) \tilde{\omega}_i^o$$ \hspace{1cm} (68)$$

where $\tilde{\omega}_i^\ast$ denotes the reaction rate for species $i$ in the fine structures and $\tilde{\omega}_i$ the reaction rate of species $i$ in the surrounding.

The close relation to the Eddy Break-Up model of Spalding (1971) and the Eddy Dissipation Combustion Model of Magnussen and Hjertager (1976) is seen in the case when the combustion is described with an irreversible single-step reaction.

In this case, the Eddy Dissipation Concept can be written

$$\tilde{\omega}_F = -C_\omega \kappa \frac{\tilde{e}}{k} \min \left[ \min \left( \tilde{Y}_F, \tilde{Y}_O \right), r_f / \left( 1 + r_f \right) \right] \left( \min \left( \tilde{Y}_F, \tilde{Y}_O \right), r_f / \left( 1 + r_f \right) \right) \gamma$$ \hspace{1cm} (69)$$

where $C_\omega$ is a constant and $\kappa$ indicates the probability of co-existence of reactants (Gran et al. 1994). In the formulation of the equation above it is assumed that $\gamma^3 \chi$
is much smaller than unity. The expression describing the probability of coexistence of reactants is expressed as

\[
\kappa = \frac{\left( \min \left[ \frac{\bar{Y}_f}{r_f}, \frac{\bar{Y}_o}{1+r_f} \right] + \frac{\bar{Y}_p}{1+r_f} \right)^2}{\left( \frac{\bar{Y}_f}{1+r_f} + \frac{\bar{Y}_p}{1+r_f} \right) \left( \frac{\bar{Y}_o}{r_f} + \frac{\bar{Y}_p}{1+r_f} \right)}
\]  

(70).

8.1 Effect of the description of the chemistry

The Eddy Dissipation Concept was first formulated assuming fast chemistry (Magnussen 1981). Therefore, it is motivated to systematically investigate the effect of the complexity of the description of the chemistry, since it is probable that a more complex description does not necessarily lead to better results. The reason for this is that the original parameters of the model were not tuned for a more complex description of the chemistry, which the model nowadays mainly is combined with.

Only few CFD studies are concerned with how the description of the chemistry affects the computed results. Gran (1994) modeled a natural gas diffusion flame in order to study the differences between the prediction obtained when using a global single-step infinitely fast irreversible reaction and that obtained using a detailed elementary reaction mechanism consisting of 50 species and 456 reactions. He found that with the fast chemistry not even a qualitative agreement between the computations and measurements could be obtained except in the case when a separate extinction model was applied. Several studies have emphasized the importance of including a model describing local extinction together with a simplified description of the reaction kinetics (see e.g., Byggstøyl and Magnussen 1983, Gran 1994, Gran et al. 1994, Brink et al. 1996). Better results were obtained with the detailed elementary reaction mechanism. Magel and co-workers (1996) modeled the unswirled natural gas diffusion flame, here referred to as combustor B, to study the influence of the use of a comprehensive reaction mechanism compared with a reaction mechanism only consisting of the most
important elementary reactions and chemical species, i.e., a skeletal mechanism. They found that both mechanisms resulted in good agreement between measurements and predictions. Only in the cold ignition zone of the flame there was a notable difference in the results obtained with the different mechanisms. Jessee and co-workers (1997) used the Eddy Dissipation Concept combined with four different reaction schemes to model swirling flames. In their investigation the simplest reaction mechanism was a two-step mechanism. The most complex reaction mechanism was a comprehensive mechanism consisting of 279 elementary reactions. The swirling flames they used in the modeling were geometrically similar and operated using the same swirl number and fuel-to-air ratio. Jessee and co-workers concluded that the more complex description of the chemistry, the better predictions. However, there was a large discrepancy between predictions and measurements that they attributed to an underestimation of the turbulent fluxes by the k-ε model.

To study the influences of the reaction mechanism, the test case described as natural gas combustor A was used. This test case has previously been used in a number of CFD studies (see e.g., Nikjooy et al. 1988, Gran 1994, Gran et al. 1994, Brink et al. 1996). The combustor was modeled using an axisymmetric description. A structured grid of 42×47 cells refined in the inlet region was used. Five cells were used for the fuel inlet, two for the tube wall and eight for the air inlet. Only half of the length of the combustor was modeled. The physical dimensions of the computational domain were 101.6 mm in the radial direction by 762 mm in the axial direction. A similar grid has been used by Gran and co-workers (1994) who found that it was sufficient in order to obtain a grid independent solution.

The turbulence was modeled with the standard k-ε model and a wall function to describe the behavior of the turbulence close to the walls. Plug flow was assumed in the setting of the boundary conditions for the fuel and the air inlet. For both inlets a turbulence intensity of 5% was used. The turbulence length scale was set to 5% of the hydraulic diameter. Gran (1994) has investigated the effect of the boundary conditions for the turbulence and found that the use of plug flow assumption instead of fully developed pipe flow affected the result, but that the
discrepancy between the different assumptions was small compared with the inaccuracies in the measurements.

During their measurement, Lewis and Smoot (1981) fired the combustor with natural gas. In the present study, all hydrocarbons were modeled as methane, but the volumetric flow rates were those reported by Lewis and Smoot. Although only 7.44 vol-% of the fuel was ethane, this simplification influences the stoichiometry significantly. In the experiments, the stoichiometric ratio was approximately 0.836 whereas in the modeling it was 0.938. The adiabatic combustion temperature of the stoichiometric fuel-air mixture was 2330 K in the experiments whereas it was 2350 K according to the modeling. Based on the flow rates reported by Lewis and Smoot the flue gas composition was, excluding inert species, 6.74 vol-% CO₂, 3.59 vol-% CO, 18.11 vol-% H₂O, and 1.71 vol-% H₂. The flue gas composition in the model was 7.48 vol-% CO₂, 2.25 vol-% CO, 18.25 vol-% H₂O, and 0.97 vol-% H₂. Argon was used as a tracer in the experiments, while N₂ replaced argon in the modeling to keep the number of species at a minimum.

The chemistry was modeled in four different ways. In approach I, thermodynamic equilibrium conditions in the reacting part were assumed. The equilibrium composition was calculated using the STANJAN program (Reynolds 1986) supplied by the CHEMKIN library (Kee et al. 1991) which uses an algorithm for minimization of Gibbs free energy. Seven species were considered in the equilibrium calculations: CH₄, CO₂, CO, O₂, H₂O, H₂, and N₂. In approach II, the three-step simplified mechanism, based on an extension of the two-step simplified mechanism, was used. This mechanism uses fast irreversible global reaction steps to describe the oxidation of CH₄ and H₂, and the empirical rate given by Howard and co-workers (1972) to describe the irreversible oxidation step of CO. In approach III, the four-step mechanism put forth by Jones and Lindstedt (1988) was used. In the present calculations the backward reaction of the H₂ oxidation reaction was not considered. The omission of the backward reaction rate is not severe in this case where the overall stoichiometry is fuel rich. In approach IV, the detail reaction mechanism for methane oxidation was used. The perfectly stirred reactor calculations required for finding the composition and temperature
of the reacting fine structures were solved with the PSR code (Glarborg et al. 1986) from the CHEMKIN library (Kee et al. 1991).

In the measurements of species concentrations, Lewis and Smoot (1981) found a large influence on the sampling method. Gran (1994) has examined the boundary conditions and the consistency of the measurements. He concluded that the species measurements are inconsistent but that the temperature measurements are more reliable than the concentration measurements. In the present study, only the temperature measurements have been utilized although concentrations of several species had been measured at a number of locations. Radiation was not accounted for, although Gran pointed out that there is a risk for soot formation that might affect the accuracy of the temperature predictions.

Figure 8.1 shows the stream function in the combustor obtained with the assumption of local equilibrium in the reacting part of the fluid, i.e., with approach I. The equilibrium approach and the simplified reaction mechanisms all predict similar flow fields. The air and fuel jets enter the combustion chamber and burn in a mixing-layer. Axial velocities dominate the flow, but an external recirculation zone is formed in the front corner region of the chamber. The re-attachment length is almost similar in these three cases: 207 mm, 207 mm, and 202 mm respectively. With the comprehensive mechanism, a re-attachment length of 247 mm was predicted. The flow field predictions were remarkably insensitive to the way the fuel chemistry was described.

![Figure 8.1. Streamlines in the combustor obtained with the thermodynamic equilibrium approach. An axisymmetric description was used in the modeling. Approximately half of the longitudinal section is shown in the figure.](image-url)
Figure 8.2. Concentration profiles of CO₂, CO, O₂, H₂O, and H₂, and the temperature profile 95 mm down stream. The modeled temperature profile is drawn with a bold line while the measurements of Lewis and Smoot (1981) are indicated with squares. The subplots are marked according to the approach used in the modeling, i.e., I) the equilibrium approach, II) the three-step mechanism, III) the four-step mechanism, and IV) the comprehensive reaction mechanism.
Figure 8.3. Concentration profiles of CO$_2$, CO, O$_2$, H$_2$O, and H$_2$, and the temperature profile 398 mm down stream. The modeled temperature profile is drawn with a bold line while the measurements of Lewis and Smoot (1981) are indicated with squares. The subplots are marked according to the approach used in the modeling, i.e., I) the equilibrium approach, II) the three-step mechanism, III) the four-step mechanism, and IV) the comprehensive reaction mechanism.
Figure 8.2 shows the radial concentration profiles and the temperature at a distance of 95 mm from the front wall of the combustor. The equilibrium approach predicts the highest CO and H₂ concentrations. The temperature peak in the reaction zone is slightly lower as compared with those predicted by the three-step and the four-step mechanism. The comprehensive mechanism predicted that reactions only take place in the recirculation zone. Temperature measurements reported by Lewis and Smoot (1981) are also shown in the figure. The measurements do not show the hot reaction zone like the one predicted by the equilibrium approach and the global mechanisms. The reason for the underestimation of the temperatures close to the centerline is according to Gran (1994) that the co-flowing air preheats the fuel before entering the combustor.

Figure 8.3 shows the radial concentration profiles and the temperature 398 mm down stream. The three-step simplified mechanism predicted the highest temperatures. At the centerline the difference in the temperature levels is at its maximum. The equilibrium approach predicted a temperature of approximately 940 K, the three-step mechanism 1470 K, the four-step mechanism 1220 K, and the comprehensive mechanism 660 K. The temperature of the fluid close to the combustor wall was more closely predicted with all four approaches.

The characteristics of the chemical approaches can readily be used to explain the trends obtained in the CFD study. In the equilibrium approach no reaction rates are used. This means that products will start to form as soon as fuel and air are mixed. In the CFD predictions this resulted in that the flame was attached to the inlet. Large amounts of the final combustion products could also be found in the immediate vicinity of the inlet. With the three-step simplified mechanism it is expected that the reactions start immediately as fuel and air are mixed whereas the CO₂ production starts slightly down-stream. This was also the case in the CFD simulations. The peak temperature was severely overestimated with the three-step mechanism approach due to an overestimation of the extent of reaction. With the four-step simplified mechanism and the comprehensive mechanisms the Eddy Dissipation Concept has the capability to predict local extinction. In these predictions this could be observed as a lift-off of the flame. For the four-step mechanism, a flame lift-off corresponding to a distance of approximately one fuel
inlet radius was predicted. The comprehensive mechanism predicted an almost complete blow-off of the flame, which is not in accordance with the measurements of Lewis and Smoot (1981).

The striking difference in the CFD predictions obtained with the four-step simplified mechanism and the comprehensive mechanism is at first surprising. The perfectly stirred reactor calculations showed that for fuel lean conditions the two mechanisms behaved similarly. However, at fuel rich conditions there was a significant difference between the results obtained with the two mechanisms. The difference could also be observed in the critical residence time calculations. The overall stoichiometry of the flame used for investigating the influence of the reaction mechanism was fuel rich. In the perfectly stirred reactor study it was found that at these conditions, the agreement in the predictions between the four-step mechanism and the comprehensive one was less satisfactory. The large differences between the results obtained using the four-step mechanism and the comprehensive one can also be explained by the degree of preheating of the air. In the present case the temperature of the air was close to 600 K. The perfectly stirred reactor study investigating the critical residence time revealed that the four-step simplified mechanism predicts faster reactions than the comprehensive mechanism for preheated mixtures. On the other hand, the approximation regarding the fuel composition led to a less fuel rich situation in the modeling compared with that in the experiments. This approximation should contribute to more similar predictions with the four-step simplified mechanism and the comprehensive one.

None of the approaches that were tested gave rise to satisfactory predictions. Although the comprehensive mechanism provides the best description of the chemistry, it resulted in the least satisfying predictions. This is in contrast to what has been found by other investigators. In these studies, the temperature predictions obtained using a separate extinction model (Gran et al. 1994) agreed closely with those obtained using a comprehensive mechanism (Gran 1994). However, in the study by Gran the local temperature changed as much as 500 K when the parameter describing the fraction of the fine structures that can react was modeled in different ways. The agreement between the computed results and
the measurements was less satisfactory when the $\chi$-factor was modeled in the way adapted in the present study, i.e., assuming $\chi = 1.0$. An alternative description of the $\chi$-factor would probably improve the quality of the predictions in approaches I-III. Unfortunately, in approach IV, where the best description of the chemistry was used, there is nothing supporting that the reduction of the reacting fraction would improve the predictions. On the contrary, it is more likely that this would have the opposite effect and make the quality of the predictions even worse. This should be compared with the findings of Magel and co-workers (1996). They used a very similar implementation of the Eddy Dissipation Concept and a comprehensive mechanism to describe the chemistry. They found an excellent agreement between measured and computed results in the study of another diffusion flame. However, Gran and Magnussen (1996) have also reported that a blow-out was predicted when modeling a bluff-body stabilized flame with the Eddy Dissipation Concept combined with a detailed reaction mechanism, although no signs of local extinction could be observed in the measurements of the case. They attributed this to shortcomings in the $k-\varepsilon$ model since no blow-out was predicted with another turbulence model. Based on the present study and those previously reported in the literature it is not safe to conclude that a better description of the chemistry will result in better descriptions overall. However, it seems clear that a more complete description of the chemistry is more sensitive to the way the turbulence-chemistry interaction model is implemented.

8.2 Effect of the characteristic mixing time

In the last section it was found that a better description of the chemistry does not necessarily contribute to better CFD predictions. With the comprehensive mechanism, in particular, the effect of local extinction was severely overestimated. The purpose of the study described in this section was to investigate whether an improvement to the predictions could be obtained through the use of an alternative time scale for the micro mixing in the Eddy Dissipation Concept.

With the standard form of the Eddy Dissipation Concept, local extinction will be predicted as the chemical time scale is of the same order as the Kolmogorov time
scale. In the classification of flames into combustion regimes by Borghi (1988), this corresponds to flames in the "wrinkled and stretched flamelet region" or "perturbed flamelet region". This is in contradiction with the assumption of perfectly stirred reactor conditions in the reacting part in the Eddy Dissipation Concept since in these combustion regions molecular diffusion plays an important role.

