Jostein Kolbu

Study of a Homogeneous Charge Compression Ignition (HCCI) Combustion Process

HOVUDOPPGÅVE HAUST-VÅR 2000/01

I

VARME- OG FORBRENNINGSTEKNIKK

for stud.tech. Jostein Kolbu

Undersøking av prosess med kompresjonstenning av fullstendig forblanda
forbrenning (HCCI, "Homogeneous Charge Compression Ignition")

DIPLOMA WORK IN HEAT AND COMBUSTION TECHNOLOGY
FALL/SPRING 2000/01

Study of a Homogeneous Charge Compression Ignition (HCCI) Combustion Process

With the increasing need to both conserve fossil fuel and minimize toxic emissions,
much effort is being focused on the advancement of current combustion technology.
One such research topic emerging in combustion society is the concept of Homoge-
neous Charge Compression Ignition (HCCI). This process is often considered a hybrid
of the conventional spark plug ignited and the compression ignited processes. As in a
spark-ignited engine, the air-fuel mixture is homogeneous; however as in compression
ignited combustion the mixture is auto-ignited by compression heating.

HCCI combustion technology offers the possibility of having advantages of both Diesel
and gasoline engines, with high thermal efficiency, low oxides of nitrogen (NOx), and
low particulate concentration. The disadvantages of HCCI engines are numerous,
including high hydrocarbon and carbon monoxide emissions, high peak pressures,
high rates of heat release, reduced operating range, lower power density than a Diesel
engine, difficulty in starting the engine and difficulty in controlling combustion timing.
There is increasing hope that these advantages will be solved through various means
with the advancement of HCCI research. The key to practical implementation of
the HCCI concept in an engine is developing methods to control combustion timing.
Control methods should be designed to tune the heat release process to occur at the
appropriate time in the engine cycle. The Combustion Analysis Lab at University of
California at Berkeley is involved in substantial research on the HCCI concept.

The candidate will investigate numerically and experimentally the operation of the
HCCI engine to establish under which conditions this HCCI process can be run
smoothly. Numerical modeling will commence by using detailed chemistry simula-
tions of the combustion chamber with a previously established model consisting of
concentric spheres of Well-Mixed Reactors. After initial runs of the model, we will
combine the model with a genetic algorithm optimization scheme. The goal will be
to optimize the many parameters of the HCCI process, including engine speed, stoi-
chiometry, inlet temperature, min NOx, compression ratio etc. Furthermore, if time

allows, other compression cycles will be explored, including so called 'free pistons' and opposed pistons (on independent shafts). Experiments will be done on an existing engine. The Combustion Lab has two single cylinders and one four cylinder HCCI engine. Test availability will determine which engine is best. Model and experiments will be compared throughout the program.

Paper published in SAE intended.

Three weeks after the start of the working period the candidate should work out a progress plan for the thesis and discuss it with the supervisors.

The thesis should be formulated as a research report with a summary both in English and Norwegian, conclusion, literature reference, tables of contents etc. During preparation of the text, the candidate should make efforts to present a well arranged and well written report. In order to ease the evaluation of the thesis, it is important to cross reference the text, tables and figures. When evaluating the report, a thorough discussion of the results will be valued.

The candidate shall follow the rules and regulations of UC Berkeley, as well as possible directions given by his superiors. The candidate is not permitted to interfere in the running of production equipment, as all orders are to be passed through the regular channels of the university.

<div align="center">

Norwegian University of Science and Technology
Department of Applied Mechanics, Thermodynamics and Fluid Dynamics, 2000

Professor Helge I. Andersson
Head of Department

</div>

Supervisors at Berkeley:

 Robert W. Dibble, Professor (experimental)

 Jyh-Yuan Chen, Professor (numerical)

Supervisors at NTNU:

 Ivar S. Ertesvåg, Associate Professor

 Bjørn F. Magnussen, Professor

Summary

The concept of Homogeneous Charge Compression Ignition (HCCI) operation of internal combustion engines has been known for over twenty years. It promises high efficiency and low emissions, and is thus under increasing focus to reduce pollution in power generation and automobiles.

Genetic algorithms have been used for parameter optimization in many types of complex problems. Well-mixed reactor simulations of the HCCI concept have previously proved successful.

The integration of genetic algorithms with well-mixed reactor simulations are investigated as a possible approach for understanding HCCI combustion and solving the control issue for this type of engine operation. The effects of parameter variation on engine performance when using methane, propane and acetylene as fuels are shown. Data from earlier propane experiments are compared to simulation results. Experiments have been performed using acetylene, showing that use of acetylene results in earlier combustion but higher gross engine efficiency.

Performance of the well-mixed reactor and genetic algorithm setup seems to provide results that follow known trends. Parameter optimization using the genetic algorithm provides new insight to the properties of HCCI combustion and appears to be a viable tool for further analysis.

Sammendrag

Kompresjonstenning av fullstendig forblandet forbrenning (Homogeneous Charge Compression Ignition, HCCI) i forbrenningsmotorer har vært et kjent fenomen i over 20 år. HCCI kjennetegnes av høy effektivitet og lave utslipp, og er derfor i økende grad tenkt brukt til kraftgenerering og i biler.

Genetiske algoritmer har blitt brukt til å optimalisere mange typer av kompliserte problemer. Velblandet reaktorsimuleringer av HCCI konseptet har tidligere blitt utført med gode resultater.

Integrasjonen av genetiske algoritmer med velblandet reaktorsimuleringer er utforsket som en mulig måte til å øke forståelsen av HCCI forbrenning og til å løse kontrollproblemene for denne motortypen. Effekten av å variere motorens driftsparametre med metan, propan og acetylen som brensel er presentert. Data fra tidligere eksperimenter med propan er sammenlignet med simuleringsresultater. Eksperimenter er utført med acetylen. Resultatene fra disse viser at acetylen fører til tidligere antenning, men høy brutto motoreffektivitet.

Velblandet reaktorsimuleringer koblet med genetiske algoritmer ser ut til å gi resultater som er i samsvar med kjente trender. Bruk av genetiske algoritmer til å optimalisere motorparametre ser ut til å være et godt verktøy til bruk i videre analyse av HCCI-prosessen.

Preface

This Thesis marks the end of my studies at the Norwegian University of Science and Technology and my Master of Science degree. It has been performed in full at the Combustion Analysis Laboratory at the University of California at Berkeley from October 2000 until February 2001.

Jostein Kolbu

February 16, 2001

Contents

List of Symbols

This list contains most of the symbols and abbreviations used in the text. Some are defined in the text where they are used and are not presented here.

Equations are referenced by their equation number. Figures and tables are referenced by the text 'Figure' or 'Table' followed by its corresponding number.

Latin Letters

C_p	specific heat capacity, constant pressure [J/kg/K]
C_v	specific heat capacity, constant volume [J/kg/K]
$\mathcal{D}$	mass diffusivity [m^2/s]
$f_{k,i}$	body force on species k in direction i [N=kg $\cdot$ m/s^2]
h_k	static specific enthalpy of species k [J/kg=m^2/s^2]
h_c	heat transfer coefficient [W/m^2/K]
k_i	reaction rate coefficient of reaction i
m	mass [kg]
M_k	molecular weight of species k [kg/kmol]
n_k	number of moles of species k [kmol]
p	static pressure [Pa = N/m^2]
q	heat transfer [W/m^2]
$\bar{R}$	universal gas constant [kJ/kmol $\cdot$ K]
S_i	normalized sensitivity of reaction i
T	temperature [K]
t	time [s]
u_j	velocity component (Euler-) in x_j-direction [m/s]
V	volume [m^3]
w	work per unit mass [kJ/kg]
X_k	mole fraction of species k
Y_k	mass fraction of species k

Greek Letters

γ	specific heat ratio
λ	thermal conductivity [W/m/K]
ρ	density [kg/m^3]
σ_{ji}	total stress tensor [Pa=N/m^2]
τ_{ij}	viscous stress tensor [Pa=N/m^2]
ω_k	chemical production of species k [kmol/m^3/s]

Superscripts

—	mean value
$\dot{}$	time derivative
^{o}	at reference state, degrees

Subscripts

e	exit
f	fuel
i	inlet
i,j,k	index
k	species
$stoich.$	stoichiometric

Abbreviations

ATDC	After Top Dead Center
BTDC	Before Top Dead Center
CAD	Crank Angle Degrees
CI	Compression Ignition
EGR	Exhaust Gas Recirculation
FMEP	Frictional Mean Effective Pressure
GA	Genetic Algorithm
HC	Hydro Carbons
HCCI	Homogeneous Charge Compression Ignition
IMEP	Indicated Mean Effective Pressure
ODE	Ordinary Differential Equation
PMEP	Pumping Mean Effective Pressure
RPM	Revolutions Per Minute
SI	Spark Ignition
TDC	Top Dead Center
VVHS	Variable Volume High Step (see Section 6.2.3)
WMR	Well-Mixed Reactor

List of Figures

List of Tables

Chapter 1

Introduction

1.1 Thesis Introduction

The concept of Homogeneous Charge Compression Ignition (HCCI) has been known for over 20 years. It is an engine concept that results in high engine efficiency and very low emissions. The problems of NO_x and soot emissions are almost completely removed. High efficiency, especially at low loads, gives it a substantial advantage over the spark-ignition and compression-ignition engines.

It has, however, some drawbacks in the difficulty of controlling the combustion process. Much work has been invested in solving this problem, and much more must be done before a satisfying solution has been found.

Numerical simulations give valuable insight into how the HCCI engine operates. The many parameters of operation makes it difficult to find the impact of each parameter on the engine operation. A search tool that has previously been proved successful on multi-parameter problems are genetic algorithms. Using the power of genetic algorithms to help in the understanding of the HCCI process was the main objective of this Thesis.

1.2 Information Found in Literature

Numerous articles have been published on the subject of HCCI. Especially in the last few years there has been a noticeable increase in the number of publishings as interest in the subject has increased. Presented here are a few of the most relevant for this report.

– Aceves et al. (2000) use the KIVA code and the HCT multi-zone well-mixed reactor model and achieve very good results compared with experiments.

– Martinez-Frias et al. (1998) do multi-parameter optimization with Super Code with a single-zone well-mixed reactor model.

– Au et al. (2001) have performed experiments for the same engine used in this report.

– A number of articles have come from the Lund Institute of Technology in Sweden. Amneus et al. (1998) and Christensen et al. (1999) have both been important sources of information for this report.

– Many articles and books on genetic algorithms are available. De Jong et al. (1993) and the book by Goldberg (1989) have been very useful reading.

1.3 Acknowledgements

The genetic algorithm setup used was made by Dr. Ryoji Homma of Tokyo Gas, while being a visiting scholar at UC Berkeley. The multi-zone well-mixed-reactor code was made by Dr. Dale Andreatta (Andreatta, 1995). The single-zone well-mixed-reactor code was made by Professor Jyh-Yuan Chen. The VW 1.9 liter engine used was modified to run in HCCI mode and operated by Michael Y. Au.

Chapter 2

Framework

This chapter presents the framework and boundaries given by all involved parties in order to document the Thesis work.

2.1   Boundaries

The Norwegian University of Science and Technology (NTNU) requires that students doing their Master Thesis abroad present their work within six months. Usually this work starts in the fall semester of the fifth year of study and represents one full semester workload.

A program of study at Berkeley was approved by the department, and freedom was given to consult with Professor Dibble on current research projects in his lab. One of the presented options was Homogeneous Charge Compression Ignition (HCCI) research, on which a draft of the Thesis text was written and sent to NTNU for final adjustments. Professor Chen provided the opportunity to work with engine simulations using the genetic algorithm. He also provided computers to run the simulations. A paper was submitted to the Western States meeting of the Combustion Institute in March 2001.

After starting work on the project at the beginning of October a finishing date some time in February of 2001 was proposed. February 16 was set as the deadline after reviewing the project status after the Holiday break in December. This would give a total of four months of work on the project.

2.2   Thesis Objectives

The objective of the Thesis was learning more about the HCCI combustion process as a part of ongoing research at University of California, Berkeley. The use of computer models coupled with genetic algorithms was a new angle of approach that the research group wanted to explore.

2.3   How to Read this Report

Chapter 1 is a general introduction to the Thesis.

Chapter 2 presents the framework and boundaries for the Thesis work.

Chapter 3 is a short documentation of the work procedure.

Chapter 4 is a general overview of the theoretical background for this Thesis. The information found here is the foundation of the later chapters.

Chapter 5 provides a brief introduction to genetic algorithms.

Chapter 6 explains internal combustion engines and the HCCI engine in more detail, as well as presenting the computer model and the experimental setup used.

Chapter 7 presents the results found through computer simulations and experiments.

Chapter 8 presents the conclusions that are drawn from this work.

Chapter 9 lays out the work ahead to improve results as seen by the author.

Chapter 3

Work Procedure

The work procedure documented below will attempt to explain how the work was done and the problems encountered and adjustments made as the project advanced.

3.1 Theory

The first four weeks were spent acquiring and reading theory on internal combustion engines, HCCI operation and genetic algorithms. The different computer codes that were available were fairly complex and a lot of work was put into the understanding of their workings.

3.2 Practical Work

At the beginning of November work started in modifying the genetic algorithm code to work with the single well-mixed reactor model. Professor Chen had already written most of the well-mixed reactor model and integrated it into the genetic algorithm. Expanding the integration so that the code accepted more parameters and dumped more data was necessary. The integration of the multi-zone model with the genetic algorithm was much more troublesome since it was originally developed as a stand-alone code. There were also practical convergence problems with the equation solver for that code when using it in HCCI simulations. The general layout of the program was somewhat modified to accept integration with the genetic algorithm. The programming work was largely done by mid-December.

Running the simulations was very time consuming. The time needed to calculate a

full dataset (usually 1000 generations with a population of 5 meaning 5000 individual simulations) for the single-zone model was from 12 hours up to five days on the fastest server available (600 MHz alpha-processor with 128 Mb of RAM), depending on computer availability and engine parameters. Tuning heat transfer rates for the multi-shell code was fairly complicated since no good model exists. It was necessary to rerun the simulations several times for both models to achieve the desired results and accuracy.

Due to time limitations and equipment availability the investigation of other engine types was canceled.

Planning of the experimental part of the Thesis began in January. This work was dependent on other projects at the lab and the availability of the equipment. After some initial planning it was decided that the experimental work would consist of a preliminary study of HCCI combustion in a converted VW 1.9 liter Diesel engine using acetylene as fuel. It was desirable to investigate the effect of acetylene compared to dimethyl ether also used as an additive to gaseous fuel in the laboratory engines. The computer modeling results would be compared to the experimental results to further validate the accuracy of the model.

3.3   Analysis

Analyzing the data from the simulations was relatively tedious work. Each simulation run would dump several megabytes of text files which had to be visualized using a software called Tecplot. It was necessary to confirm the simulation results with previously published findings to validate the model.

3.4   Computer Tools

Typesetting for this report was done with LATEX2e. Final conversion from PostScript to Adobe Portable Document Format for printing was done with Adobe Distiller 4.0.

Graphs were made using Tecplot 7.0 for Windows. Illustrations were made with Xfig 3.2 running on Unix. All computer simulation codes were written in FORTRAN77 using the Emacs editor. Code compilation was done on alpha-processor computers using the DIGITAL FORTRAN77 compiler and i686 computers using the Linux FORT77 compiler.

Chapter 4

Theoretical Background

This is an overview of the basic equations that are the foundations of this Thesis. In the following chapter these equations are presented with the background and assumptions behind their use.

4.1 Continuity Relation

The local flow velocity u_k of a species k is composed of a mean flow velocity u and mean diffusion velocity U_k, $u_k = u + U_k$. This approach disregards the Soret effect and pressure diffusion in the modeling of diffusion effects as negligible (Warnatz, Maas & Dibble, 1999:49). Taking chemical reactions into account gives a source term in the continuity equation, which is given as (Warnatz, Maas & Dibble, 1999:155):

$$\frac{\partial \rho_k}{\partial t} + \frac{\partial}{\partial x_j}(\rho_k u_j) + \frac{\partial (J_{k,j}^D)}{\partial x_j} = M_k \omega_k \qquad (4.1)$$

where $J_k^D = \rho_k U_k$. Also, introducing $\rho_k = \rho Y_k$:

$$\frac{\partial}{\partial t}(\rho Y_k) + \frac{\partial}{\partial x_j}(\rho Y_k u_j) + \frac{\partial (J_{k,j}^D)}{\partial x_j} = M_k \omega_k \qquad (4.2)$$

For the overall mixture there is no production or destruction of mass, in addition $\rho u = \sum_{k=1}^N \rho_k u_k$. This gives:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = 0, \tag{4.3}$$

$$\frac{D\rho}{Dt} + \rho \frac{\partial u_j}{\partial x_j} = 0, \tag{4.4}$$

4.2 Mass Diffusion

Transport of mass by diffusion is usually contributed to diffusion given by Fick's Law, pressure diffusion and thermal diffusion (Soret-effect). Pressure diffusion is usually negligible in combustion processes (Warnatz, Maas & Dibble, 1999:159). Thermal diffusion is only important for light or very heavy species and at low temperatures (Warnatz, Maas & Dibble, 1999:58). These simplifications leave us with a model of mass diffusion based on Fick's Law (Kuo, 1986:165):

$$-J_{k,i}^{D} = -\rho Y_k U_{k,i} = \rho \mathcal{D}_k \frac{\partial Y_k}{\partial x_i} \tag{4.5}$$

4.3 Heat Flux

Heat flux for a homogeneous medium can be described by Fourier's Law of Heat Conduction (Mills, 1995:125):

$$q_i = -\lambda \frac{\partial T}{\partial x_i} \tag{4.6}$$

For multi component situations one may have to take into account the effect of diffusion. The Dufour effect can be neglected (Warnatz, Maas & Dibble, 1999:58), meaning that the following can be used (Warnatz, Maas & Dibble, 1999:158):

$$q_i = -\lambda \frac{\partial T}{\partial x_i} + \sum_{k=1}^{N} h_k J_{k,i}^{D} \tag{4.7}$$

where $J^D_{k,i}$ is given by (4.5), thus:

$$q_i = -\lambda \frac{\partial T}{\partial x_i} - \rho \sum_{k=1}^{N} \mathcal{D}_k h_k \frac{\partial Y_k}{\partial x_i} \qquad (4.8)$$

4.4 Concentration of Species

Based on the continuity equation in (4.2) and Fick's Law in (4.5) an equation to give the concentration or mass fraction of a species in a reacting mixture is:

$$\frac{\partial}{\partial t}(\rho Y_k) + \frac{\partial}{\partial x_j}(\rho Y_k u_j) = \frac{\partial}{\partial x_j}\left(\rho \mathcal{D}\frac{\partial Y_k}{\partial x_j}\right) + \omega_k M_k. \qquad (4.9)$$

where the coefficient of diffusion $\mathcal{D}$ is set equal for all species.

4.5 Ideal Gas Law

The ideal gas law is given as (Moran & Shapiro, 1992:93):

$$pV = n\bar{R}T \qquad (4.10)$$

For a given species or mixture of molar weight M we have:

$$R = \frac{\bar{R}}{M} \qquad (4.11)$$

For a mixture of N gases we can find R as:

$$R = \sum_{k=1}^{N} Y_k R_k \qquad (4.12)$$

4.6   Conservation of Energy

The energy conservation equation in its Euler form is given as (Kuo, 1986:201):

$$\frac{\partial}{\partial t}(\rho e_t) + \frac{\partial}{\partial x_i}(\rho e_t u_i) = -\frac{\partial q_i}{\partial x_i} + \dot{Q} + \frac{\partial \sigma_{ji} u_i}{\partial x_j} + \rho \sum_{k=1}^{N} Y_k f_{k,i}(u_i + U_{k,i}) \qquad (4.13)$$

The energy equation can be expressed in many ways. Often the equation for static enthalpy is convenient (Kuo, 1986:203):

$$\rho \frac{Dh}{Dt} - \frac{Dp}{Dt} = -\frac{\partial q_j}{\partial x_j} + \tau_{ij}\frac{\partial u_i}{\partial x_j} + \dot{Q} + \rho \sum_{k=1}^{N} Y_k f_{k,i} \cdot U_{k,i} \qquad (4.14)$$

where τ_{ij} is the stress tensor.

4.7   Enthalpy

The enthalpy of a substance k is given by (Moran & Shapiro 1992:99):

$$h_k = \int_{T_o}^{T} C_{p,k}(T)dT + h_k(T_o) \qquad (4.15)$$

Given a mixture of N substances, the following is used (Moran & Shapiro 1992:544):

$$h = \sum_{i=1}^{N} y_i h_i \qquad (4.16)$$

For a pure substance k the specific heat capacity at constant pressure is given as (Moran & Shapiro 1992:84):

$$C_{p,k} = \left(\frac{\partial h_k}{\partial T}\right)_p \qquad (4.17)$$

(4.16) and (4.17) gives:

$$C_p = \left(\sum_{k=1}^{N} Y_k \frac{\partial h_k}{\partial T} + \sum_{k=1}^{N} h_k \frac{\partial Y_k}{\partial T} \right)_p = \sum_{k=1}^{N} Y_k C_{p,k} + \left(\sum_{k=1}^{N} h_k \frac{\partial Y_k}{\partial T} \right)_p \tag{4.18}$$

4.8   Internal Energy

The internal energy of a substance k is given by (Moran & Shapiro 1992:96):

$$u_k = \int_{T_o}^{T} C_{v,k}(T) dT + u_k(T_o) \tag{4.19}$$

Given a mixture of N substances, the following is used (Moran & Shapiro 1992:544):

$$u = \sum_{i=1}^{N} y_i u_i \tag{4.20}$$

For a pure substance k the specific heat capacity at constant volume is given as (Moran & Shapiro 1992:84):

$$C_{v,k} = \left(\frac{\partial u_k}{\partial T} \right)_v \tag{4.21}$$

(4.20) and (4.21) gives:

$$C_v = \left(\sum_{k=1}^{N} Y_k \frac{\partial u_k}{\partial T} + \sum_{k=1}^{N} u_k \frac{\partial Y_k}{\partial T} \right)_v = \sum_{k=1}^{N} Y_k C_{v,k} + \left(\sum_{k=1}^{N} u_k \frac{\partial Y_k}{\partial T} \right)_v \tag{4.22}$$

The relationship between internal energy and enthalpy for a substance k in a mixture is given by (Moran & Shapiro,1992:94):

$$h_k = u_k + R_k T \tag{4.23}$$

4.9   Work

Expansion or compression work in a piston can be found from (Moran & Shapiro, 1992:33):

$$W = \int_{V_1}^{V_2} p \, dV \tag{4.24}$$

4.10   Combustion Chemistry

A few basic concepts of combustion and thermodynamics are needed to understand results and discussions later.

4.10.1   Enthalpy of Combustion

The enthalpy of combustion for complete combustion is given as the difference in enthalpy between reactants and products (Moran & Shapiro 1992:621):

$$\bar{h}_{RP} = \sum_P n_e \bar{h}_e + \sum_R n_i \bar{h}_i \tag{4.25}$$

where i and e refer to the inlet and exit of the combustion chamber, and R and P refer to reactants and products respectively.

4.10.2   Adiabatic Flame Temperature

Given a steady state adiabatic reactor the temperature of the products is called the adiabatic flame temperature. This can be found by using the principle of conservation of energy for ideal gases (Moran & Shapiro, 1992:624):

$$\bar{h}_P = \bar{h}_R$$

$$\sum_P n_e (\bar{h}_f^o + \Delta \bar{h})_e = \sum_R n_i (\bar{h}_f^o + \Delta \bar{h})_i \tag{4.26}$$

The number of moles for each species, n, is obtained from a balanced chemical reaction.

4.10.3 Fuel Equivalence Ratio

The fuel equivalence ratio Φ is defined as (Warnatz, Maas & Dibble, 1999:6):

$$\Phi = \left(\frac{X_{fuel}}{X_{air}}\right) \cdot \left(\frac{X_{fuel,stoich.}}{X_{air,stoich.}}\right)^{-1} \tag{4.27}$$

4.11 NO_x Formation

Nitric oxides (NO_x, composed of NO and NO_2) have been under increasing focus due to their environmental impact through their contribution to photochemical smog and ozone at ground level. These compounds also play a role in depleting the dwindling ozone layer in the stratosphere and thereby increase incoming ultra-violet radiation from the sun. In addition NO_2 reacts to form nitric acid, a source of acid rain. Ground-near ozone will form in the presence of ultra-violet sunlight (de Nevers, 1995:492). Both NO_2 and ozone have been found to have a negative impact on plants and animals when they occur close to the ground (de Nevers, 1995:374).

