Model-Based Control of Catalytic Converters

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2012
Acknowledgments

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It is my wish to express my gratitude to Dr. Alexander Schilling, who soon will be my colleague at work, for initiating the collaboration between Liebherr Machines Bulle and the IDSC. When he supervised my bachelor thesis he sparked my interest in this research field.

Last but not least, I would like to thank my parents for their continuous support during my studies at ETH and for providing me with the chance to pursue my interests.

November 2012

Pascal Kiwic
Abstract

Catalytic converters have become the most important vehicle emission control devices to reduce the pollutants produced by combustion engines. The technical demands on the activity of these exhaust aftertreatment catalysts has been significantly increased over the years in order to be able to comply with the evermore stringent emission standards. Two major problems are still to be solved, namely the behavior of the catalyst during engine transients and the delayed light-off after cold start. This thesis addresses the first problem by making model-based control available in the application.

A framework for developing first-principle models of flow-through chemical reactors is presented. It has been optimized for control-oriented modeling, but it can easily be extended to other requirements. The framework has been implemented in an auto-code generator called camgen. With the aid of camgen it is possible to derive catalyst models within a very short time. The models are real-time capable and are optimized for fast execution.

The parameter optimization for the models derived is very challenging. The number of parameters and the non-linearity of the models demand other than gradient-based search algorithms. The particle swarm optimization (PSO) is introduced for this kind of problems. The performance of the algorithm is increased by transforming the search parameters and by limiting the search region. The simplicity of the models allows the identification of the physical and the chemical parameters in succession.

The framework has first been applied to the three-way catalytic converter (TWC). A chemical reaction scheme with only two reactions has been found to be adequate for the problem at hand. The model has been identified and validated through various kinds of test bench measurements. The relative oxygen level profile was analyzed in steady state and during transients. An explanation for the characteristic filling and
Abstract

depleting behavior of the TWC is given using simulated profiles of the oxygen level and the gas concentrations. Simulations and test bench measurements were used to derive an optimal, non-causal depletion strategy after fuel cut-off phases. This strategy significantly reduces the recovery time of the downstream oxygen sensor. The reduction in recovery time is important for the operation of a feedback TWC controller. The non-causal strategy could then be replaced by a causal depletion strategy that shows a similar performance, but requires a significantly smaller calibration effort. The causal strategy is based on an on-line observation of the relative oxygen level profile which is provided by the model introduced.

Another application of the framework is presented with the selective catalytic reduction (SCR) of nitrogen oxide with ammonia. The objective of a desired model-based controller is to keep the downstream NH$_3$ slip below a certain level while maximizing the NO$_x$ conversion efficiency. Therefore, a model for the SCR catalyst has been identified and validated through test bench measurements. The relative ammonia level profile was analyzed in steady state and during transients. An optimal NH$_3$ dosing strategy was selected from the literature and has been adapted to the model derived. The NH$_3$ slip controller performs well in simulation. The performance of the controller in the application highly depends on the quality of the model. Existing challenges within the simulation are identified for further analysis.
Zusammenfassung


Zusammenfassung


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## Nomenclature

### Latin Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{cs}$</td>
<td>cross-sectional area of catalyst</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$A_{geo}$</td>
<td>specific geometric catalytic surface</td>
<td>[m$^2$/m$^3$]</td>
</tr>
<tr>
<td>$B$</td>
<td>performance index</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$c_0$</td>
<td>total gas concentration</td>
<td>[mol/m$^3$]</td>
</tr>
<tr>
<td>$c_p$</td>
<td>specific heat capacity</td>
<td>[J/kg·K]</td>
</tr>
<tr>
<td>cpsi</td>
<td>cell density of catalyst</td>
<td>[1/in$^2$]</td>
</tr>
<tr>
<td>$E_i$</td>
<td>net mass flow of species $i$</td>
<td>[mol/m$^3$·s]</td>
</tr>
<tr>
<td>$G_i$</td>
<td>Gibbs free energy of species $i$</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$K_i$</td>
<td>chemical equilibrium constant</td>
<td>[−]</td>
</tr>
<tr>
<td>$L$</td>
<td>length</td>
<td>[m]</td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass</td>
<td>[kg/mol]</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>exhaust mass flow through catalyst</td>
<td>[kg/s]</td>
</tr>
<tr>
<td>$m$</td>
<td>mass</td>
<td>[kg]</td>
</tr>
<tr>
<td>$n_{cells}$</td>
<td>number of cells along the catalyst</td>
<td></td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>energy transfer</td>
<td>[J/s]</td>
</tr>
<tr>
<td>$q$</td>
<td>species vector</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
<td>[J/mol·K]</td>
</tr>
<tr>
<td>$R_i$</td>
<td>net reaction rate for species $i$</td>
<td>[mol/m$^3$·s]</td>
</tr>
<tr>
<td>$r_i$</td>
<td>reaction rate of reaction $i$</td>
<td>[mol/m$^3$·s]</td>
</tr>
<tr>
<td>$S$</td>
<td>any solid species</td>
<td></td>
</tr>
<tr>
<td>$SC$</td>
<td>storage capacity of the solid phase</td>
<td>[mol/m$^3$]</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$V$</td>
<td>stoichiometric coefficient matrix</td>
<td></td>
</tr>
<tr>
<td>$V_{cat}$</td>
<td>total volume of catalyst</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$W$</td>
<td>order coefficient matrix</td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>any species in the gas phase</td>
<td></td>
</tr>
</tbody>
</table>
Greek Symbols

\begin{align*}
\alpha & \quad \text{heat transfer coefficient} \quad [\text{W/m}^3\cdot\text{K}] \\
\epsilon & \quad \text{open cross-sectional fraction of catalyst} \quad [-] \\
\Gamma_i & \quad \text{scaled Gibbs free energy of species } i \quad [-] \\
\lambda & \quad \text{normalized air-fuel ratio} \quad [-] \\
\lambda_s & \quad \text{conductivity of solid phase} \quad [\text{W/m-K}] 
\end{align*}

Acronyms

\begin{itemize}
\item AFR \quad \text{air-fuel ratio}
\item CLD \quad \text{fast chemiluminescence detector}
\item CUC \quad \text{clean-up catalyst}
\item DAE \quad \text{differential algebraic equation}
\item DOC \quad \text{diesel oxidation catalyst}
\item DPF \quad \text{diesel particulate filter}
\item ECU \quad \text{engine control unit}
\item EKF \quad \text{extended Kalman filter}
\item FID \quad \text{fast flame ionization detector}
\item HFM \quad \text{hot-film air-mass meter}
\item LSF \quad \text{switch-type oxygen sensor}
\item LSU \quad \text{wide-range oxygen sensor}
\item MIL \quad \text{malfunction indicator light}
\item MS \quad \text{mass spectrometer}
\item NDIR \quad \text{nondispersive infrared detector}
\item OBD \quad \text{on-board diagnosis}
\item ODE \quad \text{ordinary differential equation}
\item OSL \quad \text{occupied surface level}
\item PSO \quad \text{particle swarm optimization algorithm}
\item RAL \quad \text{relative ammonia level (SCR)}
\item ROL \quad \text{relative oxygen level (TWC)}
\item SC \quad \text{surface storage capacity}
\item SCR \quad \text{selective catalytic reduction}
\item SP \quad \text{setpoint}
\item TWC \quad \text{three-way catalytic converter}
\item XML \quad \text{Extensible Markup Language}
\end{itemize}
Subscripts

0 before the time step
1 after the time step
X any gas species
S any surface species
cat catalyst
cs cross section
ds downstream of the catalyst
g gas phase
gg within the gas phase
gs between gas and solid phase
in inlet of the cell
opt optimal
out outlet of the cell
us upstream of the catalyst
s solid phase
ss within the solid phase
st stoichiometric

Chemical Species

CO carbon monoxide
CO$_2$ carbon dioxide
H$_2$O water
HC unburned hydrocarbon
N$_2$ nitrogen
NH$_3$ ammonia
NO nitrogen monoxide
NO$_2$ nitrogen dioxide
NO$_x$ nitrogen oxide (NO + NO$_2$)
O$_2$ oxygen
PM particulate matter
Pt platinum (empty surface of TWC)
PtO adsorbed oxygen (occupied surface of TWC)
V vanadium (empty surface of SCR)
VNH$_3$ adsorbed ammonia (occupied surface of SCR)
1 Introduction

In a general internal combustion engine, hydrocarbons are burned with an oxidizer. The heat release results in an increased pressure in the cylinder, which is then converted to mechanical energy through the pistons. The products of the desired complete combustion are carbon dioxide (CO$_2$) and water (H$_2$O).

$$C_xH_{2y} + (x + \frac{y}{2})O_2 \rightarrow xCO_2 + yH_2O + \text{energy} \quad (1.1)$$

In reality, the combustion is never complete. Furthermore, instead of pure oxygen (O$_2$), air is used as the oxidizer. This leads to products of incomplete combustion, such as carbon monoxide and unburned hydrocarbons, and to products of unwanted oxidation like nitrogen oxides. In diesel engines, a substantial amount of particulate matter is generated as well.

