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Modelling NOx-Formation in Combustion Processes

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Modeling NOx-Formation in Combustion Processes (Modellering av NOx-formation vid förbränning)

Abstract
As the regulations of pollutant emission is getting more and more strict, models of pollutant formation, as a part of system level models for control design, are needed. In this thesis NOx (nitrogen oxides) formation is modeled. A method is developed to mix equilibrium and non-equilibrium reaction equations to model NOx formation in combustion processes. This algorithm reduces high-index DAE systems by introducing ``reaction invariants''. Two models are built with help of this algorithm which describe NOx formation during combustion in a cylinder in a spark ignition car engine and in a gas turbine (for more information about the combustion models see [4] and [7]). The models use both equilibrium and non-equilibrium/dynamical reaction equations. A rough verification of the cylinder model is also done.

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Preface

This thesis is a required part for the degree of Master of Science in Engineering Physics at Lund Institute of Technology (LTH), and constitutes of 20 weeks full time university studies. The thesis has been written in cooperation with Modelon AB in Lund and the work has been performed during winter and spring 2006.

I would like to thank my supervisor at Modelon AB, Hubertus Tummescheit, for always having time to meet and talk about the work. He spent many hours discussing the work and his ideas and solution suggestions helped me get the work done. During this time I've learned very much about combustion and modeling.

Nomenclature

T	Absolute temperature in Kelvin (K)
P	Pressure in Pascal (Pa)
P_{out}	Downstream pressure (Pa)
V	Volume in m^3 if not specified otherwise (m^3)
M_i	Number of moles of substance i
M_T	Total number of moles of all substances
F_{in}	Molar rate inflow ($\frac{mole}{s}$)
F_{out}	Molar rate outflow ($\frac{mole}{s}$)
ν	Stoichiometric coefficient matrix
ν^{EQ}	Stoichiometric coefficient matrix only including equilibrium reaction equations
$\tilde{M}$	Reaction invariants
x_i	Mole fraction of substance i
R	Universal gas constant
K	Equilibrium constant
r	Reaction rate in $\frac{mole}{m^3*s}$
Φ	Equivalence ratio
ω	Null vector to ν^{EQ}
n	Total number of equations
y	Total number of substances
k	Number of equilibrium reactions
z	Number of null vectors to ν^{EQ}
ρ	Density ($\frac{kg}{m^3}$)
δ	Thermal layer thickness (m)
Pr	Prandt number
cp	Heat capacity ($\frac{J}{Kg*K}$)
μ	Viscosity ($\frac{kg}{m*s}$)
ut	Turbulent intensity ($\frac{m}{s}$)
h	Specific enthalpy ($\frac{J}{Kg}$)
s	Specific entropy ($\frac{J}{Kg*K}$)
$\tilde{h}$	Molar enthalpy ($\frac{J}{Mole}$)
$\tilde{s}$	Molar entropy ($\frac{J}{Mole*K}$)
$\tilde{g}$	Molar Gibbs free energy ($\frac{J}{mole}$)
H	Total enthalpy (J)
Q	Heat (J)
MMX	Molar mass ($\frac{Kg}{mole}$)
m	Mass (Kg)
U	Total internal energy (J)
u	Specific internal energy ($\frac{J}{Kg}$)

Chapter 1

INTRODUCTION

1.1 Background

We learn more and more about the effects of pollutants like nitrogen oxides (NOx). In the case of NOx it poses as a risk both to the environment as well as to human health. NOx reacts with moisture and other compounds to form dangerous particles when inhaled and NOx emission also contributes to the formation of ozone smog. Acid rain can also be traced back to NOx emission as well as the weakening of the ozone layer to some extent and many other negative effects. The biggest source of NOx emission comes from the fossil fuel driven part of the transportation sector, where NOx is formed in the engines during combustion. As a result more regulations concerning emission of NOx are made. These stricter rules require system level models for control design in order to decrease NOx emission.

1.2 About Modelon AB

This thesis was written in cooperation with Modelon AB in Lund. Modelon AB offer their customers model-based engineering services. This is mainly done by either deliver reusable model libraries for in-house use or custom models. The model services are done using the *Modelica language* and are well integrated with the Modelica standard libraries. Their biggest customer group is from the car industry where Modelon AB offer services in air conditioning, motor cooling and vehicle dynamics. The company is also building up libraries in the power sector such as libraries for turbines or a whole power

plant.

1.3 Objectives

The aim with this thesis is to develop a method to model NOx formation with both equilibrium and non-equilibrium reaction equations. This method will be used to build two models. The first model is simulating NOx formation in a cylinder in a spark ignition car engine. The second model is simulating NOx formation in a gas turbine using the same model classes used in the first cylinder model. The purpose of these two models is that they, in the future, will be a part of system level models, e.g. models of Flue Gas Recirculation (FGR), for control design. For this reason the models must not be too computational demanding and have to be robust, flexible and automatic. The cylinder model developed will also be roughly validated to see if it gives reasonable results.

1.4 Outline

This report is divided into four chapters. The first chapter dealt with the introduction to the subject. The second chapter deals with the theory used in the thesis. It contains some fundamental theory of combustion in internal engines and NOx formation. This chapter ends with a section elaborating an algorithm used in the models. The third chapter gives a brief introduction to the programming language *Modelica*, in which the models are written, and the program *Dymola* which was used to simulate the models. The two developed models, describing combustion in a cylinder in a spark ignition car engine and a gas turbine, are then explained. The fourth and last chapter analysis the final models and discusses simulation results from them.

Chapter 2

THEORY

In this chapter the basic theory used in the thesis will be introduced and shortly described. The chapter is divided into three sections and starts with some elementary knowledge about combustion. The second section deals with more specific theory about NOx formation during combustion. The chapter ends with a description of an algorithm to model systems with chemical equilibrium.

2.1 Combustion

In this section the elementary theory of combustion will be described and in particular the elementary theory of internal engine combustion, e.g. in turbines and cylinders in an engine.

2.1.1 Molar Gibbs free energy

A central term is Gibbs free energy, labeled $\tilde{g}$, which determines whether an equilibrium reaction proceeds in forward or reverse direction spontaneously. The molar Gibbs free energy, with units J/mole, is defined as

$$\tilde{g} = \tilde{h} - T\tilde{s} \tag{2.1}$$

where $\tilde{h}$ is enthalpy (J/mole), T is temperature (K) and $\tilde{s}$ is entropy (J/(mole*K)). The differential of $\tilde{g}$ will be

$$d(\tilde{g}) = d\tilde{h} - Td\tilde{s} - \tilde{s}dT \tag{2.2}$$

Reactions leading to a decrease of $\tilde{g}$ will happen spontaneously. By calculating the Gibbs free energy for all the reactant species in a reaction, with equation 2.1, and calling the sum of these *reactantG* and doing the same for the product species and calling it *productG*, the direction of the reaction can be determined. If

$$reactantG > productG \tag{2.3}$$

the forward reaction will occur spontaneously, this means reactants will form products. If the opposite is true

$$reactantG < productG \tag{2.4}$$

the reverse reaction will occur spontaneously, this means the products (according to the reaction formula) will form reactants. Even though the direction of a reaction can be determined by comparing the Gibbs free energy, nothing is said about the rate with which the reaction is occurring. If

$$reactantG = productG \tag{2.5}$$

the reaction is in chemical equilibrium and no net transformation of reactants to products or reverse will occur. [1]

2.1.2 Equilibrium and non-equilibrium/dynamic reactions

Reaction equations can be modeled as equilibrium reactions or non-equilibrium reactions. The first type is written

$$A + 2B \leftrightarrow C \tag{2.6}$$

whereas the later type of equation is written

$$A + 2B \rightarrow C \tag{2.7}$$

When reactants on the left side is transformed into products on the right side the reaction is said to move in the forward direction and when the opposite occur the reaction is called to go in the reverse direction. The difference between the two types of equations is that in the first type the reaction can go both ways. That is, the reactants on the left side can transform into

products on the right side but the opposite can also happen which is the products on the right side can transform into the reactants on the left side. An equilibrium will occur when the forward and reverse reaction rates are equal. Reaction 2.6 is described by the equilibrium coefficient, K, in the following way

$$K = \frac{[C]}{[A][B]^2} \tag{2.8}$$

where [ ] denotes the concentration. The value of K is calculated by using molar Gibbs free energy, for details see section 3.2. The equilibrium coefficient is only saying what this ratio will be when the system is in equilibrium. With this information and data on the different concentrations of the substances the net direction, forward or reverse (or zero in equilibrium), of an equilibrium reaction can be discovered, but nothing can be said about the reaction rate.