Minimizing NO_x has become an important issue in combustion research. Four different paths of NO_x formation have so far been identified and are presented below.

de Nevers (1995:379) ranks the importance of the different pathways by an example from coal combustion. Below 1300ºC the thermal mechanism is negligible compared to the other mechanisms, while it at the highest temperatures (above 1600ºC) is the most important. Fuel and prompt NO_x are relatively constant from 1200 to 1600ºC, with fuel-bound NO_x approximately 6-7 times larger than prompt NO_x.

The following reactions involving NO relates to the destruction and formation of NO_2 in flames (Miller & Bowman, 1989):

$$NO + HO_2 \rightleftarrows NO_2 + OH \tag{4.28}$$

$$NO_2 + H \rightleftarrows NO + OH \tag{4.29}$$

$$NO_2 + O \rightleftarrows NO + O_2 \tag{4.30}$$
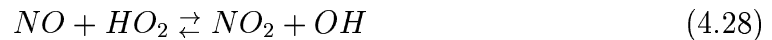
4.11.1 Thermal or Zeldovich Pathway

The following reactions make up the Zeldovich mechanism (de Nevers, 1995:380-383):

$$O + N_2 \rightleftarrows NO + N \tag{4.31}$$

$$N + O_2 \rightleftarrows NO + O \tag{4.32}$$

$$N + OH \rightleftarrows NO + H \tag{4.33}$$
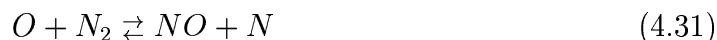
Reaction (4.31) has very high activation energy (318 kJ/mole according to Warnatz, Maas & Dibble, 1999:243), and is thus limited by temperature. This gives the mechanism its name, *thermal NO_x*, and is the reason why this mechanism produces NO in the high temperature post-flame zone. The time needed to obtain equilibrium for the reactions above is up to several seconds (de Nevers, 1995:382), thus the Zeldovich mechanism is considered slow.

4.11.2 Nitrous Oxide Pathway

The nitrous oxide mechanism relies on the presence of a third molecule to produce N_2O (Miller & Bowman, 1989):

$$N_2 + O + M \rightleftarrows N_2O + M \tag{4.34}$$

N_2O may in turn react to form NO, one pathway is (Miller & Bowman, 1989):

$$N_2O + O \rightleftarrows NO + NO \tag{4.35}$$

In lean conditions this pathway can be a significant contributor to NO_x levels (Warnatz, Maas & Dibble 1999:243) because of lower levels of CH and low temperatures. Reaction (4.34) is highly dependent on pressure because it is a three-body reaction, but little dependent on temperature because of its low activation energy (Warnatz, Maas & Dibble, 1999:243).

4.11.3   Prompt NO Pathway

Prompt, or *Fenimore NO* is formed at the flame front, resulting from radical CH (de Nevers, 1995:392). The CH reacts with nitrogen, forming HCN and in turn NO. Prompt NO is especially important in fuel-rich flames (Warnatz, Maas & Dibble, 1999:241). Compared to thermal NO_x this mechanism is usually small (Borman & Ragland, 1998:131). The low activation energy for the reaction of CH with N_2 results in prompt NO even at low temperatures since the mechanism is only weakly dependent on temperature (de Nevers, 1995:393). From Warnatz, Maas & Dibble (1999:240):

$$CH + N_2 \rightarrow HCN + N \rightarrow ... \rightarrow NO \tag{4.36}$$
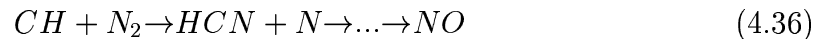
Also, from Borman & Ragland (1998:131):

$$CH_2 + N_2 \rightarrow HCN + NH \rightarrow ... \rightarrow NO \tag{4.37}$$
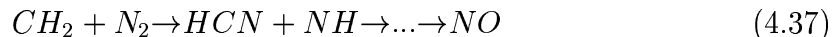
4.11.4   Fuel-Bound NO

Fuel-bound NO is produced from organic nitrogen components in the fuel. As fuels containing nitrogen are burned, hydrogen cyanide (HCN) and ammonia (NH_3) are formed (Warnatz, Maas & Dibble, 1999:243). These will in turn react further with O, OH and H to produce NO. As much as 20-50% of fuel-bound nitrogen is converted to NO (Borman & Ragland, 1998:133), where coal will contain about 1 mass-% chemically bound nitrogen (Warnatz, Maas & Dibble, 1999:243). The estimated fraction of NO_x produced by this mechanism in a standard furnace is typically 20-50%, depending on the fuel and other parameters (de Nevers, 1995:394).

This chapter forms the fundamentals on which the chapters on HCCI engines are based. After the fundamentals of genetic algorithms are explained in the next chapter, the HCCI combustion process is presented in more detail. Please reference the information found in this chapter when reading the rest of this report.

Chapter 5

Search, Optimization and Genetic Algorithms

Genetic algorithms (GAs) are search algorithms that emulate principles from evolution and genetics. The direction of the search is based on survival of the fittest solutions as well as random events. Genetic algorithms have stood out to be very robust, thus making them suited for a wide array of problem solving. They have been developed with two main principles in mind - to explain the adaptive processes of natural systems, and to design software that is based on these principles. Over the past 20-25 years the simplicity and power of genetic algorithms as a robust, adaptive system to provide solutions in multi-dimensional, complex problems have been demonstrated (see Goldberg, 1989:116-129).

5.1 Different Approaches to Search and Optimization

The traditional view of optimization is to find one or more superior solutions. That means having a clear distinction between the actual process of searching and the result itself. This is not an emphasis that is supported by natural processes. How should we judge what is the best solution? And is this optimum really our goal? The most important goal for complex systems should be improvement - we should work to achieve better solutions knowing that we may never reach an *optimal* solution that stands out from all others.

Standard, calculus-based search methods are comprised of either the direct or indirect approach. The direct methods, or *hillclimbers*, evaluate local gradients of an objective function, or to find the local optimum. Indirect methods are based on solving the set

of equations obtained from imposing zero gradient on the objective function. One of the major drawbacks of these methods is their inability to seek beyond a certain neighborhood of the current point. Second, they rely upon the existence of derivatives in every point. Real-world problems are on the other hand dominated by problems that are seldom easily evaluated, much less have smooth derivatives.

Enumerative solvers utilize another approach: evaluate the objective function values at every point within the search space. The obvious effort of computing the objective function for every value of every parameter shows the obvious disadvantage of this method for large, complex problems.

Random search on the other hand, walks through the search space blindfolded. No heed is given to the local surroundings or the search history. This very simple principle also has a major drawback in its lack of efficiency. Practical problems have many parameters and often vast search space.

The genetic algorithm is a method that uses random choice as a factor in its highly guided search of parameter space. They are stochastic search techniques based on the principles of evolution. The built-in genetic mimicking gives the routine important advantages in exploiting the history of the search as well as combining already proven good results to produce stronger offspring. Sequential generations of populations of strings as the search evolves are based on the hope that each subsequent population contains better solutions to the problem. Genetic operators work in a domain-independent fashion without knowledge of the phenotypic interpretation of the genes. Powell & Skolnick (1993) discusses non-linear constraints in engineering systems and compares GAs with other optimization techniques.

Goldberg (1989:7) points out four differences when comparing genetic algorithms and other search procedures:

1. GAs work with a coding of the parameter set, not the parameters themselves.

2. GAs search from a population of points, not a single point.

3. GAs use payoff (objective function) information, not derivatives or other auxiliary knowledge.

4. GAs use probabilistic transition rules, not deterministic rules.

Since the genetic algorithm is heavily based on nature and biology, a short overview of terminology given in Table 5.1 is useful:

Table 5.1: Comparison of biological and GA terminology. Modified from Goldberg (1989:22).

Natural	Meaning in Typical Genetic Algorithm
chromosome	string
gene	feature, character in string
allele	feature value in string
locus	string position
genotype	structure
phenotype	parameter set, condition that solution is subject to

5.2 The Layout of Genetic Algorithms

It is helpful to have an understanding of their building blocks to understand how genetic algorithms work. Below these are presented.

First the encoding of parameters in a genetic algorithm is discussed, followed by a short presentation of the population of solutions. The important concepts of fitness and penalty are introduced. Then a series of genetic operators that allow the genetic algorithm to propagate its search are shown. Some properties of selection and convergence of the search are given. The last part of this section combines all these previous parts by showing how they interact to form a genetic algorithm.

5.2.1 Encoding and Alphabets

Genetic algorithms work on strings representing the different parameters of the problem. Each parameter must be coded to a finite length using an alphabet. Many different encoding options can be chosen. Natural choices of alphabets may be binary, decimal or hexadecimal to represent numbers. A fundamental principle to take into account when considering the popularity of binary encoding is given by Goldberg (1989:80):

> '[The user] should select the smallest alphabet that permits a natural expression of the problem.'

Reeves (1993) points out that a binary coding allows for a rather small population size to cover a large part of the alleles compared to other codings like decimal. Small populations have a risk of under-covering the solution space and may lead to poor solutions. Large populations on the other hand will require a much larger computational effort.

String

1001101100011010001 0 110

Parameter   Gene
representation
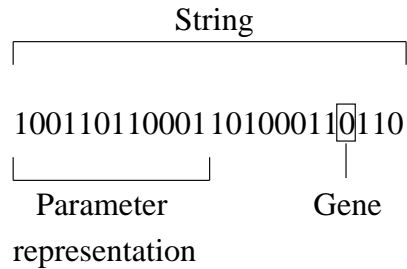
Figure 5.1: Conceptual image of a string with two twelve-digit binary sequentially encoded parameters represented in a genetic algorithm.

Another important aspect of the encoding specifics is how strings are similar to one another. More explicitly this applies to how the similarities between strings can help in guiding the search forward. A subset of strings with similarities at certain positions, called schema, is an important characteristic of the population.

One method of encoding the population would be to sequentially represent different parameters for the problem in the genetic algorithm. This would create one long string with numbers, for example binary digits, for each individual as shown in Figure (5.1).

5.2.2   The Population

Many genetic algorithms assume a constant population size during the entire search procedure. This means that for every new solution (or offspring) produced, one member of the original population must be removed through a selection procedure. As previously pointed out a small population is desirable due to low computational cost. This makes it important to have some criteria when selecting the initial members. For example it is vital that there is diversity in the characteristics, or phenotype, of the initial population. As many schemata as possible should be covered. Such criteria are difficult to generalize and it is up to the user to ensure that this is fulfilled for each problem. Reeves (1993) presents an analysis of how to run GAs with small populations.

5.2.3   Fitness and the Penalty Function

Evaluation of the individuals in a generation is important when choosing candidates for reproduction. The concept of *cost* or *fitness* of a solution or individual and the use of *penalty* are important aspects when dealing with this topic.

One given problem may have many constraints and variables. For example when optimizing some industrial process one wants to minimize the cost of input materials,

power and labor, and at the same time maximize production and profit. When the genetic algorithm is given the value of each of these parameters obtained by evaluating each individual in the population it is possible to apply a penalty function to these values. For this industrial process it may be that power is cheaper than the materials used, such that an increase in power use is more desirable than using more materials. The penalty for each parameter when it is not optimal is given by the corresponding penalty function.

When the penalties for each individual are summed up, a rank and cost for each can be found. The cost term is also used for other problems, the pollution from a furnace can be assigned a cost when the different pollutants have been given a penalty function.

An analysis of penalty functions can be found in Smith & Tate (1993).

5.2.4   Genetic Operators

The principle behind genetic algorithms is basically that of natural selection as set forth by Darwin (1859). This is the driving force that directs the search into promising areas and leaves behind what is less desirable.

Common ways of performing a reproduction or selection mechanism are for example (Goldberg, 1989:121):

- **Roulette Wheel** or **stochastic sampling with replacement** selection is based on determining selection probability according to the fitness value, or cost. A model roulette wheel is used to display these probabilities, a high fitness value gives a larger proportion of the wheel for that chromosome. The wheel is 'spun' the number of times equal to the population size, each time picking a string representing a solution.

- **Rank-based** or **stochastic tournament** selection will draw two individuals from the population using a roulette wheel and then enter the one with the highest fitness into the new population.

Crossover is an important genetic operator. Several exist, such as (Kowalczyk, 1997):

- **Uniform crossover** works by selecting two individuals from the population based on their ranking. The elements of these are randomly exchanged to produce two new offspring.

- **n-point crossover** also selects two parents, picks n crossover points at random

and exchanges the segments of the individuals bounded by these points.

Eshelman & Schaffer (1993) looks on the role of crossover in genetic algorithms.

Mutation adds another random element to the search. By randomly changing elements in the chromosomes based on a certain probability of change this mimics a very important feature found in nature. This lets the search propagate much easier into new domains.

One way of enhancing the search performance is the *elite* rank-based scheme. This ensures that the n highest ranked chromosomes in the population are always carried on to the next generation. All the remaining members are discarded in favor of the new offspring. This method will in many cases lead to faster convergence, but may also converge too quickly and end up in a local maximum or minimum. This can be helped by a higher mutation rate.

The concept of *niche* has found its place in genetic algorithms. It is based on the phenomenon found in nature that dictates that individuals in a neighborhood share and compete for resources. This is implemented in genetic algorithms by reducing the fitness value of individuals according to the population in their surroundings.

A simple genetic algorithm layout may consist of first a reproduction through the Roulette Wheel method after a ranking process. Then these new individuals are subject to the crossover mechanism by randomly coupling two strings and performing a uniform crossover. The last part would be running a mutation routine that randomly flips the value of genes.

5.2.5   Selecting the Next Generation

After producing the new offspring it is time to get rid of some of the old members of the population to ensure that the search propagates. Many strategies have been presented, such as random deletion and rank-based deletion (deletion of the n lowest ranked). Elite schemes are highly biased to remove the ones that are ranked lowest. This can lead to loss of diversity. Some solution on how to propagate the search must be found, and since no developed theory on this exists it is up to the individual user to find a scheme that works for the problem at hand.

5.2.6   Convergence

The important *Schema Theorem* given by Goldberg (1989:33) states that as the algorithm converges towards a good solution the number of individuals with optimal

Perform Generation Step ⟵ Rank Individuals | Main GA level

Initialize ⟶ Translate Strings to   GA Problem Class
Population   Problem Parameters   Evaluate Fitness   Dependent Routines

Calculate Problem Properties | Problem Specific
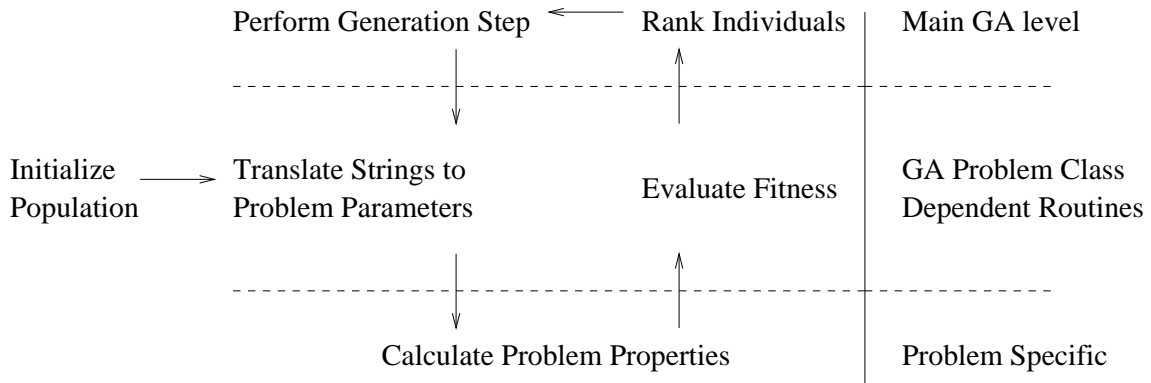
Figure 5.2: The layout of a genetic algorithm program with the different levels of operation.

schema increases. These individuals share a specific pattern of alleles, and this schema is likely to survive into the next generation.

5.2.7   Genetic Algorithm Program Layout

A general view of the genetic algorithm layout is given in Figure 5.2. The top level of GA operation consists of the routines for the genetic operators. These do their work based on a rank given by the fitness of each population member. This fitness is based on the parameter values obtained from the problem specific simulation. The simulation subroutine is given its parameter values from the genetic algorithm through a subroutine that decodes the strings in each new population. A decoding routine will be specific for each class of problems. The walk through a genetic algorithm will follow these steps: do a simulation for each individual based on its parameter values, rank each individual based on fitness then make the next generation with the use of genetic operators and so on until the algorithm is stopped.

5.3   Generalized Problems

It is necessary to express the problem in mathematical terms to use genetic algorithms, and many real-world optimization problems can be formulated using the following expressions (Goldberg, 1989:85):

$$\text{minimize} \quad g(\vec{x})$$

$$\text{subject to} \quad h_i(\vec{x}) \geq 0 \qquad i = 1, 2, ..., n$$

$$\text{where} \qquad \vec{x} \text{ is an } m \text{ vector}$$

If a penalty function is introduced into the above constrained problem, the following unconstrained form is given as (Goldberg, 1989:85):

$$\text{minimize} \quad g(\vec{x}) + r \cdot \sum_{i=1}^{N} \Phi[h_i(\vec{x})]$$

$$\text{where} \qquad \Phi \text{ is the penalty function}$$
$$r \text{ is the penalty coefficient}$$

Genetic algorithms have not yet reached the stage where they can attack any problem and guide themselves towards a solution. It is the job of the user to fine-tune the different parameters to achieve a fast and accurate result. The choice of whether or not to use features like niche and elitism, finding the best type of crossover-mechanisms and the correct mutation rates and population size can only be discovered through what accumulated experience together with trial-and error methods.

Chapter 6

The HCCI Engine

The internal combustion engine is by far the most popular engine used today. Although the term also applies to open-circuit gas turbines, it is here used in conjunction with the spark-ignition (SI) and compression-ignition (CI) piston engines. These engines are found in cars, ships, power plants and other installations around the world. SI and CI engines are presented in the following paragraphs. The HCCI engine is then shown in comparison with these two, along with a presentation of the experimental and simulation setup used.

6.1 Internal Combustion Engines

The SI engine is also referred to as the gasoline engine after its typical fuel, or the Otto engine after its inventor. The CI engine is often referred to as the Diesel engine, since the common fuel is also named after its inventor. Most common in vehicles is the four-stroke engine shown in Figure 6.1. This operates with four strokes of the piston, named the induction, compression, expansion (power) and exhaust strokes. Good introductions to engine fundamentals can be found in Stone (1999), Lumley (1999) and Heywood (1988).

Combustion (or heat addition) in an engine does not take place at constant volume (ideal Otto cycle) or constant pressure (ideal Diesel cycle). The fundamental difference between the SI and CI ignition engine is the type of combustion that occurs, namely that SI engines usually have premixed flames and CI engines usually have non-premixed flames. The SI engine maintains a close-to-stoichiometric air-to-fuel mixture to ensure ignition and subsequent flame propagation. The SI engine is also throttled to control the power output. This results in poor part load fuel economy. However it is superior to the CI engine at full load due to its better air utilization
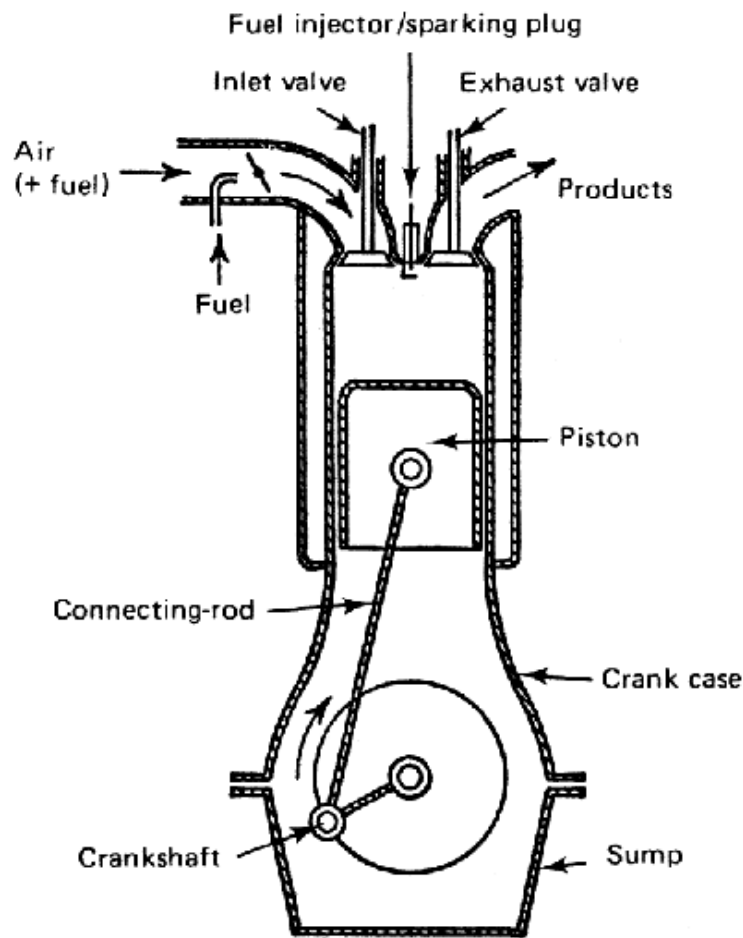
Figure 6.1: Greatly simplified model of four-stroke internal combustion engine (Stone, 1999:2).

because of the homogeneous charge in the cylinder. CI engines with fuel injection usually have stoichiometric conditions only at the flame front. The output of CI engines can be controlled by varying the amount of fuel injected, leaving the air unthrottled, thus giving it superior fuel economy at low loads. As for power-to-weight ratio the SI engine running on gasoline comes out favorably.

6.1.1 Spark-Ignition Engines

Spark-ignition engines are mostly used in passenger cars. SI engines are based on the principle of igniting a premixed charge with an electric spark. A flame front propagates through the homogeneous mixture of fuel and air from the spark plug. The combustion process is largely uncontrolled after ignition and is influenced by the

turbulent mixing of hot products from behind the flame front with unburned mixture (Smith et al., 1997). The flame front sets up high local temperatures due to its intensity. This heterogenous combustion leads to the formation of NO_x. The use of the ignition timing, lean mixtures and exhaust gas recirculation (EGR) may reduce these peak temperatures. The flame fails to reach into the crevices of the combustion chamber due to quenching through heat loss to the walls. Thus, these crevices are a source of unburned hydrocarbons in emissions. The flame propagation raises the pressure and temperature ahead of the flame front at the end of the combustion event so high that an auto-ignition process known as 'knock' can occur. This explosive self-ignition of the remaining air-fuel mixture ahead of the flame front is potentially destructive to the engine. The two most important parameters for controlling knock are found to be the compression ratio (CR) of the engine and the fuel composition (octane number for gasoline) (Ryan & Callahan, 1996).

6.1.2 Compression-Ignition Engines

The compression ignition engine uses a combustion process that is controlled by turbulent diffusion mixing. The injection of high-cetane fuel into hot, compressed air at the end of the compression stroke results in self-ignition. The mixing rate of fuel with air controls the rate of combustion since the chemical reaction rates are faster than the mixing (Ryan & Callahan, 1996). In this type of combustion the flame is stabilized between the fuel and air where the conditions are stoichiometric. Temperatures found here are thus close to the adiabatic flame temperature. NO_x will form in hot, stoichiometric regions and soot will form at the rich parts of the flame (Christensen et al., 1999). Attempting to reduce one of these emissions will tend to increase the other due to their close dependency. For example, use of EGR limits peak temperatures but increases soot since it reduces the amount of available oxygen (Ryan & Callahan, 1996).

Fuels that are able to self-ignite easily (low octane) are used in this engine, opposite to the high-octane fuels used in an SI engine. The cetane number of the fuel is an important fuel parameter for the ignition delay after the start of fuel injection. The heat release rate is controlled by the rate of fuel injection, fuel vaporization and mixing (Smith et al., 1997).