These emissions can have a great impact on people and nature [3, 45]. Carbon monoxide (CO) is very toxic to human beings since it blocks the supply of oxygen to the body tissue. Unburned hydrocarbons (HC) can cause coughing, drowsiness, or have a narcotic effect. Some of them are toxic and carcinogenic. Nitrogen dioxide (NO$_2$) is toxic by damaging the lung tissue, while nitrogen monoxide (NO) is relatively harmless to humans. But both NO and NO$_2$ play an important role in the formation of acid rain, photochemical smog, and the depletion of the ozone layer. Particulate matter (PM) can cause headaches, dizziness, or coughing in the short-term, as well as lung cancer or cardiovascular disease in the long-term. For all these reasons, the unwanted byproducts of internal combustion engines are better not emitted into the atmosphere.

The success story of exhaust gas aftertreatment for combustion engines began in 1974 with the invention of the two-way catalytic converter, which was replaced by the three-way catalytic converter in 1981. The introduction of the engine control units (ECU) in the early 1980s enabled the
1 Introduction

Figure 1.1: Flow-through catalytic converter (left) and wall-flow filter (right)

first feedback loops for catalyst control. The technological progress allowed the first emission legislation by the California Air Resource Board (CARB) in 1981. The European equivalent was not introduced until 1992 (CH: 1986). In the meantime, on-board diagnostic capabilities of the exhaust aftertreatment systems have become mandatory and the emission limits of cars, trucks, and non-road vehicles are now very stringent [27].

1.1 Catalytic converters and filters

Figure 1.1 illustrates the two main concepts of exhaust aftertreatment systems for combustion engines, namely the flow-through catalytic converter and the wall-flow filter.

An exhaust-gas catalytic converter chemically alters the toxic byproducts of the combustion to less toxic substances by way of catalyzed chemical reactions. The specific reactions vary with the washcoat loading of the surface. A catalyst consists of several channels that are open on both sides. This flow-through type of catalyst allows the exhaust gas to flow with negligible resistance. The interaction with the surface of the catalyst takes place through diffusion.

By contrast, the channels of a filter are open only on one side. The gas is forced to pass through the walls, where the particulate matter is removed from the exhaust and is deposited on the surface. This results in an increased back pressure against which the piston has to work. This back
pressure and the required regeneration of the filter lead to an increased fuel consumption of the engine.

1.2 SI engines

The exhaust aftertreatment concepts of gasoline and diesel engines must be quite different. The spark-ignited gasoline engine works with a stoichiometric gas composition, while the diesel engine is always operated under lean conditions.

The main pollutants after the combustion of a stoichiometric mixture are nitrogen monoxide (NO), carbon monoxide (CO), and unburned hydrocarbons (HC). However, the amount of oxygen in the gas phase plus the oxygen from the reduction of NO exactly matches the amount of oxygen needed to oxidize the CO and HC. Therefore, the oxygen only has to be moved from one molecule to the other.

1.2.1 Two-way catalytic converter

In 1974, the two-way catalytic converter was the first exhaust gas aftertreatment system. It was able to oxidize unburned hydrocarbons (HC) and carbon monoxide (CO), both unwanted byproducts of the combustion.

<table>
<thead>
<tr>
<th>Table 1.1: Two-way catalyst reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation: [2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2]</td>
</tr>
<tr>
<td>HC oxidation: [\text{C}<em>x\text{H}</em>{2y} + \left(x + \frac{y}{2}\right)\text{O}_2 \rightarrow x\text{CO}_2 + y\text{H}_2\text{O}]</td>
</tr>
</tbody>
</table>

Nowadays, the two-way catalytic converter is only used as the oxidation catalyst for diesel engines. On the SI engines, it was replaced by the three-way catalytic converter.

1.2.2 Three-way catalytic converter

Three-way catalytic converters (TWC) are today’s most successful exhaust gas aftertreatment devices for gasoline engines. They simultaneously reduce the harmful substances nitrogen oxides (NO\(_x\)), carbon
monoxide (CO), and unburned hydrocarbons (HC) and convert them to nitrogen (N₂), carbon dioxide (CO₂), and water (H₂O):

<table>
<thead>
<tr>
<th>Table 1.2: TWC reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation: 2 CO + O₂ → 2 CO₂</td>
</tr>
<tr>
<td>HC oxidation: CₓH₂ᵧ + (x + y/2) O₂ → x CO₂ + y H₂O</td>
</tr>
<tr>
<td>NO reduction: 2 NOₓ → N₂ + x O₂</td>
</tr>
</tbody>
</table>

The simultaneous conversion efficiencies of the reactions listed in Table 1.2 are high only under stoichiometric conditions where the amount of air matches the amount of fuel to be burned. The reduction of NOₓ fails under lean conditions, while the oxidation of CO and HC remains incomplete in rich conditions.

The storage capacity of the TWC compensates for small deviations from stoichiometric conditions. This storage capacity has to be taken into account in the design of a feedback control strategy since it introduces new dynamics to the system.

### 1.3 Diesel engines

The very efficient three-way catalytic converter cannot be used on diesel engines because the requirement of a stoichiometric combustion is not given. The nitrogen oxides (NOₓ) would not be reduced. Other exhaust aftertreatment systems are used on lean combustion engines.

#### 1.3.1 Diesel oxidation catalyst

Diesel oxidation catalysts (DOC) are comparable to the now obsolete two-way catalysts for gasoline engines. They not only eliminate the typical diesel odor; they also help to reduce the visible particulate matter.

<table>
<thead>
<tr>
<th>Table 1.3: DOC reaction scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation: 2 CO + O₂ → 2 CO₂</td>
</tr>
<tr>
<td>HC oxidation: CₓH₂ᵧ + (x + y/2) O₂ → x CO₂ + y H₂O</td>
</tr>
</tbody>
</table>
In modern diesel exhaust aftertreatment systems, the DOC also supports the oxidation of NO to NO\textsubscript{2}:

\[
2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \quad (1.2)
\]

The concentration of NO\textsubscript{2} in the exhaust gas can have a positive impact on the regeneration of a diesel particulate filter or on the efficiency of the selective catalytic reduction.

### 1.3.2 Diesel particulate filter

A diesel particulate filter (DPF) removes particulate matter (PM) from the exhaust gas of a diesel engine. Particulate matter is the term used for all the material in the exhaust pipe that is solid, such as ash and soot. Within hours, the filter is covered by combustible particles (soot) and after several thousand hours by inert solid particles (ash). The soot can be eliminated through combustion, which regenerates the filter. The ash has to be washed out, for which the filter has to be dismounted.

In 1988, the very fine particles emitted from diesel engines were classified as carcinogens by the World Health Organization (WHO). This step prompted environmental legislation in many countries to limit the amount of PM allowed in the exhaust gas.

### 1.3.3 Selective catalytic reduction

The selective catalytic reduction (SCR) is used on diesel engines to reduce the nitrogen oxides (NO\textsubscript{x}) with the aid of ammonia (NH\textsubscript{3}) to nitrogen (N\textsubscript{2}) and water (H\textsubscript{2}O). The reductant is usually stored as AdBlue, an aqueous solution with 32.5% urea, which is injected into the tailpipe upstream of the SCR catalyst. The water evaporates and the urea (CO(NH\textsubscript{2})\textsubscript{2}) decomposes into isocyanic acid (HNCO) and NH\textsubscript{3}. The HNCO decomposes further by hydrolysis to additional molecules of NH\textsubscript{3} and CO\textsubscript{2}.

Table 1.4 lists the three NO\textsubscript{x} reducing reactions and the reaction for the NH\textsubscript{3} oxidation. For vanadium-based SCR catalysts, the standard SCR reaction is the most significant since no additional DOC is used, which keeps the amount of NO\textsubcript{2} relatively low. The fast and the slow SCR reactions are required only if a DOC is used and a large amount of NO\textsubscript{2} is present in the exhaust gas.
1 Introduction

Table 1.4: SCR reaction scheme

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard SCR</td>
<td>$4 \text{NH}_3 + 4 \text{NO} + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Fast SCR</td>
<td>$4 \text{NH}_3 + 2 \text{NO} + 2 \text{NO}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Slow SCR</td>
<td>$4 \text{NH}_3 + 3 \text{NO}_2 \rightarrow \frac{7}{2} \text{N}_2 + 6 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>NH$_3$ oxidation</td>
<td>$4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

The objective of the control strategy is to maximize the NO$_x$ conversion efficiency while minimizing the urea consumption and preventing NH$_3$ slip downstream of the catalyst.

1.3.4 Lean NO$_x$ trap

The lean NO$_x$ trap (LNT) is a DeNOx system like the selective catalytic reduction. It is a discontinuous system that first stores NO$_2$ on its surface and is then regenerated with rich exhaust gas by injecting additional fuel upstream of the catalyst [31, 65]. Table 1.5 lists the complex reaction scheme of an LNT storage catalyst.