In the process of finding an appropriate turbulent time scale, three turbulent time scales were used. The first one, here referred to as $\tau_{\text{mix1}}$, is the Kolmogorov related time scale of the standard version of the Eddy Dissipation Concept, i.e., $0.41(\nu/\epsilon)^{1/2}$. The second one, $\tau_{\text{mix2}}$, is a time scale characterized by $((k/\epsilon)(\nu/\epsilon)^{1/2})^{1/2}$. This time scale, which is the geometrical mean of the eddy break-up time and the Kolmogorov time scale, has been proposed by Karlsson and Chomiak in an I.E.M.-type model (Karlsson and Chomiak 1995, Karlsson 1995). One of their arguments for this synthetic time scale for the mixing is that it is the easiest way to account for the two time scales responsible for the turbulent mixing. The third time scale investigated, $\tau_{\text{mix3}}$, is the Taylor time scale which is characterized by $4k/\epsilon$ (Visser and Weber 1990).

Figure 8.4 shows the relative time scales $\tau_{\text{mix1}}-\tau_{\text{mix3}}$ as a function of the turbulent Reynolds number defined as $k^2/\nu\epsilon$. In the normalization, the time scale in the frequently used Eddy Dissipation Combustion Model of Magnussen and Hjertager (1976), $\tau_{\text{mix}} = 0.25 k/\epsilon$, has been used.
Figure 8.4. The mixing time scale as a function of the turbulent Reynolds number, defined as $k^2/(\nu e)$, normalized by the mixing time scale of the Eddy Dissipation Combustion Model. The bold line shows the normalized $\tau_{\text{mix1}}$, the thin line the normalized $\tau_{\text{mix2}}$, and the dashed line the normalized $\tau_{\text{mix3}}$.

In the investigation of the characteristic mixing time of the reacting part, the same test case was used as in the study of the effect of the description of the chemistry, i.e., combustor A. Here too, an axisymmetric representation of the combustor was used. The structured computational grid consisted of 47 cells in the radial direction by 223 cells in the axial direction. Within the first 600 mm of the chamber, 150 of the 223 cells in the axial direction were located. The turbulence was modeled with a multiple-time-scale turbulence model proposed by Kim and Chen (1989). In this model, the spectrum of turbulence is divided into two scales. The larger scale is associated with the eddies responsible for the generation of turbulence while the smaller one is associated with the eddies in which the
dissipation of the turbulent kinetic energy into heat takes place. The model contains four transport equations: two equations for the kinetic energy of turbulence, one equation for the transport of kinetic energy from the larger scale to the smaller eddies, and one equation for the dissipation of the kinetic energy of the small eddies into heat. The total turbulent kinetic energy obtained from the turbulent kinetic energy associated with the larger eddies, and turbulent kinetic energy associated with the smaller eddies is similar to the turbulent kinetic energy predicted with the standard k-ε model. The dissipation of kinetic energy from the larger scale to the smaller eddies is similar to $\epsilon$ in the standard k-ε model.

The hydrocarbons in the natural gas were represented in the modeling with a hypothetical hydrocarbon, $C_xH_y$, and not by pure methane as in the investigation of the influence of the reaction kinetics described above. In addition, the hydrocarbon chemistry was described in a different way. Here, the modified three-step mechanism utilizing the water-shift reaction was used. This simplified description of the reaction kinetics provides a satisfactory agreement of the concentrations of the main species except at short residence times where the chemical time scale is of the same order as the mixing time. The perfectly stirred reactor calculations, required for obtaining the composition and the temperature of the fine structures, were carried out using a Newton-Raphson based algorithm. Compared to the simplified mechanisms used in the previous section, the most important difference is that here, a separate model was used to describe the behavior at short residence times. The model consisted of an algebraic expression derived from perfectly stirred reactor calculations where a comprehensive mechanism was used to describe the chemistry.

The use of a separate model to account for extinction with various versions of the Eddy Dissipation Concept has been presented in a number of studies (see e.g., Byggstøyl and Magnussen 1983, Gran et al. 1994, Ferreira et al. 1995). Byggstøyl and Magnussen (1983) suggested a model where a constant chemical time was compared with a turbulent mixing time to determine the state of the fluid. This type of model has also been used more recently (Ferreira et al. 1995). A more sophisticated model that has been used is based on a chemical time derived from calculations with a comprehensive mechanism for oxidation of methane in air.
The Eddy Dissipation Concept

(Lillehei et al. 1991, Gran et al. 1994). The model used in the work presented in this thesis is based on a similar approach, but it has been made more general to meet the needs encountered in CFD calculations. Previously, the effect of mixing with flue gas components has been omitted, although Lillehei and co-workers (1991) have pointed out this shortcoming.

In this study, the detailed mechanism was used to map the critical residence time as a function of stoichiometry, composition, and inlet temperature. The definition of the critical residence time as well as how it can be determined was described in section 6.2. Two numerical fuel mixtures were used in the mapping. The first mixture consisted mainly of methane with small amounts of CO, C₂H₆, and H₂ present. In the second mixture, the main combustable was CO, but small amounts of the other species were also present. The other species were added to the mixture because it was found that pure CH₄-air mixtures, and in particular pure CO-air mixtures, behave differently compared with mixtures including small amounts of other species as well. It is also unlikely that such pure mixtures exist in real flames. The mixtures were diluted with a product gas to various extents, so that the fresh mixtures made up 0.1 to 1.0 of the mole fraction. The product gas consisted of 18 vol-% CO₂, 12 vol-% H₂O, and 70 vol-% N₂. Ten different stoichiometric ratios were studied, i.e., λ = 0.1, 0.2, 0.35, 0.5, 1.0, 1.5, 3.0, 5.0, 7.5, and 10.0. Four different inlet temperatures were considered, i.e., 300 K, 500 K, 700 K, and 900 K. In total, 800 different mixtures were used in the mapping of the critical residence time. The perfectly stirred reactor calculations were started using the adiabatic equilibrium composition as a first estimate. Then the residence time, τ, was decreased from 1 s to 1 μs. The decrease was logarithmic in 200 steps. Each of the subsequent calculations was done using the previous solution as the initial guess.

Based on the calculated extinction behavior obtained with the comprehensive reaction mechanism, an empirical model for the critical residence time was set up. Since the model should be used in a CFD code, effort was made to keep the model as simple to compute as possible. The final expression had the form
The Eddy Dissipation Concept

\[ \tau_{ch} = 10^{\left( \max\left(0, \frac{E}{c} - \frac{1}{2} \left( \log_{10} \lambda \right)^2 \right) \right)^{1/2}} \]  (71)

In Figure 8.5 an example of the result of the numerical mapping of the critical residence time is compared with the one calculated with the empirical expression. The plots of the extinction behavior revealed that the surface is slightly asymmetric around \( \lambda = 1 \), as seen in Figure 8.5. Here, this has been taken into account modeling \( a \) as a function of the stoichiometry, i.e., \( a = a_0 + k_a \log_{10}(\lambda) \). To obtain a model as simple as possible, where the inlet temperature also is taken into account, the parameters in the model, i.e., \( a_0, k_a, b, c, \) and \( d \), were written as functions of the temperature. In the expression above, \( F \) is the freshness of the fuel-air-product gas mixture. \( F \) is one for a fuel-air mixture, whereas \( F \) is zero for flue gas. If the fuel mainly consists of \( \text{CH}_4 \), an approximate value of the freshness is given by the following expression:

\[ F = 1 - \frac{X_{\text{CO}_2} + X_{\text{H}_2\text{O}} + X_{N_2} - 3.762X_{\text{O}_2}}{\left(1 + 4.762 \frac{(1 - \lambda)}{\lambda}X_{\text{O}_2}\right)} \]  (72)

where \( X_i \) stands for mole fraction of species \( i \). The most convenient way to take the effect of the fuel composition into account was to determine two separate sets of parameters. In CFD calculations, the critical residence time is determined by a interpolation procedure, where the fuel composition is used to determine to what extent the critical residence time from the \( \text{CH}_4 \)-based and the \( \text{CO} \)-based model should be employed.

103
Figure 8.5. Results of the mapping of the critical residence time using the comprehensive mechanism (above) and results obtained with the model (below). The temperature of the entering mixtures was 300 K.

As in the investigation of the influence of the reaction kinetics, only the temperature measurements have been used when assessing the results of the CFD modeling. However, in contrast to that study, distribution of heat through radiative heat transfer within the combustion chamber was accounted for in this study. In the radiative heat transfer modeling, the local absorption coefficient was determined using the gas composition and the concentration of soot. Figure 8.6 shows the computed temperature field in a case without extinction and in a case where local extinction was accounted for by comparing the critical residence time with the Taylor time scale, i.e., $\tau_{\text{mix3}}$. If the chemical time is longer than the
mixing time the chemical source term is set to zero. It can be noted that flame lift-off is predicted when local extinction is taken into account.

![Diagram 1]

![Diagram 2]

*Figure 8.6. Computed temperature field and boundary of external recirculation zone (bold line) in the sudden expansion combustion chamber. Only the front part of the chamber is shown. Result without an extinction model (above). Result with local extinction computed with \( \tau_{\text{mix3}} (4k/\epsilon) \) as the turbulent time scale (below).*

The effect of the lift-off can also be seen in Figure 8.7 where the temperatures measured by Lewis and Smooth (1981) are compared with the numerically obtained ones. The temperature profiles are taken at an axial distance of 95 mm from the front wall of the chamber. In the case with no extinction model, the combustion starts close to the inlet pipe and causes a peak in the radial temperature profile. Figure 8.8 shows the corresponding result at a location 396 mm down stream.
Figure 8.7. Computed and measured radial temperature profiles at an axial distance of 95 mm from the front wall of the combustion chamber. The bold line shows the result when no extinction model was applied. The dotted line, the dashed line and the dash-dotted line correspond to the predicted temperature profiles when $\tau_{\text{mix}1} (0.41(\nu\varepsilon)^{1/2})$, $\tau_{\text{mix}2} ((k/\varepsilon)(\nu\varepsilon)^{1/2})^{1/2}$, and $\tau_{\text{mix}3} (4k/\varepsilon)$, respectively, were used in the extinction modeling. The circles show temperatures measured by Lewis and Smoot (1981).

A correct prediction of the length of the recirculation zone is of great importance in the prediction of the near burner region. When local extinction was not taken into account, the length of the external recirculation zone was too short to bring enough hot combustion products towards the front area of the chamber. When extinction was taken into account, the radial temperature profile at an axial distance of 95 mm has a shape similar to that obtained in the experiments. The predicted temperatures closer to the outer wall also corresponded to the measurements.
Figure 8.8. Computed and measured radial temperature profiles at an axial distance of 396 mm from the front wall of the combustion chamber. The bold line shows the result when no extinction model was applied. The dotted line, the dashed line and the dash-dotted line correspond to the predicted temperature profiles when $\tau_{\text{mix1}}$, $\tau_{\text{mix2}}$, and $\tau_{\text{mix3}}$ were used in the extinction modeling, respectively. The circles show the temperatures measured by Lewis and Smoot (1981).

In a previous section it was found that the flame shapes were similar in the cases when the break-down step of the hydrocarbon was assumed infinitely fast, which was the case in the equilibrium and the three-step approach. In that study, no additional model was used to account for extinction. In the present study too, the influence of the description of the chemistry was tested. Here the result obtained with the reaction mechanism including the water-shift reaction at fuel rich conditions was compared with the result obtained with a single-step fast irreversible reaction. The results from this comparison are shown in Figures 8.9 and 8.10.
Figure 8.9. Computed and measured radial temperature profiles at an axial distance of 95 mm from the front wall of the combustion chamber. The dotted line shows the temperature profiles obtained with the three-step simplified mechanism whereas the long-dashed line shows the temperature profiles obtained with the single-step reaction. The measurements of Lewis and Smoot (1981) are indicated with circles.
Figure 8.10. Computed and measured radial temperature profiles at an axial distance 396 mm from the front wall of the combustion chamber. The dotted line shows the temperature profiles obtained with the three-step simplified mechanism whereas the long-dashed line shows the temperature profiles obtained with the single-step reaction. The circles indicate measurements of Lewis and Smoot (1981).

In both cases the Kolmogorov related time scale of the Eddy Dissipation Concept, i.e., $\tau_{\text{mixI}}$, was used when modeling extinction. With the three-step simplified mechanism, the use of the Kolmogorov related time scale in the prediction of extinction resulted in severe overestimation of local extinction. The results with the three-step mechanism were significantly different from those obtained with the one-step mechanism. The use of a single-step global reaction led to a locally higher heat release and temperature than the use of a chemical scheme with CO and H$_2$ as intermediate species. A higher temperature made the chemical time shorter and the Kolmogorov time longer due to a higher kinematic viscosity. Altogether, the extinction condition was satisfied in a smaller region.
Based on the results with the fast single-step reaction model, the Kolmogorov related time scale appears adequate. Gran and co-workers (1994) used the same test case to compare the presumed probability density function approach to the Eddy Dissipation Concept using the fast chemistry assumption and a separate extinction model. The predictions presented in this thesis obtained with the one-step reaction approach and an extinction model agree with those that Gran and co-workers obtained. When a more complex three-step simplified mechanism is used, this time scale results in an overestimation of the lift-off of the flame. Better agreement between measurements and numerical results is obtained with the time scale given by the expression \((k/\varepsilon)(\nu/\varepsilon)^{1/2}\). The best agreement with the measurements was obtained when the extinction criterion was based on the time scale given by \(4k/\varepsilon\).

In Section 8.1, where the influence of the chemistry was investigated, two descriptions of the hydrocarbon chemistry were used which do not require a separate extinction model, i.e., the four-step mechanism of Jones and Lindstedt (1988) and the comprehensive reaction mechanism. In that study too, it was found that the extent of local extinction was overestimated, in particular when the comprehensive reaction mechanism was used. However, it should be noticed that Gran (1994) has also used the present test case in a CFD study where a detailed reaction mechanism was used to describe the chemistry. With the comprehensive mechanism, Gran's prediction agreed qualitatively with the measurements of Lewis and Smoot (1981). In the present calculations, the fine structure part was modeled using the standard version of the Eddy Dissipation Concept, although in most calculations another time scale was used in the extinction criterion. It would have been a simple task to modify the Eddy Dissipation Concept in such a way that the same turbulent time scale used in the extinction criterion also would have been used in the perfectly stirred reactor calculations the Eddy Dissipation Concept relies on. However, this would not be enough for a fully consistent model since the assumptions about the residence time in the fine structure also influences the fraction of the flow consisting of fine structures and on the mass transfer rate between the fine structures and the surrounding fluid. The errors associated with the modeling of the fine structure part are probably not that severe since in the global mechanism the hydrocarbon is oxidized instantaneously.
in the presence of oxygen. On the other hand, Borghi (1988) points out that the reaction zone usually is close to the stoichiometric contour. This would generally lead to a shorter chemical time scale. Taking the shift of the reaction zone into account would require a complete revision of the Eddy Dissipation Concept. Last, it should be remembered that in turbulent flows, there is a whole spectrum of time scales associated with the turbulence. Most probably they all have influence on the extinction.