In the other type of reaction, non-equilibrium reactions, the reactants on the left side transforms into products on the right side only. So the reaction can only move in the forward direction and is described by the reaction rate, r, which tells how fast the reaction is going.[5]

2.1.3 Stoichiometry

Stoichiometry for chemical reactions describes in what proportions chemical substances react with each other. In the following example

$$4NO + 4NH_3 + 1O_2 \rightarrow 4N_2 + 6H_20 \tag{2.9}$$

the coefficients in front of the substances, i.e. 4, 4, 1, 4, 6, are called the stoichiometric coefficients.[3]

2.1.4 Stoichiometric coefficient matrix

When dealing with a set of reaction equations it often becomes convenient to put the stoichiometric coefficients in a matrix and thereby be able to handle

all the reactions more easy and efficient in mathematical calculations. This matrix is called the *stoichiometric coefficient matrix*, ν. If, for example the set of reaction equations is the following

$$2A \leftrightarrow B \tag{2.10}$$
$$B + C \leftrightarrow 2D + E \tag{2.11}$$
$$A + C \rightarrow 2E \tag{2.12}$$

the corresponding stoichiometric matrix would look like

$$\nu = \begin{pmatrix} -2 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & -1 & -1 \\ 0 & 2 & 0 \\ 0 & 1 & 2 \end{pmatrix} \tag{2.13}$$

where each column contains the stoichiometric coefficients for one reaction. The number of columns will therefor be equal to the number of reactions. The number of rows will equal the number of substances and contain stoichiometric coefficients for the reactants A, B,..,E. The matrix including only the equilibrium reactions would then look like [3]

$$\nu^{EQ} \begin{pmatrix} -2 & 0 \\ 1 & -1 \\ 0 & -1 \\ 0 & 2 \\ 0 & 1 \end{pmatrix} \tag{2.14}$$

2.1.5 Equivalence ratio

When all oxygen is consumed in a reaction the combustion is called to be under stoichiometric condition. With the stoichiometric coefficients and the molar mass the theoretical stoichiometric fuel/air mass ratio can be calculated.

$$\frac{m_{fuel}(s)}{m_{air}(s)} \tag{2.15}$$

where the (s) stands for stoichiometric condition. The actual fuel/air mass ratio in an combustion process is normally calculated by dividing the mass flow rate of fuel, $\dot{m}_{fuel}$, with the mass flow rate of air, $\dot{m}_{air}$,

$$\frac{\dot{m}_{fuel}(a)}{\dot{m}_{air}(a)} \tag{2.16}$$

where (a) stands for actual condition. The ratio of the actual fuel/air mass ratio and the stoichiometric fuel/air mass ratio

$$\Phi = \frac{\frac{\dot{m}_{fuel}(a)}{\dot{m}_{air}(a)}}{\frac{m_{fuel}(s)}{m_{air}(s)}} \tag{2.17}$$

is called the equivalence ratio and is represented by the symbol Φ. Inverted equivalence ratio is labeled λ [4]

$$\lambda = \frac{\frac{\dot{m}_{air}(a)}{\dot{m}_{fuel}(a)}}{\frac{m_{air}(s)}{m_{fuel}(s)}} \tag{2.18}$$

2.1.6 Premixed and non-premixed/diffusion flame

For an internal combustion engine to work it needs both fuel and air. There are two different principles, premixed and non-premixed combustion. In the former the air and the fuel is already mixed before the combustion process whereas in the later the fuel and the air is mixed during combustion. The non-premixed case is usually much harder to simulate due to turbulence and other factors.[4]

2.2 NOx Formation

The term NOx usually includes nitric oxide (NO) and nitrogen dioxide (NO_2), but could also include several other oxides of nitrogen like dinitrogen oxide (N_2O), dinitrogen tetrooxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). In combustion the amount of NO is normally clearly dominating followed by a much smaller amount of NO_2. The other oxides of nitrogen occur normally in very small quantities. NOx is produced during basically all kinds of combustion and can be divided into three different types of formation. These are *thermal* NOx formation, *fuel* NOx formation and finally *prompt* NOx formation.

2.2.1 Thermal NOx formation

Thermal NOx formation describes the process when nitrogen, N_2, in the combustion air reacts with oxygen, O_2, in the combustion air to produce NOx. This process is best studied and understood. The formation requires very high temperatures and is exponentially dependent on the temperature. Because the process is very nonlinear, so called hot spots, local areas with higher temperature than the average temperature, can give very large effect on the amount of NOx produced. The maximum rather then the average temperature is therefore very important and the process is very hard to model accurately because of this. Other important factors in thermal NOx formation are the residence time, which describes how long time the combustion gas is having the high temperature. The turbulence and the amount of excess oxygen are two other important factors. The process is mainly governed by the following three equations which together are called the *Zeldovich mechanism*, here written in the form of equilibrium reaction equations:

$$N_2 + O \leftrightarrow NO + N \tag{2.19}$$

$$N + O_2 \leftrightarrow NO + O \tag{2.20}$$

$$N + OH \leftrightarrow NO + H \tag{2.21}$$

The strong triple bond in the N_2 molecule requires high temperature to break and equation 2.19 will therefore determine the rate of the thermal NOx formation. This source of NOx is usually dominating with temperatures over 1400 K (1100 C) and NOx formation is usually modeled with these three equations. Thermal NOx formation has it's maximum for temperatures over 1900 K. [6] [1]

2.2.2 Fuel NOx formation

The process where nitrogen in the fuel reacts (oxidizes) with the oxygen in the combustion air to form NOx is called fuel NOx formation. Gas fuels have a relatively low amount of bound nitrogen and therefor produce low amounts of NOx emission by this process. Coal and oil have much more bound nitrogen so fuel NOx formation is therefore a much bigger part of the total amount of NOx produced for these types of fuel compared to gaseous fuels. The mechanism for the fuel NOx formation process is not fully understood but is modeled by the following two equations:

$$N_{Complex} + OH \leftrightarrow NO + X \tag{2.22}$$

$$N_{Complex} + NO \leftrightarrow N_2 + X \tag{2.23}$$

where X symbolizes other products where the mechanism is not fully understood. [6] [1]

2.2.3 Prompt NOx formation

Prompt NOx formation is the last process describing NOx formation. In this process radical hydrocarbons are produced during the combustion of the fuel. These radicals quickly react with the nitrogen in the combustion air to form transition substances which then oxidize to NOx when they react with the oxygen in the combustion air. The following equation is the most important first step in the process.

$$CH + N_2 \leftrightarrow HCN + N \tag{2.24}$$

where the transition substance, HCN, is converted into to atomic nitrogen through a sequence of steps

$$HCN \Rightarrow NCO \Rightarrow NH \Rightarrow N \tag{2.25}$$

At higher temperature the reaction

$$C + N_2 \leftrightarrow CN + N \tag{2.26}$$

also contributes to the breaking of the N_2 bond. The nitrogen atoms from these equations are then oxidized to NO. This process is usually observed in relatively low temperatures in the beginning of the combustion process and is only relevant in very fuel-rich combustion. [1] [6]

2.2.4 Modeling NOx formation

Normally thermal NOx production is so dominating that only the three equations describing the thermal NOx process are used to model the NOx formation. There has been much research to model in more detail the NOx formation and a set of further equations, called Super-Extended Zeldovich Mechanism(SEZM), has been developed and tested by Ford Motor Company [2] and in many variations by others. The SEZM includes 67 different equations involving 13 chemical species. It is very difficult to predict NOx formation accurately but the Super-Extended Zeldovich Mechanism is shown to be able to predict the NOx formation within 10% of experimental engine test data for both fuel-rich and fuel-lean conditions and for EGR (Exhaust Gas Recirculation) dilution. Whereas the Zeldovich mechanism containing only three equations approximately gives an error of 50% or more under similair conditions in their research report. The objective for this thesis though is to develope more simple models to be used in system level models for control design. Therefore only the equations in the *Zeldovich mechanism* will be used.