Table 1.5: LNT reaction scheme

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO oxidation</td>
<td>$\text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2$</td>
</tr>
<tr>
<td>NO$_2$ storage</td>
<td>$\text{BaCO}_3 + 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Ba(NO}_3)_2 + \text{CO}_2$</td>
</tr>
<tr>
<td>Regeneration</td>
<td>$\text{Ba(NO}_3)_2 + \text{CO/H}_2/\text{HC} \rightarrow \text{BaCO}_3 + 2 \text{NO} + \text{CO}_2/\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>NO reduction</td>
<td>$\text{NO} + \text{CO/H}_2/\text{HC} \rightarrow \frac{4}{7} \text{N}_2 + \text{CO}_2/\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

The control objective is to detect a completely filled LNT catalyst and to regenerate it with as little additional fuel as possible.

1.4 Thermal and chemical deactivation

Automotive exhaust aftertreatment catalysts must efficiently clean the raw emissions of the combustion engine during the lifetime of the vehicle. Hence, the eventual deactivation of catalytic converters has to be taken into account in the design of a model-based control strategy.

Thermal and chemical aging effects induce physical and chemical modifications of the catalysts surface resulting in a deactivation of the catalyst.
1.4 Thermal and chemical deactivation

Chemical aging compounds mostly originate from engine oil additives like lead or sulfur. These aging effects are sometimes reversible. Thermal aging effects are more significant, but are irreversible. Multiple effects occur on the washcoat surface as well as on the monolith material. More information on the subject of thermal and chemical aging of exhaust gas catalysts can be found here:

| TWC: Winkler et al. [70], Zhang and Cheng [72] |
| DOC: Andersson et al. [2], Winkler et al. [71] |
| LNT: Casapu et al. [13], Ji et al. [28] |
| SCR: Brandenberger et al. [9], Kwak et al. [36] |

From a control point of view, the effects are the same: Reduced storage capacity and thus a reduced catalytic activity. Numerous approaches have been published on how to adapt to the changing storage capacity of the catalyst. For instance, Auckenthaler et al. [5] introduced an extended Kalman filter (EKF) for the adaption, whereas Ammann et al. [1] used a recursive Gauss-Newton estimation method.

A catalyst model that is used on-line in the model-based control strategy and that is being adapted to aging and poisoning effects of the catalyst can also be used for on-board diagnostics. If the adapted storage capacity falls below a certain threshold value, the catalyst is defined to be faulty.

1.4.1 On-board diagnostics

The term on-board diagnostics (OBD) refers to a vehicle’s capability for self-diagnostics and reporting. It provides access to the state of health of various vehicle sub-systems that can be useful for the driver or the repair technician. The amount of information thus obtainable has increased since this capability first was introduced in the 1980s when it was made possible by the development of the first engine control units (ECU). Modern implementations use a malfunction indicator light (MIL) to inform the driver and a standardized reporting protocol about the actual problem for the repair technician. The main reason for OBD is the importance of the environmental issues [30].
The current OBD standard includes several subsystems with their specific diagnostic requirements. The exhaust aftertreatment system is one of them. It involves the catalysts and also the exhaust gas sensors, like oxygen or NOₓ sensors. Misfire of a single cylinder must be detected because unburned fuel is converted in the catalyst which could overheat and be severely damaged. During misfire, the MIL must be blinking.

1.4.2 Catalyst OBD

The exhaust catalyst is one of the components that is monitored by the OBD. If the efficiency of the catalyst falls below a threshold, a failure is detected and the Malfunction Indicator Light (MIL) is turned on [30].

Various methods have been published to determine the state of health of the catalyst. Most of them indirectly use the storage capacity as the indicator for a failure. Fiengo et al. [24] compare the measured downstream switch-type oxygen sensor value with the output of a simplified TWC model. Muske et al. [48] published a comparable strategy using a wide-band oxygen sensor. In [47], they already stressed the advantage of a combined model-based controller and diagnostic monitor. The advantage is the reduced calibration effort. These methods require a forced excitation of the inlet gas composition. This results in delayed breakthroughs in the outlet that are detected and compared to threshold values.

The observation of the storage capacity of the catalyst can also be used to determine the end of the catalyst’s lifetime. If the storage capacity drops below a pre-defined limit, the catalyst is reported dead and has to be replaced.

1.5 Structure of the thesis

Chapter 2 presents a framework for the control-oriented modeling of chemical reactors. The framework has been implemented in an auto-code generator named camgen that is freely available for download. The difficulties in the parameterization of the catalyst models are discussed and solved in Chapter 3.

A control-oriented model of a three-way catalytic converter (TWC) is described in Chapter 4. The model is validated with several measurements
at an engine test bench and is then used to explain the asymmetric filling and depleting behavior of a TWC. An optimal depletion strategy after fuel cut-off phases is derived from the model and is validated on the engine test bench.

Chapter 5 introduces a catalyst model for the selective catalytic reduction (SCR). The model is also validated with several measurements at an engine test bench and is used to explain the filling and depleting behavior of an SCR catalyst. An optimal NH$_3$ dosing strategy is derived from the model.

Chapters 4 and 5 are structured in the same manner and can be read independently.
2 Framework for Modeling Chemical Reactors

The modeling of chemical reactors like exhaust gas catalysts has been a topic for many researchers and many different models have been derived. Most of them were built from scratch with the aid of the published models. Since the underlying first-principle approach is the same for all catalysts, a framework has been developed here that builds complete models with the desired chemical reaction scheme.

The framework has also been implemented in an auto-code generator that builds complete models out of the description of the chemical reactors. This program called camgen, with the source files and the models described in this thesis, is freely available on the homepage of the Institute for Dynamic Systems and Control (IDSC) of ETH Zurich\(^1\). It could assist other researchers in their effort at modeling chemical reactors.

Figure 2.1 illustrates the workflow when generating new models using camgen. The catalyst is defined using an XML file that includes the reaction scheme, the geometry, and the desired parameters. The XML file is then parsed by a Maple script that generates all the relevant equations. The output is optimized code in different programming languages. More information about the usage of camgen can be found on the homepage of the institute.

The use of auto-generated code has several advantages. The generation of a new model takes only a few seconds after the definition of the model in the XML file. The result is executable code that is optimized for speed and memory allocation. Typing errors are prevented because the XML file is parsed for errors and the resulting code does not have to be edited.

Böhme [8] already presented a code-generator-based software package that builds routines describing catalytic reactors. These routines are then

\(^1\)http://www.idsc.ethz.ch/camgen
linked to a PDE solver that completes the model. These PDE solvers are mostly implicit solvers that cannot be used for real-time applications. In contrast, the framework presented here builds complete models using only explicit solvers that can be run on real-time hardware and therefore can be used for model-based control strategies.

The model structure of the framework presented is based on the TWC model proposed by Möller [44]. It is simplified in order to obtain a control-oriented and real-time capable model of chemical reactors. It has been tested for three-way catalytic converters (TWC) as well as for the catalysts of the selective catalytic reduction (SCR). It is expected that the method can be applied to diesel oxidation catalysts (DOC) and SCR clean-up catalysts (CUC) as well.

The framework is designed for flow-through catalysts only. Wall-flow reactors such as diesel particulate filters (DPF) are not covered.

### 2.1 Requirements

A framework should be provided that allows the structured and fast development of control-oriented models of flow-through chemical reactors. The complexity of the model should be as low as possible in order to keep the computational demand low and thus allow its real-time operation. This implies the usage of explicit solvers.

The allowed inputs of the models are exhaust gas information available in modern cars, either directly from sensors, or as estimations from the engine control unit. These are total air mass flow, exhaust gas temperatures, and some information about the exhaust gas composition from oxygen or NO\textsubscript{x} sensors.
2.2 Chemical model

A first-principle approach is used to describe the chemical part of the model. This ensures the compliance with the energy and mass balances as well as with the chemical equilibrium at all times.

The derivation of the chemical model is explained with the chemical reaction of the three-way catalytic converter (TWC).

### 2.2.1 Reaction scheme

The development of the reaction scheme requires some knowledge about the storage capability of the catalyst and the desired net reactions. The species to be stored on the surface as well as the empty surface represent the occupied and empty site, respectively. The net reaction is then split into at least two reactions involving the two sites. In general, one reaction fills the catalyst, the others deplete the catalyst.