As with the SI engine, the CI engine also suffers from having a non-uniform temperature distribution through the combustion event. This means that while the bulk temperature is low, very high peak temperatures are found in conjunction with the flame fronts.

6.1.3 The HCCI Mode of Operation

By using a lean homogeneous air-fuel mixture and igniting it spontaneously by compression ignition, the combustion process does not depend upon flame propagation but takes place homogeneously throughout the mixture (Amneus et al., 1998). This mode of operation is called Homogeneous Charge Compression Ignition (HCCI). Since there are no flame fronts or rich parts in this mixture, soot formation is suppressed. Another advantage is that flame propagation is not a factor in the combustion process. The combustion event is shorter than with SI or CI engines (Thring, 1989). Turbulence is assumed to have little effect on HCCI combustion, but is very important as a factor in determining temperature gradients and boundary layer thickness in the cylinder (Aceves et al., 2000).

One of the major advantages of the HCCI engine is its good part-load performance compared to the SI engine. The thermal efficiency of the HCCI engine approaches that of the standard Diesel according to Thring (1989). It also runs on practically any fuel by varying the compression ratio (Christensen et al., 1999).

The HCCI combustion event is a result of self-ignition throughout the air-fuel mixture. An evenly distributed auto-ignition in the charge is dependent on high temperature and high pressure. It has been difficult to control the HCCI process in many operating conditions (Flowers et al., 2000). The engine is limited by the difficult ignition process on one hand, and the possibility of severe knock or uncontrolled combustion on the other. The explosiveness of the process can be mitigated by the use of EGR (Christensen et al., 1998b and Au et al., 2001) or excess air (Christensen et al., 1997) to control the heat release rate.

A major problem is the difficulty of controlling the combustion timing. SI engines use a spark and CI engines inject fuel at the point when combustion is desired. HCCI engines on the other hand must use more indirect control methods such as changing exhaust gas recirculation, fuel equivalence ratio and inlet temperature.

Another important drawback aside from difficulties of controlling the process is the high output of unburned hydrocarbons (Christensen et al., 1999). The low homogeneous combustion temperature of the HCCI engine prevents NO_x formation, but does not oxidize the fuel completely if the temperature drops too low at the end of the combustion event. In addition, heat losses near the engine wall result in quenching, further increasing emissions. Crevice volumes also contribute by trapping charge that does not ignite (Aceves et al., 2000). With increased CR the crevice volumes hold even more mass, thus leading to higher HC emissions.

Other disadvantages with the HCCI concept are high peak pressures, high heat release rates, reduced engine speed operating range, reduced power per displacement and difficult starting of the engine (Aceves et al., 2000).

The knock process in SI engines is virtually identical to the auto ignition in an HCCI engine (Smith et al., 1997). However, HCCI engines may experience a severe knock that may damage the engine when igniting much earlier than top dead center (TDC) as this will result in very high pressure. Ryan & Callahan (1996:161) report that the HCCI combustion must start less than 20 crank angle degrees before top dead center to avoid misfires and severe knock for their test engine. Early start usually resulted in knock, and misfires occurred if the combustion was initiated after TDC. Thring (1989) reports that when running an HCCI engine very lean, it would not generate enough power to overcome internal friction. However, the limiting factor was not misfire or erratic burning since the engine operated steady and consistent even at this setting.

A spectroscopic study of the HCCI combustion process by Noguchi et al. (1979) shows that radicals appeared in a specific temporal sequence in contradiction to SI engines where all radicals appear simultaneously, but spatially, distributed through the flame front.

One possible concept can be to operate an engine very lean in HCCI mode when running at light load, then switch to SI when full power is required. The engine would start using spark ignition. A low-pressure fuel injection system can be used to reduce the cost of engine (Thring, 1989). Information on the combustion process, thus enabling engine control, could be found from pressure transducers in the cylinders. This would require a high degree of maintenance since such equipment is not very durable, and other sensor methods may prove to be more pragmatic.

It is important to notice that the low temperature in the cylinder results in very low NO_x, very low particulate emissions and high efficiency (Martinez-Frias et al., 1998). The problem with unburned hydrocarbons can be removed by using a catalyst to treat the exhaust gases.

Among the applications for HCCI engines that have been proposed, are hybrid electric vehicles. The engine would run at near-constant conditions and would be ideal for HCCI applications. Stationary power generation also presents opportunities for HCCI engines because of its high efficiency and good emissions characteristics.

6.2   Well-Mixed Reactor Model

One way of modeling chemical reactions in an engine is by using a well-mixed reactor model. As the name implies, this type of reactor is based on the principle of having a perfectly mixed volume with uniform pressure, temperature and composition. This does not take into account fluid mechanics effects, and is a strong simplification in most cases. However, the effects of turbulent mixing for HCCI engines are not as
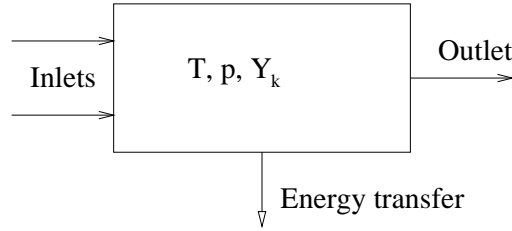
Figure 6.2: Well-mixed reactor with multiple inlets and energy transfer to surroundings via radiation or convection.

strong as for SI or CI engines since the combustion event takes place in a homogeneous mixture. A conceptual picture of a well-mixed reactor with multiple inlets can be seen in Figure 6.2.

6.2.1   Well-Mixed Reactor Theory

The mass continuity equation based on (4.3) for a well-mixed reactor can be written as:

$$\frac{dm}{dt} = \dot{m}_e + \sum_{i=1}^{N_i} \dot{m}_i \tag{6.1}$$

where N_i is the number of inlets. Since the conditions within the reactor are uniform, multiple exits can be summed up and represented with one exit stream.

The species concentration equation in (4.9) for a well-mixed reactor will be:

$$\frac{dY_k}{dt} = \frac{1}{m} \sum_{i=1}^{N_i} \dot{m}_i (Y_{k,i} - Y_k) + \frac{\dot{\omega}_k M_k}{\rho} \tag{6.2}$$

An energy balance based on (4.14) can be expressed as (Chen & Dibble, 1991 and Kuo, 1986:204):

$$\frac{dT}{dt} = \frac{1}{C_p m} \sum_{j=1}^{S} \dot{m}_j \left[\sum_{k=1}^{N} (h_{k,j} - h_k) Y_k \right] - \sum_{k=1}^{N} \frac{\dot{\omega}_k h_k M_k}{C_p m} - \frac{\dot{Q}_{loss}}{C_p m} + \frac{1}{C_p m} \frac{dp}{dt} \tag{6.3}$$

where N is the number of species and S the number of streams.

The volume of the well-mixed reactor is given by the slider-crank formula (Heywood, 1988:43) for an engine:

$$V = V_c + \frac{\pi B}{4}(l + a - a \cdot cos\Theta + (l^2 - a^2 \cdot sin^2\Theta)^{1/2}) \qquad (6.4)$$

where B is the engine bore, l is the connecting rod length, a is the crank radius, Θ is the crank angle and V_c is the clearance volume.

The heat transfer to the walls from the gas can be found from (4.6) for a steady-flow one-dimensional case (Heywood, 1988:670):

$$\dot{q} = h_c(T - T_{wall}) \qquad (6.5)$$

where B is the cylinder bore taken as characteristic length and h_c is the heat transfer coefficient. Woschni's correlation (Heywood, 1988:680) gives h_c based on engine parameters:

$$h_c = 3.26 B^{-0.2} p^{0.8} T^{-0.55} w \qquad (6.6)$$

where w is the average gas velocity in the cylinder, given as (Heywood, 1988:680):

$$w = C_1 S_p + C_2 \frac{V_d T_r}{p_r V_r}(p - p_m) \qquad (6.7)$$

where V_d is displaced volume, T_r, p_r and V_r are the working fluid temperature, pressure and volume at the reference state (for example inlet conditions) respectively. S_p is the mean piston speed. The constants C_1 and C_2 are dependent on the stroke the engine is performing. p is the cylinder pressure found from the ideal gas law in (4.10).

The Indicated Mean Effective Pressure (IMEP) is defined as (Stone, 1999:32):

$$IMEP = \frac{indicated\ work\ output\ per\ cylinder\ per\ mechanical\ cycle}{swept\ volume\ per\ cylinder}[bar] \qquad (6.8)$$

In the simulations this is calculated by using (4.24), integrating the cylinder pressure for each time-step in the compression and expansion strokes to get the work, then dividing by the swept volume.

Frictional Mean Effective Pressure (FMEP) is found from Heywood (1988:724), the following expression for diesel engines is used:

$$FMEP = 75.0 \cdot 10^3 + 48 \cdot \frac{rpm}{1000} \cdot 1.0 \cdot 10^{-5}$$ (6.9)

Pumping loss is found from an isentropic relation (Çengel & Boles, 1998:357):

$$w_{loss} = \frac{\gamma \bar{R} T_1}{\gamma - 1} \left[\left(\frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$$ (6.10)

where 1 and 2 reference the state of the surroundings and the cylinder charge at the start of the compression cycle respectively. To get Pumping Mean Effective Pressure (PMEP), the work in (6.10) is multiplied by the mass of the fresh charge in the cylinder and divided by the swept volume.

Gross indicated efficiency is obtained from (Stone, 1999:34):

$$\eta_{gr} = \frac{W_{gr}}{m_f \cdot CV_f}$$ (6.11)

where CV is the calorific value (lower heating value) of the fuel and W_{gr} is found from (4.24) as is done in (6.8).

Net indicated efficiency is found from :

$$\eta_{net} = \frac{W_{net}}{m_f \cdot CV_f}$$ (6.12)

where CV is the calorific value (lower heating value) of the fuel and W_{net} is found by subtracting the pumping and friction pressure losses from the indicated mean effective pressure and multiplying by the swept volume, see (6.8).

Indicated brake power is found by subtracting pumping losses and friction work from the gross work.

Several different approaches to simulations of the HCCI engine have been explored. The use of CFD-codes like KIVA with a simplified chemical kinetics model give more

accurate results for the fluid dynamics on the engine cylinder, but have a shortcoming when using a simplified model for chemistry due to computing intensity. A detailed chemistry code without engine fluid dynamics is another approach to the modeling problem.

Another method recently adapted has been to use a fluid dynamics code like KIVA to simulate the engine cylinder until a given time before the piston reaches TDC in the compression stroke. No combustion has occurred, and the results from this code are used to initialize a multi-zone detailed chemical kinetics model. This then runs for the remainder of the engine compression and expansion strokes. The advantages are a more accurate initialization of the multi-zone model and much reduced computational effort from doing a simulation with detailed chemical kinetics and fluid dynamics. Aceves et al. (2000) have obtained very good results using this last technique.

6.2.2 Single Well-Mixed Reactor Model for Engine Simulation

Using a single well-mixed reactor to model the workings of an engine cylinder is a rather crude simplification. Engine fluid dynamics and chemical kinetics are complicated. A reactor model will disregard the fluid mechanics and temperature gradients, greatly simplify the layout and heat transfer as well as only provide an estimate for the chemical kinetics. However, it is computationally inexpensive compared to performing a simulation with both detailed fluid dynamics and combustion.

The HCCI process has the fortunate characteristic of being relatively insensitive to turbulence and mixing effects compared to a SI or CI engine (Aceves et al., 2000). Chemistry is the controlling parameter (Amneus et al., 1998). This would lead to hopes of achieving good results even with a simple model when using a detailed model for chemistry. The single zone well-mixed reactor model assumes the combustion chamber to have uniform temperature, pressure and composition. The homogeneous nature of the HCCI engine makes this assumption easier to follow in engine simulations. Mixing effects are neglected in this model. Temperature gradients inside the cylinder are also impossible to account for with this model. This leads to underprediction of burn duration since an isothermal charge burns very rapidly (Aceves et al., 1999), over-prediction of pressure and thus NO_x and low accuracy in the prediction of CO and HC (Martinez-Frias et al., 1998). The onset of combustion is relatively well predicted since the entire charge ignites at approximately the same time in an HCCI engine.

The well-mixed reactor WMR-model version 2.9 used was made by Professor Jyh-Yuan Chen at the University of California at Berkeley. Using the DDASAC double precision ordinary differential equation (ODE) solver and CHEMKIN-II software it provides the means of doing simulations with detailed chemical kinetics. It has been

modified for integration with the genetic algorithm in HCCI mode.

The engine cylinder is treated as a homogeneous reactor with variable volume. The cylinder wall, piston and head are assumed to have a constant temperature. Necessary data for friction, pumping work and IMEP is found from Section 6.2.1.

Simulations are started at BDC, where the charge of specified pressure, temperature and composition is added to the cylinder. Step by step simulations with detailed chemical kinetics using the variable volume WMR simulates the compression and expansion strokes of the engine. Efficiencies and emissions are computed when the piston again reaches BDC. All emission values are taken at BDC.

The use of EGR in the simulations require some extra attention. First, a run with only fresh charge is calculated. The wanted percentage of this exhaust gas is then mixed with the given fresh charge and another simulation is performed. This is repeated until the resulting temperature, pressure and composition values are within tolerance levels for two consecutive runs.

6.2.3   Multiple Well-Mixed Reactor Model for Engine Simulation

A further enhancement of the single WMR model is a model consisting of several well-mixed reactors. This enables more accurate modeling of the engine cylinder. For example, one or more reactors can represent crevice volumes that do not ignite, giving a more accurate prediction of CO and unburned hydrocarbon emission. Allowing for mass transfer between the reactors and heat transfer between the reactors and the cylinder wall also gives the opportunity of having temperature and concentration gradients within the cylinder. The price is a substantial increase in computing time.

This Thesis presents results obtained with the VVHS (Variable Volume High Step) code by Dale Andreatta (Andreatta, 1995). It has been integrated with the genetic algorithm code to perform simulations of the HCCI engine and uses the DVODE double precision ODE-solver (Brown, Byrne & Hindmarsh, 1989). CHEMKIN-II software is used to perform the chemical kinetics calculations.

The VVHS code has multiple reactors in line where each reactor exchanges mass with its two neighbors, shown in Figure 6.3. This can be visualized in an engine as multiple shells in layers in the engine cylinder.

For running this code in HCCI mode, mass transfer between the zones is set to zero. This is on the assumption that compression heating is the dominant phenomenon and that the chemistry time scale is much smaller than the mixing time scale because of the fast combustion event. This is consistent with work by Aceves et al. (2000)
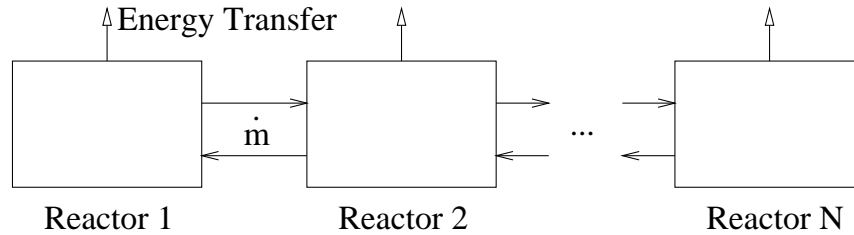
Figure 6.3: Multiple well-mixed reactors with mass exchange between neighbors and energy transfer to surroundings via radiation or convection.

and by Torres on the VVHS model (1997). Analysis by Aceves et al. (2000) suggests that diffusion effects between zones are negligible.

The volume of each zone is not constant. The total volume changes with the slider-crank formula in (6.4). The volume distribution between the zones changes due to the need to have uniform pressure in the cylinder. This is done by adjusting zone volume based on temperature, composition and mass.

Heat transfer is according to the Woschni relation in (6.6). Combustion in the core zones have been found to be insensitive to heat transfer (Aceves et al., 2000).

6.2.4 The CHEMKIN Chemical Kinetics Package

To solve the chemical kinetics in the engine simulations CHEMKIN-II has been utilized. This software package developed at the Sandia National Laboratories in California can be used to facilitate the formation, solution and interpretation of gas-phase chemical kinetics (Kee, Rupley & Miller, 1989).

Two major components make up CHEMKIN: an interpreter that reads the user's chemical reaction mechanism to produce a data linking file, and a gas-phase subroutine library. This library contains around 100 subroutines written in FORTRAN to be called in the user's program to provide information on thermodynamic properties, production rates and equation of state.

The simulation code calls the CHEMKIN interpreter to provide the linking file on startup. CHEMKIN subroutines read this data and provide information to set up arrays containing temperature, mass and mass fractions. This is then sent to the ODE-solver to perform one time step of the engine cycle. The output is run through CHEMKIN subroutines to provide mole fractions and other useful output data. This is repeated for each time step until the entire engine cycle has been completed.

6.3   Experimental Setup

A VW TDI diesel engine has been modified to run in HCCI mode. The engine used has the characteristics given in Table 6.1.

Table 6.1: Engine data for VW 1.9 liter TDI engine converted to HCCI mode.

Engine Parameter	Value
Displacement	1.896 liter
No. of cylinders	4
Bore	79.5 mm
Stroke	95.5 mm
Connecting rod length	144.0 mm
Compression ration	19.5:1

A 18 kW, 3 element quartz heater heats the intake charge. The engine flywheel is coupled to a torque transducer and a clutch/brake assembly. A 30 kW induction motor operating at 1800 rpm serves as a driver or a load for the engine depending on the operating conditions. The engine was modified to be naturally aspired. An EGR line is installed between the intake and exhaust manifold, allowing for up to 65% by mass of EGR to be fed back into the cylinders.

For data measurement four quartz pressure transducers are used. The transducers are fitted in the ports for the high-pressure fuel system originally installed on the engine. Signals are fed through a charge-amplifier with a 200 kHz low-pass filter and drift compensation before being collected by a data acquisition system on a Windows NT system. Pressure signals are recorded for every 0.1 crank angle degrees. The crank angle is measured with a crank angle degree encoder. Airflow is measured with a knife-edge orifice plate with a bore-to-pipe diameter of 0.426. Fuel flow is measured with a mass flow controller. Emissions of unburned hydrocarbons, O_2, CO, CO_2 and NO_x are measured with an emissions analyzer.

For experiments the induction motor is used to bring the engine up to speed. The intake air is preheated to the desired temperature. Fuel is then added into the intake manifold until combustion occurs. From this point further adjustments in fuel flow, intake temperature and EGR is performed. The experiments in this report use propane or acetylene as fuel.

Chapter 7

Simulations and Experiments of the HCCI Concept

The following results have been obtained using single-zone and multi-zone well-mixed reactor codes coupled with a genetic algorithm. Engine experiments have been performed with a VW 1.9 liter TDI engine modified to run in HCCI mode. Results shown are for single-zone well-mixed reactor simulations unless noted.

After a brief explanation of the setup of the simulations an example pressure trace is introduced. To validate the computer model an evaluation of simulation results is shown and discussed. The performance of the genetic algorithm is presented with a parameter optimization problem. A discussion of the NO_x mechanisms in HCCI combustion precedes a presentation of an introductory experiment with acetylene.

7.1   Simulation Setup

Each simulation run has its parameter setup listed in Appendix A. Two or three parameters are studied while the other parameters are kept constant. Varying all parameters at the same time is not an efficient use of computer resources. Only one of the four engine cylinders is simulated. The engine characteristics of the VW engine as given in Table 6.1 are used in the computer model. The fuel equivalence ratio specified is for the fresh charge, not the mixed charge in the cylinder at the start of the compression stroke when EGR is used. The EGR ratio is given as a fraction of the total volume in the cylinder charge at BDC. Inlet temperature refers to the temperature of both EGR and fresh charge. The engine wall temperature is assumed constant at 430 K throughout the simulations. Each point in the following graphs represents one simulation run with the HCCI model.

The genetic algorithm setup uses shuffled binary encoding for the six parameters inlet pressure and temperature, fuel equivalence ratio of the fresh charge, EGR rate, engine speed and compression ratio. A population size of 5 solutions is used for 1000 generations. Uniform crossover at a rate of 0.5 and a mutation and creep mutation rate of 0.04 is used. An elitism scheme is enabled.

The chemical mechanisms are listed in Appendix (B). The methane mechanism has 52 species and 323 reactions, and the propane mechanism has 55 species and 266 reactions.

7.2   Pressure Trace of Engine Cycle

The algorithm gives pressure data at each time step. It is then possible to compare pressure traces for similar operating conditions with the actual engine. As shown in Figure 7.1 the single-zone model over-predicts pressure by a substantial amount. This is to be expected since a homogeneous charge with homogeneous temperature burns all at once. This is one of the reasons that the pressure in the single-zone model is over-predicted. Another reason may be that the heat transfer is not correctly modeled.

Aceves et al. (2000) report 20% higher pressure in a single-zone model than in an actual engine. The shape of the pressure trace for the single-zone simulation in Figure 7.1 is similar to that found in Aceves et al. (2000) and Amneus et al. (1998).

The pressure trace shown for the engine is averaged over 82 cycles. It is thus much more smooth than would be found by looking at a single cycle, although HCCI combustion has small cycle-to-cycle variations compared to an SI-engine.

Also shown in Figure 7.1 are the results obtained with the multi-zone VVHS model code. As can be seen the multi-zone model predicts pressure much better than the single-zone model. This is due to the temperature gradients in the cylinder being taken into account. Similar results have been shown by Aceves et al. (2000).

A 10-zone model was used. The mass distribution between the different zones was based on work by Aceves et al. (2000), and is listed in Table A.6. This setup uses the first five zones to account for crevice volumes and boundary layers. The heat transfer from each zone was tuned so that only the inner five zones ignited, and the central two zones had a minimum of heat transfer. This is a rather crude approach, and it is probable that a much better result would come with the incorporation of results from a detailed heat transfer analysis of the engine.

Differences in the pressure trace between the two models before the combustion event can in part be due to the heat transfer model. Both use the Woschni correlation, but
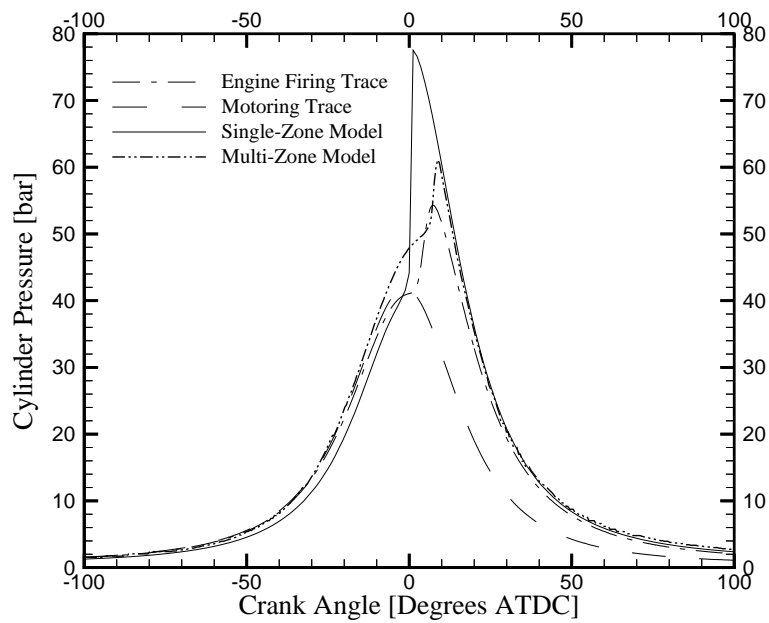
Figure 7.1: Comparable pressure traces from engine runs and simulations. Motoring trace is shown for reference. Experiments are averaged over 82 cycles for one cylinder.

the multi-zone model requires tuning of the heat transfer for each zone. The start of combustion seems to be reasonably well predicted for both models.

7.3   Engine Parameter Effect on HCCI Combustion

Single-zone well-mixed reactor simulations have been performed to investigate the effect of engine operating conditions on HCCI combustion.

Ignition timing in an HCCI engine is crucial to its operation. If the charge ignites too early, high pressure and severe knock are the results. On the other end is the possibility of misfires. Flowers et al. (2000) states that information on combustion timing is necessary for closed loop control.

As shown in Figure 7.2 the ignition timing has a noticeable effect on the overall gross engine efficiency when running with propane. Figure 7.3 shows the same results for methane fuel. The ignition timing is found from the heat release rate.