The concentration of NOx in the exhaust gas of an engine varies a lot with the equivalence ratio that was explained in section 2.1.5. As can be seen from the following figure, the NOx concentration has a maximum for slightly fuel-lean conditions.

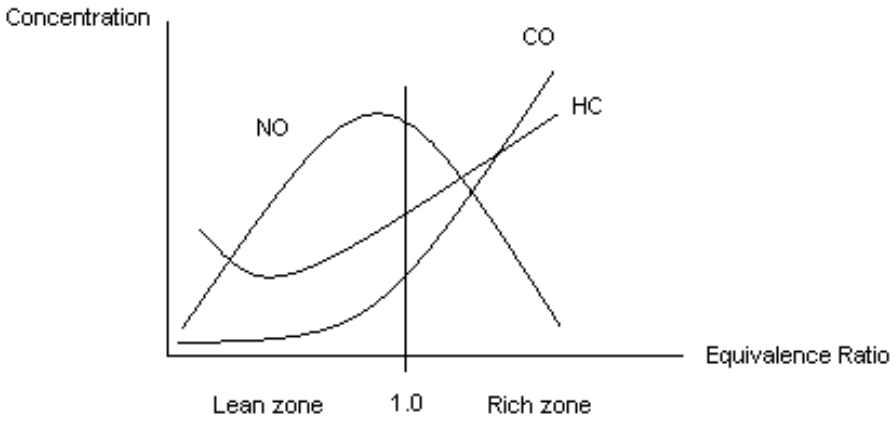

Figure 2.1: *Figure shows different emission substance concentrations qualitative dependence on the equivalence ratio*

In the figure the variations of other emission substances concentration can also be seen. It clearly shows the difficulty of trying to decrease all the emission substance concentrations with a strategy of only changing the equivalence ratio. In the far fuel-lean region, NOx and carbon oxide (CO) concentrations are low, but the concentration of hydro carbon (HC) is large. And when HC has a minimum and CO is relatively small, NOx has a maximum. And the more fuel-rich the condition gets, the higher the concentration of both HC and CO even though NOx is decreasing. [4]

2.3 Algorithm to model reactions containing both equilibrium and dynamic reactions

In this section an algorithm for modeling systems with both equilibrium and non-equilibrium reactions using reaction invariants will be presented (for more information see [3]). This section will first show two systems where the first includes a non-equilibrium reaction and the second an equilibrium equation. The later system will incur a high index problem and an index reduction method is shown in the end of the section

When modeling chemical reactors involving chemical equilibrium, high index DAE (Differential and Algebraic Equations) systems often arise with all the mathematical complications it can include. This method can solve these problems in an efficient way. Consider a well stirred reactor with constant volume as the following figure illustrates

Figure 2.2: *Constant volume reactor*

where the dynamical reaction

$$2A \rightarrow B \tag{2.27}$$

occurs. F_{in} and F_{out} are the molar rate inflow and outflow respectively. x_A and x_B are the mole fractions of substance A and B respectively in the inflow respectively outflow. P_{out} is the pressure downstream from the reactor and P the pressure inside the reactor. M_A and M_B are the total moles of the substances in the reactor. The system is mathematically described with the following set of equations

$$\frac{dM_A}{dt} = F_{in}x_A^{in} - F_{out}x_A^{out} - 2rV \tag{2.28}$$

$$\frac{dM_B}{dt} = F_{in}x_B^{in} - F_{out}x_A^{out} + rV \tag{2.29}$$

$$M_T = M_A + M_B \tag{2.30}$$

$$x_A = \frac{M_A}{M_T}; x_B = \frac{M_B}{M_T} \tag{2.31}$$

$$PV = M_T RT \tag{2.32}$$

$$F_{out} = f(P - P_{out}) \tag{2.33}$$

where the last equation describes the outflow as a function of the pressure difference in the reactor and downstream. To complete the system the reaction rate, r, is defined as

$$r = k\left(\frac{x_A P}{RT}\right)^2 \tag{2.34}$$

The system has 8 unknowns and 8 equations and with arbitrary start values for M_A and M_B, the system can easily be solved. If however the reaction is an equilibrium equation

$$2A \leftrightarrow B \tag{2.35}$$

equation 2.34 will be replaced by equilibrium relation

$$K = \frac{x_B}{x_A^2} \tag{2.36}$$

where K is the equilibrium constant. It turns out the system is now a high index DAE system where the start values for M_A and M_B not can be specified arbitrary due to the fact that M_A and M_B are related by

$$\frac{KRT}{PV} = \frac{M_B}{M_A^2} \tag{2.37}$$

Also, unique start values for r, $\frac{dM_A}{dt}$ and $\frac{dM_B}{dt}$ can not be calculated. An index reduction can be done by rearranging and differentiating equation 2.37 and adding this equation to the system, which transforms it to an index 1 system. With more complex systems this method will turn out to be very complicated and ineffective. A strategy could instead be to try and eliminate r from the system, because it is not an interesting variable and only added to complete the system. This can be done by combining the only to equation where r is occurring, eq. 2.28 and 2.29, and gives

$$\frac{dM_A}{dt} + 2\frac{dM_B}{dt} = F_{in}(x_A^{in} + 2x_B^{in}) - F_{out}(x_A + 2x_B) \tag{2.38}$$

A new variable is defined as

$$\tilde{M} = M_A + 2M_B \tag{2.39}$$

which is a so called "reaction invariant" due to the fact that it doesn't change by the reaction $2A \leftrightarrow B$. Equation 2.38 can now be written as

$$\frac{d\tilde{M}}{dt} = F_{in}(x_A^{in} + 2x_B^{in}) - F_{out}(x_A + 2x_B) \tag{2.40}$$

The new DAE system also includes 8 unknowns with $\tilde{M}$ instead of r and 8 equations (2.30-2.33, 2.36, 2.39-2.40). This system turns out to have an index of 1 and is solvable by standard methods. The reason why a higher index DAE can be transformed to a index 1 system without any differentiations is because not all variables in the original system are calculated, in this case variable r which was eliminated by purely algebraic manipulation.

In a more standardized method, equation 2.39 and 2.40 can be obtained in the following way. Similar to above as many reaction rates, r, will be eliminated as there are equilibrium reactions in the system. This is as before done by forming linear combinations of the substance balances $\frac{dM_{1..y}}{dt}$, where y is the number of substances and n will be the total number of equations. This gives

$$\sum_{i=1}^{y} \omega_i \frac{dM_i}{dt} = F_{in} \sum_{i=1}^{y} \omega_i x_i^{in} - F_{out} \sum_{i=1}^{y} \omega_i x_i^{out} + V \sum_{i=1}^{y} \omega_i \sum_{j=1}^{n} \nu_{ij} r_j \tag{2.41}$$

The last term is rearranged to

$$+V \sum_{j=1}^{n} r_j \sum_{i=1}^{y} \omega_i \nu_{ij} \tag{2.42}$$

ν is the stoichiometric matrix for the system. To eliminate $r_{1..k}$, where k is the number of equilibrium equations, the coefficients $\omega_{1..y}$ are chosen such that

$$\sum_{i=1}^{y} \omega_i \nu_{i1} = \sum_{i=1}^{y} \omega_i \nu_{i2} = .. = \sum_{i=1}^{y} \omega_i \nu_{ik} = 0 \tag{2.43}$$

This is equivalent to

$$\omega^T \nu^{EQ} = 0 \tag{2.44}$$

where ν^{EQ} is the part of the stoichiometric matrix ν that only includes the equilibrium equations. This goal can be achieved by choosing ω as the null vectors of the matrix ν^{EQ}. The number of null vectors, z, will be the difference between the number of rows and the rank of the matrix ν^{EQ}. The substance balance equations used to form equation 2.41 can now be replaced by the following equations

$$\frac{d\tilde{M}_f}{dt} = F_{in}x\omega^{(f)} - F_{out}x\omega^{(f)} - \nu^T_{:,k+1}\omega^f Vr_{k+1} + .. + \nu^T_{:,n}\omega^f Vr_n \qquad (2.45)$$

where f=1,2,..,z. $\nu_{:,k+1},..,\nu_{:,n}$ stands for column k+1,..,n of ν, The new variables $\tilde{M}_f$ are defined as

$$\tilde{M}_f = M\omega^{(f)} \qquad (2.46)$$

M is a column vector of the substance masses $M_1, M_2, .., M_y$.