For example, the TWC is known to store considerable amounts of oxygen because of the platinum (Pt) loading on the surface. Therefore, the empty site Pt and the occupied site PtO are introduced. The desired net reaction is the oxidation of CO to CO$_2$:

\[
O_2 + 2\text{CO} \rightarrow 2\text{CO}_2
\]

(2.1)

This net reaction is not intuitive for a TWC but it will be explained later why this fulfills the needs. The net reaction then takes place on the catalyst’s surface resulting in the following reaction scheme:

\[
\begin{align*}
O_2 + 2\text{Pt} & \rightleftharpoons 2\text{PtO} \\
\text{CO} + \text{PtO} & \rightleftharpoons \text{CO}_2 + \text{Pt}
\end{align*}
\]

(2.2)

This reaction scheme should only be extended if the desired characteristics of the catalyst are not reproduced by the model. The derivation of the TWC reaction scheme and the consequences of the simplifications are described in Chapter 4.
2 Framework for Modeling Chemical Reactors

2.2.2 Definitions

The vector $q^m$ stores all $m$ gas and solid species that are involved in the reaction scheme (2.2).

$$q = (\text{CO} \quad \text{CO}_2 \quad \text{O}_2 \quad \text{Pt} \quad \text{PtO}) \quad (2.3)$$

The matrix $V^{n \times m}$ describes the stoichiometric coefficients of all $m$ species in $q$ for all $n$ reactions of reaction scheme (2.2). A positive value identifies the species as a reactant of that reaction while a negative value defines it as a product.

$$V = \begin{pmatrix} 0 & 0 & -1 & -2 & 2 \\ -1 & 1 & 0 & 1 & -1 \end{pmatrix} \quad (2.4)$$

The net reaction rate $R_j$ of each species $q_j$ is the inner product of the $j$-th row of the matrix $V$ and the reaction rates $r$ of all $n$ reactions. This ensures its compliance with the mass balance.

$$R_j = \sum_i V_{i,j} \cdot r_i \quad (2.5)$$

The following net reactions can be calculated for the species in $q$:

$$R_{\text{CO}} = -r_2 \quad R_{\text{Pt}} = -2r_1 + r_2$$

$$R_{\text{CO}_2} = r_2 \quad R_{\text{PtO}} = 2r_1 - r_2$$

$$R_{\text{O}_2} = -r_1 \quad (2.6)$$

The matrix $W^{n \times m}$ describes the reaction order of all $m$ species in $q$ for all $n$ reactions. Again, reactants have a negative sign, while products have a positive sign. By default, the reaction order matrix is chosen to be $W = V$. The reaction order is not necessarily related to the stoichiometry of the reaction, but it is a good initial guess.

$$W = \begin{pmatrix} 0 & 0 & -1 & -2 & 2 \\ -1 & 1 & 0 & 1 & -1 \end{pmatrix} \quad (2.7)$$

The reaction rates are calculated as differences between forward and backward reaction rates with the reaction constants $k_i^f$ and $k_i^b$. 

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2.2 Chemical model

\[ r_i = k_i^f \cdot \prod_{j, W_{i,j} > 0} [q_j]^{W_{i,j}} - k_i^b \cdot \prod_{j, W_{i,j} < 0} [q_j]^{W_{i,j}} \]  
\hspace{10cm} (2.8)

The reaction rates \( r \) in the example are then calculated as follows:

\[ r_1 = k_1^f \cdot [O_2] \cdot [Pt]^2 - k_1^b \cdot [PtO]^2 \]  
\hspace{10cm} (2.9)

\[ r_2 = k_2^f \cdot [CO] \cdot [PtO] - k_2^b \cdot [CO_2] \cdot [Pt] \]  
\hspace{10cm} (2.10)

2.2.3 Reaction kinetics

The forward reaction constants \( k_i^f \) are based on the Arrhenius equation, which describes the temperature dependence of the reaction rate constant of a chemical reaction as follow:

\[ k_i^f = A_i \cdot \exp\left(-\frac{E_i}{R \cdot T}\right) \]  
\hspace{10cm} (2.11)

where \( A_i \) is the pre-exponential factor, \( E_i \) is the activation energy of the reaction \( i \), \( R \) is the universal gas constant, and \( T \) is the temperature in kelvin. Any other equation for the reaction kinetics could be used for the forward reaction rate as well.

The backward reaction rate constants \( k_i^b \) are linked to \( k_i^f \) using the chemical equilibrium constants \( K_i \). This coupling ensures compliance with the chemical equilibrium at all times and decouples the dynamics from the equilibrium state. The total gas concentration \( c_0 = p/R \cdot T \) compensates for possible non-mole preserving reactions \[42\]. The pressure \( p \) is assumed to be ambient throughout the catalyst.

\[ k_i^b = \frac{k_i^f}{K_i} \cdot \prod_j c_0^{W_{i,j}} \]  
\hspace{10cm} (2.12)

Reaction (2.9) does not conserve the mole balance because the number of gas species available before and after the reaction is different. Therefore, \( k_1^b \) is corrected with \( c_0 \). Reaction (2.10) does conserve the mole balance and thus does not have to be corrected.
The chemical equilibrium constants \( K_i \) depend on the changes in the Gibbs energy \( \Delta G_i \) of each reaction. For the sake of convenience, the scaled Gibbs energy \( \Gamma_i = G_i/R \cdot T \) is introduced, as follows:

\[
K_i = \exp\left(-\frac{\Delta G_i}{R \cdot T}\right) = \exp(-\Delta \Gamma_i) \tag{2.14}
\]

The change in the scaled Gibbs energy \( \Delta \Gamma \) of reaction \( i \) is the difference between the scaled Gibbs energies of its products and its reactants multiplied by their reaction order.

\[
\Delta \Gamma_i = \sum_j W_{i,j} \cdot \Gamma_j \tag{2.15}
\]

The changes in the scaled Gibbs energies in the example are the following:

\[
\Delta \Gamma_1 = 2 \Gamma_{PtO} - 2 \Gamma_{Pt} - \Gamma_{O2} \tag{2.16}
\]
\[
\Delta \Gamma_2 = \Gamma_{PtO} + \Gamma_{CO2} - \Gamma_{Pt} - \Gamma_{CO} \tag{2.17}
\]

### 2.2.4 Gibbs approximation

The scaled Gibbs energies of gases are well known functions of the temperature. The NASA tables \([11]\) list the seven coefficients of the following polynomial for each gas species:

\[
\frac{G(T)}{R \cdot T} = a_1 (1 - \ln(T)) - \frac{a_2 T}{2} - \frac{a_3 T^2}{6} - \frac{a_4 T^3}{12} - \frac{a_5 T^4}{20} + \frac{a_6}{T} - a_7 \tag{2.18}
\]

In order to reduce the complexity of the model, the scaled Gibbs energies are approximated using the following formulation:

\[
\Gamma(T) = \frac{G(T)}{R \cdot T} = g_1 \cdot \frac{T}{T + g_2} \tag{2.19}
\]
2.2 Chemical model

Table 2.1 lists the values derived for the most important gas species of the TWC and the SCR catalysts fitted to their expected temperature range. Figure 2.2 shows that this approximation is justified. The error introduced is well below 1% when using the approximated values instead of the exact values from Equation (2.18).

Table 2.1: Approximations of the scaled Gibbs energies for gases

<table>
<thead>
<tr>
<th>species</th>
<th>( g_1 ) [K(^{-1})]</th>
<th>( g_2 ) [-]</th>
<th>( g_3 ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>-54.92</td>
<td>-2.158 \times 10^5</td>
<td>9.195 \times 10^3</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>-28.54</td>
<td>-8.044 \times 10^3</td>
<td>-5.982 \times 10^1</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>-33.06</td>
<td>-4.065 \times 10^4</td>
<td>-2.669 \times 10^1</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>-27.62</td>
<td>-2.070 \times 10^2</td>
<td>9.509 \times 10^1</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>-29.44</td>
<td>1.266 \times 10^4</td>
<td>4.192 \times 10^1</td>
</tr>
<tr>
<td>( \text{NO}_2 )</td>
<td>-35.40</td>
<td>3.337 \times 10^3</td>
<td>1.779 \times 10^2</td>
</tr>
</tbody>
</table>

The Gibbs energies of the site species are not known. But since the Gibbs energies of the occupied site species always appear as the difference to the Gibbs energy of the empty site, the latter is set to zero. The scaled Gibbs energies of the occupied site are approximated by Equation (2.19) with \( g_1, g_2, \) and \( g_3 \) being parameters of the model.
2 Framework for Modeling Chemical Reactors

2.2.5 Concentration of empty surface

The concentrations of all site species add up to the storage capacity (SC) of that surface.

$$\sum_i S_i = SC \quad (2.20)$$

Therefore, the concentration of the empty site can be calculated using the concentrations of all non-empty site species subtracted from the storage capacity. For the TWC example, this results in the following equation:

$$[\text{Pt}] = SC_O - [\text{PtO}] \quad (2.21)$$

2.2.6 Static species

Some gas species might take part in the reaction scheme, but their change in the concentration is negligible. These species can be set to a constant value, which simplifies the calculation. In the TWC example, CO$_2$ is such a species.

$$[\text{CO}_2] = 12\% \cdot c_0 \quad (2.22)$$

2.2.7 Irreversible reactions

In general, all chemical reactions are modeled reversibly. No additional parameters are introduced because the chemical equilibrium is used to determine the backward reaction rate, see Equation (2.12).

If the chemical equilibrium lies far on one side, numerical problems can be the consequence. The change in the Gibbs energy thus is large, and the chemical equilibrium constant $K_i$ becomes even larger, see Equation (2.14). Under these circumstances, the backward reaction should be omitted. Its impact on the concentrations is negligible anyway.

A reaction $i$ can be set irreversible by setting all negative elements of the corresponding row in the reaction order matrix $W$ to zero.

$$W_{i,j} = \max(W_{i,j}, 0) \quad \forall j \quad (2.23)$$
2.3 Physical model

The monolith of a flow-through catalytic converter is modeled as a single one-dimensional channel divided into several cells along the flow direction. Each cell consists of one gas phase and one solid phase, see Figure 2.3. The outlet of one cell is the next cell’s inlet. The input and output of the total catalyst are denoted as upstream (us) and downstream (ds). The number of cells is a design parameter.