These figures indicate that the HCCI process has a window of the highest efficiency of about 5 CAD, from 5 to 10 degrees ATDC for propane, and slightly higher for methane. Flowers et al. (2000) observed a similar trend of increased efficiency for later combustion timing for their experiments. Their timing varied between 3 degrees BTDC and 8 degrees ATDC for experiments with propane. Their simulations using a single-zone model also show the same basic trends as given in Figure 7.2.

Heat transfer may be an important parameter in the ignition timing. Fiveland and Assanis (2000) point out that the Woschni-model was developed for direct-injection Diesel engines by fitting data to the correlation form. It is not necessarily valid for premixed combustion, and they present results where the difference between a Woschni correlation and a zero-dimensional $k - \epsilon$ based heat transfer model (Assanis and Heywood, 1986) is about 8 crank angle degrees in the ignition timing, a significant value. Thus the accurate modeling of engine heat transfer appears to be very important.

Figure 7.4 shows that high maximum cycle pressure is not optimal. This is also shown in Figure 7.2 where the efficiency is highest for combustion initiation after TDC. This is due to lower peak pressure since the combustion event takes place in expanding volume.

Early ignition will result in very high pressure as shown in Figure 7.5. The decrease in peak pressure as combustion timing occurs later in the cycle is consistent with the volume change in the cylinder. With combustion before TDC the peak temperature occurs when the volume is very small, thus leading to higher pressure. Flowers et al. (2000) also show the same overall trend in the results for experiments and single-zone
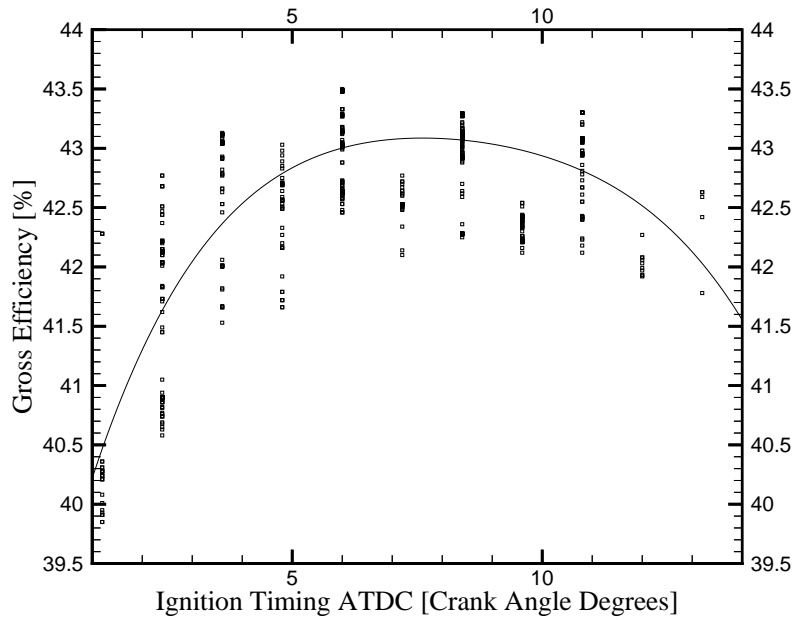
Figure 7.2: Gross engine efficiency shown versus ignition timing. Curve-fit to data shown. Engine parameters given in Table A.1.
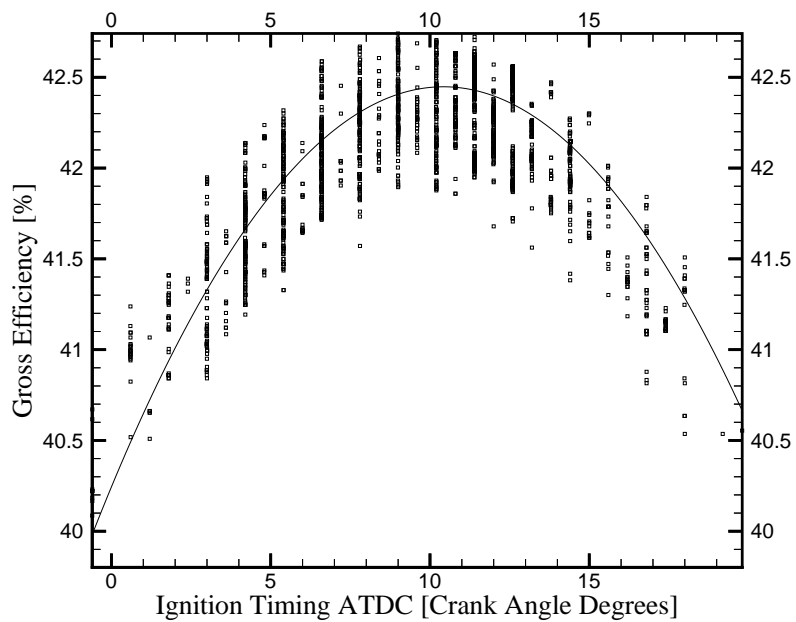
Figure 7.3: Gross engine efficiency shown versus ignition timing. Curve-fit to data shown. Engine parameters given in Table A.3.
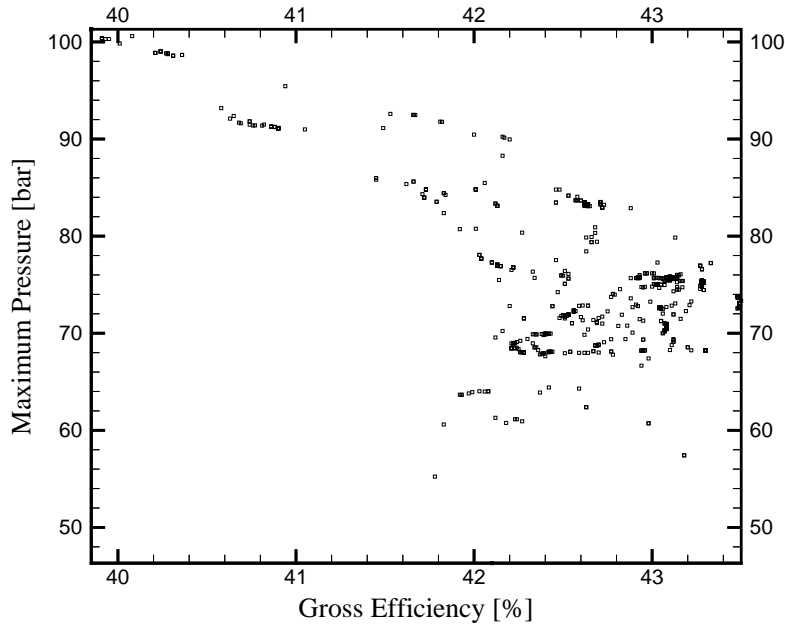
Figure 7.4: Maximum pressure versus gross efficiency. Engine parameters given in Table A.1.

modeling.

Burn duration in Figure 7.6 is found from one simulation to be between 6 and 18 CAD depending on the maximum pressure in the cylinder and thus maximum temperature and ignition timing. The duration is determined to be the time between 90% and 10% fuel remaining. This has previously been used with good results to measure combustion duration (Christensen et al., 1998a).

More fuel added (higher fuel equivalence ratio) leads to higher pressure and temperature. More fuel gives shorter combustion duration since the overall chemical reactions speed up. Lower temperatures, for example from lower intake temperature, leads to longer combustion duration.

Most of the ignition results from the simulation were between 6 and 15 CAD. This is somewhat lower than for the real engine, shown in Au et al. (2001) to be between 7 and 23 CAD depending on EGR rate. However since a single-zone model is used the burn duration is expected to be under-predicted (Smith et al., 1997). This is due to the isothermal charge simplification in this model. The overall combustion rate is very dependent on fuel equivalence ratio, combustion temperature and combustion timing (Christensen et al., 1999). Flowers et al.(2000) present experimental results for propane ranging from 7 to 9 CAD. It seems from Figure 7.6 that the propane mechanism used is quite accurate and gives good results for burn duration.
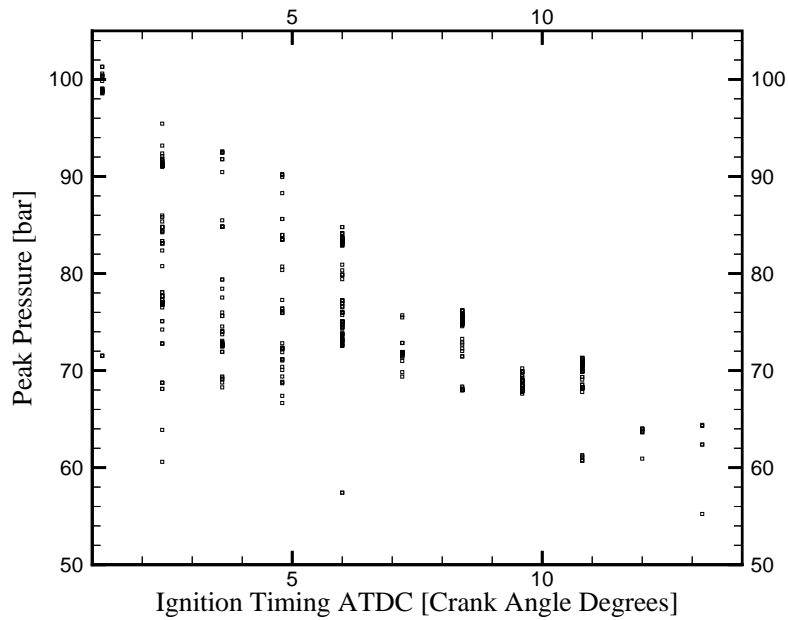
Figure 7.5: Maximum pressure shown versus ignition timing. Parameter set in Table A.1.
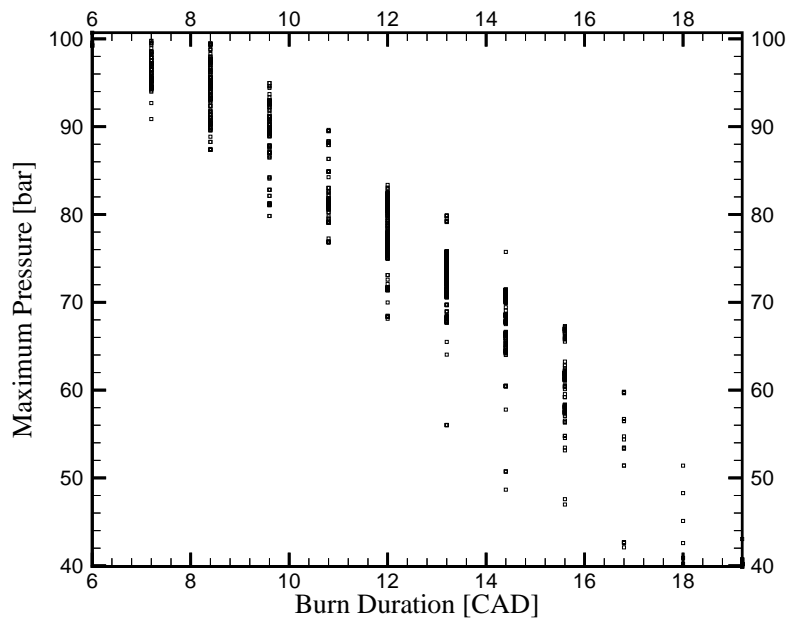
Figure 7.6: Maximum pressure versus burn duration. Engine parameters given in Table A.2.
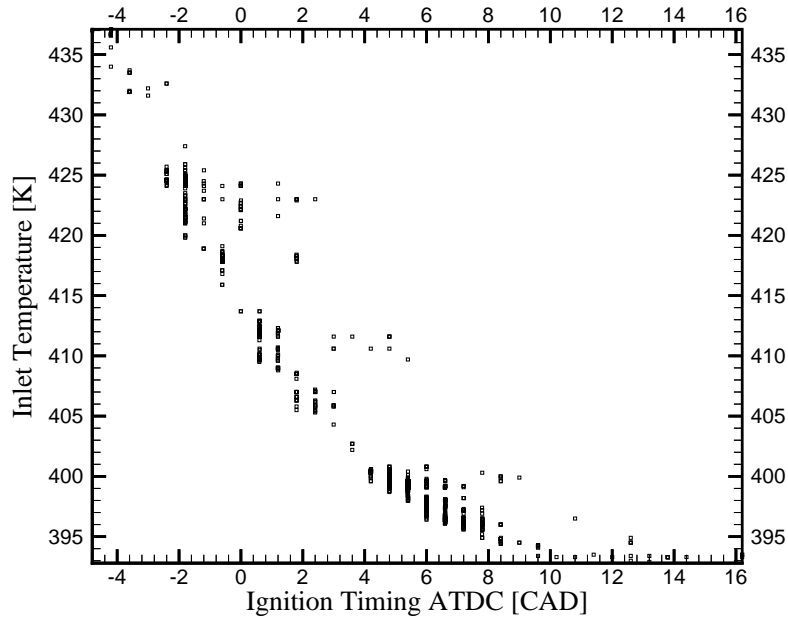
Figure 7.7: Inlet temperature versus ignition timing. Fuel is propane. Engine parameters given in Table A.2.

The considerable impact of inlet temperature on the ignition timing is shown in Figure 7.7. Inlet temperature has been previously shown to be a controlling factor for HCCI combustion. Amneus et al. (1998:567) state that HCCI combustion is extremely dependent on initial temperature, much lesser on pressure, fuel-air ratio and engine speed. Higher temperature results in earlier formation of radicals, thus earlier combustion. This seems to be well represented in the performed simulations.

Figure 7.8 shows how the engine efficiency is not optimal at the point of maximum brake power. This is consistent with the findings of Smith et al. (1997), and means that the HCCI engine has considerable advantages over the SI engine at low loads. Let it be noted that super-charging will improve the HCCI power output (Christensen et al., 1998b).

7.4   Parameter Optimization

It is desirable to know how the genetic algorithm would perform when asked to optimize the performance of the HCCI process. The penalty function was set as a linear function of the indicated brake efficiency given in (6.12). It was presumed that a simple penalty function would allow the genetic algorithm to search more
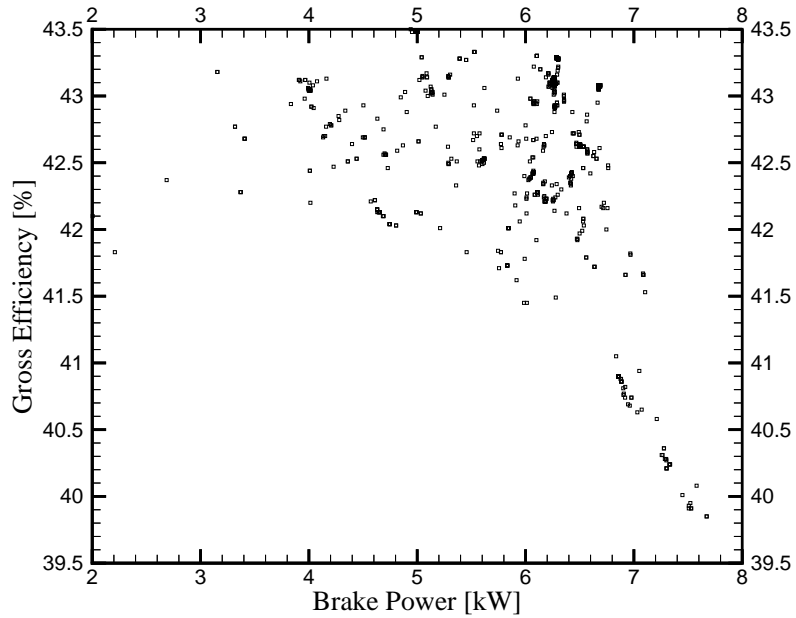
Figure 7.8: Brake power versus gross engine efficiency. Engine parameters given in Table A.1.

efficiently, although any number and combinations of engine parameters, emissions and performance could be used.

The engine parameters used are listed in Table A.1. EGR rate and fuel equivalence ratio was varied while all other parameters were kept constant. The results of the optimization are given below.

7.4.1 Optimization Analysis

Ryan & Callahan (1996) show experiments that use EGR will initiate start of combustion earlier. However, they state that this effect is primarily due to the higher intake temperature that results from use of EGR. When the temperature of both the EGR and fresh charge is kept constant, and the EGR and fresh charge fuel equivalence ratios are varied, results in Figure 7.9 show that low EGR rates result in earlier combustion. An EGR rate of 0.3 corresponds to 30% of the total charge by volume at BDC being recycled exhaust gases. Also interesting is that an EGR rate of between 0.3 and 0.35 leads to the desired late combustion timing, although these values also are found with early combustion timing. This is due to the combined effect of fuel equivalence and EGR ratios.
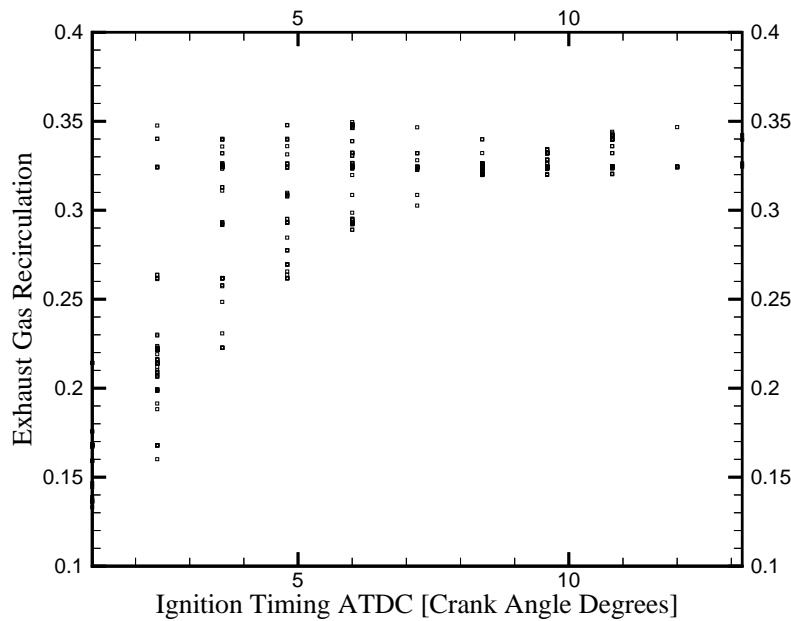
Figure 7.9: Rate of EGR versus ignition timing for single-zone model. Engine parameters given in Table A.1.

Exhaust gas recirculation will raise the temperature of the charge entering the cylinder. This will reduce the need of pre-heating in an actual engine. Second it will also dilute the charge in the cylinder. This results in lower peak temperature and pressure. The residual gases in the cylinder and the EGR will change the fuel-air ratio of the charge.

Figure 7.10 shows the simulation values of fuel equivalence ratio versus ignition timing. Flowers et al. (2000) show for experiments and multi-zone model experiments that increasing the equivalence ratio results in earlier start of combustion, opposite to what is shown in (7.10). By only varying the fuel equivalence ratio a similar result as that found by Flowers et al. (2000) is obtained. The combined effects of the fuel equivalence ratio and EGR result in this discrepancy.

Figure 7.11 shows that an EGR ratio between 0.3 and 0.35 is needed to get peak efficiencies. It also appears from the simulation results that the fuel equivalence ratio should approach the limit of the parameter range, in this case at least 0.7. Ryan & Callahan (1996) also found in their experimental results with diesel fuel that a close-to-stoichiometric fuel equivalence ratio for the fresh charge and EGR rates of 30-60% produced acceptable power in HCCI mode. This choice of EGR and fuel equivalence ratios are due to the penalty function. More fuel and less oxygen means that more of the charge in the cylinder reacts and produces heat and thus work.
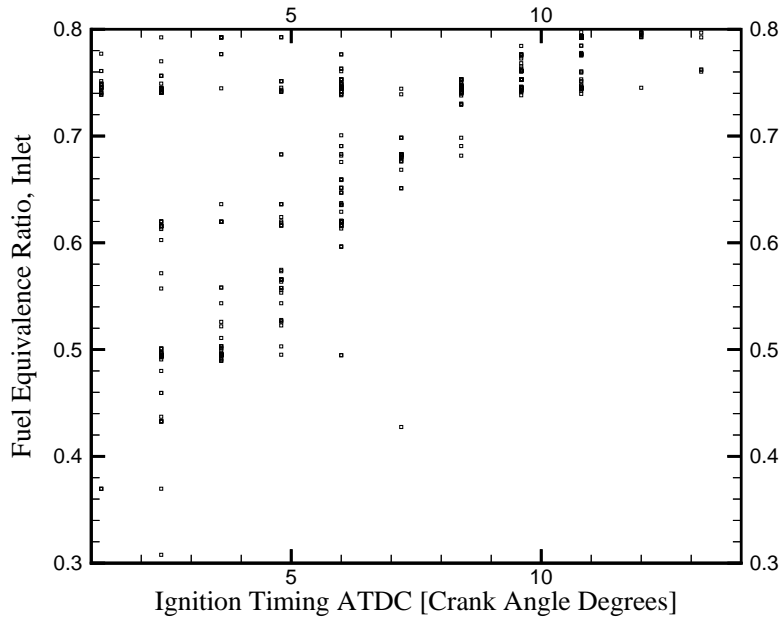
Figure 7.10: Fuel equivalence ratio shown versus ignition timing. Parameter set in Table A.1.

Figure 7.12 shows the three-dimensional map effects of the various EGR and fuel equivalence ratios on gross efficiency. A two-dimensional rendering of the figure removes much information, but it is shown to validate the optimal values for EGR and fuel equivalence ratios given. When rotated in three dimensions the simulation points appear spatially distributed, and an optimal region is easily identified.

Again, the heat transfer model may be introducing error into the results. The heat losses will increase as more heat is released in the combustion. This will affect the efficiency of the engine.

It is possible that a richer charge (e.g. a fuel equivalence ratio above 0.5) will lead to severe knock in a real engine (Olsson et al., 2000) since the rate of combustion will be high.

7.4.2 Performance of the Genetic Algorithm

The genetic algorithm performed a multi-parameter exploration of the HCCI combustion. Figure 7.13 shows how the parameter for EGR rate is varied for the first 200 generations of the search for the simulation run given in Table A.1. It appears that a close-to-optimal value is found within 30 generations, although one can observe the
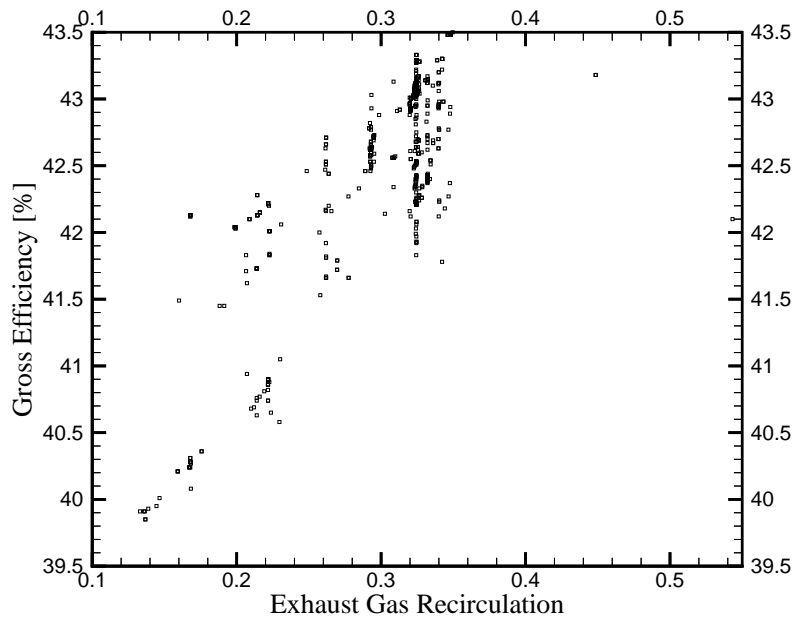
Figure 7.11: The impact of EGR on gross engine efficiency. Parameter set in Table A.1.

random elements of the search exploring other possibilities as the search evolves.

Figure 7.14 shows how the engine gross efficiency changes with each generation. It appears to quickly reach a high value.

Little work on the investigation of population size was made. However it is noted that a population size of five individuals may give reasonable results with two or three parameters, but is probably too small for more complex problems. The effects of change in mutation parameters and other features like elitism were not investigated.

When running with more than three parameters the search had problems with stabilizing on an optimal value for each parameter. The data from the simulations were also very difficult to analyze since the complex interactions of the parameters made it hard to discern any trends.