Chapter 3

MODELS

In this chapter the models of the car engine cylinder and gas turbine will be explained. The models are written in the programming language Modelica with the program Dymola. A short introduction of the programming language Modelica and the program Dymola will therefore start this chapter.

3.1 Modelica and Dymola

Modelica is a object oriented programming language well suited for building models and simulating advanced systems involving many different domains like electrical, mechanical, hydraulical, automatic control, thermodynamics and more. The Modelica Association owns and administrates incorporeal rights related to the language. The language is acausal which gives it advantages in modeling, but can sometimes also create difficulties, especially if the user is more familiar to causal programming languages, e.g. Java. In acausal modeling, models are based on equations instead of assignment statements. Equations do not state which variables are inputs and which are outputs as an assignment statement does, where variables on the left side are outputs and variables on the right side are inputs. The causality of the equations will be specified only when the equation system is solved. For this reason acausal models are more flexible and easier to reuse. Dymola is a graphical modeling and simulation environment for Modelica models. The program is developed by the company Dynasim in Lund.

3.2 Model of a cylinder in a spark ignition car engine

The model describes a cylinder in a car engine during one cycle. The cycle starts at maximum cylinder volume. The piston then moves into the cylinder and the cylinder volume decreases. Shortly before minimum cylinder volume is reached ignition starts. After minimum cylinder volume is reached the piston moves out from the cylinder until maximum cylinder volume is reached again. While the cylinder volume is decreasing the piston is doing work on the gas and while the cylinder volume is increasing the gas is doing work on the piston.

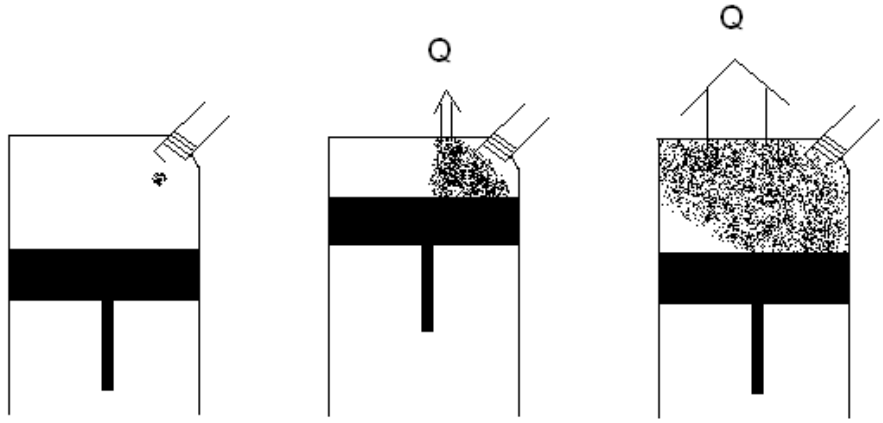

Figure 3.1: *Figures show the system, a cylinder in a spark ignition car engine, to be modeled. A spark ignites the gas and the flame is propagating throughout the cylinder while the piston is moving first to decrease and then to increase the volume in the cylinder. While the flame is propagating heat is flowing from the burned gas to the surrounding walls.*

At first all the gas, which is a mixture of fuel (gasoline) and air, is unburned. After ignition a flame is developed which spreads throughout the cylinder and the fraction of gas unburned inside the cylinder decreases and the fraction of burned gas increases. This happens while the volume inside the cylinder changes due to the piston movements. The area of the flame increases and grows in all directions until the flame front hits the cylinder walls or the piston. When the flame front has hit all the surrounding walls including the piston, all gas is burned.

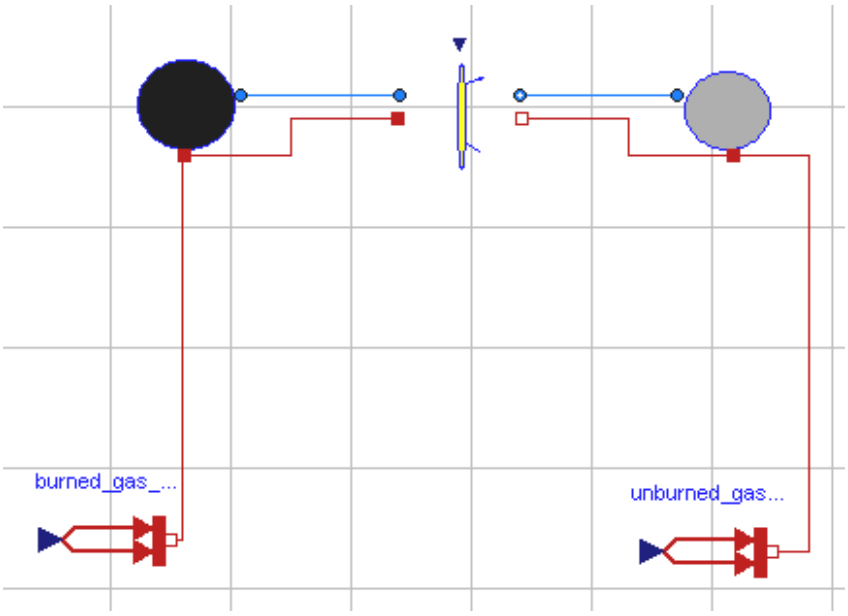

Figure 3.2: *The model over a cylinder in a spark ignition car engine viewed in the program Dymola. The essential components of the model are shown with the top left icon representing the burned gas zone, the top right icon representing the unburned gas zone and the top center icon representing the flame. The lower left icon models the surrounding walls in contact with the burned gas zone and the lower right icon models the surrounding wall in contact with the unburned zone.*

In figure 3.2 the model is viewed in Dymola. In the model no substances can enter or leave the cylinder, i.e. the gas change process is not included in the model, but heat can enter and leave through the cylinder walls. The cylinder is divided up in two zones, unburned and burned gas zone, and are described

by two different models (for more information about the two zones model see [4] and [2]). In both zones the gas is modeled as an ideal gas govern by the ideal gas law:

$$P * V = M * R * T \tag{3.1}$$

where M is the number of moles and R is the universal gas constant. In the cylinder model the pressure will be the same in the two zones.

In figure 3.2 the icon representing the model for the burned gas zone is the upper left and the upper right represents the model for the unburned gas zone. In the middle is the model for the flame. The lower two icons represents the cylinder wall through which heat can flow into and out from the cylinder. The lower left represents the part of the cylinder wall in contact with the burned gas zone and the lower right represents the part of the cylinder wall in contact with the unburned zone. At start the burned zone volume is approximately zero (for numerical reasons it will have a very small volume with air). After ignition gas is transported from the unburned zone to the burned zone. The flame front is considered indefinitely small with no volume and contains therefore no gas.

Figure 3.3: *Mass flow from unburned to burned zone*

The rate at which this transportation is taking place is calculated by the following function

$$MassRate = d_{ubz} * Af * ST \tag{3.2}$$

where d_{ubz} is the density of the gas in the unburned zone, Af is the flame area and ST is turbulent burning velocity. At first the mass rate of gas transported