The mass flow through the catalyst is assumed to be constant. Inlet pressure drops [51] as well as pressure profiles [22] along the catalyst are neglected. The pressure throughout the catalyst is assumed ambient.

Simulations show that radial diffusion is not a limiting factor for the chemical reaction rates in the catalysts observed, and since axial diffusion is negligible in the presence of axial convection, no diffusion process has to be taken into account.

Heat convection is modeled between the gas phase and the solid phase within each cell. Heat releases caused by enthalpy changes, radial heat losses, as well as heat transfer in the solid phases are neglected. Therefore, no temperature profile is generated for a constant engine operating point.

The physical reactor model of the catalyst is kept simple in order to keep the computational demand low. A more detailed description of the

\[ T_{in} \quad X_{in} \quad T_{out} \quad X_{out} \]

\[ T_{us} \quad T_{ds} \]

\[ X_{us} \quad X_{ds} \]

**Figure 2.3:** Inputs and outputs of a single axial cell with illustrated mass and energy transfer

The formulas derived still hold. The calculation of the reaction rate $r_i$ according to Equation (2.8) results in a forward reaction only. The change in the scaled Gibbs energy (2.15) does not have to be determined because no backward reaction rate constant $k_i^b$ has to be calculated.
transport phenomena in a catalytic monolith is given by Santos and Costa [57].

2.3.1 Mass balance

The concentration of any solid species $S$ of each cell changes with the net reaction rate $R_S$ calculated according to Equation (2.5).

$$\frac{d}{dt} S = R_S \quad (2.24)$$

The concentration of any gas species $X$ of each cell changes not only with the net reaction rate $R_X$ but also with the net mass flow $E_X$ through the cell:

$$\frac{d}{dt} X = E_X + R_X \quad (2.25)$$

The net mass flow of the species $X$ is a function of the inlet and outlet concentrations of that species, the total mass flow $\dot{m}$, the average molar mass of the exhaust gas $M_{exh}$, the catalyst volume $V_{cat}$, and the number of cells $n_{cells}$:

$$E_X = ([X]_{in} - [X]_{out}) \cdot \frac{\dot{m}}{M_{exh}} \cdot \frac{n_{cells}}{V_{cat}} \quad (2.26)$$

2.3.2 Energy balance

The energy transfers modeled in the framework are illustrated in Figure 2.3. The energy transfer through gas exchange depends on the thermal capacity $c_{pg}$ of the exhaust gas, which is assumed to be constant, and the mass flow $\dot{m}$ through the catalyst:

$$\dot{Q}_g = (T_{in} - T_{out}) \cdot c_{pg} \cdot \dot{m} \quad (2.27)$$

The heat exchange between the gas and the solid phase is modeled with the equation for the forced convection:

$$\dot{Q}_{gs} = (T_g - T_s) \cdot \alpha \cdot A_{geo} \cdot \frac{V_{cat}}{n_{cells}} \quad (2.28)$$
2.3 Physical model

Figure 2.4: Cross-sectional view of the catalyst with the cross-sectional area $A$ of one channel and the side length $b$ of the open fractional area.

The heat transfer coefficient $\alpha$ is a parameter of the model. The specific geometric catalytic surface $A_{geo}$ is a function of the cell density cpsi and of the open cross-sectional fraction $\epsilon$ of the catalyst.

$$A_{geo} = \frac{\text{reaction surface}}{\text{catalyst volume}} \quad (2.29)$$

Figure 2.4 shows a cross-sectional view of the catalyst. The cross-sectional area $A$ of a single channel is calculated by inverting the cell density cpsi. A factor transforms the units from inches to meters.

$$A = \frac{.0254^2}{\text{cpsi}} \quad (2.30)$$

One side $b$ of the open fractional area is calculated as the square root of that area.

$$b = \sqrt{\epsilon \cdot A} \quad (2.31)$$

The specific geometric catalytic surface $A_{geo}$ is then derived with the outline over the area:

$$A_{geo} = \frac{4 \cdot b}{A} = 4 \cdot \sqrt{\frac{\epsilon}{A}} = 4 \cdot \sqrt{\epsilon \cdot \frac{\text{cpsi}}{.0254^2}} \quad (2.32)$$
The final gradients for the temperatures are functions of the energy transfers, the thermal capacity of the solid and the gas phases \((c_{ps}, c_{pg})\), and the masses of the gas and solid phases \((m_{gas}, m_{cat})\):

\[
\frac{m_{cat}}{n_{cells}} \cdot c_{ps} \cdot \frac{d}{dt} T_s = \dot{Q}_{gs} \tag{2.33}
\]

\[
\frac{m_{gas}}{n_{cells}} \cdot c_{pg} \cdot \frac{d}{dt} T_g = \dot{Q}_g - \dot{Q}_{gs}. \tag{2.34}
\]

Section 2.4.1 below shows that the total mass of the gas phase \(m_{gas}\) does not have to be calculated. The framework neglects any heat transfer within the solid phase as well as any heat losses. However, it can easily be extended at the expense of an additional computational demand.

### 2.4 Resolution of model equations

Most catalyst models, including the one presented here, are described as an implicit system of differential algebraic equations (DAE). These equations are written in the form \(F(t, y, y') = 0\) for which special DAE solvers like DASSL \([52]\) provide the numerical solutions. The computational demand and their robustness are the major problems of these solvers, especially for numerically stiff systems like the catalyst model introduced. Manca et al. \([40]\) provide a robust and efficient numerical integration method to solve these problems. However, the performance of the solver remains insufficient.

Therefore, a method has been developed with an explicit, fixed step solver that shows the required performance. Some adjustments have been made to ensure the robustness.

#### 2.4.1 Quasi-static gas phase

The gas exchange from one cell to the next can result in very large gradients in the gas concentrations as well as in the gas temperature. In combination with the relatively small gradients in the occupied surface level (OSL) and the surface temperature, this leads to a stiff system.

The large gradients can be eliminated by assuming steady-state conditions in the gas phase, which resolves the problem of the stiff system. For
2.4 Resolution of model equations

the chemical system, Equation (2.25) is set to zero leading to the following system of equations:

\[ \begin{align*}
\frac{d}{dt} S &= R_S \\
0 &= E_X + R_X
\end{align*} \]  

(2.35)

The physical model is simplified by setting Equation (2.34) to zero, which leads to following system of equations:

\[ \begin{align*}
\frac{m_{\text{cat}} \cdot c_{ps}}{n_{\text{cells}}} \cdot \frac{dT_s}{dt} &= \dot{Q}_{gs} \\
0 &= \dot{Q}_g - \dot{Q}_{gs}
\end{align*} \]  

(2.36)

The assumption of the quasi-static gas phase reduces the states of the model to only the temperature of the solid phase $T_s$ and all occupied surface species $S$ for each cell. No information about the gas phase needs to be stored.

2.4.2 Approximation of states in gas phase

The states of the gas concentrations $X$ and the gas temperature $T_g$ have been eliminated in the previous section. However, these states are needed to calculate the net reaction rates and heat transfer between gas and solid phase in Equations (2.8) and (2.28). Therefore, the states in the gas phase are approximated with their inlet values, which is accurate for a large number of cells:

\[ \begin{align*}
X &= X_{\text{in}} \\
T_g &= T_{\text{in}}
\end{align*} \]  

(2.37)

The accuracy of the model can be increased by approximating $X$ and $T_g$ with the mean of their corresponding inlet and outlet values. While such approximations increase the accuracy especially for a small number of cells, they induce implicit systems of equations. The implicit representations are overcome by explicitly solving for the state update and the outlet conditions.

\[ \begin{align*}
X &= \frac{1}{2} \cdot (X_{\text{in}} + X_{\text{out}}) \\
T_g &= \frac{1}{2} \cdot (T_{\text{in}} + T_{\text{out}})
\end{align*} \]  

(2.38)
Chapter 4 illustrates the advantages of these approximations with respect to those in Equations (2.37). The modeling error is significantly reduced for a small number of cells while the computational demand is increased only slightly.

### 2.4.3 Real-time solver

The state update of the solid temperature and the solid species concentrations in Equations (2.35) and (2.36) can be performed with the semi-implicit Runge-Kutta method by Cash [14]. This ordinary differential equation (ODE) solver requires the calculation of the Jacobian, which can be done analytically. This method adapts the step size and can therefore only be used in simulation.