One of the powers of the genetic algorithm is multi-dimensional data that is generated. Figure 7.15 gives an example of a three dimensional visualization of two engine parameters and their effects on the maximum cycle pressure. A three-dimensional plane can be made out, and much of the search performed by the genetic algorithm appears to be done for low temperatures. This type of information could be a powerful tool in engine performance mapping.
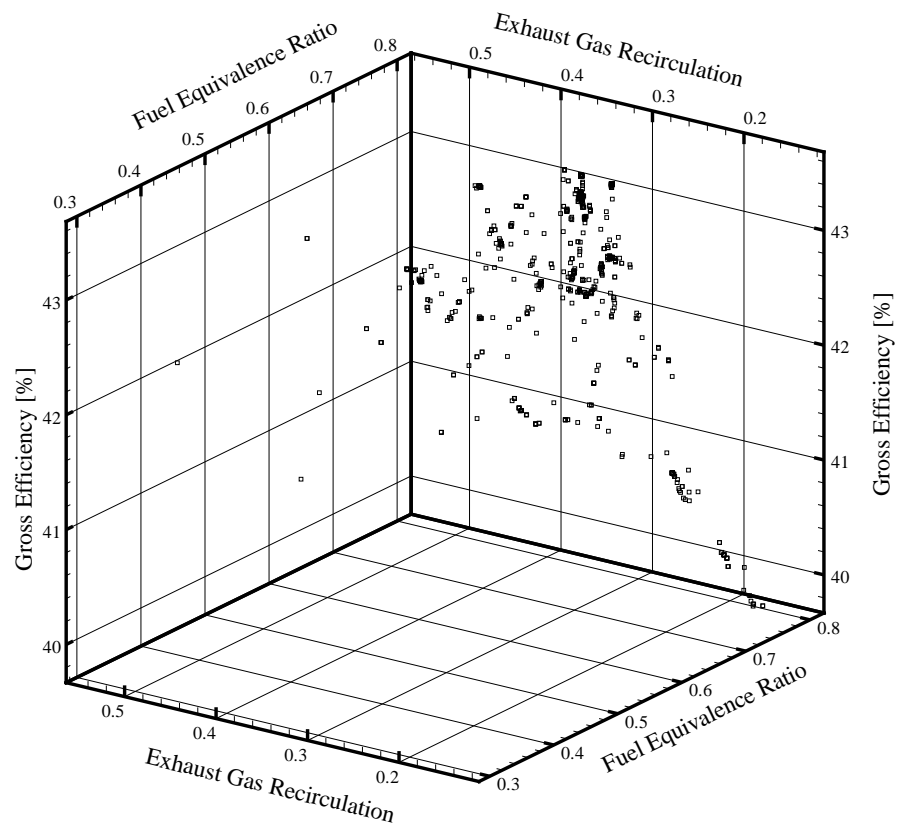
Figure 7.12: Gross engine efficiency versus EGR and fuel equivalence ratios. Engine parameters from Table A.1.
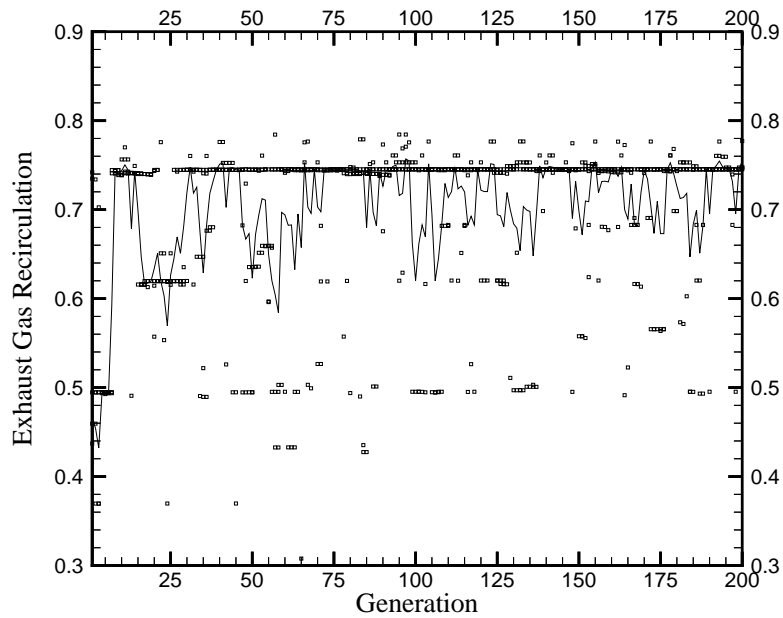
Figure 7.13: Variation of EGR in search propagation. Parameter set in Table A.1. Average value curve fit for each generation is shown.
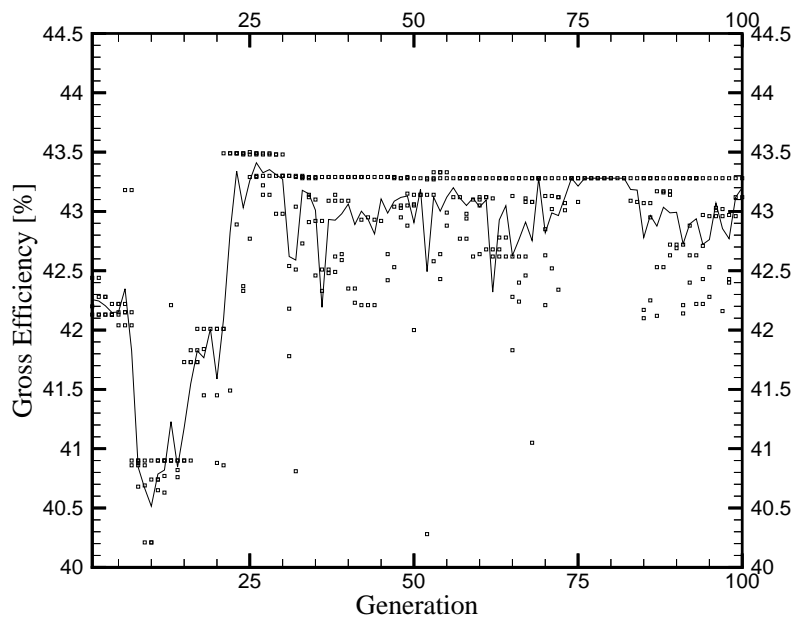
Figure 7.14: Efficiency in search propagation. Parameter set in Table A.1. Average value curve fit for each generation is shown.
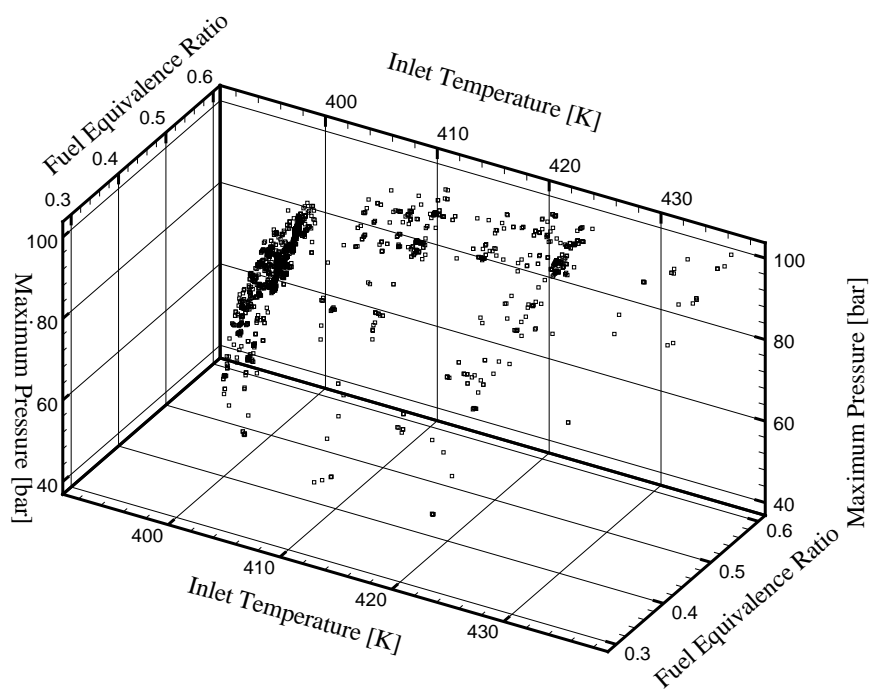
Figure 7.15: Demonstration of the multi-dimensional capabilities of GAs. Parameters in Table A.2.

7.5 NO_x Emissions

Previous work with single-zone models has pointed out the difficulty of predicting HC and CO emissions because of the lack of thermal gradients and no quenching or boundary layers in the model. NO_x emissions have been predicted with some success (Flowers et al., 2000). However, with the pressure over-prediction in a single-zone model NO_x formation will be somewhat over-predicted as well. Analysis efforts were put towards NO_x formation for the results at hand.

Reaction sensitivity data was taken from CHEMKIN and analyzed to find the controlling steps in NO production in HCCI engines running on propane. The sensitivity information identifies rate-limiting steps in complex reaction mechanisms, an introduction to this can be found in Warnatz, Maas & Dibble (1999:91).

The engine parameters used can be found in Table A.5. The total output of NO_x was 8.3 ppm for this run, of which 96% was in the form of NO.

The sensitivity analysis performed for NO used the following normalized value for each reaction i in each time step:

$$S_i = \frac{\partial X_k}{\partial k_i} \cdot \left[max \left(\left| \frac{\partial X_k}{\partial k_j} \right|_{j=1..N} \right) \right]^{-1} \tag{7.1}$$

where N is the number of reactions and k is the species, in this case NO.

As seen in Figure 7.16 the most prominent reaction steps are those of the thermal (Zeldovich) and nitrous oxide mechanism. The prompt mechanism is hardly active at all. The burn duration was found to be 14 CAD (10-90% fuel burned) for this simulation, a value that is well within the probable range for HCCI combustion.

The pressure and temperature is over-predicted in single-zone models as previously discussed. It is therefore likely that the thermal mechanism for NO_x is over-predicted as well.

With HCCI combustion the assumption is that temperature will be fairly uniform in the combustion chamber due to the homogeneous combustion. The use of lean mixtures means that the maximum temperature will be low compared to SI or CI engines. The formation of NO_x through the thermal mechanism is very temperature sensitive as discussed in Section 4.11. The residence time at high temperatures is also important, so a high inlet temperature will mean an increase in NO_x formation. This is due to the fact that the temperature at the start of the compression stroke greatly influences the the ignition and thus the temperature after combustion. The maximum temperature in HCCI combustion running at very lean fuel equivalence ratios will probably approach the limit of thermal NO_x production of approximately
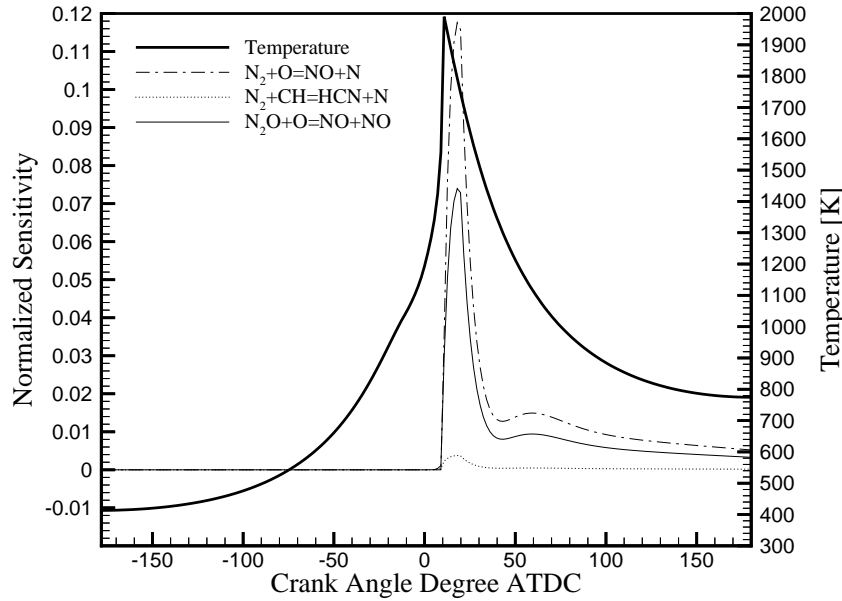
Figure 7.16: NO sensitivity analysis using propane as fuel. Engine parameters from Table A.5.

1700 K (Warnatz, Maas & Dibble, 1999:240).

Figure 7.17 shows the dependency of NO_x production on the maximum cycle temperature for methane combustion. As expected for the thermal NO_x pathway it rises approximately exponentially with temperature.

The importance of the nitrous oxide pathway is also found by Nicol et al. (1995). The low NO_x of lean premixed combustion in gas turbines receives a significant value of the total NO_x formation from the nitrous oxide pathway. The very low significance of the prompt NO_x pathway may be due to the occurrence and timing of radicals found in HCCI combustion.

It is important to notice that all results for HCCI combustion agree that very low NO_x is produced.

7.6   Investigation of HCCI Operation with Acetylene

The experimental investigation with acetylene in HCCI combustion was done with the VW 1.9 liter engine. Compressed acetylene was added to the air stream at equivalence ratios between 0.14 and 0.24. 10 different settings of inlet temperature
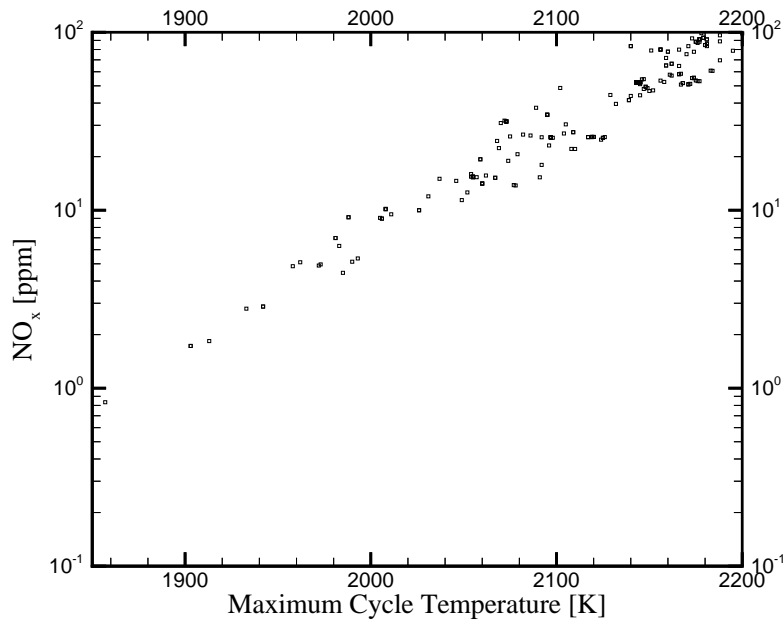
Figure 7.17: NO_x versus maximum temperature, logarithmic scale. Engine parameters from Table A.3.

and fuel equivalence ratio were used. As this was a preliminary investigation only little fuel was added because of the extremely flammable nature of acetylene.

As can be seen in Figure 7.18 the pressure trace for acetylene combustion has a similar but somewhat more gradual pressure rise after combustion than the one shown for propane in Figure 7.1. Also notice the pressure fluctuations that appear after a 82 cycle averaging process has been performed.

The ignition timing for acetylene combustion was very early (before TDC), as can be seen in Figure 7.19. Simulations indicate that combustion later than TDC will be difficult to achieve without the use of EGR or other means. Experiments using a lower intake temperature than the ones shown did not fire. It is possible that using more fuel would make the engine fire even at lower intake temperatures, however that was not investigated due to safety concerns with the explosive nature of acetylene. The simulation results fit the experiments quite well.

As for propane and methane, ignition much before TDC with acetylene results in low efficiency. This is shown in Figure 7.20. Notice the high efficiency obtained with acetylene compared to propane or methane.

A three-dimensional picture of the acetylene combustion can be made using genetic algorithms as seen in Figure 7.21.
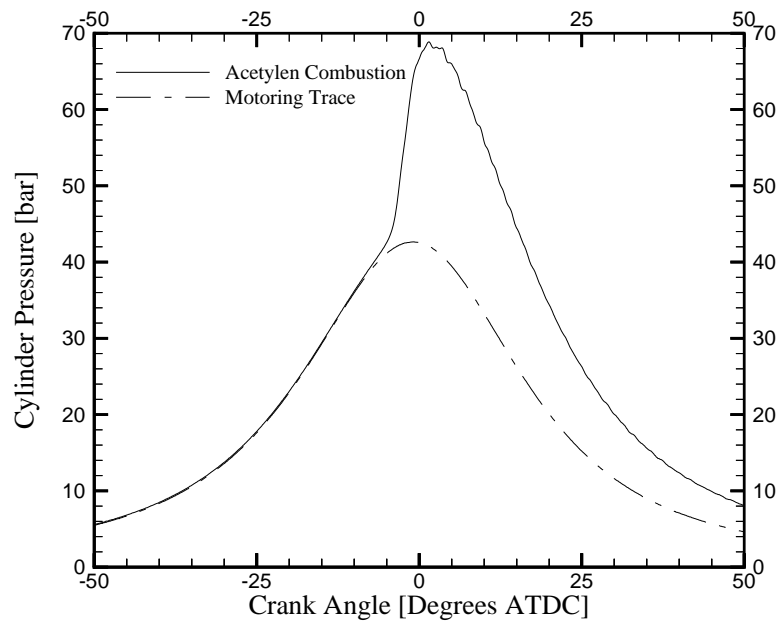
Figure 7.18: Example pressure trace for experiments with acetylene. Engine parameters from Table A.4, using inlet temperature at 79^oC and Φ equal to 0.193. Experiments averaged for 82 cycles.
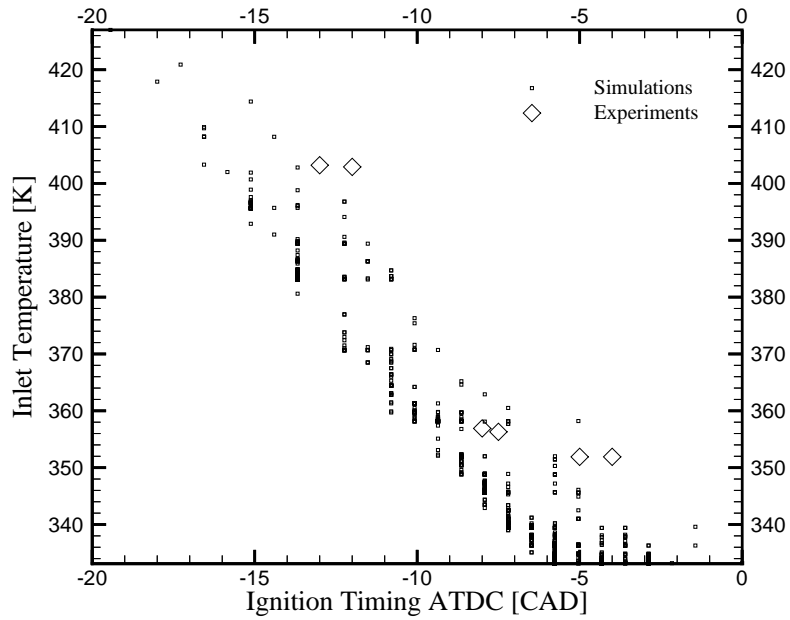
Figure 7.19: Inlet temperature versus ignition timing. Engine parameters from Table A.4.
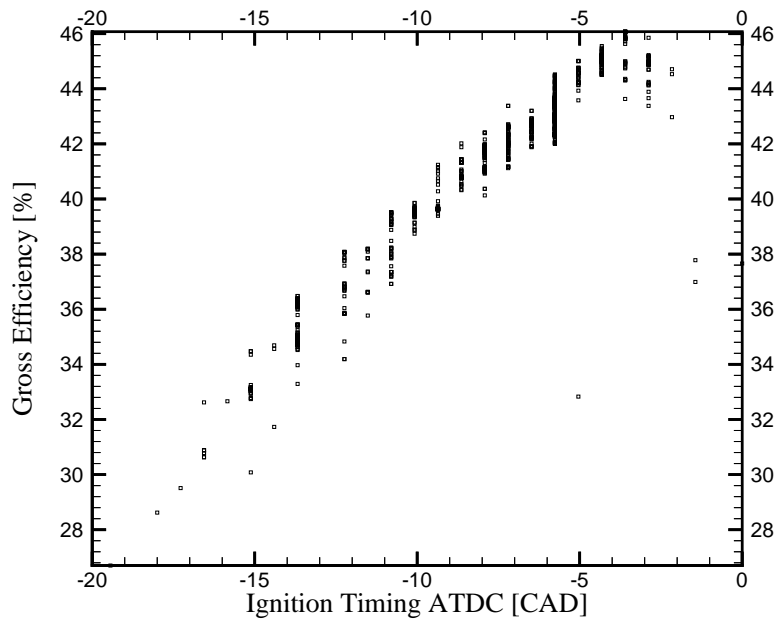
Figure 7.20: Efficiency versus ignition timing. Engine parameters from Table A.4.
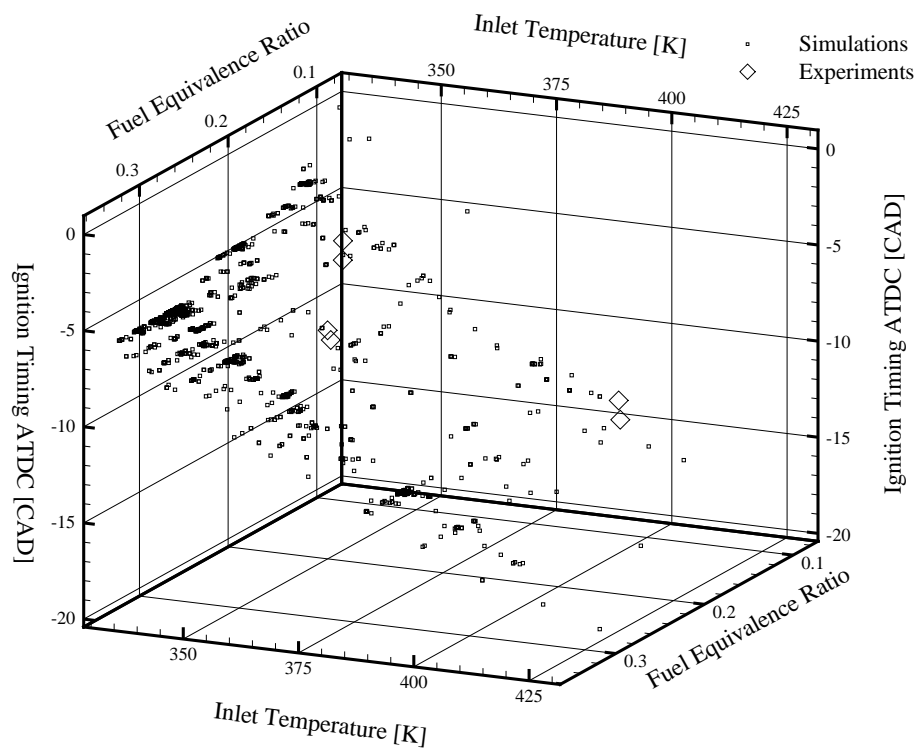
Figure 7.21: Ignition timing versus inlet parameters. Engine parameters from Table A.4.

Chapter 8

Conclusions

1. From the simulation results with propane the NO_x emissions in HCCI combustion, although very low, are found to be mainly caused by the thermal (Zeldovich) and nitrous oxide mechanisms.

2. The use of a genetic algorithm with the single-zone model is successful in predicting important engine performance parameters in HCCI combustion.

3. The use of genetic algorithms provides valuable insight into HCCI combustion through multi-parameter optimization. From the optimization data it appears that running the HCCI engine with about 35% EGR and a fuel equivalence ratio of about 0.7 gives very high gross engine efficiency.

4. Using the VVHS multi-zone model seems to provide more accurate simulation results through improved pressure prediction and the inclusion of temperature gradients. However, much work is left on this model in terms of the heat transfer modeling.

5. Acetylene used for HCCI combustion resulted in early ignition (before TDC), but high efficiency.

Chapter 9

Future Work

1. A more thorough analysis of engine heat transfer could provide the information needed in tuning the heat transfer coefficients for the multi-zone model to the particular engine being studied.