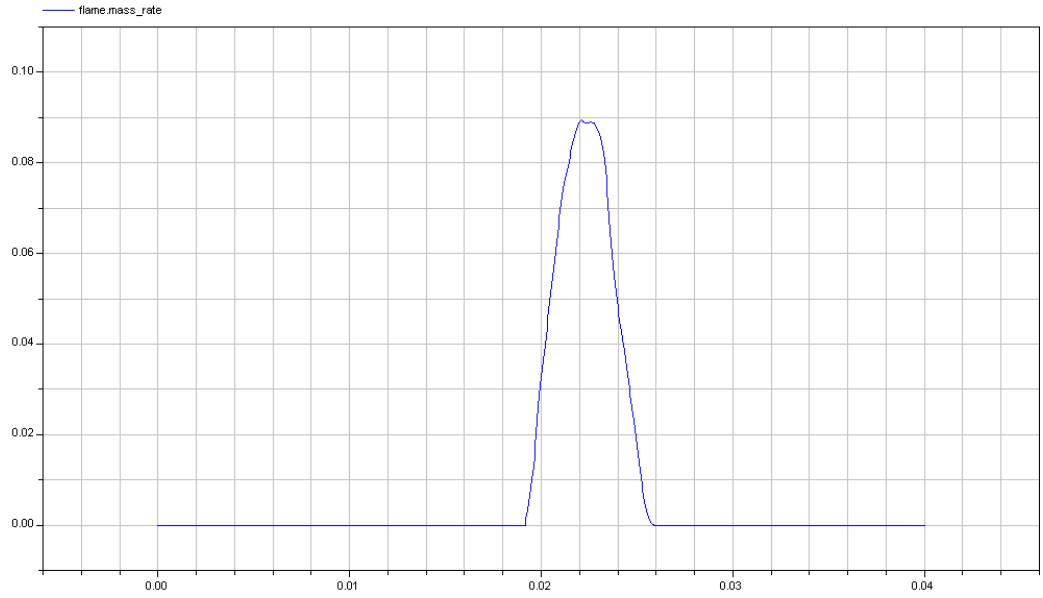

Figure 3.4: *Graph showing the mass flow rate from unburned to burned zone as a function of time. Just before half cycle at time 0.02 a spark ignite the gas and the mass rate increases very fast until enough flame area has hit the surrounding walls for the mass rate to start decrease until the mass rate finally is zero again when all gas is burned.*

from the unburned zone to the burned zone increases until enough of the flame area has hit the surrounding walls and the mass rate starts to decrease until it is zero again and all gas is burned as figure 3.4 shows.

At the start no part of the cylinder wall is in contact with the burned gas zone. As the flame propagates through the cylinder, more and more of the burned gas and less and less of the unburned gas will get in contact with the cylinder walls. The heat flow between the burned gas zone and the cylinder walls is modeled with the equation

$$heatflow = A * hc * \Delta T \tag{3.3}$$

where A is the area of the burned zone in contact with the cylinder walls, hc is the heat transfer coefficient for the burned gas zone and ΔT is the temperature difference between the burned gas zone and the cylinder walls.

The same equation is used to calculate the heat flow between the unburned gas zone and the walls. hc is calculated with the following function

$$hc = \frac{Cf * \rho * ut * cp * Pr^{-\frac{2}{3}}}{2} \tag{3.4}$$

where Cf is calculated with the function

$$Cf = \alpha * (\rho * ut * \delta/\mu)^{-\frac{1}{4}} \tag{3.5}$$

where α is a model parameter, ρ is the density of the gas, ut is the turbulent density with values taken from a turbulent data table, δ is the burned gas layer thickness with values taken from a geometrical table, Pr is Prandt number, μ is the viscosity of the gas calculated with

$$\mu = \frac{3.3 * 10^{-7} * T^{0.7}}{1 + 0.027 * \Phi} \tag{3.6}$$

where data for the last equation is taken from [4]. cp is the specific heat capacity for every substance used in the model, calculated with the following equation

$$\frac{c_p(T)}{R} = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \tag{3.7}$$

For more information about heat transfer see [9]. The last equation, for heat capacity, is empirical and data is taken from [10]. For every substance there is a set of coefficients, a_{1-7}, stored in a table in the model.

Both the unburned and the burned zone is modeled as zero dimensional, that means perfect mixing within each zone is approximated. The temperature, pressure, density and so on is therefore uniform over the whole zone. This is a good approximation if the time scales that characterizes the turbulent mixing process in the burned gas zone is much smaller than the overall burning time. If the opposite was true then a unmixed model would be more accurate. The situation in reality is somewhere in between these two models.

The model of the flame propagation is three dimensional and more complex. It uses geometrical data describing a cylinder with position and measurements of the cylinder volume, the piston and so on. The model of flame

propagation also uses turbulence data to determine the wrinkled flame surface [9]. The data is used to precalculate different tables used in the model. With help of these tables the area of the wall in contact with the flame front at a given moment is found. These data in the table effect the NOx result from simulations very much, due to the exponential dependence of NOx formation of temperature. How large area of burned gas zone in contact with the cylinder walls and the heat transfer coefficient are examples of factors that strongly will influence the NOx formation.

The gas inside the cylinder is modeled in a media class called GasMedium, which is replaceable if other fuels were to be simulated. The media class contains all necessary equations to describe the gas. This class also contains the stoichiometric coefficient matrix (see section 2.1.4) where all the reactions, both equilibrium and non-equilibrium reactions, are defined. From this matrix, the matrix only containing the equilibrium equations is calculated and used to compute the null vectors (see section 2.3).

In the unburned zone, no reactions are taking place, but the state of the gas is changing due to pressure changes, changes in temperature and transportation of mass out from the unburned zone. In addition to these changes, with the exception that mass is flowing in and not out, the state of the gas in the burned zone is also changed by reactions among the substances. The system of reaction equations are implemented with the method described in section 2.3.

A system can either be in chemical equilibrium or not. When modeling a system with equilibrium reaction equations there is an assumption that the system is in equilibrium or close to it. Whether to model the system with equilibrium equations or dynamical equations depends on the time constants of the controlling chemical reactions. If they are short compared to the rate of change of the systems condition (e.g. pressure, temperature) the system can be modeled as in equilibrium. Air-pollutant formation (e.g. NOx formation) in engines is usually an example of non-equilibrium phenomena and is therefore modeled with dynamical equations. This means that such processes are controlled by the rates which the actual chemical reactions which converts reactants to products occur. Because of this the NOx formation was modeled with dynamical reaction equations.

In general, the higher the system temperature gets the faster the reactions go, which means that the system reaches equilibrium faster and can be accurately modeled with only equilibrium reaction equations. If the system gets cooler the reactions start going slower and it takes longer time to reach equilibrium. In this case both equilibrium and dynamical reaction equations can be used to model the system. If the temperature of the system is low enough the reactions are going so slow the process can be modeled by only dynamical reaction equations. In a car engine there are very high temperature systems that can be modeled by only equilibrium reaction equations or a combination with dynamic reactions, e.g. the general combustion in a cylinder, and there are systems with low enough temperature to be modeled by dynamical reaction equations or in combination with equilibrium reaction equations, e.g. the catalyst.

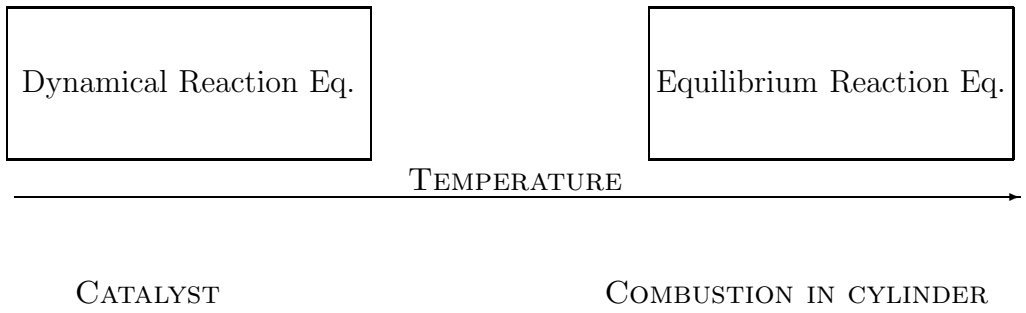

Figure 3.5: *Choice of reaction equation type depends on temperature. For a relative warm system, e.g. combustion in a cylinder, equilibrium reaction equations can be used exclusively or in a combination with dynamic reaction equations, whereas in a colder system, e.g. a catalyst, dynamic reaction equations are used exclusively or in a combination with equilibrium reaction equations.*

As stated in the NOx formation section in the second chapter (2.2.1) thermal NOx formation is usually the most dominating. The thermal NOx formation in the cylinder is modeled with the *Zeldovich mechanism* (see 2.2.1), and are in the form of dynamic reaction equations as can be seen in table 3.1

The rate constants are taken from Heywood [4]. They are empirically de-

Reaction	**Rate constant (cm^3/mole/s)**
$O + N_2 \rightarrow NO + N$	$7.6 * 10^{13} exp[-38000/T]$
$N + NO \rightarrow N_2 + O$	$1.6 * 10^{13}$
$N + O_2 \rightarrow NO + O$	$6.4 * 10^{8} exp[-3150/T]$
$O + NO \rightarrow O_2 + N$	$1.5 * 10^{8} exp[-19500/T]$
$N + OH \rightarrow NO + H$	$4.1 * 10^{13}$
$H + NO \rightarrow OH + N$	$2.0 * 10^{14} exp[-23650/T]$

Table 3.1: *Dynamic reactions used in the model to describe the NOx formation*

termined and can vary quite a lot between different sources in the literature. These rate constants are used to calculate the reaction rate, r, stated in the algorithm explained in section 2.3.