Real-time capability implies an explicit, fixed time step solver. The solid species are thus updated with the Euler forward method with a step size $dt$ while the gas concentrations are in the equilibrium state. The following system of equations is solved explicitly for $S^1$ and $X_{\text{out}}$. The gas concentrations $X$ are approximated by Equation (2.38).

$$
\begin{bmatrix}
S^1 \\
0
\end{bmatrix} = \begin{bmatrix}
S^0 + dt \cdot R_S \\
E_X + R_X
\end{bmatrix}
$$

(2.39)

The updates of the temperatures are carried out analogously. The solid temperature is updated with the Euler forward step while the gas temperature is in the equilibrium state. The following system of equations is solved explicitly for $T^1_s$ and $T_{\text{out}}$. The gas temperature $T_g$ is approximated by Equation (2.38).

$$
\begin{bmatrix}
T^1_s \\
0
\end{bmatrix} = \begin{bmatrix}
T^0_s + dt \cdot \dot{Q}_{gs} \cdot \frac{n_{\text{cells}}}{m_{\text{cat}} \cdot c_{ps}} \\
\dot{Q}_g - \dot{Q}_{gs}
\end{bmatrix}
$$

(2.40)

### 2.4.4 Solvability of concentration update

The system of equations (2.39) might not be solvable if the reaction order of a gaseous species $X$ for a reaction $i$ is higher than one. The reaction rate $r_i$ (2.8) and thus also the net reaction rate $R_X$ (2.5) of that species would become nonlinear in $X$. The quasi-static equation $0 = E_X + R_X$
2.4 Resolution of model equations

The robustness of the derived models is one of the key features of the framework. The model needs to be stable even though a fixed step solver is used and high gradients are expected. A solution was found by limiting the reaction rates \( r \) such that the concentrations do not turn negative and the occupied surface stays between zero and one.

Figure 2.5 illustrates the method for one time step. If the concentration in the gas phase became negative (red), the reaction rate is lowered such that the concentration becomes zero (blue). The change in the occupied surface is calculated using the corrected reaction rate in order to maintain the mass balance.

Note that the use of a more sophisticated solver like an explicit Runge-Kutta method cannot prevent this problem without reducing the step size.
In the case of reaction rate limitations, the reaction sequence plays an important role. If there are not enough reactants to serve all reactions, the reaction with the highest priority is calculated first. The subsequent reactions then use the remaining reactants.

The following reaction scheme is used to illustrate the impact on the output concentrations:

\[
SA + B \rightarrow S + AB \quad (2.42) \\
SA + C \rightarrow S + AC \quad (2.43)
\]

Figure 2.6 shows the resulting output concentrations for various orders of reaction priority. First, reaction (2.42) is given priority over reaction (2.43), then the reaction order is reversed. The reaction rates of both reactions are large, and the initial position is the same for both orders.
2.5 Adaption of storage capacity

There is not enough of A stored on the surface S to fully reduce the reactants B and C. Depending on the order of the reaction priority, the outlet concentration of either B or C is non-zero.

2.4.7 Steady-state output

The steady-state behavior of the catalyst is defined by setting the change of the surface species concentration in Equation (2.35) to zero:

\[
\begin{align*}
0 & = R_S \\
0 & = E_X + R_X
\end{align*}
\]  

(2.44)

This system of equation is analytically solved for the steady-state OSL profile and the steady-state outlet concentrations \(X_{out}\). The resulting functions can be used for the identification of the conversion efficiencies, as shown in Chapter 5, or for the setpoint generation of the control strategy, as shown in Chapter 4.

2.5 Adaption of storage capacity

The desired control strategies highly depend on the accuracy of the underlying catalyst model which is not given over the lifetime of the catalyst. This model is accurate when the catalyst is first delivered, but it becomes inaccurate during operation because of aging and poisoning.

A first approach to model aging or poisoning is an adaption of the storage capacity of the catalyst. Such an adaption not only affects the filling and depleting behavior of the catalyst, but it also reduces the reaction rates \(r\) according to Equation (2.8) because they depend on the surface concentrations.

The presented model is well suited for the adaptive strategy presented by Auckenthaler et al. [5], which observes the changing storage capacity of the chemical reactor by using an extended Kalman filter (EKF). This observed storage capacity then can be used not only for control purposes but also for on-board diagnostics.
3 Parameter Identification

3.1 Model parameters

The parameters of the model can be divided into two types that can be identified successively. The physical model parameters only affect the temperatures while the chemical model parameters only influence the concentrations. The physical model parameters need to be identified first, since the chemical model highly depends on the temperatures in the catalyst.

The properties of the catalyst listed in Table 3.1 are expected to be known.

<table>
<thead>
<tr>
<th>Table 3.1: Properties of the catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{cat}}$</td>
</tr>
<tr>
<td>$A_{\text{cs}}$</td>
</tr>
<tr>
<td>$m_{\text{cat}}$</td>
</tr>
<tr>
<td>cpsi</td>
</tr>
<tr>
<td>$\epsilon$</td>
</tr>
</tbody>
</table>

3.1.1 Physical model

The physical parameters listed in Table 3.2 can be identified with a few load steps on the engine that result in a change in the exhaust temperature. The objective is to predict the downstream temperature of the catalyst if the upstream temperature and the total mass flow are given.

<table>
<thead>
<tr>
<th>Table 3.2: Number of physical model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>parameter</td>
</tr>
<tr>
<td>heat transfer coefficient $\alpha$</td>
</tr>
<tr>
<td>specific heat capacity of the solid $c_{ps}$</td>
</tr>
</tbody>
</table>
3 Parameter Identification

3.1.2 Chemical model

The chemical part of the model does not generate any energy flows that could affect the temperatures. This is a simplification of the framework that can easily be changed. However, the possibility to separate the physical model parameters from the chemical parameters would be lost. The number of parameters mainly depends on the number of reactions and site species. Table 3.3 summarizes the parameters for the chemical model.

Table 3.3: Number of chemical model parameters

<table>
<thead>
<tr>
<th>parameter</th>
<th>quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface storage capacity</td>
<td>1 per surface</td>
</tr>
<tr>
<td>Gibbs energy of site species</td>
<td>3 per occupied site species</td>
</tr>
<tr>
<td>reaction kinetics</td>
<td>2 per reaction</td>
</tr>
</tbody>
</table>

The storage capacity of each surface is a scalar. This is the sum of available sites per catalyst volume. At the moment, the framework is optimized for only one surface.

The scaled Gibbs energy of each occupied site species is approximated by Equation (2.19) and results in three parameters per site species. The Gibbs energy of the empty site is set to zero.

Each reaction has two parameters for the activation energy $E_i$ and the pre-exponential factor $A_i$ from the Arrhenius equation (2.11). No additional parameters are needed for the backward reaction rate because it is defined through the chemical equilibrium.

3.2 Identification trajectories

The identification of the chemical model parameters can be accelerated by a suitable choice of the identification measurements taken. The trajectories should be simple and reproducible. Ideally, the engine is operated at constant load and speed, which results in a constant mass flow and a constant temperature of the exhaust gas. The system is always in steady state before a new operating point is approached.

The identification trajectories serve as the basis for the observation of the filling and depleting behavior and the steady-state conversion effi-
ciencies of the catalyst. The chemical parameters can only be identified correctly if the reaction rates are the limiting factors for the conversion efficiencies of the upstream gas composition. A smaller catalyst or an increased mass flow can prevent the reactants from vanishing completely if the conversion rates are high.

Preconditioning of the catalyst might be necessary prior to the identification measurements. Depending on the type of catalyst, a predefined filling and depleting trajectory is applied or the catalyst is thermally preconditioned. Peyton Jones and Schallock [53] have found preconditioning to be necessary for the TWC.

### 3.3 Parameter optimization

The search for the optimal parameters is very difficult in chemical systems. The number of parameters and the non-linearity of the models demand other than gradient-based search algorithms. The particle swarm optimization (PSO) algorithm is a stochastic search method inspired by the coordinated motion of animals living in groups. The PSO algorithm has shown good performance on this kind of problems. Some adjustments have to be made to the parameters in order to increase the performance and reliability of the algorithm.

#### 3.3.1 Particle swarm optimization

In 1995, the PSO algorithm was introduced by Kennedy and Eberhart [29]. It is a numerical search algorithm which is used to find parameters that minimize a given fitness function. This fitness function can be nonlinear and can be subjected to any number of linear and nonlinear constraints.

The desired number of particles are randomly spread within the defined bounds and are given a random initial velocity. The velocity of each particle is a function of its previous velocity, the differences from the current position to the particle’s best position, and to the global best position. Figure 3.1 illustrates the PSO method.

Equation (3.1) shows the calculation of the velocity and the position update. The inertia $\Phi$ and the acceleration constants $\alpha_{1,2}$ are tuning
parameters of the method, while $\gamma_{1,2} \in [0, 1]$ are uniformly distributed random values.

\[
v_i^{k+1} = \Phi v_i^k + \alpha_1 [\gamma_{1,i} (P_i - x_i^k)] + \alpha_2 [\gamma_{2,i} (G - x_i^k)]
\]
\[
x_i^{k+1} = x_i^k + v_i^{k+1}
\]

(3.1)

Ebbesen et al. [21] introduced a generic MATLAB function for the particle swarm optimization. It is well suited for the identification of the model presented. The usage of the function is described in the paper, while the MATLAB function itself is freely available for download\footnote{http://www.idsc.ethz.ch/pso}.