Conceptually, the use of a mixing time related to the break-up of eddies is not in agreement with the basis of the Eddy Dissipation Concept. On the other hand, there are many indications supporting the use of a turbulent mixing time scale longer than a Kolmogorov related one. For example, in the classification of the combustion into various regimes by Borghi (1988), the line where the Kolmogorov and the chemical time scale are of equal duration separates the “wrinkled and stretch flamelets” region from the “perturbed flamelets” region. If the Eddy Dissipation Concept predicts extinction as soon as the chemical time scale is longer than the Kolmogorov time scale, the model can only be applied to flames in the “wrinkled and stretched flamelets” region. Then neither is the model general, nor is it a good one since molecular diffusion is not taken into account although it is of great importance in this combustion regime. More support for the use of a longer mixing time in the determination of extinction can also be obtained from, e.g., the work of Meneveau and Poinset (1991), and Norris and Pope (1995). Meneveau and Poinset used detailed numerical simulations to study the interaction of a vortex pair with a premixed laminar flame front. They found that the use of the Kolmogorov scale as a basis for quenching modeling led to an overestimation of the quenching. Norris and Pope used the Velocity-Dissipation-Composition probability density function to study extinction in a turbulent diffusion flame. They obtained reasonable agreement between the predicted results and the measured ones when using a mixing model based on $k$ and $\varepsilon$. On the other hand, Yoshida and co-workers (1997) found that the Kolmogorov micro scale is of importance for extinction in diffusion flames. Close to extinction they were able to observe non-reactive holes that appeared intermittently in the flame they studied.
8.3 Effect of the characteristic mixing time and reacting fraction

In the last section, the mixing time associated with the reacting part was investigated. It was found that the use of a longer mixing time than that used in the standard version of the Eddy Dissipation Concept is motivated. In the previous section it was also pointed out that a change of the mixing time has to be accompanied by a complete revision of the model. The purpose of the study described in the present section was to develop a new version of the Eddy Dissipation Concept where an alternative description of the micro mixing time is used. At the same time the change of the part of the model associated with the reacting part should be reflected in the other part of the model in a consistent way.

One time scale that appeared more promising than the Kolmogorov related time scale of the Eddy Dissipation Concept was the synthetic time scale proposed by Karlsson and Chomiak (Karlsson and Chomiak 1995, Karlsson 1995), referred to as $\tau_{\text{mix2}}$ in this thesis. This time scale is based on the two scales of turbulence responsible for the turbulent mixing. Karlsson and Chomiak put forth this synthetic time scale when developing a new turbulence-chemistry interaction model. As in the Eddy Dissipation Concept, the fluid is divided into two parts in their model. The mean mass fraction of a species $i$ can then be calculated from

$$\bar{Y}_i = \kappa Y^R_i + (1 - \kappa)Y^N_i$$

(73)

where the superscript $N$ refers to the non-reacting part, and $R$ to the reacting part. The parameter $\kappa$ indicates the part of the fluid that is reacting. The two states are treated as separate fluid particles, both described using a Lagrangian approach. The model of Karlsson and Chomiak is related to the I.E.M. model although trajectories for the fluid particles are solved for. In the case where only the gas phase is considered the trajectories for the fluid particles are given by
The Eddy Dissipation Concept

\[
\frac{\partial}{\partial t} Y_i^R + \frac{\partial}{\partial x_\alpha} (u + u')_\alpha Y_i^R = \frac{\bar{Y}_i - Y_i^R}{\tau_{mix2}} + \dot{\omega}_i \tag{74}
\]

\[
\frac{\partial}{\partial t} Y_i^N + \frac{\partial}{\partial x_\alpha} (u + u')_\alpha Y_i^N = \frac{\bar{Y}_i - Y_i^N}{\tau_{mix2}} \tag{75}
\]

To account for the turbulent diffusion, they used a random-walk approach where a randomly chosen fluctuation was added to the mean velocity and acted during the minimum of the eddy lifetime or residence time in the computational cell.

The use of fluid particle trajectories makes this model computationally demanding, but it is still possible to use not only the mixing time scale proposed by Karlsson and Chomiak, but also the way they calculated the reacting fraction. In the Eddy Dissipation Concept model, the reacting part was given by \(\chi Y^3\), i.e., the part sufficiently heated and mixed times the fraction of the fluid mixed on a molecular level. Karlsson and Chomiak proposed that the fraction of the fluid in which reactions are going on should be proportional to the chemical time, \(\tau_{ch}\), and the total of the chemical and the mixing time, i.e.,

\[
\kappa = \frac{\tau_{ch}}{\tau_{mix2} + \tau_{ch}} \tag{76}
\]

In the model by Karlsson and Chomiak, the chemical time scale is estimated from

\[
\frac{1}{\tau_{ch}} = \frac{dc}{dt} \tag{77}
\]

where \(c\) is a chemical progress variable. Another suggestion given by Karlsson and Chomiak on how to estimate the chemical time scale is

\[
\frac{1}{\tau_{ch}} = -\frac{\dot{\omega}_{fuel}}{Y_{min}} \tag{78}
\]

113
where $\dot{\omega}_{\text{fuel}}$ is the reaction rate of the fuel, and $Y_{\min}$ the minimum of $Y_{\text{fuel}}$ and $Y_O$, divided by the stoichiometric coefficient for the global reaction taken from the flow into the reacting part. For the fuel rich case, a slight modification to the equation has to be made. In the case of a complex description of the chemistry, in particular, the definition of a single chemical time scale seems to be problematic. Here the time scale of the CO oxidation was considered as a representative choice for the chemical time scale. This time scale was chosen since the time scale for the CO oxidation process in one of the slowest. There also exist several empirical rate expressions for this reaction that are easy to use. In the present study, the empirical reaction rate for CO oxidation in post flame conditions proposed by Howard and co-workers (1972) was used to describe the reaction rate.

In the work presented here, the Eddy Dissipation Concept (Magnussen 1981, Magnussen 1989) and the I.E.M.-type model of Karlsson and Chomiak (Karlsson and Chomiak 1995, Karlsson 1995) have been combined. Despite its shortcomings, the Eddy Dissipation Concept is still one of the few turbulence-chemistry interaction models that can utilize the chemical knowledge collected in a comprehensive mechanism. This is partly due to its simplified description of the fluctuations, but perhaps mainly because of the use of the perfectly stirred reactor as an integral part of the model. The use of the perfectly stirred reactor also has the additional advantage that the great number of reactions used in the reaction scheme only has to be taken into account when solving the perfectly stirred reactor sub-problem. Unfortunately, although mathematically well defined, the perfectly stirred reactor problem requires a substantial computational effort, which limits the use of comprehensive reaction mechanisms in engineering calculations. All together, the structure of the Eddy Dissipation Concept has many benefits. In Table I is the new model compared with the standard version of the Eddy Dissipation Concept.

This complete revision of the Eddy Dissipation Concept also fulfills the requirement that the change of mixing time should also be reflected in the other parts of the model. This was not the case in the versions of the Eddy Dissipation Concept used to investigate the micro scale mixing time in Section 8.2.
Table I. Equations describing the new model compared with the equations used in the standard version of the Eddy Dissipation Concept.

<table>
<thead>
<tr>
<th>The present model</th>
<th>Standard EDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\psi} = \kappa \psi^R + (1 - \kappa) \psi^N )</td>
<td>( \bar{\psi}_i = \gamma^3 \chi \psi^<em>_i + (1 - \gamma^3 \chi) \psi^</em>_i )</td>
</tr>
<tr>
<td>( \tilde{\omega}<em>i = \frac{\kappa}{\tau</em>{mix2}} (Y^N_i - Y^R_i) )</td>
<td>( \tilde{\omega}_i = \frac{\gamma^{(233)} \chi}{\tau^<em>} (Y^</em>_i - Y^*_i) )</td>
</tr>
<tr>
<td>( \tau_{mix2} = \sqrt{\frac{k}{e} \left( \frac{V}{\varepsilon} \right)} )</td>
<td>( \tau^* = 0.41 \left( \frac{V}{\varepsilon} \right)^{1/2} )</td>
</tr>
<tr>
<td>( \kappa = \frac{\tau_{ch}}{\tau_{ch} + \tau_{mix2}} )</td>
<td>( \gamma^3 \chi = 2.13 (\nu c / k^2)^{1/4} \cdot f(Y_F, Y_O, Y_P) )</td>
</tr>
</tbody>
</table>

In the mathematical modeling, the CO/H₂/N₂-air jet flame investigated by Drake and co-workers (1984) was used as a test case. This test case was partly chosen because its geometry is simple but most of all because the fuel was doped with NH₃, which provided possibilities to test fuel-N modeling as well. The combustor was modeled using an axisymmetric representation. To enable this approach, the square duct was modeled as a round pipe. The diameter of the pipe was chosen such that the velocities and the fuel–air ratio were kept the same as in the experiments conducted by Drake and co-workers (1984). In the modeling, 47 cells were used in the axial direction and 19 cells in the radial direction. The structured grid extended from 2 cm upstream of the fuel inlet to 16 cm downstream of the fuel inlet. Five cells in the axial direction were used from the start of the grid to the position where the fuel pipe ended. Then 11, 10, 11, and 11 cells were used in the segments \( x/d = 0-10, 10-25, 25-50, \) and 50-100, respectively. In the radial direction, three cells were used to resolve the inner radius of the pipe, two to resolve the wall of the pipe and fourteen for the rest of the duct. At the fuel inlet a turbulence intensity of 10% and a characteristic length of 1.6 mm were used. For
The Eddy Dissipation Concept

the co-flowing air, a turbulence intensity of 1.3% and a characteristic length of 75 mm were used. The turbulence intensities are based on the data of Drake and co-workers, whereas the characteristic length scales are based on the physical dimensions of the combustion device. Radiation was not accounted for in the CFD modeling. The composition of the numerical fuel was 39.4 mol-% CO, 29.7 mol-% H₂, 29.5 mol-% N₂, and 0.7 mol-% CH₄. In the modeling the H₂O content of the air stream was set to 0.9 mol-%. For both the fuel and air stream an inlet temperature of 300 K was assumed. In this study, the case where 0.8 mol-% NH₃ was added has been modeled.

As a first approach, the chemistry was described with the comprehensive reaction mechanism. The main chemistry as well as the nitrogen chemistry were included. The direct use of a comprehensive mechanism with this large number of species in a CFD calculation was associated with a number of problems. First, solving transport equations for all species was computationally demanding. To reduce the number of transport equations certain simplifications had to be made. For example, it would be possible to assume that the radicals in the non-reacting part are in steady state with the radicals in the reacting part. In this way it would not have been necessary to solve transport equations for the radicals. However, the drawback of this approach is that the radicals will be present in super-equilibrium levels in the whole computational cell, which may be a poor assumption. The approach used in this thesis was to form stable species of the radicals and consider only transport equations for the stable species. The most interesting species that were treated in this way were the nitrogen-containing species. Thus, the radicals NH₂, NH, N, NNH, and N₂H₂ were added to the NH₃ concentration. Of these, the NH₂ radical concentration was considerable in large regions. Similarly, HNCO, HOCN, and NCO were added to the HCN concentration. No other radicals were added to the NO and NO₂ concentrations. The drawback of this approach is the additional computational costs associated with the correction of the enthalpy of the mixture leaving the reacting part.

The comprehensive mechanism was used in three different ways. In the first approach, i.e., approach I, it was used in the calculations of the source terms in the species transport equations, and for the enthalpy equation. In the two other
The Eddy Dissipation Concept

approaches, approaches IIa and IIb, the comprehensive mechanism was only used in the computations of the nitrogen chemistry, i.e., all other variables were fixed except NH$_3$, HCN, NO, and NO$_2$. In approach IIa, the temperature of the reacting part was taken from the main calculation. In approach IIb, the comprehensive mechanism was used to solve a constant enthalpy case where only the inlet temperature was taken from the main calculations. The behavior of the reacting part was solved with the PSR code (Glarborg et al. 1986) from the CHEMKIN library (Kee et al. 1991). In the main calculations preceding approaches IIa and IIb, the main chemistry was described with the four-step mechanism of Jones and Lindstedt (1988). Since this mechanism only includes four reactions and no combustion radicals, perfectly stirred reactor calculations with this mechanism are considerably easier to perform than with a comprehensive mechanism. In approach IIIa and in approach IIIb the empirical mechanisms of Mitchell and Tarbell (1982) and of de Soete (1974) were used in combination with the mechanism of Jones and Lindstedt. In these approaches, the nitrogen chemistry was accounted for simultaneously as the main chemistry, i.e., the post-processing technique was not used. In the approach using the empirical mechanism of Mitchell and Tarbell, the HCN reactions were also included.

There was a clear difference between the predicted results and the measured ones. Using approach I, the lift-off height was severely overestimated. With the empirical four-step mechanism of Jones and Lindstedt, the predictions of the temperature and of the main species concentration were in better agreement, although here too, the lift-off of the flame seem to be overestimated. Figure 8.11 shows a comparison between predicted radial temperature profiles and measured ones. This test case is also used in the assessment of the Eddy Dissipation Combustion Model presented in next chapter. That study suggests that the reason for the poor predictions is that this case requires that the reaction rates should be evaluated taking fluctuations into account.
Figure 8.11. Measured (symbols) and computed temperatures (line) as a function of the radial distance (normalized by the fuel tube radius). The calculated temperatures have been obtained with the four-step mechanism of Jones and Lindstedt (1988). a) x/d=10, b) x/d=25, and c) x/d=50, where x is the axial distance and d the inner diameter of the fuel tube.

Approach IIa, IIb, and IIIa resulted in qualitatively similar NH$_3$ fields. Moreover, the predicted NO distributions were similar for these approaches. With approach IIa, the NO mole fraction peaked at 2150 ppm, while it with IIb peaked at 2035 ppm and with IIIa at 2620 ppm, respectively. With approach IIa, the predicted molar yield of NO was 79.5% and of NO$_2$ 5.8%. With this approach, it was
predicted that 10.1% of the initial NH$_3$ left the computational domain without reacting. With approach IIb, the molar yield of NO was 71.4% and of NO$_2$ 9.4%. At the end of the domain 9.2% of the NH$_3$ had still not reacted. With approach IIIa, the molar yield of NO was 87.9%, whereas 11.6% of the NH$_3$ was still found at the end of the computational domain. With approach IIIb, a much slower oxidation rate of NH$_3$ was predicted. The peak level of NO was only 920 ppm. The molar yield of NO was 40.0 %, which is lower than with approaches IIa, IIb, and IIIa. However, 66.8% of the NH$_3$ left the computational domain without reacting. All yields are based on the reacted NH$_3$ amount. In the empirical mechanisms used in approaches IIIa and IIIb, NO$_2$ is not separately accounted for. An overview of the results can be seen in Table II.