To model the other reaction processes going on during combustion the following equilibrium reactions were used.

The equilibrium constants, K, (see section 2.1.2) for the equilibrium re-

$$
\begin{array}{l}
CO_2 \leftrightarrow CO + \frac{1}{2}O_2 \\
H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \\
H_2O \leftrightarrow \frac{1}{2}H_2 + OH \\
\frac{1}{2}H_2 \leftrightarrow H \\
\frac{1}{2}O_2 \leftrightarrow O \\
\frac{1}{2}N_2 \leftrightarrow N
\end{array}
$$

Table 3.2: *Equilibrium reactions used in the model to describe the general combustion*

actions are calculated by using molar Gibbs free energy (see section 2.1.1). Molar Gibbs free energy (J/mole), is calculated for all substances with

$$\tilde{g} = (h - Ts) * MMX \tag{3.8}$$

where h is specific enthalpy, T is temperature, s is specific entropy and MMX is molar mass. To calculate the specific enthalpy, h, and specific entropy , s, for all different substances in the model the following two equations are used in the model

$$\frac{h(T)}{RT} = -a_1 T^{-2} + a_2 T^{-1} ln(T) + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3} + a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{b_1}{T} \tag{3.9}$$

$$\frac{s(T)}{R} = -a_1\frac{T^{-2}}{2} - a_2T^{-1} + a_3ln(T) + a_4T + a_5\frac{T^2}{2} + a_6\frac{T^3}{3} + a_7\frac{T^4}{4} + b_2 \quad (3.10)$$

These equations and the coefficients (a_{1-7}, $b_{1,2}$) are empirical and data is taken from [10]. In the model a set of these coefficients for every substance is stored in a table. By multiplying the vector containing the molar Gibbs free energy for all substances with the equilibrium stoichiometric matrix ν^{EQ} a vector is calculated in which the change of Gibbs free energy for each equilibrium reaction is stored. By dividing this vector element wise with R*T, a new vector containing all the equilibrium constants is calculated.

Energy conservation is maintained with the following two equations

$$U = u * m \quad (3.11)$$

$$\frac{d(U)}{dt} = H_{in} + Q - P * \frac{d(V)}{dt} \quad (3.12)$$

where U is internal energy (J), u is specific internal energy ($\frac{J}{Kg}$), m is mass (Kg), H_{in} is the total inflow of enthalpy(J), Q is heat (J), P is pressure (Pa) and V is volume (m^3). Many times you can see a quantity of heat energy added or subtracted in equations of energy for exothermic and endothermic reactions. This is not seen in equation 3.12 because it has rearranged the form in which energy is held. When a exothermic equation occur in the model the energy conservation will hold and the temperature will increase and vice versa for endothermic reactions. For more information about the energy conservation theory used here see [3].

The dynamic reaction equations describing the NOx formation can be viewed as the differential equations in a DAE system whereas the equilibrium reaction equations can be seen as the algebraic equations in the DAE system. The later ones cause the constraints which cause the high index. This problem is resolved by transforming the system to a DAE system with index 1 with the algorithm describes in 2.3.

3.3 Model of Gas Turbine

This model is much simpler compared to the former cylinder model. The same models for the unburned and burned zones are used with very small

modifications. In this model the volumes for both zones are constant and the pressure can be different in the two zones, in contrast to the previous model of a cylinder. In reality the flame is kept fixed located by whirls of gas or a flame holder (a warm metal net). Because the primary purpose of the model is to simulate NOx formation and not mass flow the model is simplified by setting the mass flow, transporting gas from the unburned to the burned zone, to a constant. The system is modeled as a premixed (see section 2.1.6) flame for simplicity because non-premixed/diffusion flame systems are much harder and more complicated to model.

The unburned zone is modeled as a never ending source of premixed, air and fuel, gas. The burned gas zone is now modeled to have an inflow and an outflow where the mass outflow is an function of the pressure difference inside the combustion chamber and outside (atmospheric pressure).

$$MassOutFlow = k * (P_{bz} - P_{amb}) \tag{3.13}$$

where k is a constant, P_{bz} the pressure in the burned zone, P_{amb} the ambient pressure.

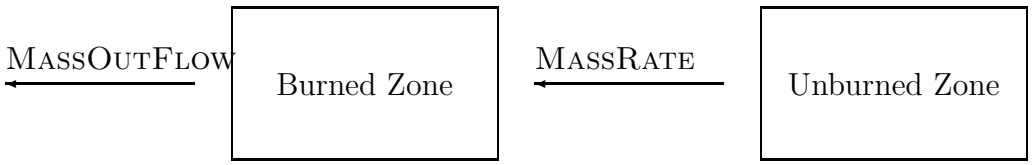

Figure 3.6: *The unburned zone is modeled as a never ending source of unburned gas with a mass rate flow into and out from the burned gas zone*

Chapter 4

SIMULATIONS and ANALYSIS

In this chapter the two models will be analysed and simulation results will be discussed. Results from the cylinder model will first be presented and compared with results from other published model results and data from a test engine. Thereafter will the results from the turbine model simulation be presented and commented. The chapter ends with a section which gives the conclusions from this thesis.

4.1 Verification of Cylinder model

As described in section 2.2.4 NOx concentration depends very much on the equivalence ratio (see section 2.1.5). In figure 4.1 NOx concentration in ppm is plotted as a function of the equivalence ratio. In the figure data from a real test engine is also plotted as a reference (data taken from [2]).

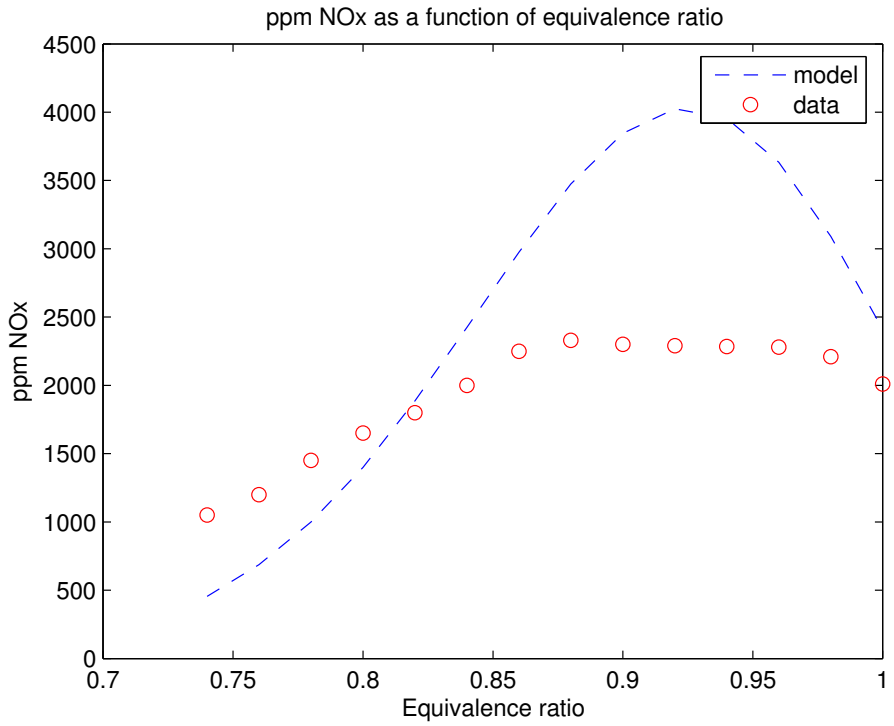

Figure 4.1: *Graph showing concentration of NOx as a function of equivalence ratio. Simulation from the developed model and data from a real test engine are shown.*

As described in the theory NOx concentration has a maximum in the fuel-lean zone ($\Phi < 1$). This maximum comes from the amount of excess oxygen existing in the fuel-lean region. As stated in section 2.2.1 thermal NOx formation depends on the amount of excess oxygen. The setup of the test engine isn't known so the comparison is very rough. The purpose is only to see if the simulation results are reasonable which they seem to be.