### 3.3.2 Reaction rate transformation

The sensitivities of the pre-exponential factor $A$ and the activation energy $E$ on the reaction rate are very different. Therefore, the reaction rates are transformed to discrete values at two different temperatures ($T_1 < T_2$). Furthermore, the actual optimization parameter $u_i$ is the natural logarithm of the reaction rates $k_i$.

\[
u_i^1 = \ln (k_i(T_1)) \quad \quad u_i^2 = \ln (k_i(T_2))
\]

(3.2)
3.3 Parameter optimization

The search region becomes less weighted and the problem with negative reaction rates during the optimization is avoided when searching for the logarithm. The parameters $A_i$ and $E_i$ can then be found with the following equations:

$$A_i = e^{u_1} \cdot (e^{u_1-u_2})^{\frac{T_2}{T_1-T_2}}$$  \hspace{1cm} (3.3)

$$E_i = \frac{(u_1-u_2) \cdot R \cdot T_1 \cdot T_2}{T_1-T_2}$$  \hspace{1cm} (3.4)

Since the reaction rate is expected to rise with a higher temperature, the following constraints are defined:

$$u_1^i < u_2^i$$  \hspace{1cm} (3.5)

3.3.3 Gibbs energy constraints

The change of the Gibbs energies of a reaction defines its chemical equilibrium. Empirical values on the functionality of the catalyst might define boundaries of a feasible region to the unknown scaled Gibbs energy of the occupied surface.

Since a TWC reduces $O_2$ and oxidizes CO, the chemical equilibrium of these reactions is expected to lie on the right hand side (PtO and $CO_2$). The changes in the scaled Gibbs energies according to Equation (2.15) are therefore negative. Figure 3.2 shows the expected range for the Gibbs energy of the occupied surface defined by the expected chemical equilibrium. The derivation of the boundaries is explained in more detail in the Chapters 4 and 5.

The sensitivities of the parameters to the scaled Gibbs energies vary greatly. Three temperature nodes ($T_1 < T_2 < T_3$) are used instead since the approximation of the scaled Gibbs energies requires three parameters per site species, see Equation (2.19).

$$g_1^i = \Gamma(T_1) \hspace{1cm} g_2^i = \Gamma(T_2) \hspace{1cm} g_3^i = \Gamma(T_3)$$  \hspace{1cm} (3.6)

The shape of the plotted scaled Gibbs energies of all site or gas species is either convex or concave with a decreasing gradient for higher temper-
Figure 3.2: Expected region of the scaled Gibbs energy for the occupied site for the TWC and SCR catalysts

atures. Therefore, the following constraints are defined depending on the expected shape of the scaled Gibbs energy for the occupied site species.

The constraints for an expected convex shape of the scaled Gibbs energy are shown in (3.7):

\[
\begin{aligned}
g_1^i &> g_2^i > g_3^i \\
(g_1^i - g_2^i) &> (g_2^i - g_3^i)
\end{aligned}
\] (3.7)

If the expected shape of the scaled Gibbs energy is concave, the following constraints are valid:

\[
\begin{aligned}
g_1^i &< g_2^i < g_3^i \\
(g_1^i - g_2^i) &< (g_2^i - g_3^i)
\end{aligned}
\] (3.8)

These constraints are needed in order to obtain a solution to all combinations of \(g_i\).
4 Three-Way Catalytic Converter

The main purpose of a three-way catalytic converter (TWC) has already been mentioned in the introduction. The full reaction scheme (1.2) is too complex when it comes to control-oriented modeling because of the high computational demand and the large number of parameters. Therefore, a much simpler model needs to be derived.

A substantial amount of research has been conducted on developing chemical first-principle models of TWCs that can be used to predict the exhaust gas composition downstream of the catalyst [10, 15, 37, 38, 67]. This information helps to estimate the absolute amount of harmful substances that could not be eliminated for a given input. The fact that these models often require more than ten reactions results in a high calibration effort and causes a high computational demand. In addition, they make extensive use of the upstream gas composition, which disqualifies them for on-line control purposes since this information is not available in production cars.

Some control-oriented models have also been presented in literature. Peyton Jones et al. [46, 54] and Balenović [7] developed lumped parameter models where the catalyst is reduced to only one cell. While they are real-time capable, their simplicity limits their accuracy.

Auckenthaler et al. [6] stated that a first-principle modeling approach is essential for TWC control because of the adaptability and the applicability of the model. The model presented here uses first-principle approaches and is discretized along the flow direction. The state of each cell of the catalyst is described by its relative oxygen level (ROL) and its temperature of the solid. Nevertheless, the real-time capability of the model is preserved.

The first part of the chapter introduces the simplified TWC model that is then validated with several measurements at an engine test bench. The second part of the chapter describes optimal depletion strategies after fuel
cut-off phases derived from the model. A non-causal strategy introduced first is later replaced by a causal strategy.

4.1 Control-oriented model

A real-time capable TWC model was to be developed that accurately predicts the oxygen storage dynamics of the catalyst. Only then, the model can be used for control purposes.

The model inputs are total air mass flow, exhaust gas temperature, and upstream air-fuel ratio. These values are available in modern cars, either directly from sensors or as estimations from the engine control unit. The model outputs are the downstream air-fuel ratio and the relative oxygen level (ROL) profile along the catalyst.

The derivation of the model is explained in detail in the Chapter 2. Only a summary is given here.

4.1.1 Reaction scheme

The exhaust gas information from the oxygen sensors distinguishes only between lean and rich. Therefore, the complete TWC reaction scheme presented in Table 1.2 is too complex for a control-oriented model.

The most important property of a TWC for the control design is its oxygen storage capability. This property is considered by introducing two site species. One is the reduced form of the noble metal Pt; the other is the oxidized form of the noble metal PtO. An oxidizing gas species \( \text{O}_2 \) and a reducing gas species \( \text{CO} \) are required to cause an exchange between the gas phase and the solid phase.

\[
\begin{array}{c|c}
\text{O}_2 + 2 \text{Pt} & \iff \text{2PtO} \\
\text{CO} + \text{PtO} & \iff \text{CO}_2 + \text{Pt}
\end{array}
\] (4.1)

The reaction scheme (4.1) represents an Eley-Rideal mechanism, the simplest of all mechanisms in heterogeneous catalysis. Nibbelke et al. in [49] and other publications show the Langmuir-Hinshelwood mechanism to be more appropriate for the oxidation of CO with \( \text{O}_2 \). This is not contradictory, because the reaction scheme (4.1) is a representation of
many different paths of oxidizing and reducing the noble metal and the underlying ceria.

Since the noble metal is not wasted, the reaction scheme (4.1) results in a very simple net reaction:

\[ \text{O}_2 + 2\text{CO} \rightleftharpoons 2\text{CO}_2 \hspace{1cm} (4.2) \]

### 4.1.2 Reaction kinetics

The reaction species vector \( q \) is derived directly from reaction scheme (4.1).

\[ q = (\text{CO}, \text{CO}_2, \text{O}_2, \text{Pt}, \text{PtO}) \hspace{1cm} (4.3) \]

The matrix of the stoichiometric coefficients \( V \) is derived from the reaction scheme (4.1) and the species vector \( q \). The order coefficient matrix \( W \) was chosen equal to \( V \).

\[ V = W = \begin{pmatrix} 0 & 0 & -1 & -2 & 2 \\ -1 & 1 & 0 & 1 & -1 \end{pmatrix} \hspace{1cm} (4.4) \]

The default order coefficient matrix \( W = \text{sign}(V) \) is not suitable for this problem. The characteristic filling and depleting behavior cannot be reproduced with the default \( W \) matrix.

The reaction rates \( r \) are then calculated according to Equation (2.8).

\[ r_1 = k_1^f \cdot [\text{O}_2] \cdot [\text{Pt}]^2 - k_1^b \cdot [\text{PtO}]^2 \hspace{1cm} (4.5) \]
\[ r_2 = k_2^f \cdot [\text{CO}] \cdot [\text{PtO}] - k_2^b \cdot [\text{CO}_2] \cdot [\text{Pt}] \hspace{1cm} (4.6) \]

Since the change in the \( \text{CO}_2 \) concentration due to the reaction rates are negligible, \( \text{CO}_2 \) is defined as a static gas with a fixed concentration of 12%. The empty site Pt can be represented as the storage capacity minus the occupied site.

\[ [\text{Pt}] = \text{SC}_O - [\text{PtO}] \hspace{1cm} (4.7) \]
\[ [\text{CO}_2] = 12\% \cdot c_0 \hspace{1cm} (4.8) \]
The backward reaction rate constants $k^b_i$ are determined using the chemical equilibrium constant and a correction for the mole balance according to Equation (2.12). Reaction (4.6) does conserve mole balance, but Reaction (4.5) does not.

$$k^b_1 = \frac{k^f_i}{K_1} \cdot c_0$$
$$k^b_2 = \frac{k^f_i}{K_2}$$

(4.9)

The resulting net reactions for the considered species are:

$$R_{PtO} = 2 r_1 - r_2$$
$$R_{O_2} = -r_1$$
$$R_{CO} = -r_2.$$  

(4.10)

(4.11)

(4.12)

\subsection*{4.1.3 Gibbs energy constraints}

The chemical equilibrium constant $K_i$ depends on the change in the scaled Gibbs energies of the reaction $i$ in (4.1). It is calculated according to Equation (2.15).