**Table II. An overview of the results of the nitrogen chemistry predictions.**

<table>
<thead>
<tr>
<th>Approach</th>
<th>NO yield</th>
<th>NO$_2$ yield</th>
<th>non-reacted NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measurements</td>
<td>23 %*</td>
<td>*</td>
<td>not mentioned</td>
</tr>
<tr>
<td>Approach I</td>
<td>no result</td>
<td>no result</td>
<td>no result</td>
</tr>
<tr>
<td>Approach IIa</td>
<td>79.5 %</td>
<td>5.8 %</td>
<td>10.1%</td>
</tr>
<tr>
<td>Approach IIb</td>
<td>71.4 %</td>
<td>9.4 %</td>
<td>9.2 %</td>
</tr>
<tr>
<td>Approach IIIa</td>
<td>87.9 %</td>
<td>-</td>
<td>11.6 %</td>
</tr>
<tr>
<td>Approach IIIb</td>
<td>40.0 %</td>
<td>-</td>
<td>66.8 %</td>
</tr>
</tbody>
</table>

*NO and NO$_2$ reported as NO$_x$ in the measurements data

The success in modeling of the main flow, temperature, and concentration fields of the main components influences the quality of the prediction of the conversion of NH$_3$ to NO and N$_2$. In the part of the flame where most of the fuel was oxidized the mass fraction of O$_2$ entering the reacting structures exceeded 0.05. In the reacting structures too, the mass fraction of O$_2$ never obtained values below 0.007. In the measurements of Drake and co-workers (1984) this part of the flame is poor in O$_2$. Without such an O$_2$-poor region, the path leading to NO is favored

119
in the calculations. Here, the predicted molar NOx yield exceeds 80% when post-processing is performed with a comprehensive mechanism, whereas the measurements only showed a molar NOx yield of 23%. Moreover, the results obtained with approach IIIa, i.e., post-processing with the empirical mechanism of Mitchell and Tarbell, are similar to those obtained with approach IIa and IIB, although the computational demand with this approach is substantially smaller. In this study, the empirical mechanism of de Soete, which has been derived from experiments with a higher flame temperature, predicted a NH3 conversion that was too slow. None of the mechanisms including HCN predicted any substantial amounts of this species. Small amounts of HCN could be formed since the fuel contained a small amount of CH4. However, the O2-rich reaction zone does not favor this reaction path.

Apart from taking measurements in the flame used in this study, Drake and co-workers (1984) also modeled the flame. They used equilibrium chemistry with a presumed pdf shape for the mixture fraction. In their calculations, the mean reaction rates for the nitrogen chemistry were calculated by convolution with the local mixture fraction pdf. Although their calculations resulted in too high temperatures in the flame, their NOx yield was overestimated by approximately 50% whereas in this study, using a comprehensive reaction mechanism, it was overestimated by almost 400%. This result too supports the suggestion that the turbulent fluctuations need to be accounted for in this case.

8.4 Summary of the investigation of the Eddy Dissipation Concept

The investigations showed that a more accurate description of the chemistry does not necessarily contribute to a better quality of the predictions. The investigation also pointed out problems associated with inclusion of reaction mechanisms accounting for radical reactions. If transport equations for the radicals were included, the number of species would have increased from less than 10 to more than 50 in the case nitrogen chemistry was of interest. If these radicals were included in the same way as the main species, it would have implied that the highly reactive radicals would have been considered as inert species in most of the fluid. A solution to the problem with a large number of radicals that must be
transported has been presented in the literature (Magel et al. 1996). In this approach the radicals in the non-reacting part of the fluid are assumed to be in steady state with the radicals in the reacting part. However, in this way, the super-equilibrium levels of the radicals in the reacting part will also be present in the non-reacting part and the contradictory situation with highly reactive radicals behaving as inert species in most of the fluid remains. In this study, a solution was proposed where the radicals were merged together to stable species. In contrast to the super-equilibrium level of radicals in the non-reacting fraction obtained by the first approach, the non-reacting part will be free of radicals in this approach. This approach too is physically poorly motivated.

The investigation of the Eddy Dissipation Concept showed that predictions of a similar quality could be obtained if the turbulent mixing time of the reacting part was chosen differently compared with suggestions of Magnussen (1981,1989). According to the Borghi-diagram, the interaction with turbulent structures of the Kolmogorov scale is of greatest importance in the flamelet region. The use of the Kolmogorov time scale could thus imply that the Eddy Dissipation Concept is suitable for modeling flows in this combustion region. However, in the Eddy Dissipation Concept the effect of molecular diffusion on the structure of the flamelets are neglected since the reacting structures are modeled using the perfectly stirred reactor concept.

The derivation of the Eddy Dissipation Concept relies on the use of the Kolmogorov related time scale. If another time scale is chosen, the whole model has to be modified. However, already the modification of the expression for the exchange rate of mass between the reacting and the non-reacting part, i.e., the use of $\gamma^3/\tau^*$ instead of $\gamma^3/\tau^*$, leaves certain loose ends in the standard version of the Eddy Dissipation Concept as well. Since this modification explicitly was based on the argument that the fine structures mainly exchange mass with the fine structure regions they are located in, the composition of the inflow from the surrounding should no longer be calculated using the expression giving the relation between the mean, the value in the non-reacting part, and the reacting part.
In this thesis, a new turbulence-chemistry interaction model relying on the structure of the Eddy Dissipation Concept has been presented. This model is similar to a model presented by Karlsson and Chomiak (Karlsson and Chomiak 1995, Karlsson 1995) but does not require the use of a Lagrangian description. Compared to the standard Eddy Dissipation Concept, in particular the assumption that the reacting fraction is dependent on both the turbulence and the chemistry seems to be a big improvement. Still, this model too relies on a simplified description of the fluctuations, and predictions of processes that are sensitive to fluctuations, including the formation of thermal-NO, are not more reliable than with the standard Eddy Dissipation Concept. As this model no longer uses the Kolmogorov related time scale of the Eddy Dissipation Concept, which is derived from the analyze of the cascade process for transportation of turbulent kinetic energy from the energy containing structures down to the dissipative structures, it should probably not be called an Eddy Dissipation Concept even though the model shares the structure of the Eddy Dissipation Concept.
9. The Eddy Dissipation Combustion Model

Although the Eddy Dissipation Concept (Magnussen 1981 and 1989) is a versatile model, in practice, many CFD studies of combustion devices and burners (Peters and Weber 1995, Magel et al. 1995, Ferreira et al. 1995, Peters and Weber 1997) are still based on the Eddy Dissipation Combustion Model of Magnussen and Hjertager (1976). This model is closely related to the Eddy-Break Up model of Spalding (1971), but takes into account that there must be both fuel and oxygen present before reactions can occur. The Eddy Dissipation Combustion Model has been developed assuming that in most technical applications the chemical reaction rates are fast compared with the mixing rate. Thus, the reaction rate is determined by the rate of intermixing of fuel and oxygen containing eddies, i.e., by the rate of the dissipation of the eddies. The expression for the reaction rate, already given in the literature review section, is

\[
\tilde{\omega}_f = A \frac{\bar{\varepsilon}}{k} \min \left[ \tilde{Y}_f, \frac{\tilde{Y}_{O_2} B}{1 + r_f}, r_f \right] \tag{79}
\]

where \( Y \) is the mass fraction, and \( r_f \) the stoichiometric coefficient for the over all reaction written on mass basis. \( A \) and \( B \) are experimentally determined constants, whereas \( k \) is the turbulent kinetic energy, and \( \varepsilon \) its dissipation rate. The product dependence for the reaction rate is a deviation from the pure fast chemistry assumption, since the idea here is that without hot products, the temperature will be too low for reactions to occur.

In many recent studies, the Eddy Dissipation Combustion Model is used in an extended form, which allows for the use of finite rate chemistry. In this case, the model can be written

\[
\tilde{\omega}_{R_i} = \min \left[ A \frac{\bar{\varepsilon}}{k} \tilde{Y}_{R_i}, A \frac{\bar{\varepsilon}}{k} \frac{\tilde{Y}_{R_i}}{r_i}, \tilde{\omega}_{\text{kinetic}, R_i} \right] \tag{80}
\]
The subscript $R_i$ indicates that reactant 1 is considered. In this form, it is possible to take multi-step reaction kinetics into account with the Eddy Dissipation Combustion Model. In the equation above, $r_i$ is the stoichiometric coefficient, expressed on mass bases, for the reaction between reactant $R_1$ and reactant $R_2$. If a global reaction is used where more than two reactants take part in the reaction, the expression needs to be modified accordingly. In the expression above, the term dependent on the mass fraction of products has been replaced by a term describing the reaction kinetics. The motivation for replacing the term depending on the mass fraction of products is that the kinetic rate expression too will be dependent on the presence of hot combustion products. Therefore, it seems unnecessary to include this dependence twice. However, in many implementations of this model, the product dependency is maintained in the finite rate chemistry formulation.

Although the Eddy Dissipation Combustion Model is an 
*ad hoc* model, Duclos and co-workers (1993) have pointed out that in the premixed case, when there is a local equilibrium between production and dissipation of flame surface density, a number of flamelet models reduces to an Eddy Break-Up model, similar to the Eddy Dissipation Combustion Model. For non-premixed flames too, it has been shown that a similar model can be derived theoretically assuming fast chemistry, see Brizuela and Bilger (1996) for further references.

**9.1 Effect of the description of the chemistry**

In the form given by Equation 80 above, the Eddy Dissipation Combustion Model can handle a description of the chemistry such as the one proposed by Jones and Lindstedt (1988). To test the capability of the Eddy Dissipation Combustion Model to model combustion with such a mechanism, three test cases were used.

As a first test case, the natural gas combustor B was modeled. The 102 by 70 cells structured grid describes the entire combustion chamber as well as a part of the outlet. A grid twice as dense was also tested to ensure that the solution was grid
independent. In this study, the results obtained with the finite rate approach were not only compared with available measurements, but also to the predictions obtained with the fast chemistry approach. In the calculations with fast chemistry approach, the formulation of the Eddy Dissipation Combustion Model in which the products also are occurring was used.

The composition of the natural gas was assumed to be 90 vol-% methane and 10 vol-% N₂. Heavier hydrocarbons present in the natural gas were neglected in the modeling. This approach was suggested by Garréton and Simonin (1994), who have compiled the data necessary to model this test case. In the calculations, the wall temperature was set to 120°C, the temperature of the natural gas entering the reactor to 40°C, and the temperature of the air to 50°C. The relative humidity of the air was 80%, which corresponds to a H₂O content of approximately 6.5%. The boundary conditions for the turbulence as well as the flow profiles at the inlets were set according to the suggestions of Garréton and Simonin. The influence of radiation on the predictions was tested, and although the influence of radiation was significant, it was much smaller than the influence of the description of the reaction kinetics. The influence of radiation was also much larger when the fast chemistry approach was used compared with when the four-step mechanism was used. The reason for this was the much higher temperatures predicted with the first approach.

Figure 9.1 shows measured and computed temperatures along the centerline. Figure 9.2 shows measured and computed radial temperature profiles at a location 612 mm from the inlets, a distance approximately ten times the fuel pipe diameter. From the figures it can be seen that the results obtained with the four-step mechanism agree well with the measured ones.
Figure 9.1. Temperatures along the centerline of the sudden-expansion combustor. The continuous line represents the results with the four-step mechanism. The dashed line represents the results with the fast chemistry approach. The squares represent the temperatures measured by Garréton and Simonin (1994).

Figure 9.2. Radial temperature profiles 612 mm from the burner in the sudden-expansion combustor. The continuous line represents the results with the four-step mechanism. The dashed line represents the results with the fast chemistry approach. The squares represent temperatures reported by Garréton and Simonin (1994).
As a second test case in the evaluation of the Eddy Dissipation Combustion Model, the natural combustor C was used. In this case, the hydrocarbons in the natural gas were modeled as a hypothetical hydrocarbon with the molecular formula $C_{1.104}H_{4.208}$. The mass fractions of the other species in the natural gas were taken from the natural gas composition. The combustion air was assumed to contain 1.0 vol-% of water vapor. The stoichiometric coefficients of the first to reaction in the four-step mechanism of Jones and Lindstedt (1988) were changed so that this hypothetical hydrocarbon could be used in the calculations. To account for the chemistry of the NH$_3$ present in the fuel stream the mechanism of Mitchell and Tarbell (1982) was used. However, the reaction describing the formation of thermal-NO was not included in the description of the nitrogen chemistry. The temperatures of the fuel and the air, as well as the temperature of the walls were set according to the values given in the description of the test case. Radiative heat transfer in the combustion chamber was modeled with the 4-flux model. The absorption coefficient was set to 0.3. The burner geometry was relatively complex, and a 3D model would have been necessary to resolve the 8 gas injection nozzles. To reduce the computational effort, an axisymmetric representation was used. This approach required that the nozzles were modeled as a single slit. The width of the inlet was chosen such that the area of the slit corresponded to the area of the nozzles. The body fitted grid had 75 cells in the axial direction and 40 in the radial direction. Especially the boundary conditions for the swirling air were difficult to establish since no measurements inside the burner were available. To solve the problem with uncertainties in the boundary conditions, the modeling was started inside the burner. The radial velocity component was set such that it corresponded to the volumetric flow rate and then, by means of iteration, the swirl component was set such that the theoretical swirl number was 1.0 at the location where the air emerged from the burner. During this iterative procedure, the natural gas flow was set to zero. At the air inlet, a turbulence intensity of 50% was used and the characteristic length was set to 5 mm. At the natural gas inlet, a turbulence intensity of 5% was used and the characteristic length was taken from the dimensions of the air nozzles. Two turbulence models were employed in the present study, i.e., the k-$\varepsilon$ model and the Reynolds stress model.
Figure 9.3 shows the calculated hydrocarbon \((C_{1.104}H_{4.208})\) profile compared with the measured CH\(_4\) profile at an axial distance of 90 mm from the natural gas inlet. There is a significant difference in the hydrocarbon profiles predicted with the various approaches, although at this location the flow field predictions are similar.

![Graph showing hydrocarbon profile](image)

**Figure 9.3.** Computed \(C_{1.104}H_{4.208}\) and measured CH\(_4\) mole fraction 90 mm from the natural gas inlet.

In the computations with the fast chemistry approach, the hydrocarbon mole fractions were much higher than the measured ones. With the \(k-\varepsilon\) model, the hydrocarbon mole fraction peaked at 35 vol-%, whereas with the Reynolds stress model it peaked at 52 vol-%. With the finite rate chemistry approach, the hydrocarbon profiles agreed better with the measured ones. However, inside the internal recirculation zone, the predicted hydrocarbon mole fraction was considerably lower than the measured one. The discrepancy in the hydrocarbon mole fraction was also reflected in the predictions of the other species. Inside the internal recirculation zone, in particular, the agreement was poor. With the fast chemistry approach, the O\(_2\) mole fraction was very close to zero. With the finite rate chemistry approach, the predicted O\(_2\) mole fraction was slightly lower than the
predicted hydrocarbon mole fraction, which is in contradiction with the measurements. The mole fractions of CO and H₂ are also higher than the measured ones since compared with the measurements too much of the hydrocarbons were oxidized. Most notable was the difference in the H₂ prediction. In the calculations, a peak was predicted in the H₂ profile at the outer boundary of the internal recirculation zone. However, no corresponding peak in the H₂ profile was found in the experiments of Stapf and Leuckel (1993). They reported that the H₂ mole fraction increased as the centerline was approached.

Further downstream, the difference in the predictions between each approach was more evident. Figure 9.4 shows the axial velocity component 360 mm from the natural gas inlets.