As discussed in section 2.2.4 accurate modeling of NOx formation is very difficult and the purpose of the developed model is a not too computational demanding model describing NOx formation reasonably well to be part in a system level model, which also emphasizes the perspective of a very rough comparison. These concentrations of NOx are well above the regulation limits and will be reduced by the catalyst before emitted into the surrounding air.

The next figure (figure 4.2) shows a comparison between results from the developed model and other models found in a doctoral thesis by Rolf Egnell [8]. Results from the developed model in this thesis is labeled *thesis model* and uses both equilibrium and dynamic reactions. The combustion process is modeled with equilibrium reactions and the NOx formation is modeled with dynamic reactions. The *Original Zeldovich* data is taken from [8] and uses a equilibrium approach combining a simple combustion model and the first two equations in the *Zeldovich mechanism*. The results labeled *Extended Zeldovich*, also from [8], uses the same equilibrium approach as the former model but includes all three equations in the *Zeldovich mechanism*. The last results, labeled *Full kinetic*, uses dynamic reactions to model the combustion and the full extended *Zeldovich mechanism*, and are also taken from [8].

As can be seen in the figure the model results with the equilibrium approach, *Original Zeldovich* and *Extended Zeldovich*, give higher concentration than the *Full kinetic* model result. This implies that the NOx concentration don't have time to reach the equilibrium concentration. Because the developed model uses both equilibrium and non-equilibrium reactions you would expect its result to be between the equilibrium and dynamic models. The peak result from the developed model is between the peak results from the models taken from [8]. The result curve from the developed model seem to be shifted to the right in a comparison to the other results. The reason for this can be many. The model is not very well tuned. In the model it is assumed that the reactions modeling the combustion are fast enough to be modeled with equilibrium reaction equations and the reactions modeling the NOx formation are slow enough to be modeled with dynamic reaction equations. More work need to be done in analysing which equations that are fast enough (in this temperature range) to be modeled as equilibrium reactions and which to be modeled with dynamic reactions. A simple way of doing this could be to

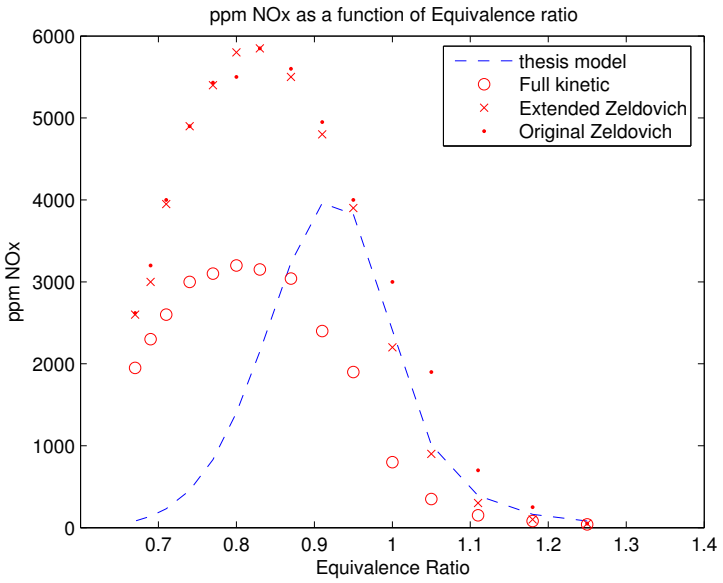

Figure 4.2: *Graph showing a comparison of NOx concentration from the developed model and three other models found in a doctoral thesis by Rolf Egnell [8]. The two models using a equilibrium approach give higher NOx peak results compared with the model using a dynamic/full kinetic approach. The developed model uses a combination of dynamic approach to describe NOx formation and equilibrium approach to describe the general combustion, and gives result with a peak height between the other two approaches*

calculate and compare the reactions rates for all the equations in the appropriate temperature range. More tuning is also needed on the parameters of the model, especially the ones effecting the temperature in the cylinder, e.g. the heat transfer coefficient between the burned gas and the cylinder walls. Different fuel models can also effect the NOx values and for what equivalence ratio the NOx concentration has its peak.

To avoid these factors that make the comparison between different models so hard, a comparison is made with two variations of the developed model. The developed model is compared when simulating with the same approach as before, that is with both equilibrium and non-equilibrium/dynamic reaction equations, and with only equilibrium reaction equations over one cycle. All other parameters except which type of reaction equations used are the same

in the two simulations. The result from these simulations are seen in figure 4.3 and 4.4. In figure 4.4 the temperatures in the burned gas zone for the

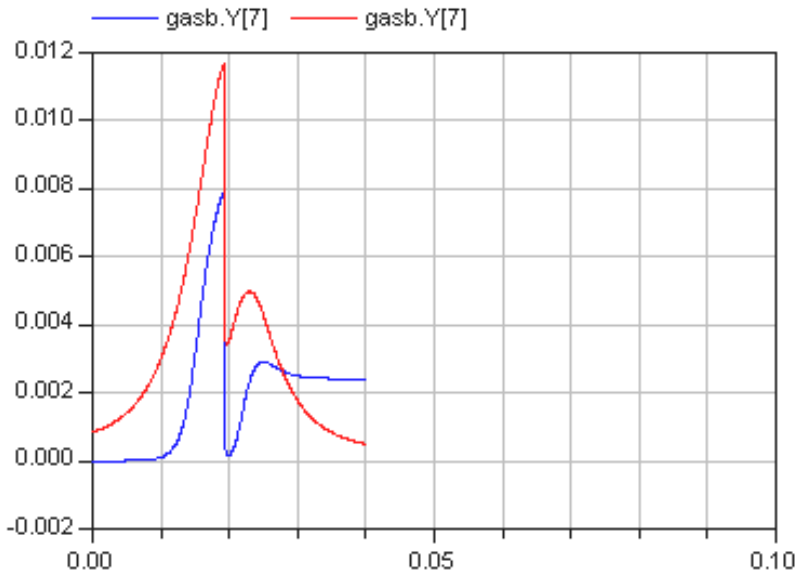

Figure 4.3: *Graph showing a comparison of NOx concentration, during one cycle, for two variations of the developed model as a function of time. The two model variations are with equilibrium approach, in red, and with partial equilibrium, in blue. As can be seen in figure 4.4 the temperature will be almost the same for the two approaches, but the equilibrium approach usually give higher concentration of NOx. In the end of the cycle when the equilibrium approach give lower concentrations compared to the partial equilibrium approach can be explained by a probable cause of the the phenomena called freezing.*

two variations of the developed model are plotted as a function of time. As can be seen in the figure the temperature difference between the two model variations is very small. In figure 4.3 on the other hand a clear difference appear between the two model variations. The red line with the higher concentration of NOx for most of the cycle is the result from the developed model with equilibrium approach and the blue line with lower concentration of NOx for most of the cycle is the developed model with equilibrium reaction equations for the general combustion and dynamic reaction equations for the NOx formation. As described before the equilibrium approach give

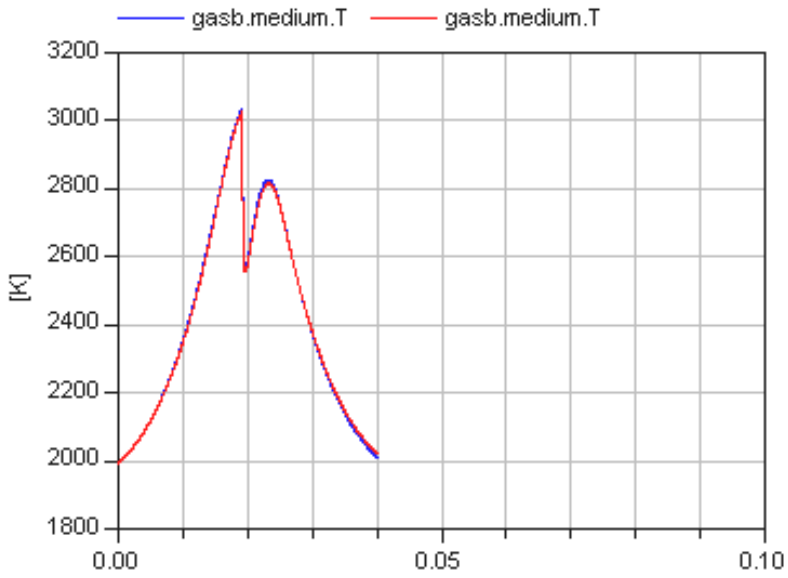

Figure 4.4: *Graph showing a comparison of the temperature in the burned gas zone, during one cycle, for two variations of the developed model as a function of time. The two model variations are with equilibrium approach and will partial equilibrium. The temperature is almost the same during the whole cycle, but as can be seen in figure 4.3 the concentration of NOx will usually be higher when using the equilibrium approach.*

the highest concentration because the assumption of instant chemical equilibrium is made. This can clearly be seen in the beginning of the cycle when the concentration of NOx instantly is higher with this approach compared to the model with only partial equilibrium.