2. The results for the genetic algorithm parameter optimization of the HCCI combustion process using the multi-zone model should be compared to results from using the single-zone model.

3. The power of the genetic algorithm setup for engine simulations should be explored further and hopefully provide more detailed knowledge of HCCI combustion through the exploration of engine performance.

4. An analysis of the genetic algorithm efficiency looking at population size and other parameters should be performed to improve the efficiency of the method.

5. Further investigations with acetylene should explore if later ignition could be achieved with lower inlet temperature while increasing the fuel equivalence ratio.

References

Aceves, Salvador M., Daniel L. Flowers, Charles K. Westbrook, J. Ray Smith, William Pitz, Robert Dibble, Magnus Christensen and Bengt Johansson *A Multi-Zone Model for Prediction of HCCI Combustion and Emissions.* SAE Paper No. 2000-01-0327, 2000.

Aceves, S.M., J.R. Smith, C.K. Westbrook and W.J. Pitz *Compression Ratio Effect on Methane HCCI Combustion.* ASME Journal of Engineering for Gas Turbines and Power, Vol. 121, pp. 569-574, 1999.

Andreatta, Dale Allan *The Use of Reformed Natural Gas as a Fuel for Reciprocating Engines.* Doctor of Philosophy Thesis in Mechanical Engineering, University of California at Berkeley, 1995.

Assanis, Dennis N. and J. B. Heywood *The Effect of Chamber Geometry on Spark-Ignition Engine Combustion.* SAE Paper No. 860329, 1986.

Au, Michael Y., James W. Girard, Robert Dibble, Daniel Flowers, Salvador Aceves, Joel Martinez-Frias, Ray Smith, Christian Seibel and Ulrich Maas *1.9-Liter Four Cylinder HCCI Engine Operation with Exhaust Gas Recirculation.* SAE Paper No. 01FL-159, 2001.

Borman, Gary and Kenneth W. Ragland *Combustion Engineering.* McGraw-Hill, 1998.

Brown, Peter N., George D. Byrne and Alan C. Hindmarsh *VODE, a Variable-Coefficient ODE Solver.* SIAM Journal on Scientific and Statistical Computing, Vol. 10, No. 5, pp. 1038-1051, September 1989.

Çengel, Yunus A. and Michael A. Boles *Thermodynamics - An Engineering Approach.* 3rd ed., McGraw-Hill, 1998.

Chen, Jyh-Yuan and Robert Dibble *A Perfectly-Stirred-Reaction Description of Chemistry in Turbulent Nonpremixed Combustion of Methane in Air.* Combust. Sci.

and Tech., Vol. 84, pp.45-50, 1991.

Christensen, Magnus, Anders Hultqvist and Bengt Johansson *Demonstrating the Multi Fuel Capability of a Homogeneous Charge Compression Ignition Engine with Variable Compression Ratio.* SAE Paper No. 1999-01-3679, 1999.

Christensen, Magnus, Bengt Johansson, Per Amneus and Fabian Mauss *Supercharged Homogeneous Charge Compression Ignition* SAE Paper No. 980787, 1998a.

Christensen, M., and B. Johansson *Influence of Mixture Quality on Homogeneous Charge Compression Ignition.* SAE Paper No. 982454, 1998b.

Christensen, M., P. Einewall and B. Johansson *Homogeneous Charge Compression Ignition (HCCI) Using Iso-Octane, Ethanol and Natural Gas - A Comparison to Spark Ignition Operation.* SAE Paper No. 972874, 1997.

Darwin, Charles *On The Origin of Species by Means of Natural Selection or the Preservation of Favored Races in the Struggle for Life.* London, 1859.

De Jong, Kenneth and William Spears *On the State of Evolutionary Computing* Proceedings of the Fifth International Conference on Genetic Algorithms, 1993.

de Nevers, Joel *Air Pollution Control Engineering.* McGraw-Hill, Inc., 1995.

Eshelman, Larry J. ad J. David Schaffer *Crossover's Niche.* Proceedings of the Fifth International Conference on Genetic Algorithms, 1993.

Fiveland, Scott B. and Dennis N. Assanis *A Four-Stroke Homogeneous Charge Compression Ignition Engine Simulation for Combustion and Performance Studies.* SAE-Paper No. 2000-01-0332, 2000.

Goldberg, David E. *Genetic Algorithms in Search, Optimization, and Machine Learning.* Addison-Wesley Publishing Company, Inc., 1989.

Gen, Mitsuo and Runwei Cheng *Genetic Algorithms and Engineering Optimization.* John Wiley & Sons, Inc., 2000.

Heywood, John B. *Internal Combustion Engine Fundamentals.* McGraw-Hill, Inc., 1988.

Kee, Robert J., Fran M. Rupley and James A. Miller *CHEMKIN-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics.* SAND89-8009, Sandia National Laboratories, Livermore, California, 1989.

Kowalcsyk, Ryszard *Constrained Genetic Operators Preserving Feasibility of Solutions in Genetic Algorithms.* Genetic Algorithms in Engineering Systems: Innovations and Applications. 2-4 September 1997, Conference Publication.

Kuo, Kenneth Kuan-yun *Principles of Combustion.* John Wiley & Sons, Inc., 1986.

Lumley, John L. *Engines - An Introduction.* Cambridge University Press, 1999.

Maigaard, Peter, Fabian Mauss and Markus Kraft *Homogeneous Charge Compression Ignition Engine: A Simulation on the Effects of Inhomogenities.* ASME Spring Engine Technology Conference, Texas, April 9-12, 2000.

Martinez-Frias, Joel, Salvador M. Aceves, Daniel Flowers, J. Ray Smith and Robert Dibble *HCCI Engine Control by Thermal Management.* SAE Paper No. 2000-01-2869, 1998.

Miller, James A. and Craig T. Bowman *Mechanism and Modeling of Nitrogen Chemistry in Combustion.* Prog. Energy Combust. Sci., Vol. 15, pp. 287-338, 1989.

Moran, Michael J. and Howard N. Shapiro *Fundamentals of Engineering Thermodynamics.* 2nd. edition (US), John Wiley & Sons, Inc., 1992.

Nicol, D. G., R. C. Steele, N. M. Marinov and P. C. Malte *The Importance of the Nitrous Oxide Pathway to NO_x in Lean Premixed Combustion.* Journal of Engineering for Gas Turbines and Power, Vol. 117, pp 100-111, January 1995.

Noguchi, M., Y. Tanaka, T. Tanaka and Y. Takeuchi *A Study of Gasoline Engine Combustion by Observation of Intermediate Reactive Products During Combustion.* SAE Paper No. 790840, 1979.

Powell, David and Michael M. Skolnick *Using Genetic Algorithms in Engineering Design Optimization with Non-Linear Constraints.* Proceedings of the Fifth International Conference on Genetic Algorithms, 1993.

Reeves, Colin R. *Using Genetic Algorithms with Small Populations.* Proceedings of the Fifth International Conference on Genetic Algorithms, 1993.

Ryan III, Thomas W. and Timothy J. Callahan *Homogeneous Charge Compression Ignition of Diesel Fuel.* International Spring Fuels & Lubricants Meeting, May 6-8, 1996. SAE Paper No. 961190.

Smith, Alice E. and David M. Tate *Genetic Optimization Using a Penalty Function.* Proceedings of the Fifth International Conference on Genetic Algorithms, 1993.

Smith, J. Ray, Salvador M. Aceves, Charles Westbrook and William Pitz *Modeling of Homogeneous Charge Compression Ignition (HCCI) of Methane.* Fall Technical Conference of the ASME, Paper No. 97-ICE-68, 1997.

Stone, Richard *Introduction to Internal Combustion Engines.* SAE, 2nd ed. 1993.

Stone, Richard *Introduction to Internal Combustion Engines.* SAE, 3rd ed. 1999.

Thring, R. H. *Homogeneous Charge Compression Ignition (HCCI) Engines.* SAE Paper No. 892068, 1989.

Torres, John R. *Combustion of Natural Gas Augmented with Dimethyl Ether, Performed in a Homogeneous Charge Compression Ignited Engine.* Master of Science Thesis in Mechanical Engineering, University of California at Berkeley, 1997.

Warnatz, Jürgen, Ulrich Maas and Robert W. Dibble *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation.* Springer-Verlag, Berlin Heidelberg, 1999.

Appendix A

Simulation Parameters

This appendix contains the parameters used in the engine simulations.

A.1 Parameter Setup for Simulations

Table A.1: Engine parameters used in simulation run A.

Engine Parameter	Value
Pressure at cylinder inlet	0.9 bar
Temperature at cylinder inlet	115ºC
EGR rate	0.3 - 0.6
Fuel equivalence ratio	0.3 - 0.8
Engine speed	1800 rpm
Compression ratio	19.5:1
Fuel	Propane

Table A.2: Engine parameters used in simulation run B.

Engine Parameter	Value
Pressure at cylinder inlet	0.9 bar
Temperature at cylinder inlet	115 - 165ºC
EGR rate	0.0
Fuel equivalence ratio	0.25 - 0.6
Engine speed	1800 rpm
Compression ratio	18.5 - 19.5:1
Fuel	Propane

Table A.3: Engine parameters used in simulation run C.

Engine Parameter	Value
Pressure at cylinder inlet	0.9 - 1.5 bar
Temperature at cylinder inlet	115 - 165°C
EGR rate	0.0
Fuel equivalence ratio	0.25 - 0.6
Engine speed	1800 rpm
Compression ratio	19.5:1
Fuel	Methane

Table A.4: Engine parameters used in simulation run D.

Engine Parameter	Value
Pressure at cylinder inlet	0.91 bar
Temperature at cylinder inlet	60 - 160°C
EGR rate	0.0
Fuel equivalence ratio	0.05 - 0.35
Engine speed	1800 rpm
Compression ratio	19.5:1
Fuel	Acetylene

Table A.5: Engine parameters used in NO_x sensitivity analysis.

Engine Parameter	Value
Pressure at cylinder inlet	0.9 bar
Temperature at cylinder inlet	140°C
EGR rate	0.0
Fuel equivalence ratio	0.35
Engine speed	1800 rpm
Compression ratio	19.5:1
Fuel	Propane

Table A.6: Mass distribution in multi-zone model. From Aceves et al. (2000). Zone 10 is the central zone.