![Graph showing axial velocity component](image)

**Figure 9.4. Axial velocity component 360 mm from the natural gas inlet.**

With the k-ε model, a significantly wider internal recirculation zone was predicted than experimentally observed. However, more interesting to notice is the effect of the chemical reaction scheme on the flow field when the turbulence was modeled with the Reynolds stress model. With the fast chemistry approach, the flow field was similar to that predicted with the k-ε model. With the finite rate chemistry
approach, on the other hand, the predicted flow field was in better agreement with the measured one. Although this model combination resulted in a significantly better agreement, it did not work completely satisfactorily. The main shortcoming in the predictions obtained with this combination was an overestimation of the length of the internal recirculation zone. This tendency can already be spotted at the 360 mm location, where the velocity in the reverse flow along the centerline is larger than the measured one. This discrepancy is not due to the computational grid, since predictions obtained with a denser grid showed the same feature.

Figure 9.5 shows the distribution of nitrogen containing species at the 90 mm location. These predictions were obtained using the finite rate chemistry approach and the Reynolds stress model combination.

![Graph showing mole fractions of NO, HCN, and NH₃](image)

*Figure 9.5. Predictions and measurements of the mole fractions of NO, HCN, and NH₃ 90 mm from the natural gas inlet.*

The figure shows a fair agreement in NO away from the center of the combustor. The quality of the predictions is less satisfactory closer to the centerline. In the calculations, the NO mole fraction at the centerline was approximately 300 ppm whereas the measurements showed less that 100 ppm NO. Yet, the measurements
showed that the HCN mole fraction was slightly higher than 400 ppm. In the CFD calculations, HCN was not included in the reaction scheme. It is also worth noting that inside the internal recirculation zone, the predicted NH$_3$ concentrations were higher than the measured ones. This finding is interesting since the NH$_3$ was injected with the natural gas stream and the NH$_3$ should react as the fuel reacts. Inside the internal recirculation zone, the predicted hydrocarbon concentrations were lower than the measured ones.

Although the Reynolds stress model significantly improved the description of the flow field, its influence on the NO$_x$ predictions was not as drastic. With the finite rate approach combined with the Reynolds stress model, the predicted NO mole fraction was 620 ppm, whereas combined with the k-ε model it was 650 ppm.

The calculations show that for the quality of the flow predictions, not only the description of the hydrocarbon oxidation was important; a more advanced turbulence model was also needed. However, based on the present study, it is not possible to make the general conclusion that the combination of finite rate chemistry and the Reynolds stress model will provide the best result in the modeling of swirling natural gas flames. For instance, Batley and Lamers (1997) have reported two stable solutions using this combination when modeling a laboratory scale combustor equipped with a swirl burner.

Although the turbulence model had a large influence on the flow predictions, the NO concentration in the flue gas was only slightly influenced by the turbulence model. In both cases the agreement was fair, which in this case partly must be explained as a coincident. A probable reason for the insensitivity with respect to the turbulence model is the shortcomings in the descriptions of the NO$_x$ chemistry. It should also be remembered that the thermal-NO formation was not included in the description of the nitrogen chemistry. Stapf and Leuckel (1993) estimated that the contribution to the final NO from NO formed via the thermal-NO path is close to 100 ppm in this case. In addition, when combining the Reynolds stress model with the Eddy Dissipation Combustion Model, the constant $A$ (and $B$) has not been tuned for use with the Reynolds stress model. In the
present study, this could be observed as a difference in the mixing determined reaction rate in the vicinity of the diffusor zone.

The previous test cases showed that the Eddy Dissipation Combustion Model combined with the four-step mechanism provides an adequate description of the reactions in the modeling of natural gas combustors, although the modeling of the swirling flame was depending on a more complex turbulence model. As a last test case in the evaluation of the Eddy Dissipation Combustion Model the CO/H₂/N₂ jet flame was used. This test case was also used in Chapter 8. Again, the combustor was modeled by use of an axisymmetric representation, i.e., the square duct was modeled as a pipe. The velocities and the fuel to air ratio were the same as in the experiments conducted by Drake and co-workers (1984). The 96 by 78 cells structured grid extends from 20 mm upstream of the fuel inlet to 320 mm downstream of the fuel inlet. This grid was denser than the one used with the model based on Eddy Dissipation Concept and the model of Karlsson and Chomiak, but the boundary conditions were set identical to those used in that study. That is, at the fuel inlet a turbulence intensity of 10% and a characteristic length of 1.6 mm were used. For the co-flowing air, a turbulence intensity of 1.3% and a characteristic length of 75 mm were used. In the mathematical modeling, the composition of the fuel was 39.4 mol-% CO, 29.7 mol-% H₂, 29.5 mol-% N₂, and 0.7 mol-% CH₄. The NH₃ content of the fuel stream was 0.8 mol-%. The H₂O content of the air stream was 0.9 mol-%. The inlet temperature was set to 300 K. It was ensured that the solution was grid-independent by testing a grid that was twice as dense. Radiation was not accounted for.

The measured and computed center line temperature profiles are shown in Figure 9.6. Figure 9.7 shows the radial temperature profiles at an axial distance of 32 mm. This distance is ten times the fuel pipe diameter. In this case, neither of the two mechanisms agreed well. The predictions with the fast chemistry agreed qualitatively better with the measurements since the use of the four-step reaction mechanism of Jones and Lindstedt (1988) predicted complete blow-out of the jet flame.
Figure 9.6. Temperatures along the center of the CO/H$_2$/N$_2$-jet. The dashed line represents the fast chemistry approach. The squares represent measured temperatures. Blow-out was predicted with the four-step mechanism (not shown in the figure).

Figure 9.7. Radial temperature profiles in the CO/H$_2$/N$_2$-jet 32 mm from the burner. The dashed line represents the fast chemistry approach. The squares represent measured temperatures. Blow-out was predicted with the four-step mechanism (not shown in the figure)
9.2 Importance of fluctuations

The purpose of the investigations reported in this section is to determine the conditions where a finite rate chemistry description could be used with the Eddy Dissipation Combustion Model.

In Chapter 6, where the influence of temperature fluctuations was investigated, it was shown that the temperature fluctuations at certain conditions could change the trends of the nitrogen chemistry compared with those found in the steady state perfectly stirred reactor calculations. The influence of the temperature fluctuations was not as important for the main species part, whereas the fluctuations had a significant effect on the concentrations of the most important radicals. The insensitivity of the main chemistry with respect to fluctuations in the temperature was indirectly supported by the findings of the previous section. There it was found that the Eddy Dissipation Combustion Model, which only relies on the mean values of temperature and concentrations, worked well together with a multi-step mechanism for the test cases where hydrocarbons were the primary combustibles. However, in the CO/H₂/N₂-air flame case this formulation did not work well, and the much simpler one-step mechanism provided a better description.

Brizuela and Bilger (1996) made one study that can be used as a starting point when trying to understand when the finite rate chemistry version of the Eddy Dissipation Combustion Model can be used. They used a presumed pdf approach to calculate the constant \( A \) in the Eddy Dissipation Combustion Model. With their approach, a fuel dependent value of \( A \) was obtained as a function of mixture fraction and mixture fraction variance. They assumed fast chemistry, and the dependence on the fuel could only be seen as a dependence on the value of the stoichiometric mixture fraction.
The presumed pdf approach is a well-establish technique that is used in several models, including flamelet models (Peters 1984). The true shape of the pdf is difficult to assess, but Brizuela and Bilger (1996) found that the results were not sensitive to whether a clipped Gaussian pdf or a Beta pdf was used. Jones and Priddin (1978) too found that when using the fast chemistry assumption, the influence of the presumed pdf shape is not of importance. Kent and Bilger (1976), on the other hand, found that although the shape of the pdf does not have a large influence on the flow field and on temperature predictions, it had a significant influence on the predictions of NO in a hydrogen-air diffusion flame.

In the investigation presented here, the pdf is presumed to be of a clipped Gaussian form. The clipped Gaussian pdf consists of a Gaussian pdf

\[
\tilde{f}_{\xi-Gauss}(\xi) = \frac{1}{\sqrt{2\pi \sigma^2}} e^{-\frac{(\xi - \bar{\xi})^2}{2\sigma^2}}
\]  

(81)

and of a Delta-function added at \( \xi = 0 \) in order to fulfill the definition of a pdf, i.e., \( \int f_{\xi}(\xi) d\xi = 1 \). In the expression above, \( \xi_{\bar{}} \) is the overall mixture fraction of the fuel-air mixture, \( \xi \) the local mixture fraction, and \( \xi^{*2} \) the local mixture fraction variance.

Figure 9.8 shows the clipped Gaussian pdf for a stoichiometric CH\(_4\)-air mixture. The larger the mixture fraction variance, the broader is the distribution. The figure also shows the meaning of clipped. Since the center of the distribution is much closer to 0 than to 1, a continuous distribution curve would require negative mixture fractions. Since this is not possible, a Delta-function is added at \( \xi = 0 \). In the figure, the magnitude of the Delta-function peaks is not shown in whole. Similarly, the width of the distribution curve as the variance approaches zero is due to the resolution used in the calculations used to produce the figure.
Figure 9.8. Clipped Gaussian pdf for a stoichiometric natural gas-air mixture.

The aim of the study of Brizuela and Bilger (1996) was to calculate a fuel dependent value of $A$ as a function of mixture fraction and mixture fraction variance. In the present study the aim is to analyze at which conditions the for finite rate chemistry version of the Eddy Dissipation Combustion Model can be applied.

In order to assess the reason for why the Eddy Dissipation Combustion Model performs well with the finite rate chemistry formulation for natural gas flames but not for the CO/H$_2$/N$_2$-air jet flame, attention was paid to the differences in the fuels. If the reactions are fast and reversible, the adiabatic combustion temperature will be a function of the mixture fraction. Figure 9.9 shows a plot of $T_{ad}(\xi)$, i.e., the adiabatic temperature as function of mixture fraction for the two cases used in the assessment of the influence of fluctuations. A mixture fraction of 1 means that the mixture consists of fuel and a mixture fraction of 0 that the mixture consists of air.
Figure 9.9. Adiabatic combustion temperature as a function of mixture fraction. The bold line represents the result for the natural gas used in the modeling of the sudden-expansion combustor. The thin line represents the result for the CO/H₂/N₂-mixture used in the modeling of the jet flame.

The figure shows that these two fuel-air mixtures behave very differently. The stoichiometric mixture fraction of a natural gas-air mixture is approximately 0.06. This means that of 1 kg mixture, only 60 grams originate from the natural gas whereas the rest originates from the air. Already a small change in the mixture fraction will bring the mixture far away from the stoichiometric conditions with the resulting drop in the adiabatic combustion temperature. For the CO/H₂/N₂-air mixture, on the other hand, the stoichiometric mixture fraction is around 0.3. As in the previous case, this means that of 1 kg stoichiometric mixture, 300 g originates from the fuel mixture and the rest from the air. Here, a small change in
the mixture fraction does not lead to a drastic drop in the adiabatic combustion temperature. Although the temperature of the fresh CO/H\(_2\)/N\(_2\)-air mixture was 25\(^\circ\)C, the equilibrium calculation showed that the temperature of this mixture at its thermodynamics equilibrium state is considerably higher. The combustion kinetics will not support such a high temperature, but equilibrium calculation by definition disregards from the kinetics.

So far, also this study relies on fast reactions, although, in the equilibrium analysis, the reactions are not assumed to be irreversible. However, using temperature–mixture fraction relation, i.e., \(T_{ad}(\xi)\), the kinetically controlled reaction rate can be estimated if it is assumed that the reaction rate mainly is a function of the temperature. In this case, the reaction rate can be written \(\dot{\omega} = k \exp\left(-\frac{E_A}{RT}\right)\). The mean reaction rate, where the temperature fluctuations are taken into account, i.e., pdf weighted mean reaction rate, is then given by

\[
\tilde{\omega} = \int_{0}^{1} \tilde{f}_\xi(\xi) ke^{-\frac{E_A}{RT_{ad}(\xi)}} d\xi \tag{82}
\]

Figures 9.10, 9.12, and 9.14 show the mean reaction rate for the natural gas-air mixture as a function of the activation energy in the case when the temperature fluctuations are taken into account. The frequency factor \(k\) was in these calculations set to unity. Figures 9.11, 9.13, and 9.15 show the mean reaction rate in the case when the mean reaction rate was evaluated using the mean temperature only, i.e.,

\[
\tilde{\omega} = ke^{-\frac{E_A}{RT_{ad}(\xi)}} \tag{83}
\]
Figure 9.10. The pdf weighted mean reaction rate as a function of mixture fraction and mixture fraction variance for the natural gas-air mixture used in the modeling of combustor B. An activation energy of 20 kcal/molK was assumed.

Figure 9.11. The mean reaction rate based on the pdf weighted temperature as a function of mixture fraction and mixture fraction variance for the natural gas-air mixture used in the modeling of combustor B. An activation energy of 20 kcal/molK was assumed.
Figure 9.12. The pdf weighted mean reaction rate as a function of mixture fraction and mixture fraction variance for the natural gas-air mixture used in the modeling of combustor B. An activation energy of 30 kcal/molK was assumed.

Figure 9.13. The mean reaction rate based on the pdf weighted temperature as a function of mixture fraction and mixture fraction variance for the natural gas-air mixture used in the modeling of combustor B. An activation energy of 30 kcal/molK was assumed.
Figure 9.14. The pdf weighted mean reaction rate as a function of mixture fraction and mixture fraction variance for the natural gas-air mixture used in the modeling of combustor B. An activation energy of 40 kcal/molK was assumed.

Figure 9.15. The mean reaction rate based on the pdf weighted temperature as a function of mixture fraction and mixture fraction variance for the natural gas-air mixture used in the modeling of combustor B. An activation energy of 40 kcal/molK was assumed.
From Figures 9.10-9.15 it can be seen that for the natural gas-air mixture only a small mixture fraction variance can be allowed for if a significant reaction rate is to be obtained. There is no significant difference in the results whether the mean reaction rate is computed according to the principles of Equation 82 or Equation 83. This result is also insensitive to the activation energy level.

In the CO/H₂/N₂-air case the situation is very different. Figures 9.16 and 9.17 show corresponding plots for this case. In Figure 9.16 it can be noted that a significant reaction rate is predicted also for large values of the mixture fraction variance when the mean reaction rate is evaluated using thepdf weighted reaction rate, i.e., according to the principles of Equation 82. Figure 9.17, on the other hand, shows that if only the mean temperature is used in the evaluation of the mean reaction rate, the predicted reaction rate drops significantly for large values of the mixture fraction variance.

![Figure 9.16. The pdf weighted mean reaction rate as a function of mixture fraction and mixture fraction variance for the CO/H₂/N₂–air mixture used in the modeling of the CO/H₂/N₂–air jet flame.](image)

Figure 9.16. The pdf weighted mean reaction rate as a function of mixture fraction and mixture fraction variance for the CO/H₂/N₂–air mixture used in the modeling of the CO/H₂/N₂–air jet flame.
Figure 9.17. The mean reaction rate based on the pdf weighted temperature as a function of mixture fraction and mixture fraction variance for the CO/H₂/N₂–air mixture used in the modeling of the CO/H₂/N₂–air jet flame.