When the time is 0.028 the concentration from the equilibrium approach drops below the model with both equilibrium and dynamic reaction equations. This is due to a phenomenon called freezing, described in [11]. It comes from the fact that the forward reactions in the *Zeldovich mechanism*, with dynamic reaction equations, have a much stronger temperature dependence than the reverse reactions. This will lead to that NOx formation at high temperatures is much faster than the destruction, but the opposite, that the destruction is much faster than the formation at low temperatures, is not true. This gives the result that the NOx concentration, modeled with

dynamic reaction equations, will remain high even if the temperature drops, whereas the the NOx formation, modeled with equilibrium equations, will drop when the temperature drops because the freezing phenomenon does not appear in the equilibrium approach.

The sudden drop in both the concentration of NOx and the temperature in both figures just before the time is 0.02 comes from the fact that the ignitions starts at this time. Before ignition the burned gas zone is modeled as a very small volume with air for numerical reasons. The dilution, when gas is entering the burned zone from the unburned zone, is the reason for this drop.

4.2 Simulation results from the Gas turbine model

As mentioned in section 2.2.1 thermal NOx formation is dependent on residence time, which is how long time combustion gas stays in the warm combustion area. The reason for this dependence is that it takes some time until the chemical system has reached equilibrium. If the residence time is short enough the concentration of NOx isn't as high as it would be if time was given for the system to reach chemical equilibrium.
Residence time can be seen as a function of both the volume and the volume flow rate out from the combustion chamber in the following way

$$ResidenceTime = \frac{Volume}{VolumeFlowRate} \tag{4.1}$$

Figure 4.5 shows a plot from simulation results where NOx concentration is shown as a function of the mass flow rate from the unburned to the burned zone.

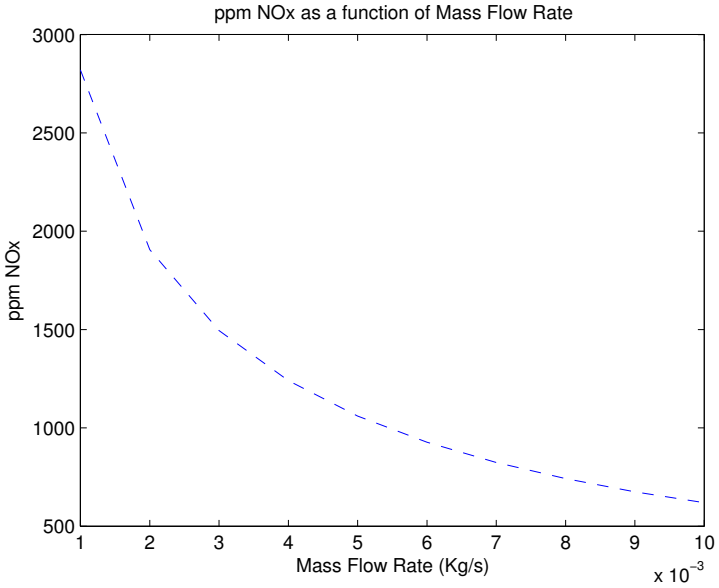

Figure 4.5: *Graph showing ppm NOx as a function of the mass flow rate*

As the mass flow rate from the unburned to the burned zone increases the volume flow rate out from the burned zone increases. This leads to an decrease of the residence time which results in lower NOx concentration. When changing the mass flow rate from the unburned to the burned zone one has to remember though that more than the residence time is changing. The temperature for instance is also effected due to cold gas is entering at a different mass rate which alters the NOx formation because of its strong dependence of the temperature. Figure 4.6 shows a plot of temperature as a function of mass flow rate for the same situation as above.

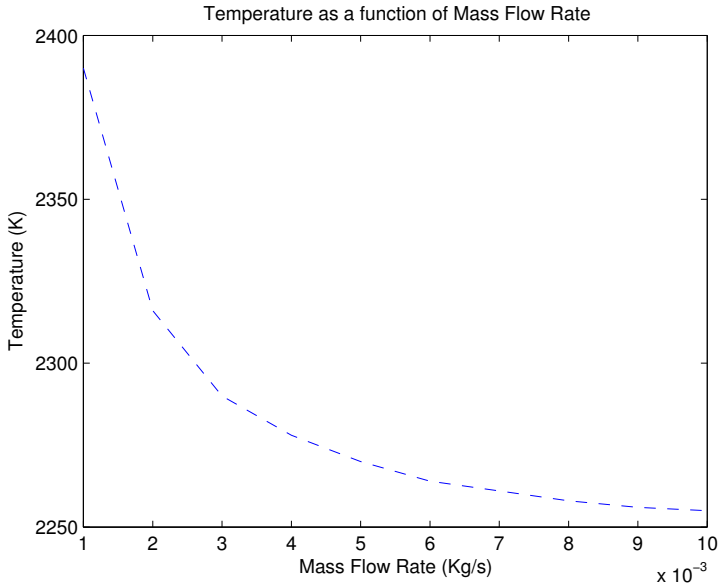

Figure 4.6: *Graph showing temperature as a function of the mass flow rate*

Both the lower temperature and the lower residence time for higher mass flow rate will cause the concentration of NOx to decrease. Even though the temperature change is small the change in concentration of NOx becomes very big because of the exponential dependence.

4.3 Conclusion

Chemical reactions in combustion processes is a very complicated and difficult area to model. This is especially true for NOx modeling which is very hard to predict with good accuracy. The different values of reaction constants for the dynamical reaction equations called *Zeldovich mechanism* found in the literature is also an result of the difficulty of NOx modeling.

There are very many different factors that effect the formation of NOx but the single most important is the temperature. Another important factor is the amount of excess air due to the fact that NOx formation is dependent on the equivalence ratio and has a maximum in the fuel-lean region.

In this thesis a method has been developed to model NOx formation in combustion processes. The method mixes both equilibrium and non-equilibrium reaction equations. The general combustion is modeled with equilibrium reactions whereas the NOx formation is modeled with dynamical reactions. The two developed models built with this method, a cylinder in a spark ignition car engine and a gas turbine, have been tested and the simulation results have been briefly analysed. The model of a cylinder has been roughly validated with help of other published model results and data from a test engine. It seems to give reasonable results, but more testing is needed. A comparison between two model variations of the cylinder model, one with only equilibrium reaction equations and the other with both equilibrium and non-equilibrium reaction equations, is made. The equilibrium approach usually give higher concentrations of NOx but does not have the phenomenon called freezing, which can make the concentration from the equilibrium approach drop below the approach with both equilibrium and non-equilibrium reaction equations if the temperature is high and then rapidly drops. The models also seem to be robust and fairly flexible. The objective to have automatic models with no manual work needed in the algorithms is also achieved.

More work is especially needed in tuning the model. This includes analysing more carefully when equations can be modeled with equilibrium reaction equations and when they have to be modeled with dynamic reaction equations. Parameters of the model also need to be tuned, especially parameters that effect the temperature in the cylinder, e.g. the heat transfer coefficient between the burned gas and the cylinder walls.

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