Zone number	1	2	3	4	5	6	7	8	9	10
% of total mass in zone	1	1	1	1	1	2	6	17	30	40

Appendix B

Chemical Reaction Mechanisms

B.1   GRI-Mech 3.0 CH_4 Mechanism

```
!  GRI-Mech Version 3.0 3/12/99 CHEMKIN-II format
!  See README30 file at anonymous FTP site unix.sri.com, directory gri
!  WorldWideWeb home page http://www.me.berkeley.edu/gri_mech/ or
!  through http://www.gri.org , under 'Basic Research',
!  for additional information, contacts, and disclaimer
ELEMENTS
O H C N
END
SPECIES
H2 H O O2 OH H2O HO2 H2O2
C CH CH2 CH2(S) CH3 CH4 CO CO2
HCO CH2O CH2OH CH3O CH3OH C2H C2H2 C2H3
C2H4 C2H5 C2H6 HCCO CH2CO HCCOH N NH
NH2 NH3 NNH NO NO2 N2O HNO CN
HCN H2CN HCNN HCNO HOCN HNCO NCO
C3H7 C3H8 CH2CHO CH3CHO N2
END
!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
REACTIONS
2O+M<=>O2+M 1.200E+17 -1.000 .00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/
O+H+M<=>OH+M 5.000E+17 -1.000 .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
O+H2<=>H+OH 3.870E+04 2.700 6260.00
O+HO2<=>OH+O2 2.000E+13 .000 .00
O+H2O2<=>OH+HO2 9.630E+06 2.000 4000.00
O+CH<=>H+CO 5.700E+13 .000 .00
O+CH2<=>H+HCO 8.000E+13 .000 .00
O+CH2(S)<=>H2+CO 1.500E+13 .000 .00
O+CH2(S)<=>H+HCO 1.500E+13 .000 .00
O+CH3<=>H+CH2O 5.060E+13 .000 .00
O+CH4<=>OH+CH3 1.020E+09 1.500 8600.00
O+CO(+M)<=>CO2(+M) 1.800E+10 .000 2385.00
LOW/ 6.020E+14 .000 3000.00/
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/
O+HCO<=>OH+CO 3.000E+13 .000 .00
O+HCO<=>H+CO2 3.000E+13 .000 .00
O+CH2O<=>OH+HCO 3.900E+13 .000 3540.00
O+CH2OH<=>OH+CH2O 1.000E+13 .000 .00
O+CH3O<=>OH+CH2O 1.000E+13 .000 .00
O+CH3OH<=>OH+CH2OH 3.880E+05 2.500 3100.00
O+CH3OH<=>OH+CH3O 1.300E+05 2.500 5000.00
O+C2H<=>CH+CO 5.000E+13 .000 .00
O+C2H2<=>H+HCCO 1.350E+07 2.000 1900.00
O+C2H2<=>OH+C2H 4.600E+19 -1.410 28950.00
```

```
O+C2H2<=>CO+CH2 6.940E+06 2.000 1900.00
O+C2H3<=>H+CH2CO 3.000E+13 .000 .00
O+C2H4<=>CH3+HCO 1.250E+07 1.830 220.00
O+C2H5<=>CH3+CH2O 2.240E+13 .000 .00
O+C2H6<=>OH+C2H5 8.980E+07 1.920 5690.00
O+HCCO<=>H+2CO 1.000E+14 .000 .00
O+CH2CO<=>OH+HCCO 1.000E+13 .000 8000.00
O+CH2CO<=>CH2+CO2 1.750E+12 .000 1350.00
O2+CO<=>O+CO2 2.500E+12 .000 47800.00
O2+CH2O<=>HO2+HCO 1.000E+14 .000 40000.00
H+O2+M<=>HO2+M 2.800E+18 -.860 .00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/
H+2O2<=>HO2+O2 2.080E+19 -1.240 .00
H+O2+H2O<=>HO2+H2O 11.26E+18 -.760 .00
H+O2+N2<=>HO2+N2 2.600E+19 -1.240 .00
H+O2<=>O+OH 2.650E+16 -.6707 17041.00
2H+M<=>H2+M 1.000E+18 -1.000 .00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/
2H+H2<=>2H2 9.000E+16 -.600 .00
2H+H2O<=>H2+H2O 6.000E+19 -1.250 .00
2H+CO2<=>H2+CO2 5.500E+20 -2.000 .00
H+OH+M<=>H2O+M 2.200E+22 -2.000 .00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/
H+HO2<=>O+H2O 3.970E+12 .000 671.00
H+HO2<=>O2+H2 4.480E+13 .000 1068.00
H+HO2<=>2OH 0.840E+14 .000 635.00
H+H2O2<=>HO2+H2 1.210E+07 2.000 5200.00
H+H2O2<=>OH+H2O 1.000E+13 .000 3600.00
H+CH<=>C+H2 1.650E+14 .000 .00
H+CH2(+M)<=>CH3(+M) 6.000E+14 .000 .00
LOW / 1.040E+26 -2.760 1600.00/
TROE/ .5620 91.00 5836.00 8552.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+CH2(S)<=>CH+H2 3.000E+13 .000 .00
H+CH3(+M)<=>CH4(+M) 13.90E+15 -.534 536.00
LOW / 2.620E+33 -4.760 2440.00/
TROE/ .7830 74.00 2941.00 6964.00 /
H2/2.00/ H2O/6.00/ CH4/3.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+CH4<=>CH3+H2 6.600E+08 1.620 10840.00
H+HCO(+M)<=>CH2O(+M) 1.090E+12 .480 -260.00
LOW / 2.470E+24 -2.570 425.00/
TROE/ .7824 271.00 2755.00 6570.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+HCO<=>H2+CO 7.340E+13 .000 .00
H+CH2O(+M)<=>CH2OH(+M) 5.400E+11 .454 3600.00
LOW / 1.270E+32 -4.820 6530.00/
TROE/ .7187 103.00 1291.00 4160.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+CH2O(+M)<=>CH3O(+M) 5.400E+11 .454 2600.00
LOW / 2.200E+30 -4.800 5560.00/
TROE/ .7580 94.00 1555.00 4200.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+CH2O<=>HCO+H2 5.740E+07 1.900 2742.00
H+CH2OH(+M)<=>CH3OH(+M) 1.055E+12 .500 86.00
LOW / 4.360E+31 -4.650 5080.00/
TROE/ .600 100.00 90000.0 10000.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+CH2OH<=>H2+CH2O 2.000E+13 .000 .00
H+CH2OH<=>OH+CH3 1.650E+11 .650 -284.00
H+CH2OH<=>CH2(S)+H2O 3.280E+13 -.090 610.00
H+CH3O(+M)<=>CH3OH(+M) 2.430E+12 .515 50.00
LOW / 4.660E+41 -7.440 14080.0/
TROE/ .700 100.00 90000.0 10000.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+CH3O<=>H+CH2OH 4.150E+07 1.630 1924.00
H+CH3O<=>H2+CH2O 2.000E+13 .000 .00
H+CH3O<=>OH+CH3 1.500E+12 .500 -110.00
H+CH3O<=>CH2(S)+H2O 2.620E+14 -.230 1070.00
H+CH3OH<=>CH2OH+H2 1.700E+07 2.100 4870.00
H+CH3OH<=>CH3O+H2 4.200E+06 2.100 4870.00
H+C2H(+M)<=>C2H2(+M) 1.000E+17 -1.000 .00
LOW / 3.750E+33 -4.800 1900.00/
TROE/ .6464 132.00 1315.00 5566.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+C2H2(+M)<=>C2H3(+M) 5.600E+12 .000 2400.00
LOW / 3.800E+40 -7.270 7220.00/
TROE/ .7507 98.50 1302.00 4167.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+C2H3(+M)<=>C2H4(+M) 6.080E+12 .270 280.00
LOW / 1.400E+30 -3.860 3320.00/
TROE/ .7820 207.50 2663.00 6095.00 /
```

```
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+C2H3<=>H2+C2H2 3.000E+13 .000 .00
H+C2H4(+M)<=>C2H5(+M) 0.540E+12 .454 1820.00
LOW / 0.600E+42 -7.620 6970.00/
TROE/ .9753 210.00 984.00 4374.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+C2H4<=>C2H3+H2 1.325E+06 2.530 12240.00
H+C2H5(+M)<=>C2H6(+M) 5.210E+17 -.990 1580.00
LOW / 1.990E+41 -7.080 6685.00/
TROE/ .8422 125.00 2219.00 6882.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+C2H5<=>H2+C2H4 2.000E+12 .000 .00
H+C2H6<=>C2H5+H2 1.150E+08 1.900 7530.00
H+HCCO<=>CH2(S)+CO 1.000E+14 .000 .00
H+CH2CO<=>HCCO+H2 5.000E+13 .000 8000.00
H+CH2CO<=>CH3+CO 1.130E+13 .000 3428.00
H+HCCOH<=>H+CH2CO 1.000E+13 .000 .00
H2+CO(+M)<=>CH2O(+M) 4.300E+07 1.500 79600.00
LOW / 5.070E+27 -3.420 84350.00/
TROE/ .9320 197.00 1540.00 10300.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
OH+H2<=>H+H2O 2.160E+08 1.510 3430.00
2OH(+M)<=>H2O2(+M) 7.400E+13 -.370 .00
LOW / 2.300E+18 -.900 -1700.00/
TROE/ .7346 94.00 1756.00 5182.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
2OH<=>O+H2O 3.570E+04 2.400 -2110.00
OH+HO2<=>O2+H2O 1.450E+13 .000 -500.00
DUPLICATE
OH+H2O2<=>HO2+H2O 2.000E+12 .000 427.00
DUPLICATE
OH+H2O2<=>HO2+H2O 1.700E+18 .000 29410.00
DUPLICATE
OH+C<=>H+CO 5.000E+13 .000 .00
OH+CH<=>H+HCO 3.000E+13 .000 .00
OH+CH2<=>H+CH2O 2.000E+13 .000 .00
OH+CH2<=>CH+H2O 1.130E+07 2.000 3000.00
OH+CH2(S)<=>H+CH2O 3.000E+13 .000 .00
OH+CH3(+M)<=>CH3OH(+M) 2.790E+18 -1.430 1330.00
LOW / 4.000E+36 -5.920 3140.00/
TROE/ .4120 195.0 5900.00 6394.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
OH+CH3<=>CH2+H2O 5.600E+07 1.600 5420.00
OH+CH3<=>CH2(S)+H2O 6.440E+17 -1.340 1417.00
OH+CH4<=>CH3+H2O 1.000E+08 1.600 3120.00
OH+CO<=>H+CO2 4.760E+07 1.228 70.00
OH+HCO<=>H2O+CO 5.000E+13 .000 .00
OH+CH2O<=>HCO+H2O 3.430E+09 1.180 -447.00
OH+CH2OH<=>H2O+CH2O 5.000E+12 .000 .00
OH+CH3O<=>H2O+CH2O 5.000E+12 .000 .00
OH+CH3OH<=>CH2OH+H2O 1.440E+06 2.000 -840.00
OH+CH3OH<=>CH3O+H2O 6.300E+06 2.000 1500.00
OH+C2H<=>H+HCCO 2.000E+13 .000 .00
OH+C2H2<=>H+CH2CO 2.180E-04 4.500 -1000.00
OH+C2H2<=>H+HCCOH 5.040E+05 2.300 13500.00
OH+C2H2<=>C2H+H2O 3.370E+07 2.000 14000.00
OH+C2H2<=>CH3+CO 4.830E-04 4.000 -2000.00
OH+C2H3<=>H2O+C2H2 5.000E+12 .000 .00
OH+C2H4<=>C2H3+H2O 3.600E+06 2.000 2500.00
OH+C2H6<=>C2H5+H2O 3.540E+06 2.120 870.00
OH+CH2CO<=>HCCO+H2O 7.500E+12 .000 2000.00
2HO2<=>O2+H2O2 1.300E+11 .000 -1630.00
DUPLICATE
2HO2<=>O2+H2O2 4.200E+14 .000 12000.00
DUPLICATE
HO2+CH2<=>OH+CH2O 2.000E+13 .000 .00
HO2+CH3<=>O2+CH4 1.000E+12 .000 .00
HO2+CH3<=>OH+CH3O 3.780E+13 .000 .00
HO2+CO<=>OH+CO2 1.500E+14 .000 23600.00
HO2+CH2O<=>HCO+H2O2 5.600E+06 2.000 12000.00
C+O2<=>O+CO 5.800E+13 .000 576.00
C+CH2<=>H+C2H 5.000E+13 .000 .00
C+CH3<=>H+C2H2 5.000E+13 .000 .00
CH+O2<=>O+HCO 6.710E+13 .000 .00
CH+H2<=>H+CH2 1.080E+14 .000 3110.00
CH+H2O<=>H+CH2O 5.710E+12 .000 -755.00
CH+CH2<=>H+C2H2 4.000E+13 .000 .00
CH+CH3<=>H+C2H3 3.000E+13 .000 .00
CH+CH4<=>H+C2H4 6.000E+13 .000 .00
CH+CO(+M)<=>HCCO(+M) 5.000E+13 .000 .00
LOW / 2.690E+28 -3.740 1936.00/
```

```
TROE/ .5757 237.00 1652.00 5069.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
CH+CO2<=>HCO+CO 1.900E+14 .000 15792.00
CH+CH2O<=>H+CH2CO 9.460E+13 .000 -515.00
CH+HCCO<=>CO+C2H2 5.000E+13 .000 .00
CH2+O2=>OH+H+CO 5.000E+12 .000 1500.00
CH2+H2<=>H+CH3 5.000E+05 2.000 7230.00
2CH2<=>H2+C2H2 1.600E+15 .000 11944.00
CH2+CH3<=>H+C2H4 4.000E+13 .000 .00
CH2+CH4<=>2CH3 2.460E+06 2.000 8270.00
CH2+CO(+M)<=>CH2CO(+M) 8.100E+11 .500 4510.00
LOW / 2.690E+33 -5.110 7095.00/
TROE/ .5907 275.00 1226.00 5185.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
CH2+HCCO<=>C2H3+CO 3.000E+13 .000 .00
CH2(S)+N2<=>CH2+N2 1.500E+13 .000 600.00
CH2(S)+O2<=>H+OH+CO 2.800E+13 .000 .00
CH2(S)+O2<=>CO+H2O 1.200E+13 .000 .00
CH2(S)+H2<=>CH3+H 7.000E+13 .000 .00
CH2(S)+H2O(+M)<=>CH3OH(+M) 4.820E+17 -1.160 1145.00
LOW / 1.880E+38 -6.360 5040.00/
TROE/ .6027 208.00 3922.00 10180.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
CH2(S)+H2O<=>CH2+H2O 3.000E+13 .000 .00
CH2(S)+CH3<=>H+C2H4 1.200E+13 .000 -570.00
CH2(S)+CH4<=>2CH3 1.600E+13 .000 -570.00
CH2(S)+CO<=>CH2+CO 9.000E+12 .000 .00
CH2(S)+CO2<=>CH2+CO2 7.000E+12 .000 .00
CH2(S)+CO2<=>CO+CH2O 1.400E+13 .000 .00
CH2(S)+C2H6<=>CH3+C2H5 4.000E+13 .000 -550.00
CH3+O2<=>O+CH3O 3.560E+13 .000 30480.00
CH3+O2<=>OH+CH2O 2.310E+12 .000 20315.00
CH3+H2O2<=>HO2+CH4 2.450E+04 2.470 5180.00
2CH3(+M)<=>C2H6(+M) 6.770E+16 -1.180 654.00
LOW / 3.400E+41 -7.030 2762.00/
TROE/ .6190 73.20 1180.00 9999.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
2CH3<=>H+C2H5 6.840E+12 .100 10600.00
CH3+HCO<=>CH4+CO 2.648E+13 .000 .00
CH3+CH2O<=>HCO+CH4 3.320E+03 2.810 5860.00
CH3+CH3OH<=>CH2OH+CH4 3.000E+07 1.500 9940.00
CH3+CH3OH<=>CH3O+CH4 1.000E+07 1.500 9940.00
CH3+C2H4<=>C2H3+CH4 2.270E+05 2.000 9200.00
CH3+C2H6<=>C2H5+CH4 6.140E+06 1.740 10450.00
HCO+H2O<=>H+CO+H2O 1.500E+18 -1.000 17000.00
HCO+M<=>H+CO+M 1.870E+17 -1.000 17000.00
H2/2.00/ H2O/ .00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HCO+O2<=>HO2+CO 13.45E+12 .000 400.00
CH2OH+O2<=>HO2+CH2O 1.800E+13 .000 900.00
CH3O+O2<=>HO2+CH2O 4.280E-13 7.600 -3530.00
C2H+O2<=>HCO+CO 1.000E+13 .000 -755.00
C2H+H2<=>H+C2H2 5.680E+10 0.900 1993.00
C2H3+O2<=>HCO+CH2O 4.580E+16 -1.390 1015.00
C2H4(+M)<=>H2+C2H2(+M) 8.000E+12 .440 86770.00
LOW / 1.580E+51 -9.300 97800.00/
TROE/ .7345 180.00 1035.00 5417.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H5+O2<=>HO2+C2H4 8.400E+11 .000 3875.00
HCCO+O2<=>OH+2CO 3.200E+12 .000 854.00
2HCCO<=>2CO+C2H2 1.000E+13 .000 .00
N+NO<=>N2+O 2.700E+13 .000 355.00
N+O2<=>NO+O 9.000E+09 1.000 6500.00
N+OH<=>NO+H 3.360E+13 .000 385.00
N2O+O<=>N2+O2 1.400E+12 .000 10810.00
N2O+O<=>2NO 2.900E+13 .000 23150.00
N2O+H<=>N2+OH 3.870E+14 .000 18880.00
N2O+OH<=>N2+HO2 2.000E+12 .000 21060.00
N2O(+M)<=>N2+O(+M) 7.910E+10 .000 56020.00
LOW / 6.370E+14 .000 56640.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HO2+NO<=>NO2+OH 2.110E+12 .000 -480.00
NO+O+M<=>NO2+M 1.060E+20 -1.410 .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
NO2+O<=>NO+O2 3.900E+12 .000 -240.00
NO2+H<=>NO+OH 1.320E+14 .000 360.00
NH+O<=>NO+H 4.000E+13 .000 .00
NH+H<=>N+H2 3.200E+13 .000 330.00
NH+OH<=>HNO+H 2.000E+13 .000 .00
NH+OH<=>N+H2O 2.000E+09 1.200 .00
NH+O2<=>HNO+O 4.610E+05 2.000 6500.00
NH+O2<=>NO+OH 1.280E+06 1.500 100.00
```

```
NH+N<=>N2+H 1.500E+13 .000 .00
NH+H2O<=>HNO+H2 2.000E+13 .000 13850.00
NH+NO<=>N2+OH 2.160E+13 -.230 .00
NH+NO<=>N2O+H 3.650E+14 -.450 .00
NH2+O<=>OH+NH 3.000E+12 .000 .00
NH2+O<=>H+HNO 3.900E+13 .000 .00
NH2+H<=>NH+H2 4.000E+13 .000 3650.00
NH2+OH<=>NH+H2O 9.000E+07 1.500 -460.00
NNH<=>N2+H 3.300E+08 .000 .00
NNH+M<=>N2+H+M 1.300E+14 -.110 4980.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
NNH+O2<=>HO2+N2 5.000E+12 .000 .00
NNH+O<=>OH+N2 2.500E+13 .000 .00
NNH+O<=>NH+NO 7.000E+13 .000 .00
NNH+H<=>H2+N2 5.000E+13 .000 .00
NNH+OH<=>H2O+N2 2.000E+13 .000 .00
NNH+CH3<=>CH4+N2 2.500E+13 .000 .00
H+NO+M<=>HNO+M 4.480E+19 -1.320 740.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HNO+O<=>NO+OH 2.500E+13 .000 .00
HNO+H<=>H2+NO 9.000E+11 .720 660.00
HNO+OH<=>NO+H2O 1.300E+07 1.900 -950.00
HNO+O2<=>HO2+NO 1.000E+13 .000 13000.00
CN+O<=>CO+N 7.700E+13 .000 .00
CN+OH<=>NCO+H 4.000E+13 .000 .00
CN+H2O<=>HCN+OH 8.000E+12 .000 7460.00
CN+O2<=>NCO+O 6.140E+12 .000 -440.00
CN+H2<=>HCN+H 2.950E+05 2.450 2240.00
NCO+O<=>NO+CO 2.350E+13 .000 .00
NCO+H<=>NH+CO 5.400E+13 .000 .00
NCO+OH<=>NO+H+CO 0.250E+13 .000 .00
NCO+N<=>N2+CO 2.000E+13 .000 .00
NCO+O2<=>NO+CO2 2.000E+12 .000 20000.00
NCO+M<=>N+CO+M 3.100E+14 .000 54050.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
NCO+NO<=>N2O+CO 1.900E+17 -1.520 740.00
NCO+NO<=>N2+CO2 3.800E+18 -2.000 800.00
HCN+M<=>H+CN+M 1.040E+29 -3.300 126600.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HCN+O<=>NCO+H 2.030E+04 2.640 4980.00
HCN+O<=>NH+CO 5.070E+03 2.640 4980.00
HCN+O<=>CN+OH 3.910E+09 1.580 26600.00
HCN+OH<=>HOCN+H 1.100E+06 2.030 13370.00
HCN+OH<=>HNCO+H 4.400E+03 2.260 6400.00
HCN+OH<=>NH2+CO 1.600E+02 2.560 9000.00
H+HCN(+M)<=>H2CN(+M) 3.300E+13 .000 .00
   LOW / 1.400E+26 -3.400 1900.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H2CN+N<=>N2+CH2 6.000E+13 .000 400.00
C+N2<=>CN+N 6.300E+13 .000 46020.00
CH+N2<=>HCN+N 3.120E+09 0.880 20130.00
CH+N2(+M)<=>HCNN(+M) 3.100E+12 .150 .00
   LOW / 1.300E+25 -3.160 740.00/
   TROE/ .6670 235.00 2117.00 4536.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
CH2+N2<=>HCN+NH 1.000E+13 .000 74000.00
CH2(S)+N2<=>NH+HCN 1.000E+11 .000 65000.00
C+NO<=>CN+O 1.900E+13 .000 .00
C+NO<=>CO+N 2.900E+13 .000 .00
CH+NO<=>HCN+O 4.100E+13 .000 .00
CH+NO<=>H+NCO 1.620E+13 .000 .00
CH+NO<=>N+HCO 2.460E+13 .000 .00
CH2+NO<=>H+HNCO 3.100E+17 -1.380 1270.00
CH2+NO<=>OH+HCN 2.900E+14 -.690 760.00
CH2+NO<=>H+HCNO 3.800E+13 -.360 580.00
CH2(S)+NO<=>H+HNCO 3.100E+17 -1.380 1270.00
CH2(S)+NO<=>OH+HCN 2.900E+14 -.690 760.00
CH2(S)+NO<=>H+HCNO 3.800E+13 -.360 580.00
CH3+NO<=>HCN+H2O 9.600E+13 .000 28800.00
CH3+NO<=>H2CN+OH 1.000E+12 .000 21750.00
HCNN+O<=>CO+H+N2 2.200E+13 .000 .00
HCNN+O<=>HCN+NO 2.000E+12 .000 .00
HCNN+O2<=>O+HCO+N2 1.200E+13 .000 .00
HCNN+OH<=>H+HCO+N2 1.200E+13 .000 .00
HCNN+H<=>CH2+N2 1.000E+14 .000 .00
HNCO+O<=>NH+CO2 9.800E+07 1.410 8500.00
HNCO+O<=>HNO+CO 1.500E+08 1.570 44000.00
HNCO+O<=>NCO+OH 2.200E+06 2.110 11400.00
HNCO+H<=>NH2+CO 2.250E+07 1.700 3800.00
HNCO+H<=>H2+NCO 1.050E+05 2.500 13300.00
HNCO+OH<=>NCO+H2O 3.300E+07 1.500 3600.00
```

```
HNCO+OH<=>NH2+CO2 3.300E+06 1.500 3600.00
HNCO+M<=>NH+CO+M 1.180E+16 .000 84720.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
HCNO+H<=>H+HNCO 2.100E+15 -.690 2850.00
HCNO+H<=>OH+HCN 2.700E+11 .180 2120.00
HCNO+H<=>NH2+CO 1.700E+14 -.750 2890.00
HOCN+H<=>H+HNCO 2.000E+07 2.000 2000.00
HCCO+NO<=>HCNO+CO 0.900E+13 .000 .00
CH3+N<=>H2CN+H 6.100E+14 -.310 290.00
CH3+N<=>HCN+H2 3.700E+12 .150 -90.00
NH3+H<=>NH2+H2 5.400E+05 2.400 9915.00
NH3+OH<=>NH2+H2O 5.000E+07 1.600 955.00
NH3+O<=>NH2+OH 9.400E+06 1.940 6460.00
NH+CO2<=>HNO+CO 1.000E+13 .000 14350.00
CN+NO2<=>NCO+NO 6.160E+15 -0.752 345.00
NCO+NO2<=>N2O+CO2 3.250E+12 .000 -705.00
N+CO2<=>NO+CO 3.000E+12 .000 11300.00
O+CH3=>H+H2+CO 3.370E+13 .000 .00
O+C2H4<=>H+CH2CHO 6.700E+06 1.830 220.00
O+C2H5<=>H+CH3CHO 1.096E+14 .000 .00
OH+HO2<=>O2+H2O 0.500E+16 .000 17330.00
DUPLICATE
OH+CH3=>H2+CH2O 8.000E+09 .500 -1755.00
CH+H2(+M)<=>CH3(+M) 1.970E+12 .430 -370.00
LOW/ 4.820E+25 -2.80 590.0 /
TROE/ .578 122.0 2535.0 9365.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
CH2+O2=>2H+CO2 5.800E+12 .000 1500.00
CH2+O2=>O+CH2O 2.400E+12 .000 1500.00
CH2+CH2=>2H+C2H2 2.000E+14 .000 10989.00
CH2(S)+H2O=>H2+CH2O 6.820E+10 .250 -935.00
C2H3+O2<=>O+CH2CHO 3.030E+11 .290 11.00
C2H3+O2<=>HO2+C2H2 1.337E+06 1.610 -384.00
O+CH3CHO<=>OH+CH2CHO 5.840E+12 .000 1808.00
O+CH3CHO=>OH+CH3+CO 5.840E+12 .000 1808.00
O2+CH3CHO=>HO2+CH3+CO 3.010E+13 .000 39150.00
H+CH3CHO<=>CH2CHO+H2 2.050E+09 1.160 2405.00
H+CH3CHO=>CH3+H2+CO 2.050E+09 1.160 2405.00
OH+CH3CHO=>CH3+H2O+CO 2.343E+10 0.730 -1113.00
HO2+CH3CHO=>CH3+H2O2+CO 3.010E+12 .000 11923.00
CH3+CH3CHO=>CH3+CH4+CO 2.720E+06 1.770 5920.00
H+CH2CO(+M)<=>CH2CHO(+M) 4.865E+11 0.422 -1755.00
LOW/ 1.012E+42 -7.63 3854.0/
TROE/ 0.465 201.0 1773.0 5333.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
O+CH2CHO=>H+CH2+CO2 1.500E+14 .000 .00
O2+CH2CHO=>OH+CO+CH2O 1.810E+10 .000 .00
O2+CH2CHO=>OH+2HCO 2.350E+10 .000 .00
H+CH2CHO<=>CH3+HCO 2.200E+13 .000 .00
H+CH2CHO<=>CH2CO+H2 1.100E+13 .000 .00
OH+CH2CHO<=>H2O+CH2CO 1.200E+13 .000 .00
OH+CH2CHO<=>HCO+CH2OH 3.010E+13 .000 .00
CH3+C2H5(+M)<=>C3H8(+M) .9430E+13 .000 .00
LOW/ 2.710E+74 -16.82 13065.0 /
TROE/ .1527 291.0 2742.0 7748.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
O+C3H8<=>OH+C3H7 1.930E+05 2.680 3716.00
H+C3H8<=>C3H7+H2 1.320E+06 2.540 6756.00
OH+C3H8<=>C3H7+H2O 3.160E+07 1.800 934.00
C3H7+H2O2<=>HO2+C3H8 3.780E+02 2.720 1500.00
CH3+C3H8<=>C3H7+CH4 0.903E+00 3.650 7154.00
CH3+C2H4(+M)<=>C3H7(+M) 2.550E+06 1.600 5700.00
LOW/ 3.00E+63 -14.6 18170./
TROE/ .1894 277.0 8748.0 7891.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
O+C3H7<=>C2H5+CH2O 9.640E+13 .000 .00
H+C3H7(+M)<=>C3H8(+M) 3.613E+13 .000 .00
LOW/ 4.420E+61 -13.545 11357.0/
TROE/ .315 369.0 3285.0 6667.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
H+C3H7<=>CH3+C2H5 4.060E+06 2.190 890.00
OH+C3H7<=>C2H5+CH2OH 2.410E+13 .000 .00
HO2+C3H7<=>O2+C3H8 2.550E+10 0.255 -943.00
HO2+C3H7=>OH+C2H5+CH2O 2.410E+13 .000 .00
CH3+C3H7<=>2C2H5 1.927E+13 -0.320 .00
END
```