The finding, that in a hydrocarbon flame the reaction rate is much more sensitive to fluctuations in the mixture fraction variance than in a CO/H₂/N₂ flame, is also confirmed if the mixture fraction and mixture fraction variance are studied in the regions where most of the reactions occur in the combustor B and in the CO/H₂/N₂–air jet.

In Figure 9.18 it can be seen that the O₂ consumption occurs when the mixture fraction is between 0.03 and 0.08. The maximum reaction rate is found close to where the mixture fraction has its stoichiometric value. In the figure, the O₂ consumption rate is based on the rate given by the four-step mechanism. With this mechanism, the temperature and composition predictions are in agreement with the measurements. Studying the mixture fraction variance in the region where the reactions occur reveals that the mixture fraction variance is generally less than 0.005. This explains why the four-step mechanism, although based on mean quantities, performs well. This also suggests, that for hydrocarbon fuels, the fast chemistry approach generally seems to be a poor description.
Figure 9.18. Consumption rate of $O_2$ in the sudden-expansion reactor. The darkest field corresponds to an $O_2$ consumption rate of approximately 3.5 kg/m$^3$s. Iso-contours for the mixture fraction are also shown.

Figure 9.19. Consumption rate of $O_2$ in the CO/H$_2$/N$_2$–air jet. The darkest field corresponds to an $O_2$ consumption rate of 20 kg/m$^3$s. The maximum $O_2$ consumption rate is locally considerably higher. Iso-contours for the mixture fraction are also shown.
In Figure 9.19, the corresponding information is shown for the CO/H₂/N₂–air jet flame, although the reaction rate is given for the single-step irreversible reaction. The reason for taking the O₂ consumption rate from this reaction in this case is that with this approach the predicted temperature distribution agrees with the measurements. As shown in the same figure, the O₂ consumption starts in a region where the mixture fraction variance is around 0.2 and the mean mixture fraction is 0.5. At such conditions a mean reaction rate based on a pdf weighted reaction rate is substantially larger than a reaction rate based on mean quantities alone. This also explains why the mixed-is-burned approach is better in this case.

In the CO/H₂/N₂-air case, where the value of the stoichiometric mixture fraction is much higher than in the natural gas-air case, the use of only one single Delta-function is not fully justified. Here, it would be better to use two Delta-functions, one at ξ = 0 of a magnitude corresponding to \[\int_0^\xi \bar{J}_\xi \text{Gauss}(\xi) d\xi\] and one at ξ = 1 of a magnitude corresponding to \[\int_1^\infty \bar{J}_\xi \text{Gauss}(\xi) d\xi\]. Another way to overcome this problem would be to use a \(\beta\)-function. However, this function is numerically difficult to evaluate for large values of the variance.

9.3 Outline of an Eddy Dissipation Combustion/ PDF Model

The analysis of the Eddy Dissipation Combustion Model using the presumed pdf approach cannot only be used to explain why a certain description of the chemistry is to prefer with the Eddy Dissipation Combustion Model in a certain case. This approach can also be used to construct an improved version of the Eddy Dissipation Combustion Model. Now, instead of using the simplified pdf weighted reaction rate for explaining why the Eddy Dissipation Combustion Model works in a certain case, this information is directly used in the calculation of the reaction rate. This requires that the pdf-weighted reaction rate is calculated in advance and stored in a form that easily can be accessed in the CFD calculations. Moreover, the pre-calculated pdf-weighted reaction rate has to be calculated for each case since it relies on the adiabatic combustion temperature. In addition, a separate calculation has to be undertaken for each activation energy occurring in the reaction scheme. In the calculation of the adiabatic combustion
temperature, it must be assumed that the chemistry is fast whereas the results are used in finite rate kinetic expressions. Further, only fluctuations in the temperature are considered. This assumption will require the use of an additional parameter, $C$, that reduces the value of the purely kinetic reaction rate. This parameter should not be a constant but a link between the conditions used in the pdf-based evaluation of the kinetic rate and the conditions in the flow modeling. However, such an approach is not very straightforward and easy to realize, since it is likely that it would introduce additional instability into the flow calculations.

For a reaction between reactants $R$ and $S$, where the reaction kinetics can be described by the modified Arrhenius expression $\dot{\omega} = kT^\beta \left[ \frac{[R]^\gamma}{[S]^\delta} \right] \exp\left(-\frac{E_a}{RT}\right)$, the mean reaction rate according to this modified Eddy Dissipation Combustion Model is

$$\tilde{\omega}_R = \min\left[ A \frac{\tilde{\gamma}_R}{k}, A \frac{\tilde{\gamma}_S}{k}, \frac{C}{r} \int_0^1 \tilde{f}_\xi(\xi) kT^\beta \left[ \frac{[R]^\gamma}{[S]^\delta} \right] e^{-\frac{E_a}{RT_{av}(\xi)}} d\xi \right]$$

(84).

An alternative way to create a link between the conditions used in the pdf based evaluation of the kinetic rate and the conditions in the flow modeling is to include the term of Magnussen and Hjertager's Eddy Dissipation Combustion Model that was depending on the presence of hot products. In this case, the full expression describing the modified Eddy Dissipation Combustion Model is

$$\tilde{\omega}_R = \min\left[ A \frac{\tilde{\gamma}_R}{k}, A \frac{\tilde{\gamma}_S}{k}, AB \left( \frac{\tilde{\gamma}_{products}}{1+r} \right), C \int_0^1 \tilde{f}_\xi(\xi) kT^\beta \left[ \frac{[R]^\gamma}{[S]^\delta} \right] e^{-\frac{E_a}{RT_{av}(\xi)}} d\xi \right]$$

(85).

In the expressions above, $r$ is the stoichiometry of the reaction expressed on mass base. It should be noted that the parameters shared with the normal Eddy Dissipation Combustion Model most probably need to be adjusted.

This version of the Eddy Dissipation Combustion Model is more general in the context that it will allow for the use of a multi-step reaction mechanism also in the cases where the standard Eddy Dissipation Combustion Model fails. However,
this model will also suffer from the restriction of the presumed pdf approach, i.e., it is based on the mixture fraction concept, and is thus only suitable for diffusion flames.

9.4 Summary of the investigation of the Eddy Dissipation Combustion Model

In the present study, the simpler Eddy Dissipation Combustion Model (Magnussen and Hjertager 1976) was able to provide as good a prediction of the non-swirled natural gas flame as the more complicated Eddy Dissipation Concept (Magnussen 1981 and 1989). Unfortunately, the same test case was not used with the Eddy Dissipation Combustion Model as with the Eddy Dissipation Concept. However, Magel and co-workers (1996) have modeled the test case used in the evaluation of the Eddy Dissipation Combustion Model with the Eddy Dissipation Concept combined with a detailed reaction mechanism. Their temperature and main component predictions are almost identical to those obtained here with the Eddy Dissipation Combustion Model.

For the hydrocarbon flames encouraging results were obtained when the hydrocarbon chemistry was described with the four-step mechanism of Jones and Lindstedt (1988). In the swirling flame case, the Reynolds stress model was required to model the turbulence properly. Even though the four-step mechanism provides a reasonable description of the oxidation of the CO/H₂/N₂–air mixture in perfectly stirred reactor calculations, the Eddy Dissipation Combustion Model combined with the four-step mechanism did not provide a good description in the jet flame case.

At first, it is difficult to understand the reason for that the Eddy Dissipation Combustion Model, in which the calculation of the reaction rate is only based on mean quantities successfully, can describe the turbulence-chemistry interaction. The presumed pdf analysis showed that the reason for this is that in order to achieve a high flame temperature, where the reactions proceed at a high rate, the fuel and the air should be well mixed. The same study also revealed that in the CO/H₂/N₂–air flame case the use of mean quantities in the modeling of the
reaction kinetics is not correct because in this case the reaction rate is significant also in the case when the mixture fraction variance is large.

As such, the two versions of the Eddy Dissipation Combustion Model, i.e., the version for fast chemistry, and for finite rate chemistry, are much more different from each other than they first may occur. The fast chemistry version is based on the assumption that the effective reaction rate is limited by turbulent mixing. Then, the Eddy Dissipation Combustion Model is suitable for modeling flames with a low turbulence level. However, if the finite rate chemistry version of the model is used, the reaction kinetic rates are relying only on mean values of the quantities needed for the rate expressions. In this version, the model is not at all suitable for flames with a low turbulence level. It is here required that the turbulence intensity is that high that the conditions locally resemble those in a perfectly stirred reactor.

Based on the results of the presumed pdf analysis, a modified version of the Eddy Dissipation Combustion Model has also been presented. This model should be capable of successfully modeling many types of fuel. Nevertheless, this model will suffer from the drawback associated with the use of the mixture fraction concept.
10. Discussion

10.1 Steady state reactor studies

The comparison of the predictions with the available simplified mechanisms with those of the comprehensive one shows that the chemistry of the main components can be described with a four-step mechanism under a broad range of conditions. Evidently, there are differences in the predictions with the two mechanisms, but keeping in mind that the simplified mechanism only consists of four global reactions whereas in the comprehensive mechanism the hydrocarbon chemistry is described with 156 elementary reactions, the situation is satisfactorily. Generally, the four-step mechanism of Jones and Lindstedt (1988) is slightly faster than the comprehensive one.

On the nitrogen chemistry side the situation is less satisfactory. Here, there exist a number of simplified mechanisms, but most of them are restricted to the description of a few reaction paths, e.g., the oxidation of NH$_3$ or HCN to NO at oxidizing conditions. One problem with the nitrogen chemistry mechanisms is that they require that the concentrations of the main components are correct. Although it was found that the four-step mechanism of Jones and Lindstedt (1988) could be used to model the main chemistry, the combination of a reaction mechanism for the main chemistry with a simplified mechanism for the nitrogen chemistry does not lead to a satisfying situation. In this work, a problem that was encountered was the main chemistry consumed most of the oxygen before the oxidation of the nitrogen containing species started. The mechanism of Mitchell and Tarbell (1982) is an exception since they used a simplified reaction mechanism for the main chemistry as they determined the reaction rates for the nitrogen chemistry. However, their main chemistry in the gas phase is not as advanced as that proposed by Jones and Lindstedt. Although the mechanism proposed by Mitchell and Tarbell for the gas phase nitrogen chemistry is reasonably complex, certain problems with the mechanism were found in the investigations conducted in this work. One severe shortcoming of this mechanism was its inability to predict the conversion of HCN from NH$_3$ at the studied conditions. The reason for this inability is probably that with this mechanism, HCN can only be formed from NH$_3$ via NO. For NO to be formed, oxidizing
conditions are needed. To convert the NO further to HCN, hydrocarbon is needed. However, at the conditions modeled in this work the hydrocarbon was oxidized to CO and H₂ as the NH₃ was oxidized to NO. In conclusion, there is a big need for the development of a “comprehensive” simplified reaction scheme where not only the main chemistry is described but also the nitrogen chemistry. The development of such a scheme is not an easy task, but it should be undertaken.

10.2 Transient reactor studies

In the investigation of the chemistry, a transient perfectly stirred reactor was modeled. Using such a simple system it was easy to have full control over the conditions even though the transient perfectly stirred reactor allowed for fluctuations. Here, only the temperature was allowed to fluctuate. In a turbulent reacting flow, other quantities fluctuate as well, but temperature fluctuations are probably among the most important ones because of the exponential temperature dependence of the reaction rates. The transient perfectly stirred reactor study with the fluctuating temperature showed that the concentrations of the main components were relatively insensitive to the temperature fluctuations. The concentrations of the most important radicals, on the other hand, were extremely sensitive to the temperature fluctuations. This sensitivity to fluctuations suggests that it is likely that a turbulence-chemistry interaction model that does not take fluctuation into account still can predict the behavior of the main components in a satisfying way. As expected, the chemistry of the nitrogen containing species was sensitive to the temperature fluctuations. However, here several remarkable differences compared with the behavior of the most important radicals were found. The oscillations in the concentrations of the most important radicals very quickly became periodical, whereas the oscillations in the nitrogen containing species very slowly became periodical. As it is well known that the thermal-NO formation is highly temperature dependent, the increased formation of NO at fuel lean conditions with a fluctuating temperature compared with the case when the perfectly stirred reactor was held at steady state was no surprise. More surprising was the finding that at fuel rich conditions the conversion of fuel-N, here NH₃, to N₂ was efficient when the temperature was fluctuating. In the steady state case, large amounts of NH₃ and HCN could be found. This suggests that not only the
Discussion

modeling of thermal-NO requires that fluctuations are accounted for, but the rest of the nitrogen chemistry should be treated in a similar way. The perfectly stirred reactor study with the fluctuating temperatures also showed that the way the fluctuations occur is of considerable importance. The implication of this finding is that it is not enough to use a simple pdf approach to account for these effects.

10.3 Studies of the Eddy Dissipation Concept

In the investigation of the effect of the description of the chemistry on the quality of predictions with the Eddy Dissipation Concept, problems were encountered with the comprehensive reaction mechanism. The reason was an overestimation of the extinction effects in the vicinity of the burner. In the literature, several slightly different versions of the Eddy Dissipation Concept can be found. The lack of a generally accepted version of the model suggests that it on beforehand may be difficult to estimate the quality of the predictions obtained in the modeling.

Another important issue when using a comprehensive mechanism with the Eddy Dissipation Concept is how to treat the radicals. The transient perfectly stirred reactor calculations showed that the radicals are much more sensitive to fluctuations in temperature than the main species. The Eddy Dissipation Concept is not detailed enough to properly model these fluctuations. On the other hand, the finding in the transient perfectly stirred reactor study that the main radicals almost immediately follow the main components suggests that the way the radicals are treated is not of extreme importance. Consequently, less than expected may be gained by including radicals in the calculations. However, this brings up the need for a “comprehensive” simplified mechanism, since at present, the comprehensive mechanisms, consisting of numerous elementary reactions, are the only alternative when a reasonable description of the nitrogen chemistry is required. One exception from this is the chemistry describing the thermal-NO path, which successfully can be described with a global mechanism.

In the study of the mixing time associated with the reacting part in the Eddy Dissipation Concept, it was found that accurate predictions could be obtained
when a turbulent mixing time scale longer than the Kolmogorov time scale was used. Since the name of the model stems from the derivation following the dissipative process, which led to the Kolmogorov related time scale, the use of another time scale would call for a revision of the model name as well. Although a Kolmogorov related time scale is used in the Eddy Dissipation Concept to account for the micro scale interactions between turbulence and chemistry, molecular diffusion does not influence the reacting structures. On the other hand, according to the Borghi-diagram, the Kolmogorov time scale is associated with the flamelet regime. In this combustion regime, molecular diffusion is of great importance for the local conditions. In addition, the use of the Kolmogorov related time scale in the Eddy Dissipation Concept leads to a situation where local extinction is likely to be predicted as soon as combustion takes place outside the flamelet regime. Nevertheless, it should be kept in mind that when the Eddy Dissipation Concept was first presented, the chemistry was described using the fast chemistry approach. Using the fast chemistry assumption, the Eddy Dissipation Concept reduces to an eddy break-up model, much similar to the Eddy Dissipation Combustion Model. In this case, the Kolmogorov related time scale of the fine structure, obtained through the analysis of the dissipative process is only of importance for establishing the mean reaction rate and not the reaction rate in the fine structures.