B.2 C_3H_8 Mechanism

```
ELEMENTS H O N C END
SPECIES
H2 H O2 O OH HO2 H2O2 H2O N
NH NH2 NH3 HNO NO N2O NO2 N2H N2H2
HCN CN NCO HNCO CO CO2
CH CH2(S) CH2 CH3 CH4 C2H C2H2
C2H3 C2H4 C2H5 C2H6 C3H4 C3H5 C3H6 C3H8
C4H2 CHO CHCO CH2O CH3O CH2OH CH3OH
CH3O2 CH2CO CH3CO CH2CHO CH3CHO CH3O2H
I*C3H7 N*C3H7 N2
END
REACTIONS caloriers/mole
!konvertiert von KJOULES/MOLE nach CAL/MOL
! A n () E
! mol,cm3,sec cal/mol
!   MECHANISM C1, P = 3.0 1.0 0.0253 BAR, HIGH TEMP,

[-2ex] ! --------------------------------------
!  PRINT = "3.1 CH Verbrauch"
! --------------------------------------
CH + O = CO + H 3.30E+13 0 0
CH + O2 = CHO + O 3.00E+13 0 0
CH + CO2 = CHO + CO 3.40E+12 0 693.1
CH + H2O = CH2 + OH 5.70E+12 0 -764.8
! --------------------------------------
!  PRINT = "3.2 CHO Verbrauch"
! --------------------------------------
CHO + M = CO + H + M 7.10E+14 0 16801.7
CHO + H = CO + H2 9.00E+13 0 0
CHO + O = CO + OH 3.00E+13 0 0
CHO + O = CO2 + H 3.00E+13 0 0
CHO + OH = CO + H2O 1.00E+14 0 0
CHO + O2 = CO + HO2 3.00E+12 0 0
CHO + CHO = CH2O + CO 3.00E+13 0 0
! --------------------------------------
!  PRINT = "3.3.a 3-CH2 Verbrauch"
! --------------------------------------
CH2 + H = CH + H2 6.00E+12 0 -1792.5
CH2 + O => CO + H + H 8.43E+12 0 0
!CH2 + CH2 = C2H2 + H2 1.20E+13 0 812.6
CH2 + CH2 = C2H2 + H + H 1.10E+14 0 812.6
CH2 + CH3 = C2H4 + H 4.20E+13 0 0
CH2 + O2 = CO + OH + H 1.30E+13 0 1481.8
CH2 + O2 = CO2 + H2 1.20E+13 0 1481.8
! --------------------------------------
!  PRINT = "3.3.b 1-CH2 Bildung und Verbrauch"
! --------------------------------------
CH2(S) + M = CH2 + M 1.20E+13 0 0
CH2(S) + O2 = CO + OH + H 3.10E+13 0 0
CH2(S) + H2 = CH3 + H 7.20E+13 0 0
! --------------------------------------
!  PRINT = "3.4 CH2O Verbrauch"
! --------------------------------------
CH2O + M = CHO + H + M 5.00E+16 0 76480
CH2O + H = CHO + H2 2.30E+10 1.05 3274.3
CH2O + O = CHO + OH 4.15E+11 0.57 2772.4
CH2O + OH = CHO + H2O 3.40E+09 1.2 -454.1
CH2O + HO2 = CHO + H2O2 6.00E+08 0 0
CH2O + CH3 = CHO + CH4 1.00E+11 0 6094.5
CH2O + O2 = CHO + HO2 6.00E+13 0 40797.3
! --------------------------------------
!  PRINT = "3.5 CH3 Verbrauch"
! --------------------------------------
CH3 + M = CH2 + H + M 1.00E+16 0 90581
CH3 + H = CH2 + H2 6.00E+13 0 15057
CH3 + O = CH2O + H 8.43E+13 0 0
! --------------------------------------
!  Warnix
! --------------------------------------
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 3 BAR
! CH3 + H = CH4 4.59E+35 -6.7 9392.7
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 1 BAR
! CH3 + H = CH4 1.93E+36 -7 9082
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 0.0253 BAR
! CH3 + H = CH4 3.77E+35 -7.3 8604
! --------------------------------------
!  pressure dependent (Troe)
```

```
! -----------------------------------------
!  troe
CH3 + H (+M) = CH4 (+M) 2.11E+14 0 0
LOW /2.97E+09 -1.8 0/
TROE /0.577 2370.0 0.0 1.0/
! -----------------------------------------
CH3 + OH => CH3O + H 2.26E+14 0 15487.2
CH3O + H => CH3 + OH 4.75E+16 -0.1 21032
CH3 + O2 => CH2O + OH 3.30E+11 0 8938.6
CH3 + HO2 = CH3O + OH 1.80E+13 0 0
CH3 + HO2 = CH4 + O2 3.60E+12 0 0
CH3 + CH3 => C2H4 + H2 1.00E+16 0 32026
! -----------------------------------------
!  Warnix
! -----------------------------------------
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 3 BAR
! CH3 + CH3 = C2H6 1.32E+49 -11 18087.52
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 1 BAR
! CH3 + CH3 = C2H6 1.69E+53 -12 19416.36
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 0.0253 BAR
! CH3 + CH3 = C2H6 3.23E+58 -14 18591.81
! -----------------------------------------
!  pressure dependent (Troe)
! -----------------------------------------
!  troe
CH3 + CH3 (+M) = C2H6 (+M) 3.61E+13 0 0
LOW /1.41E+28 -7 2762.84 /
TROE /0.38 73.0 0.62 1180.0/
! -----------------------------------------
!  PRINT = "3.6 CH3O Bildung und Verbrauch"
! -----------------------------------------
CH3O + M = CH2O + H + M 5.00E+13 0 25095
CH3O + H = CH2O + H2 1.80E+13 0 0
CH3O + O2 = CH2O + HO2 4.00E+10 0 2127.1
CH2O + CH3O => CH3OH + CHO 6.00E+11 0 3298.2
CH3OH + CHO => CH2O + CH3O 6.50E+09 0 13670.8
CH3O + O = O2 + CH3 1.10E+13 0 0
CH3O + O = OH + CH2O 1.40E+12 0 0
! -----------------------------------------
!  PRINT = "3.7 CH2OH Verbrauch"
! -----------------------------------------
CH2OH + M = CH2O + H + M 5.00E+13 0 25095
CH2OH + H = CH2O + H2 3.00E+13 0 0
CH2OH + O2 = CH2O + HO2 1.00E+13 0 7170
! -----------------------------------------
!  PRINT = "3.8 CH3O2 Verbrauch"
! -----------------------------------------
CH3O2 + M => CH3 + O2 + M 7.24E+16 0 26552.9
CH3 + O2 + M => CH3O2 + M 1.41E+16 0 -1099.4
CH3O2 + CH2O => CH3O2H + CHO 1.30E+11 0 9010.3
CH3O2H + CHO => CH3O2 + CH2O 2.50E+10 0 10109.7
CH3O2 + CH3 => CH3O + CH3O 3.80E+12 0 -1195
CH3O + CH3O => CH3O2 + CH3 2.00E+10 0 0
CH3O2 + HO2 => CH3O2H + O2 4.60E+10 0 -2605.1
CH3O2H + O2 => CH3O2 + HO2 3.00E+12 0 39028.7
CH3O2 + CH3O2 => CH2O + CH3OH + O2 1.80E+12 0 0
CH2O + CH3OH + O2 => CH3O2 + CH3O2 0.00E+00 0 0
CH3O2 + CH3O2 => CH3O + CH3O + O2 3.70E+12 0 2198.8
CH3O + CH3O + O2 => CH3O2 + CH3O2 0.00E+00 0 0
! -----------------------------------------
!  PRINT = "3.9 CH4 Verbrauch"
! -----------------------------------------
CH4 + H = H2 + CH3 1.30E+04 3 8030.4
CH4 + O = OH + CH3 6.92E+08 1.56 8484.5
CH4 + OH = H2O + CH3 1.60E+07 1.83 2772.4
CH4 + HO2 = H2O2 + CH3 1.10E+13 0 24640.9
CH4 + CH = C2H4 + H 3.00E+13 0 -406.3
CH4 + CH2 = CH3 + CH3 1.30E+13 0 9536.1
! -----------------------------------------
!  PRINT = "3.10 CH3OH Verbrauch"
! -----------------------------------------
!  DECOMPOSITION. VALUE KASSEL AT P = 0.0253 BAR.
CH3OH = CH3 + OH 2.17E+24 -3.3 87952
CH3OH + H = CH2OH + H2 4.00E+13 0 6094.5
CH3OH + O = CH2OH + OH 1.00E+13 0 4684.4
CH3OH + OH = CH2OH + H2O 1.00E+13 0 1696.9
CH3OH + HO2 => CH2OH + H2O2 6.20E+12 0 19382.9
CH2OH + H2O2 => HO2 + CH3OH 1.00E+07 1.7 11448.1
CH3OH + CH3 = CH4 + CH2OH 9.00E+12 0 9822.9
CH3O + CH3OH => CH2OH + CH3OH 2.00E+11 0 7002.7
CH2OH + CH3OH => CH3O + CH3OH 2.20E+04 1.7 10850.6
```

```
CH3OH + CH2O => CH3O + CH3O 1.53E+12 0 79634.8
CH3O + CH3O => CH3OH + CH2O 3.00E+13 0 0
! -------------------------------------
!  PRINT = "3.11 CH3O2H Verbrauch"
! -------------------------------------
CH3O2H = CH3O + OH 4.00E+15 0 43139.5
OH + CH3O2H = H2O + CH3O2 2.60E+12 0 0
! -------------------------------------
!  PRINT = "4.1 C2H Verbrauch"
! -------------------------------------
C2H + O = CO + CH 1.00E+13 0 0
C2H + O2 = CHCO + O 3.00E+12 0 0
! -------------------------------------
!  PRINT = "4.2 CHCO Verbrauch"
! -------------------------------------
CHCO + H = CH2 + CO 1.50E+14 0 0
CHCO + O => CO + CO + H 9.60E+13 0 0
CHCO + CH2 = C2H3 + CO 3.00E+13 0 0
! -------------------------------------
!  PRINT = "4.3 C2H2 Verbrauch"
! -------------------------------------
C2H2 + M = C2H + H + M 3.60E+16 0 106594
C2H2 + H = C2H + H2 1.50E+14 0 19024.4
C2H2 + O = CH2 + CO 1.72E+04 2.8 501.9
C2H2 + O = CHCO + H 1.72E+04 2.8 501.9
C2H2 + OH = H2O + C2H 6.00E+13 0 12953.8
!  C2H2 + C2H = C4H2 + H 3.00E+13 0 0
CH2 + CH2 = C2H2 + H2 5.20E+13 0 0
!  C2H2 + O2 = CHCO + OH 2.00E+08 0 30114
! -------------------------------------
!  PRINT = "4.4 CH2CO Verbrauch"
! -------------------------------------
CH2CO + M = CH2 + CO + M 1.00E+16 0 59272
CH2CO + H = CH3 + CO 4.20E+13 0 3847.9
CH2CO + O = CHO + CHO 2.30E+12 0 693.1
CH2CO + OH = CH2O + CHO 1.00E+13 0 0
! -------------------------------------
!  PRINT = "4.5 C2H3 Verbrauch"
! -------------------------------------
!  Warnix
! -------------------------------------
!  NEXT VALUE OBTAINED FROM K0/KINF CEE 3 BAR /3
!  C2H3 = C2H2 + H 1.89E+42 -9.1 47704.4
!  NEXT VALUE OBTAINED FROM K0/KINF CEE 1 BAR /3
!  C2H3 = C2H2 + H 4.70E+40 -8.8 46485.5
!  NEXT VALUE OBTAINED FROM K0/KINF CEE 0.0267 BAR
!  C2H3 = C2H2 + H 9.40E+37 -8.5 45433.9
! -------------------------------------
!  pressure dependent (Troe)
! -------------------------------------
!  troe
C2H3 (+M) = C2H2 + H (+M) 2.00E+14 0 39743.31
LOW /5.94E+27 -7.5 5762.29/
TROE /0.35 1.000E+98 0.0 999.99/
! -------------------------------------
C2H3 + OH = C2H2 + H2O 5.00E+13 0 0
C2H3 + H = C2H2 + H2 1.20E+13 0 0
C2H3 + O = C2H2 + OH 1.00E+13 0 0
C2H3 + O = CH3 + CO 1.00E+13 0 0
C2H3 + O = CHO + CH2 1.00E+13 0 0
C2H3 + O2 = C2H2 + HO2 5.40E+12 0 0
! -------------------------------------
!  PRINT = "4.6 CH3CO Verbrauch"
! -------------------------------------
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 3 BAR
! CH3CO = CH3 + CO 4.37E+27 -5.2 19335.1
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 1 BAR
CH3CO = CH3 + CO 2.32E+26 -5 17948.9
!  NEXT VALUE OBTAINED FROM KASSEL AT P = 0.0253 BAR
! CH3CO = CH3 + CO 4.13E+23 -4.7 16371.5
CH3CO + H = CH2CO + H2 2.00E+13 0 0
CH3CO + CH3 = C2H6 + CO 5.00E+13 0 0
! -------------------------------------
!  PRINT = "4.7 C2H4 Verbrauch"
! -------------------------------------
C2H4 + M = C2H2 + H2 + M 2.50E+17 0 76432.2
C2H4 + M = C2H3 + H + M 1.70E+18 0 96556
C2H4 + H = C2H3 + H2 1.70E+15 0 15033.1
C2H4 + O = CH2CHO + H 5.20E+05 2.08 0
C2H4 + O = CHO + CH3 1.21E+06 2.08 0
C2H4 + OH = C2H3 + H2O 6.50E+13 0 5951.1
```

```
! ----------------------------------------
! PRINT = "4.8 CH3CHO Verbrauch"
! ----------------------------------------
CH3CHO + M = CH3 + CHO + M 7.00E+15 0 81929.2
CH3CHO + H = CH3CO +H2 2.10E+09 1.16 2413.9
CH3CHO + H = CH2CHO +H2 2.00E+09 1.16 2413.9
CH3CHO + O = CH3CO +OH 5.00E+12 0 1816.4
CH3CHO + O = CH2CHO +OH 8.00E+11 0 1816.4
CH3CHO + O2 = CH3CO +HO2 4.00E+13 0 39267.7
CH3CHO + OH = CH3CO +H2O 2.30E+10 0.73 -1123.3
CH3CHO + HO2 = CH3CO +H2O2 3.00E+12 0 11950
CH3CHO + CH2 = CH3CO +CH3 2.50E+12 0 3800.1
CH3CHO + CH3 = CH3CO +CH4 2.00E-06 5.54 2461.7
! ----------------------------------------
! PRINT = "4.9 C2H5 Consumption"
! ----------------------------------------
! Warnix
! ----------------------------------------
! NEXT VALUE OBTAINED FROM KASSEL AT P = 3 BAR
! C2H5 = C2H4 + H 6.09E+41 -8.6 54133.5
! NEXT VALUE OBTAINED FROM KASSEL AT P = 1 BAR
! C2H5 = C2H4 + H 1.02E+43 -9.1 53583.8
! NEXT VALUE OBTAINED FROM KASSEL AT P = 0.0253 BAR
! C2H5 = C2H4 + H 2.65E+42 -9.5 50213.9
! ----------------------------------------
! pressure dependent (Golden und Larson)
! ----------------------------------------
! golden ??? aber Eingabe in TROE ???
C2H5 (+M) = C2H4 + H (+M) 3.20E+13 0 39913
LOW /7.69E+02 0 -9799/
TROE /0.411 73.4 422.8/
! ----------------------------------------
C2H5 + H = CH3 + CH3 3.00E+13 0 0
C2H5 + O = CH3CHO + H 5.00E+13 0 0
C2H5 + O = CH2O + CH3 1.00E+13 0 0
C2H5 + O2 = C2H4 + HO2 1.10E+10 0 -1505.7
C2H5 + CH3 = C2H4 + CH4 2.80E+13 0 0
C2H5 + C2H5 = C2H4 + C2H6 1.40E+12 0 0
! ----------------------------------------
! PRINT = "4.9 C2H6 Verbrauch"
! ----------------------------------------
C2H6 + H = C2H5 + H2 1.40E+09 1.5 7432.9
C2H6 + O = C2H5 + OH 1.00E+09 1.5 5831.6
C2H6 + OH = C2H5 + H2O 7.20E+06 2 860.4
C2H6 + HO2 = C2H5 + H2O2 1.70E+13 0 20530.1
C2H6 + O2 = C2H5 + HO2 6.00E+13 0 51863
C2H6 + CH2 = C2H5 + CH3 2.20E+13 0 8675.7
C2H6 + CH3 = C2H5 + CH4 1.50E-07 6 6070.6
! ----------------------------------------
! PRINT = "5.1 C3H2 Verbrauch"
! ----------------------------------------
! ----------------------------------------
! PRINT = "5.2 C3H3 Bildung und Verbrauch"
! ----------------------------------------
! C3H3 + O = CO + C2H3 3.80E+13 0 0
! C3H3 + O2 = CHCO + CH2O 6.00E+12 0 0
! ----------------------------------------
! PRINT = "5.3 C3H4 Bildung und Verbrauch"
! ----------------------------------------
C3H4 + O = CH2O + C2H2 1.00E+12 0 0
C3H4 + O = CHO + C2H3 1.00E+12 0 0
C3H4 + OH = CH2O + C2H3 1.00E+12 0 0
C3H4 + OH = CHO + C2H4 1.00E+12 0 0
! ----------------------------------------
! PRINT = "5.4 C3H5 Bildung und Verbrauch"
! ----------------------------------------
C3H5 = C3H4 + H 3.98E+13 0 70050.9
C3H5 + H = C3H4 + H2 1.00E+13 0 0
C3H5 + O2 = C3H4 + HO2 6.00E+11 0 10014.1
! ----------------------------------------
! PRINT = "5.5 C3H6 Bildung und Verbrauch"
! ----------------------------------------
C3H6 = C3H5 + H 1.00E+13 0 77914
C3H6 = C2H3 + CH3 3.15E+15 0 85801
H + C3H6 = C3H5 + H2 5.00E+12 0 1505.7
C3H6 + O = C2H4 + CH2O 5.90E+13 0 5019
C3H6 + O = C2H5 + CHO 3.60E+12 0 0
C3H6 + O = CH3 + CH3CO 5.00E+12 0 597.5
C3H6 + OH = C2H5 + CH2O 7.90E+12 0 0
OH + C3H6 = CH3 + CH3CHO 5.10E+12 0 0
C3H6 + OH = C3H5 + H2O 4.00E+12 0 0
```

```
CH3 + C3H6 = CH4 + C3H5 8.96E+12 0 8508.4
C3H6 + C2H5 = C3H5 + C2H6 1.00E+11 0 9201.5
! ----------------------------------------
!  PRINT = "5.6.a n-C3H7 Verbrauch"
! ----------------------------------------
N*C3H7 = CH3 + C2H4 9.60E+13 0 31022.2
N*C3H7 = H + C3H6 1.25E+14 0 37021.1
N*C3H7 + O2 = C3H6 + HO2 1.00E+12 0 4995.1
! ----------------------------------------
!  PRINT = "5.6.b i-C3H7 Verbrauch"
! ----------------------------------------
I*C3H7 = H + C3H6 6.30E+13 0 36925.5
I*C3H7 = CH3 + C2H4 2.00E+10 0 29516.5
I*C3H7 + O2 = C3H6 + HO2 1.00E+12 0 4995.1
! ----------------------------------------
!  PRINT = "5.7 C3H8 Verbrauch"
! ----------------------------------------
C2H5 + CH3 = C3H8 7.00E+12 0 0
H + C3H8 = H2 + I*C3H7 1.00E+14 0 8341.1
H + C3H8 = H2 + N*C3H7 1.30E+14 0 9703.4
C3H8 + O = I*C3H7 + OH 2.60E+13 0 4469.3
C3H8 + O = N*C3H7 + OH 3.00E+13 0 5759.9
C3H8 + OH = I*C3H7 + H2O 2.80E+12 0 860.4
C3H8 + OH = N*C3H7 + H2O 3.70E+12 0 1649.1
C3H8 + HO2 => I*C3H7 + H2O2 2.00E+12 0 17016.8
I*C3H7 + H2O2 => C3H8 + HO2 4.16E+11 0 7432.9
C3H8 + HO2 => N*C3H7 + H2O2 1.70E+13 0 20482.3
N*C3H7 + H2O2 => C3H8 + HO2 2.33E+12 0 9822.9
CH3 + C3H8 => CH4 + I*C3H7 1.30E+12 0 11615.4
CH4 + I*C3H7 => CH3 + C3H8 1.01E+13 0 18570.3
CH3 + C3H8 => CH4 + N*C3H7 4.00E+11 0 9512.2
CH4 + N*C3H7 => CH3 + C3H8 3.12E+12 0 16467.1
C3H8 + O2 => I*C3H7 + HO2 4.00E+13 0 47537.1
I*C3H7 + HO2 => C3H8 + O2 2.08E+12 0 0
C3H8 + O2 => N*C3H7 + HO2 4.00E+13 0 47537.1
N*C3H7 + HO2 => C3H8 + O2 2.08E+12 0 0
C3H8 + CH3O => N*C3H7 + CH3OH 3.00E+11 0 7002.7
N*C3H7 + CH3OH => C3H8 + CH3O 1.22E+10 0 9201.5
C3H8 + CH3O => I*C3H7 + CH3OH 3.00E+11 0 7002.7
I*C3H7 + CH3OH => C3H8 + CH3O 1.22E+10 0 9201.5
! ----------------------------------------
!END OF FILE
! MECHANISM CO-CO2, P = 3.0 1.0 0.0253 BAR, HIGH TEMP,
!  LIST OF SPECIES
! H = "H"
!  O = "O"
!  OH = "OH"
!  HO2 = "HO2"
!  O2 = "O2"
!  CO = "CO"
!  CO2 = "CO2"
!  THIRD BODY EFFICIENCY
! M'
! H2O = 6.5
!  O2 = 0.4
!  N2 = 0.4
!  AR = 0.35
!  CO = 0.75
!  CO2 = 1.5
!  M' H2O/6.5/ O2/0.4/ N2/0.4/ AR/0.35/ CO/0.75/ CO2/1.5/
!  END
! END OF THIRD BODY EFFICIENCY
! ----------------------------------------
!  PRINT = "2.  CO/CO2 Reaktionen"
! ----------------------------------------
CO + OH = CO2 + H 6.00E+06 1.5 -740.9
CO + HO2 = CO2 + OH 1.50E+14 0 23589.3
CO + O + M = CO2 + M 7.10E+13 0 -4541
CO + O2 = CO2 + O 2.50E+12 0 47800
! ----------------------------------------
!END OF FILE
! MECHANISM H2/O2, P = 3.0 1.0 0.0253 BAR, HIGH TEMP,
! ----------------------------------------
!  PRINT = "1.  C3 Kinetik"
!  PRINT = "1.1 H2/O2 Reaktionen"
! ----------------------------------------
O2 + H = OH + O 2.00E+14 0 16801.7
H2 + O = OH + H 5.06E+04 2.67 6285.7
H2 + OH = H2O + H 1.00E+08 1.6 3298.2
OH + OH = H2O + O 1.50E+09 1.14 100.38
! ----------------------------------------
```

```
!  PRINT = "1.2 HO2 Bildung und Verbrauch"
! ----------------------------------------
H + O2 + M = HO2 + M 2.30E+18 -0.8 0
HO2 + H = OH + OH 1.50E+14 0 1003.8
HO2 + H = H2 + O2 2.50E+13 0 693.1
HO2 + H = H2O + O 3.00E+13 0 1720.8
HO2 + O = OH + O2 1.80E+13 0 -406.3
HO2 + OH = H2O + O2 6.00E+13 0 0
! ----------------------------------------
!  PRINT = "1.3 H2O2 Bildung und Verbrauch"
! ----------------------------------------
HO2 + HO2 = H2O2 + O2 2.50E+11 0 -1242.8
OH + OH + M = H2O2 + M 3.25E+22 -2 0
H2O2 + H = H2 + HO2 1.70E+12 0 3752.3
H2O2 + H = H2O + OH 1.00E+13 0 3585
H2O2 + O = OH + HO2 2.80E+13 0 6405.2
H2O2 + OH = H2O + HO2 5.40E+12 0 1003.8
! ----------------------------------------
!  PRINT = "1.4 Rekombinationsreaktionen"
! ----------------------------------------
H + H + M = H2 + M 1.80E+18 -1 0
O + O + M = O2 + M 2.90E+17 -1 0
H + OH + M = H2O + M 2.20E+22 -2 0
! ----------------------------------------
!END OF FILE
! MECHANISM NO, P = 3.0 1.0 0.0253 BAR, HIGH TEMP,
! ----------------------------------------
!  PRINT = "6.   NO MECHANISM" "
! ----------------------------------------
!!  PRINT = "6.0 NH3 Bildung aus Harnstoff"
! ----------------------------------------
!  CH4N2O = NH3 + HNCO 4.42E+05 0.7 17925
! ----------------------------------------
!  PRINT = "6.1 NH3 Verbrauch"
! ----------------------------------------
NH3 + M = NH2 + H + M 9.20E+15 0 84797.2
NH3 + H = NH2 + H2 2.50E+13 0 17088.5
NH3 + OH = NH2 + H2O 9.60E+12 0 7289.5
! ----------------------------------------
!  PRINT = "6.2 NH2 Verbrauch"
! ----------------------------------------
NH2 + H = NH + H2 6.00E+12 0 0
NH2 + O = NH + OH 6.30E+14 -0.5 0
NH2 + OH = NH3 + O 2.00E+10 0.4 501.9
NH2 + NH2 = NH3 + NH 6.30E+12 0 9990.2
NH2 + HO2 = NH3 + O2 1.60E+13 0 0
! ----------------------------------------
!  PRINT = "6.3 NH Verbrauch"
! ----------------------------------------
NH + H = N + H2 1.00E+13 0 0
NH + O = N + OH 6.30E+11 0.5 7887
NH + OH = NO + H2 2.40E+13 0 0
NH + OH = N + H2O 2.40E+13 0 0
NH + O2 = HNO + O 3.80E+10 0 1529.6
NH + O2 = NO + OH 3.80E+10 0 1529.6
! ----------------------------------------
!  PRINT = "6.4 HNO Verbrauch"
! ----------------------------------------
HNO + M = H + NO + M 8.60E+16 0 48708.2
H2O/6.5/ O2/0.4/ N2/0.4/ CO/0.75/ CO2/1.5/
HNO + H = NH + OH 2.00E+11 0.5 13001.6
HNO + H = NO + H2 4.80E+12 0 0
HNO + OH = NO + H2O 3.60E+13 0 0
HNO + N = NO + NH 1.00E+13 0 1983.7
HNO + NH2 = NO + NH3 5.00E+13 0 1003.8
! ----------------------------------------
!  PRINT = "6.5 N Verbrauch"
! ----------------------------------------
N + OH = NO + H 3.00E+13 0 0
N + O2 = NO + O 6.40E+09 1 6237.9
! ----------------------------------------
!  PRINT = "6.6 NO Verbrauch"
! ----------------------------------------
NO + NH => N2 + OH 4.30E+14 -0.5 0
NO + NH2 = N2 + H2O 3.12E+11 0 -1290.6
NO + NH2 = N2 + H + OH 3.12E+11 0 -1290.6
NO + NH2 = N2H + OH 3.12E+11 0 -1290.6
!  NO + CH3 = HCN + H2O 5.00E+12 0 0
NO + CH3 => HCN + H2O 1.20E+14 0 28966.8
NO + CH2 = HNCO + H 2.90E+12 0 -597.5
NO + CH = HCN + O 1.10E+14 0 0
```

```
! ----------------------------------------
!  PRINT = "6.7 HCN Verbrauch"
! ----------------------------------------
HCN + O = NCO + H 1.40E+06 2.1 2762.84
! ----------------------------------------
!  PRINT = "6.8 CN Verbrauch"
! ----------------------------------------
CN + H2 = HCN + H 5.45E+11 0.7 4875.6
CN + O = CO + N 1.00E+13 0 0
CN + OH = NCO + H 3.00E+13 0 0
CN + OH = HCN + O 3.00E+13 0 0
CN + O2 = NCO + O 6.60E+12 0 -406.3
CN + H2O = HCN + OH 3.90E+12 0 7456.8
CN + H2O = HNCO + H 3.90E+12 0 7456.8
CN + CH4 = HCN + CH3 9.00E+12 0 1864.2
! ----------------------------------------
!  PRINT = "6.9 HNCO Verbrauch"
! ----------------------------------------
HNCO + H = H2 + NCO 2.05E+14 -0.3 20243.3
! ----------------------------------------
!  PRINT = "6.10 NCO Verbrauch"
! ----------------------------------------
NCO + M = N + CO + M 2.60E+15 0 46700.6
H2O/6.5/ O2/0.4/ N2/0.4/ CO/0.75/ CO2/1.5/
NCO + H = NH + CO 5.20E+13 0 0
NCO + O = NO + CO 4.20E+13 0 0
NCO + N = N2 + CO 2.00E+13 0 0
! ----------------------------------------
!  PRINT = "6.11 N₂H Verbrauch"
! ----------------------------------------
N2H + OH = N2 + H2O 3.00E+13 0 0
N2H + M = N2 + H + M 2.00E+14 0 20004.3
N2H + NO = N2 + HNO 5.00E+13 0 0
! ----------------------------------------
!  PRINT = "6.12 N₂ Verbrauch"
! ----------------------------------------
N2 + O = NO + N 1.80E+14 0 76241
N2 + CH = HCN + N 4.40E+12 0 21988
! ----------------------------------------
!  PRINT = "6.13 N₂O Bildung und Verbrauch"
! ----------------------------------------
NO + NH = N2O + H 2.40E+15 -0.8 0
NCO + NO = N2O + CO 1.00E+13 0 -391.96
N2H + O = N2O + H 1.00E+14 0 0
N2O + M = N2 + O + M 1.60E+14 0 51576.2
N2O + H = N2 + OH 7.60E+13 0 15198.01
N2O + OH = N2 + HO2 2.00E+12 0 9999.76
N2O + O = NO + NO 1.00E+14 0 28202
N2O + O = N2 + O2 1.00E+14 0 28202
N2O + CN = NCO + N2 1.00E+13 0 0
! ----------------------------------------
!  PRINT = "6.14 NO₂ Bildung und Verbrauch"
!  aus meth
! ----------------------------------------
!  REF. SALIMIAN
N2O + NO = N2 + NO2 1.00E+14 0 49712
!  REF. JOHNSON
NO + O + M = NO2 + M 2.75E+15 0 -1868.98
H2O/6.5/ O2/0.4/ N2/0.4/ CO/0.75/ CO2/1.5/
!  REF. MILLER
!  NO2 + M = NO + O + M 2.50E+16 0 65940.1
!  H2O/6.5/ O2/0.4/ N2/0.4/ CO/0.75/ CO2/1.5/
!  REF. HOWARD
NO + HO2 = NO2 + OH 2.11E+12 0 -478
!  REF. CERNANSKY
NO2 + H = NO + OH 3.50E+14 0 1505.7
!  REF. KOSHI
NO2 + O = NO + O2 1.00E+13 0 597.5
! ----------------------------------------
!END OF FILE
!Hi Wei-Chen,
!
!The problem is, that this mechanism has grown and was changed since it
!was first established, and now there are a couple of different mechanisms
!"on the market".  But nobody has ever since published one of this new
!versions (as far as I know).  So here's how I usually reference the mechanism:
!The calculations were performed using a detailed reaction scheme for the
!C/H/N/O-system [13], which includes the most recent evaluated kinetic
!  data of the CEC evaluation group [14].  The NO mechanism is taken from
!  Bockhorn [15a,b], completed with the latest data for the
!"reburn-reaction" CH3 + NO -> HCN + H2O from Gardiner [16] and extended by
```

```
!NO2 <-> NO reactions from Miller and Bowman [17].  The complete mechanism
!comprises 488 elementary reactions among 53 chemical species.
!REFERENCES
!13.  Warnatz, J., in Combustion Chemistry (W. C. Gardiner, Jr., Ed.)
!Springer, Berlin, 1984.
!14.  Baulch, D. L., Cobos, C. J., Cox, R. A., Esser, C., Frank, P., Just,
!Th., Kerr, J. A., Pilling, M.J., Troe, J., Walker, R. W. and Warnatz, J.,
!J. Phys.  Chem.  Ref.  Data 21:411 (1992).

!15a.  Bockhorn, H., Chevalier, Ch., Warnatz, J. and Weyrauch, V., ASME
!HTD-Vol.  166, Book No.  G00629, 1991.

!15b.  Bockhorn, H., Chevalier, Ch., Warnatz, J. and Weyrauch, V., VDI
!Berichte Nr.  922, VDI Verlag, D=FCsseldorf, 1991.

!16.  Gardiner, W., Lissianski, V., Okoroanyanwu, U., Yang, H. X., Zhao, M.
!and Shin, K.S., Proceedings Second Int.  Conf.  on Comb.  Technol.  for a
!Clean Environment, 19-22 July 1993, Portugal.

!17.  Miller, J. A., Bowman, C. T., Prog.  Energy Combust.  Sci., 15:287-338
!(1989).
```