The flame in the case used to investigation of the mixing time in the Eddy Dissipation Concept is similar to that in the test case used in the study of the Eddy Dissipation Combustion Model. The conclusion from that study was that the fluctuating temperature is of less importance in hydrocarbon flames since a temperature, high enough for the combustion to occur can only be obtained if the fuel and the air are well mixed. In the test cases, where the flame is not swirled, this occurs some distance down stream from the fuel and the air inlets. A separate extinction model, which the present study also relies on, has been used with the Eddy Dissipation Concept by several authors to improve the results of the modeling, i.e., to get the flame in the right place. If the investigation in this thesis points in the right direction, this extinction model is in fact accounting for that large variance in the flow composition cannot be allowed for if hydrocarbons are going to combust. The extinction model does not rely on an analysis of the
“mixedness” of the fluid for this, but includes a chemical time scale that is so short that it can only be reached in well mixed regions.

In this thesis, the model combining the structure of the Eddy Dissipation Concept with Karlsson’s and Chomiak’s suggestions on how to estimate the mixing time and the reacting fraction (Karlsson and Chomiak 1995, Karlsson 1995), still needs development. There are, however, several features in this model that makes it attractive, in particular the fact that the reacting fraction depends on both the chemistry and on the turbulence in a clear and logical way. Nevertheless, a clear way of estimating a representative time scale of the chemistry is especially needed. This problem is probably not easy to solve since there exist a variety chemistry time scales in combustion. The model also needs to be applied to several other test cases, since the CO/H₂/N₂-jet flame seems to require a turbulence-chemistry interaction model that accounts for temperature fluctuations before it can be properly modeled. This also points to the weakness this combined model shares with the Eddy Dissipation Concept.

10.4 Studies of the Eddy Dissipation Combustion Model

The Eddy Dissipation Combustion Model combined with a multi-step reaction mechanism proved to be a good model for the main chemistry in the tested hydrocarbon flames. In the CO/H₂/N₂-jet flame case, on the contrary, better agreement was predicted with the fast chemistry model. As the Eddy Dissipation Concept, the Eddy Dissipation Combustion Model was developed assuming fast chemistry. When introducing the Eddy Dissipation Concept, the possibilities to include a complex description of the chemistry were already pointed out. In the Eddy Dissipation Combustion Model, on the other hand, the modification of the model required to account for finite rate chemistry was introduced at a later stage. When using a multi-step reaction mechanism with the Eddy Dissipation Combustion Model, certain peculiarities may occur. First, some of the reactions may be mixing limited whereas other reactions are kinetically limited. In some cases this is probably not far from the real situation, but if the same radical pool is shared, it should probably be the mixing of only one of the reactants that is limiting. Second, an even more peculiar situation occurs when reversible
reactions are included in the reaction mechanism. The backward rates can principally be handled in two ways. The most straightforward approach is to treat the backward reaction as a separate one. However, in this case, the backward rate may become mixing limited, which is not reasonable since the reactants involved in it are already mixed. One way to overcome this problem is to use an effective reaction rate to represent the forward and the backward reaction rates. As long as the forward reaction rate is larger than the backward rate the "reactants" are reactants, but as soon as the backward rate becomes larger than the forward rate the "products" become reactants. In this way it is partly taken into account that the products are present where the reaction occurs. However, with this implementation too, a situation can occur where the backward rate is modeled as mixing limited. When species being reactants in a backward reaction are also present in the fuel or air stream, the situation is even less clear, since now the possibility arises that at certain locations of the combustion device this backward reaction indeed should be mixing limited. In the Eddy Dissipation Concept, the situation is less confusing, because of the use of the perfectly stirred reactor concept.

In both the Eddy Dissipation Concept and the Eddy Dissipation Combustion Model fluctuations are not accounted for. The Eddy Dissipation Concept tries to account for non-uniformities by separating between a reacting and a non-reacting part, but this is still an enormous simplification of the fluctuations in a turbulent reacting flow. The analysis presented in this thesis, using a pdf for the temperature based on the mixture fraction and the mixture fraction variance, indicates that in hydrocarbon flames it is important that the fuel and the air are well mixed before the fuel oxidation reactions can occur. This in turn indicates that the use of mean quantities when evaluating the kinetically controlled reaction rate can be motivated in such flames. Although in the fast chemistry versions, the Eddy Dissipation Concept and the Eddy Dissipation Combustion Model are almost identical, there are differences in these models which result in that the findings of the presumed pdf analysis is only applicable to the Eddy Dissipation Combustion Model. With the Eddy Dissipation Combustion Model, a high turbulence intensity implies that the conditions locally resemble those of a perfectly stirred reactor. In the Eddy Dissipation Concept, on the other hand, the
reacting fraction becomes smaller as the turbulence mixing becomes more intense. This decrease of the reacting fraction is at the same time followed by a higher exchange rate between the reacting fraction and the non-reacting fraction of the fluid, which makes the fluid locally uniform. However, the residence time in the reacting fraction also becomes shorter, which easily leads to the prediction of local extinction. In the new model combining the structure of the Eddy Dissipation Concept with the findings of Karlsson and Chomiak, the situation resembles more that in the Eddy Dissipation Combustion Model. In the new combined model, the fraction of the fluid where reactions occur becomes larger as the turbulence intensity increases.

Based on the findings from the pdf analysis of the reaction rates, a modification of the Eddy Dissipation Combustion Model, where the kinetically controlled term is evaluated using a reaction rate obtained taking the pdf of the mixture into account, has been suggested. This model should be able to use a multi-step reaction mechanism both in the modeling of the hydrocarbon flames as well as in the modeling of the CO/H₂/N₂-jet flame. The version of this model outlined in this thesis is only preliminary, and further investigations are required to solve certain problems associated with it. The probably most difficult one is to find a connection between the mean temperature predicted by the pdf and the mean temperature in the CFD simulations. This connection will be particularly difficult to establish in situations where heat transfer by radiation is important. The use of a presumed pdf results in that the combined Eddy Dissipation Combustion/PDF Model suffers from the same limitations as other presumed pdf models, i.e., only one type of fuel and air streams is allowed. On the other hand, the model will not only be applicable to a larger set of applications, it should also be able to model processes where temperature fluctuations are of a great importance, e.g., processes where the NO formation is significant.
11. Conclusions

In this thesis, seven tasks have been completed. This contributes to understanding of models suitable for CFD modeling of practical combustion devices such as boilers and furnaces with a finite rate description of the chemistry.

- Available simplified reaction mechanisms have been investigated by comparing predictions obtained with these models with those obtained with a comprehensive mechanism. It was found that the main chemistry could reasonably well be described with a four-step mechanism. However, none of the investigated simplified mechanisms for nitrogen chemistry was adequate.

- The comprehensive mechanism has been used to investigate the influence of temperature fluctuations on the main chemistry, on the most important radicals, and on the nitrogen containing species. It was found that although the main chemistry was not particularly sensitive to temperature fluctuations, the concentrations of the most important radicals were. For the nitrogen chemistry part, the temperature fluctuations had not only a large influence on the thermal-NO formation, as expected, but also on the conversion of NH$_3$ at fuel rich conditions.

- The influence of the way the chemistry is described on the predictions with the Eddy Dissipation Concept has been investigated. It was found that the features of the chemical reaction mechanism could be identified in the predictions. When using a comprehensive reaction mechanism, the predictions became poor due to an overestimation of the extinction effects.

- The time scale associated with the mixing in the reacting part of the Eddy Dissipation Concept has been investigated. It was found that the Kolmogorov related time scale used in the modeling of the reacting part of the fluid probably is too short, and that a time scale related to the eddy break-up rate could provide better agreement.
Conclusions

- A new turbulence-chemistry interaction model combining the structure of the Eddy Dissipation Concept with ideas put forth by Karlsson and Chomiak has been suggested and tested. Compared to the standard Eddy Dissipation Concept, the chemistry has a more important role when calculating the state of the reacting fluid. However, the test case used for this model would probably require a turbulence-chemistry interaction model that accounts for temperature fluctuations in a more detailed way. This model still needs further evaluation.

- Situations where the finite rate chemistry version of the Eddy Dissipation Combustion Model can be used have been identified and a theoretical explanation for the reasons for this has been put forth. It was found that the most probable reason for the good predictions of the main species in the hydrocarbon flame obtained using the Eddy Dissipation Combustion Model, although the reaction rates are evaluated using mean quantities in this model, was that in a hydrocarbon flame the fuel and the air need to be well mixed before a sufficiently high temperature can be reached. In the CO/H₂/N₂-air jet flame case, reaction could occur in a broad range of stoichiometry, which led to that the Eddy Dissipation Combustion Model with a finite rate chemistry failed.

- A new version of the finite rate Eddy Dissipation Combustion Model that uses a presumed pdf approach in the evaluation of the mean kinetic reaction rate has been outlined. This model uses a mixture fraction–mixture fraction variance based presumed pdf to evaluate the effect of the fluctuations on the kinetically controlled reaction rate, which is one of the terms in the Eddy Dissipation Combustion Model.
12. Literature


Literature


162
Kilpinen, P., Aho, M., Seetula, J., and Hupa, M., 1994. Gas Phase Chemistry of NO\textsubscript{x} and N\textsubscript{2}O at Pressurized Combustion Conditions between Temperatures 700 and 1000\degree C, In 6\textsuperscript{th} International Workshop on Nitrous Oxide Emissions, pp. 333-344, Åbo Akademi University Report 94-10, Turku, Finland.


Literature


Literature


Appendix A: Hydrocarbon chemistry mechanism

\( k = A T^b \exp(-E/RT) \)

**REACTIONS CONSIDERED**

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168
### Appendix A: Hydrocarbon chemistry mechanism

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Low pressure limit: 0.800E+27 -0.30E+01 0.000E+00

169
### Appendix A: Hydrocarbon chemistry mechanism

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### Appendix A: Hydrocarbon chemistry mechanism

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**Appendix A: Hydrocarbon chemistry mechanism**

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<th>Reaction</th>
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<th>Preexponential Factor</th>
<th>TROE Centering</th>
<th>Low Pressure Limit</th>
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<tr>
<td>C + OH = CO + H</td>
<td>5.00E+13</td>
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<td>0.3200E+42 -0.7030E+01 0.27620E+04</td>
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<td>C + O2 = CO + O</td>
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<td><strong>CO2</strong> Enhanced by 3.000E+00</td>
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<td><strong>H2O</strong> Enhanced by 5.000E+00</td>
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### Appendix A: Hydrocarbon chemistry mechanism

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<th>Rate Constant</th>
<th>Preexponential Factor</th>
<th>Pressure Limit</th>
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<td>C2H2+O=HCCO+H</td>
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Low pressure limit: 0.3600E+16 0.0000E+00 0.5927E+05

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<td>C3H3+H=CH3H2+H2</td>
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<td>C3H3+OH=CH3H2+H2O</td>
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**Appendix B: Nitrogen chemistry mechanism**

\( k = A T^b \exp(-E/RT) \)

**REACTIONS CONSIDERED**

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<th>b</th>
<th>E</th>
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<td>CN+H2=HCN+H</td>
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<td>HCN+O=NCO+H</td>
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<tr>
<td>HCN+O=CN+OH</td>
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<tr>
<td>HCN+O=NH+CO</td>
<td>3.50E+03</td>
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<tr>
<td>CN+H2O=HCN+OH</td>
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<tr>
<td>HCN+OH=HOCN+H</td>
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<td>HCN+OH=HNCO+H</td>
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<tr>
<td>HCN+OH=NH2+CO</td>
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<td>C2N2+O=CN+NCO</td>
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<td>C2N2+OH=CN+HOCN</td>
<td>1.90E+11</td>
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</tr>
<tr>
<td>NCN+H=HCN+N</td>
<td>1.00E+14</td>
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<tr>
<td>NCN+O=CN+NO</td>
<td>1.00E+14</td>
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<td>0</td>
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<tr>
<td>NCN+OH=HCN+NO</td>
<td>5.00E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCN+O2=NO+NCO</td>
<td>1.00E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CN+O=CO+N</td>
<td>7.70E+13</td>
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<td>0</td>
</tr>
<tr>
<td>CN+OH=NCO+H</td>
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<td>0</td>
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<tr>
<td>CN+O2=NCO+O</td>
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<td>CN+CO2=NCO+CO</td>
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<td>CN+NO=NCN+N</td>
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<td>CN+NO2=NCO+NO</td>
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<td>CN+HNO=HCN+NO</td>
<td>1.80E+13</td>
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<tr>
<td>CN+HONO=HCN+NO2</td>
<td>1.20E+13</td>
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<td>0</td>
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<tr>
<td>CN+N2O=NCN+NO</td>
<td>3.80E+03</td>
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<td>HOCN+H=HNCO+H</td>
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<td>HOCN+OH=NCO+H2O</td>
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<td>HOCN+O=NCO+OH</td>
<td>1.50E+04</td>
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<td>HNCO+M=CO+NH</td>
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</table>

\( \text{N2} \) Enhanced by \( 1.500E+00 \)
Appendix B: Nitrogen chemistry mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Quantum Yield</th>
<th>Limiting Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNCO + H = NH2 + CO</td>
<td>2.20E+07</td>
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<td>HNCO + O = NCO + OH</td>
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<td>HNCO + O = NH + CO2</td>
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<td>HNCO + O = HNO + CO</td>
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<td>44012</td>
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<td>HNCO + OH = NCO + H2O</td>
<td>6.40E+05</td>
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<td>2560</td>
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<tr>
<td>HNCO + HO2 = NCO + H2O2</td>
<td>3.00E+11</td>
<td>0</td>
<td>29000</td>
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<tr>
<td>HNCO + NH2 = NH3 + NCO</td>
<td>5.00E+12</td>
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<td>6200</td>
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<tr>
<td>HNCO + NH = NH2 + NCO</td>
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<tr>
<td>HNCO + NO2 = HNNO + CO2</td>
<td>2.50E+12</td>
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<td>26200</td>
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<tr>
<td>HNCO + CN = HCN + NCO</td>
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<td>0</td>
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<td>NCO + M = N + CO + M</td>
<td>3.10E+16</td>
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</table>

N2 Enhanced by 1.500E+00

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Quantum Yield</th>
<th>Limiting Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCO + H = CO + NH</td>
<td>5.00E+13</td>
<td>0</td>
<td>0</td>
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<tr>
<td>NCO + O = NO + CO</td>
<td>4.70E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCO + H2 = HNCO + H</td>
<td>7.60E+02</td>
<td>3</td>
<td>4000</td>
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<tr>
<td>NCO + OH = HCO + NO</td>
<td>5.00E+12</td>
<td>0</td>
<td>15000</td>
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<tr>
<td>NCO + O2 = NO + CO2</td>
<td>2.00E+12</td>
<td>0</td>
<td>20000</td>
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<tr>
<td>NCO + HCO = HNCO + CO</td>
<td>3.60E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCO + CH2O = HNCO + HCO</td>
<td>5.00E+12</td>
<td>0</td>
<td>0</td>
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<tr>
<td>NCO + N = N2 + CO</td>
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<td>0</td>
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<tr>
<td>NCO + NO = N2O + CO</td>
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<td>-1.7</td>
<td>763</td>
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<tr>
<td>NCO + NO = N2 + CO2</td>
<td>7.80E+17</td>
<td>-1.7</td>
<td>763</td>
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<td>NCO + NO2 = CO + NO + NO</td>
<td>1.30E+13</td>
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<td>0</td>
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<tr>
<td>NCO + NO2 = CO2 + N2O</td>
<td>5.40E+12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCO + HNO = HNCO + NO</td>
<td>1.80E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCO + HONO = HNCO + NO2</td>
<td>3.60E+12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCO + NCO = CO + CO + N2</td>
<td>1.80E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NCO + CN = NCN + CO</td>
<td>1.80E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH3 (+M) = NH2 + H (+M)</td>
<td>5.50E+15</td>
<td>0</td>
<td>107731</td>
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Low pressure limit: 0.2200E+17 0.0000E+00 0.93470E+05

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<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Quantum Yield</th>
<th>Limiting Temperature</th>
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</thead>
<tbody>
<tr>
<td>NH3 + H = NH2 + H2</td>
<td>6.40E+05</td>
<td>2.4</td>
<td>10171</td>
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<td>NH3 + O = NH2 + OH</td>
<td>9.40E+06</td>
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<td>6460</td>
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<tr>
<td>NH3 + OH = NH2 + H2O</td>
<td>2.00E+06</td>
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<td>566</td>
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<tr>
<td>NH3 + HO2 = NH2 + H2O2</td>
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<td>0</td>
<td>22000</td>
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</table>
### Appendix B: Nitrogen chemistry mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Energy (kcal/mol)</th>
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<tbody>
<tr>
<td>NH₂+H=NH+H₂</td>
<td>4.00E+13</td>
<td>0</td>
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<tr>
<td>NH₂+O=HNO+H</td>
<td>6.60E+14</td>
<td>-0.5</td>
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<tr>
<td>NH₂+O=NH+OH</td>
<td>6.80E+12</td>
<td>0</td>
</tr>
<tr>
<td>NH₂+OH=NH+H₂O</td>
<td>4.00E+06</td>
<td>2</td>
</tr>
<tr>
<td>NH₂+HO₂=H₂NO+OH</td>
<td>2.50E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH₂+HO₂=NH₃+O₂</td>
<td>1.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>H₂NO+O=NH₂+O₂</td>
<td>4.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH₂+NH₂=N₂H₂+H₂</td>
<td>8.50E+11</td>
<td>0</td>
</tr>
<tr>
<td>NH₂+NH₂=NH₃+NH</td>
<td>5.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH₂+NH=N₂H₂+H</td>
<td>5.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH₂+N=N₂+2H</td>
<td>7.20E+13</td>
<td>0</td>
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<tr>
<td>NH₂+NO=NNH+OH</td>
<td>2.80E+13</td>
<td>-0.6</td>
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<tr>
<td>NH₂+NO=N₂+H₂O</td>
<td>1.30E+16</td>
<td>-1.3</td>
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</table>

Declared duplicate reaction...

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Energy (kcal/mol)</th>
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<tbody>
<tr>
<td>NH₂+NO=NH₂+H₂O</td>
<td>-2.80E+13</td>
<td>-0.6</td>
</tr>
<tr>
<td>NH₂+NO₂=N₂O+H₂O</td>
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<td>-2.2</td>
</tr>
<tr>
<td>NH+H=N+H₂</td>
<td>3.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH+O=NO+H</td>
<td>9.20E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH+OH=HNO+H</td>
<td>2.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH+OH=NN+H₂O</td>
<td>5.00E+11</td>
<td>0.5</td>
</tr>
<tr>
<td>NH+O₂=HNO+O</td>
<td>4.60E+05</td>
<td>2</td>
</tr>
<tr>
<td>NH+O₂=NO+OH</td>
<td>1.30E+06</td>
<td>1.5</td>
</tr>
<tr>
<td>NH+N=N₂+H</td>
<td>3.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>NH+NH=N₂+2H</td>
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<td>0</td>
</tr>
<tr>
<td>NH+NO=N₂O+H</td>
<td>2.90E+14</td>
<td>-0.4</td>
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Declared duplicate reaction...

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Energy (kcal/mol)</th>
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</thead>
<tbody>
<tr>
<td>NH+NO=N₂+OH</td>
<td>-2.20E+13</td>
<td>-0.2</td>
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Declared duplicate reaction...

<table>
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<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Energy (kcal/mol)</th>
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</thead>
<tbody>
<tr>
<td>NH+NO=N₂+OH</td>
<td>2.20E+13</td>
<td>-0.2</td>
</tr>
<tr>
<td>NH+NO₂=N₂O+OH</td>
<td>1.00E+13</td>
<td>0</td>
</tr>
<tr>
<td>N+OH=NO+H</td>
<td>3.80E+13</td>
<td>0</td>
</tr>
<tr>
<td>N+O₂=NO+O</td>
<td>6.40E+09</td>
<td>1</td>
</tr>
<tr>
<td>N+NO=N₂+O</td>
<td>3.30E+12</td>
<td>0.3</td>
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</table>

176
## Appendix B: Nitrogen chemistry mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate 1</th>
<th>Rate 2</th>
<th>Rate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>N + CO(_2) = NO + CO</td>
<td>1.90E+11</td>
<td>0</td>
<td>3400</td>
</tr>
<tr>
<td>NO + OH((+\text{M})) = HONO((+\text{M}))</td>
<td>2.00E+12</td>
<td>-0.1</td>
<td>-721</td>
</tr>
</tbody>
</table>

- **Low pressure limit:** 0.5000E+24 -0.2510E+01 -0.6800E+02

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate 1</th>
<th>Rate 2</th>
<th>Rate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2) Enhanced by</td>
<td>1.000E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)O Enhanced by</td>
<td>5.000E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO + HO(_2) = NO(_2) + OH</td>
<td>2.10E+12</td>
<td>0</td>
<td>-480</td>
</tr>
<tr>
<td>HCO + NO = CO + HNO</td>
<td>7.20E+12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO(_2)((+\text{M})) = NO + O((+\text{M}))</td>
<td>1.40E+14</td>
<td>0</td>
<td>70950</td>
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</table>

- **Low pressure limit:** 0.1100E+17 0.0000E+00 0.6600E+05

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate 1</th>
<th>Rate 2</th>
<th>Rate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_2)+H = NO + OH</td>
<td>3.50E+14</td>
<td>0</td>
<td>1500</td>
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<tr>
<td>NO(_2)+O = NO + O2</td>
<td>1.00E+13</td>
<td>0</td>
<td>600</td>
</tr>
<tr>
<td>NO(_2)+NO(_2) = NO + NO + O(_2)</td>
<td>1.60E+12</td>
<td>0</td>
<td>26123</td>
</tr>
<tr>
<td>CO + NO(_2) = CO(_2) + NO</td>
<td>9.00E+13</td>
<td>0</td>
<td>33800</td>
</tr>
<tr>
<td>HCO + NO(_2) = CO + HONO</td>
<td>2.10E+00</td>
<td>3.3</td>
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<tr>
<td>HCO + NO(_2) = H + CO(_2) + NO</td>
<td>8.40E+15</td>
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<tr>
<td>NO(_3) = NO + O2</td>
<td>2.50E+06</td>
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<td>12000</td>
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<tr>
<td>NO(_3)+H = NO(_2) + OH</td>
<td>6.00E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO(_3)+O = NO(_2) + O(_2)</td>
<td>1.00E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO(_3)+OH = NO(_2) + HO(_2)</td>
<td>1.40E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO(_3)+HO(_2) = NO(_2) + O(_2) + OH</td>
<td>1.40E+12</td>
<td>0</td>
<td>-338</td>
</tr>
<tr>
<td>NO(_3)+NO(_2) = NO + NO(_2) + O(_2)</td>
<td>1.90E+05</td>
<td>1.6</td>
<td>2047</td>
</tr>
<tr>
<td>NO(_3)+NO(_3) = NO(_2) + NO(_2) + O(_2)</td>
<td>5.10E+11</td>
<td>0</td>
<td>6750</td>
</tr>
<tr>
<td>HNO((+\text{M})) = H + NO((+\text{M}))</td>
<td>1.20E+16</td>
<td>-0.4</td>
<td>49490</td>
</tr>
</tbody>
</table>

- **Low pressure limit:** 0.1500E+17 0.0000E+00 0.4868E+05

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate 1</th>
<th>Rate 2</th>
<th>Rate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O Enhanced by</td>
<td>1.000E+01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_2) Enhanced by</td>
<td>2.000E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(_2) Enhanced by</td>
<td>2.000E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2) Enhanced by</td>
<td>2.000E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO + H = NO + H(_2)</td>
<td>4.40E+11</td>
<td>0.7</td>
<td>650</td>
</tr>
<tr>
<td>HNO + O = NO + OH</td>
<td>1.00E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HNO + OH = NO + H(_2)O</td>
<td>3.60E+13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HNO + O(_2) = NO + HO(_2)</td>
<td>1.00E+13</td>
<td>0</td>
<td>25000</td>
</tr>
<tr>
<td>HNO + NH(_2) = NO + NH(_3)</td>
<td>2.00E+13</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>HNO + NO = N(_2)O + OH</td>
<td>2.00E+12</td>
<td>0</td>
<td>26000</td>
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</tbody>
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177
### Appendix B: Nitrogen chemistry mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponential Factor</th>
<th>Temperature (K)</th>
</tr>
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<tbody>
<tr>
<td>HNO+NO₂=HONO+NO</td>
<td>6.00E+11</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td>HNO+HNO=N₂O+H₂O</td>
<td>4.00E+12</td>
<td>0</td>
<td>5000</td>
</tr>
<tr>
<td>HCO+HNO=NO+CH₂O</td>
<td>6.00E+11</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td>H₂NO+M=HNO+H+M</td>
<td>5.00E+16</td>
<td>0</td>
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<td>H₂NO+H=HNO+H₂</td>
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<td>H₂NO+H=NH₂+OH</td>
<td>5.00E+13</td>
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<tr>
<td>H₂NO+O=HNO+OH</td>
<td>3.00E+07</td>
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<tr>
<td>HONO+H=NO₂+H₂</td>
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<td>HONO+O=NO₂+OH</td>
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<td>HONO+OH=NO₂+H₂O</td>
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<tr>
<td>HCO+HONO=NO₂+CH₂O</td>
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<td>N₂H₂+M=NNH+H+M</td>
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Enhanced by:

- H₂O: 1.500E+01
- H₂: 2.00E+00
- N₂: 2.000E+00
- O₂: 2.000E+00

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponential Factor</th>
<th>Temperature (K)</th>
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<tbody>
<tr>
<td>N₂H₂+H=NNH+H₂</td>
<td>5.00E+13</td>
<td>0</td>
<td>1000</td>
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<tr>
<td>N₂H₂+O=NH₂+NO</td>
<td>1.00E+13</td>
<td>0</td>
<td>1000</td>
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<tr>
<td>N₂H₂+O=NNH+OH</td>
<td>2.00E+13</td>
<td>0</td>
<td>1000</td>
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<tr>
<td>N₂H₂+OH=NNH+H₂O</td>
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<tr>
<td>N₂H₂+NH=NNH+NH₂</td>
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<td>1000</td>
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<tr>
<td>N₂H₂+NH₂=NNH+NH₃</td>
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<tr>
<td>N₂H₂+NO=NN₂+NH₂</td>
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<td>NNH=N₂+H</td>
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<td>NNH+H=N₂+H₂</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>NNH+NH=N₂+NH₂</td>
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<td>0</td>
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<tr>
<td>NNH+NH₂=N₂+NH₃</td>
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<td>0</td>
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<tr>
<td>NNH+NO=N₂+HNO</td>
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<td>HNNO+M=N₂O+H+M</td>
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</table>
## Appendix B: Nitrogen chemistry mechanism

<table>
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<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponential Factor</th>
<th>Preexponential Factor</th>
</tr>
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<tbody>
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<td>HNNO+M=N2+OH+M</td>
<td>1.00E+15</td>
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<td>HNNO+H=N2O+H2</td>
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<tr>
<td>HNNO+H=NNH+OH</td>
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<td>0</td>
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<tr>
<td>HNNO+O=N2O+OH</td>
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<td>0</td>
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<tr>
<td>HNNO+O=NNH+O2</td>
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<td>0</td>
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<tr>
<td>HNNO+OH=N2O+H2O</td>
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<tr>
<td>HNNO+OH=NNH+HO2</td>
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<td>0</td>
</tr>
<tr>
<td>HNNO+NO=N2O+HNO</td>
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<td>0</td>
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<tr>
<td>HNNO+NO=NNH+NO2</td>
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<td>270</td>
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<tr>
<td>HNNO+NO2=NNH+NO3</td>
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<td>0</td>
</tr>
<tr>
<td>HNNO+NO2=N2O+HONO</td>
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<td>0</td>
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<tr>
<td>N2O(+M)=N2+O(+M)</td>
<td>1.30E+11</td>
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Low pressure limit: 0.40000E+15 0.00000E+00 0.56100E+05

<table>
<thead>
<tr>
<th>Species</th>
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<tr>
<td>N2</td>
<td>1.700E+00</td>
</tr>
<tr>
<td>O2</td>
<td>1.400E+00</td>
</tr>
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<td>CO2</td>
<td>3.000E+00</td>
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<tr>
<td>H2O</td>
<td>1.200E+01</td>
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N2O+H=N2+OH 3.30E+10 0 4729

Declared duplicate reaction...

N2O+H=N2+OH 4.40E+14 0 19254

Declared duplicate reaction...

N2O+O=NO+NO 2.90E+13 0 23150
N2O+O=N2+O2 1.40E+12 0 10800
N2O+OH=N2+HO2 2.00E+12 0 40000
N2O+CO=N2+CO2 2.70E+11 0 20237
H2CN+M=HCN+H+M 3.00E+14 0 21857
CH3+N=H2CN+H 7.10E+13 0 0
CH3+NO=HCN+H2O 5.30E+11 0 14902
CH3+NO=H2CN+OH 5.30E+11 0 14902
CH2+N=HCN+H 5.00E+13 0 0
CH2+N2=HCN+NH 1.00E+13 0 73519
CH2+NO=NCO+H2 3.50E+12 0 -1093
HCNO+H=HCN+OH 1.00E+14 0 6000
CH2*+NO=HCN+OH 1.00E+14 0 0
### Appendix B: Nitrogen chemistry mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Preexponential Factor</th>
<th>Preexponential Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH+N=CN+H</td>
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<td>0</td>
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<td>CH+N2=HCN+N</td>
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<td>CH+NO=HCN+O</td>
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<td>0</td>
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<tr>
<td>CH+N2O=HCN+NO</td>
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<td>-994</td>
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<tr>
<td>C+N2=CN+N</td>
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<tr>
<td>C+NO=CN+O</td>
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<td>C+NO=CO+N</td>
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<tr>
<td>C2H3+N=HCN+CH2</td>
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<tr>
<td>HCCO+N=HCN+CO</td>
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<tr>
<td>C2H+NO=HCN+CO</td>
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<tr>
<td>C3H3+N=HCN+C2H2</td>
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</tr>
</tbody>
</table>
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