$$\Delta \Gamma_1 = \Gamma_{O_2} + 2 \Gamma_{Pt} - 2 \Gamma_{PtO}$$
$$\Delta \Gamma_2 = \Gamma_{CO} + \Gamma_{PtO} - \Gamma_{CO_2} - \Gamma_{Pt}$$

(4.13)

(4.14)

The scaled Gibbs energy for the empty surface Pt is zero, while the one for the occupied surface PtO is a parameter of the system. The chemical equilibrium of all reactions is expected to lie on the right-hand side because the catalyst is known to work well in the desired operating conditions. This information can be used to define a feasible region for $\Gamma_{PtO}$ by setting Equations (4.13) and (4.14) smaller than zero. This results in two inequalities for the unknown scaled Gibbs energy of the occupied surface $\Gamma_{PtO}$.

$$\Gamma_{PtO} < \frac{1}{2} \Gamma_{O_2}$$
$$\Gamma_{PtO} > \Gamma_{CO_2} - \Gamma_{CO}$$

(4.15)

(4.16)
Figure 4.1 shows the calculated boundaries that limit the feasible region for $\Gamma_{\text{PtO}}$. The identification procedure finds the three optimization nodes $g^1$, $g^2$, $g^3$ from Section 3.3.3 to lie in that region. The resulting scaled Gibbs energy of the occupied surface PtO remains in the feasible region even for very low temperatures.

The two boundaries in Figure 4.1 intersect at about 1340 K. Beyond that temperature, the chemical equilibrium of reaction (4.2) switches to the left side and the reaction becomes endergonic. The TWC catalyst would create CO and O$_2$ out of CO$_2$ if it could withstand the high temperatures.

### 4.1.4 Number of parameters

The very simple reaction scheme keeps the number of parameters small, which helps the parameter identification process. The physical model parameters $\alpha$ (heat transfer coefficient) and $c_{ps}$ (specific heat capacity of the solid) are identified separately in advance. Table 4.1 lists the chemical parameters for the TWC model derived. The parameters for the scaled Gibbs energy and for the reaction kinetics are the transformed values according to Section 3.3.2.
Table 4.1: Number of chemical parameters for TWC model

<table>
<thead>
<tr>
<th>parameter</th>
<th>quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen storage capacity</td>
<td>1 (SCO)</td>
</tr>
<tr>
<td>scaled Gibbs energy of PtO</td>
<td>3 ($g_1$, $g_2$, $g_3$)</td>
</tr>
<tr>
<td>reaction kinetics</td>
<td>4 ($u^1_1$, $u^2_1$, $u^1_2$, $u^2_2$)</td>
</tr>
</tbody>
</table>

### 4.1.5 Inlet gas composition

The only information required about the inlet gas composition is taken from the upstream wide-range oxygen sensor. Equation (4.17) puts the measured value of $\lambda$ in relation to the concentrations of $O_2$, CO, and $CO_2$. This definition is taken from Auckenthaler [3] and is reduced to the species regarded in the reaction mechanism (4.1).

$$\lambda = \frac{2 [O_2] + [CO] + 2 [CO_2]}{2 [CO] + 2 [CO_2]}$$ (4.17)

Some assumptions on the absolute values of the concentrations have to be made in order to obtain a fully defined inlet gas composition using only $\lambda$. The following inlet gas composition is derived from Guzzella and Onder [26] who presented values for the measured raw emissions of a gasoline engine at stoichiometric conditions.

$$[O_2]^* = 1\% \cdot c_0$$
$$[CO]^* = 2\% \cdot c_0$$
$$[CO_2]^* = 12\% \cdot c_0$$ (4.18)

For other than stoichiometric conditions, one of the inlet concentrations for CO or $O_2$ is adapted such that Equation (4.17) holds:

$$[O_2]_{us} = \max ([O_2]^*, (\lambda_{us} - \frac{1}{2}) \cdot [CO]^* + (\lambda_{us} - 1) \cdot [CO_2]^*)$$
$$[CO]_{us} = \max ([CO]^*, \frac{[O_2]^* + (1 - \lambda_{us}) \cdot [CO_2]^*}{\lambda_{us} - \frac{1}{2}})$$ (4.19)

Figure 4.2 illustrates the calculated inlet gas concentrations (solid lines). As mentioned above, the $CO_2$ concentration is fixed to 12%.
4.1 Control-oriented model

4.1.6 Outlet gas composition

The concentration of CO\(_2\) has been set constant for the chemical model. This leads to an error when calculating the downstream \(\lambda\) according to Equation (4.17) if the concentration of CO is reduced and the concentration of CO\(_2\) does not rise to the same degree. Therefore, \([\text{CO}_2]_{ds}\) is adapted with the following equation:

\[
[\text{CO}_2]_{ds} = [\text{CO}_2]_{us} + [\text{CO}]_{us} - [\text{CO}]_{ds}
\]  \hspace{1cm} (4.20)

For large catalysts, the downstream concentrations of either CO or O\(_2\) are zero for steady-state conditions. The amount of CO that is oxidized is limited by the stoichiometric inlet concentration of CO for lean conditions and of O\(_2\) for rich conditions. The amount of oxidized CO is the same for all conditions, namely the stoichiometric inlet concentration of CO. Hence, the downstream concentration of CO\(_2\) is constant.

\[
[\text{CO}_2]_{ds} = [\text{CO}_2]^* + [\text{CO}]^* = 14\% \cdot c_0
\]  \hspace{1cm} (4.21)

The resulting steady-state output for all concentrations is illustrated in Figure 4.2 (dashed lines). Even though this relation is exact only for

\[\text{Figure 4.2: Inlet (solid) and outlet (dashed) steady-state gas concentrations depending on the upstream air-fuel ratio}\]
steady-state conditions, it is also used during transients. Only a small error is introduced when both concentrations of CO and O$_2$ are non-zero.

### 4.2 Test bench

The measurements in this chapter were taken on a test bench at the IDSC with a production type VW 2.5 l SI engine with port fuel injection. The dynamometer is suitable for both steady-state and driving cycle experiments. The complete engine control system is implemented on a real-time hardware system which allows full on-line access to all measured and manipulated variables with a sample rate of 1 kHz. Table 4.2 summarizes the specifications of the engine.

<table>
<thead>
<tr>
<th>Table 4.2: Engine specifications of the TWC test bench</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
</tr>
<tr>
<td>Injection system</td>
</tr>
<tr>
<td>Number of cylinders</td>
</tr>
<tr>
<td>Displacement volume</td>
</tr>
<tr>
<td>Compression ratio</td>
</tr>
<tr>
<td>Maximum output power</td>
</tr>
<tr>
<td>Maximum output torque</td>
</tr>
</tbody>
</table>

### 4.2.1 Catalysts

Commercial three-way catalytic converters from Umicore AG are used throughout the project. The catalysts contain a ceria/zirconia mixed oxide oxygen storage compound and are thermally aged in two stages (24 h at 1200° C and 8 h at 985° C). Table 4.3 summarizes the data sheet of the two catalysts that only vary in length and therefore in volume and mass.

### 4.2.2 Sensors

The test bench is equipped with a wide-range oxygen sensor (LSU) upstream of the catalyst that provides quantitative information about the
4.2 Test bench

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Catalyst 1</th>
<th>Catalyst 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume $V_{\text{cat}}$</td>
<td>1.00 l</td>
<td>0.66 l</td>
</tr>
<tr>
<td>length $L_{\text{cat}}$</td>
<td>90 mm</td>
<td>60 mm</td>
</tr>
<tr>
<td>mass $M_{\text{cat}}$</td>
<td>540 g</td>
<td>360 g</td>
</tr>
<tr>
<td>cell density cps</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>open fraction $\epsilon$</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>loading Pt/Pd/Rh</td>
<td>3/0/2</td>
<td>3/0/2</td>
</tr>
</tbody>
</table>

Table 4.3: Characteristics of the three-way catalysts

Air-fuel ratio. A switch-type oxygen sensor (LSF) is used downstream of the catalyst that is very exact for stoichiometric conditions.

The setup for the identification and validation measurements includes an additional LSU sensor downstream of the catalyst. This signal is used as a reference for the simulated downstream AFR. The downstream LSF sensor is used to calibrate the upstream LSU sensor offset prior to the identification measurement. The signal from the hot-film air-mass meter (HFM) is used to calculate the mass flow through the catalyst.

Operating conditions are defined to be stoichiometric if the downstream LSF shows 600 mV, which is slightly rich. The closer the chosen value is to the true stoichiometric value of 450 mV, the more difficult the prevention of NOx breakthroughs becomes because of the higher steady-state oxygen filling level in the catalyst. The offsets of both LSU sensors are adjusted accordingly.

4.2.3 Downstream LSU gain correction

Standard wide-range oxygen sensors are calibrated for raw exhaust gas emissions and thus cannot be used downstream of the catalyst without adjustments. Figure 4.3 shows a pulse excitation on the AFR setpoint and the resulting LSU signal downstream of the catalyst (red).

First, the offset $p_1$ of the measured signal is determined. The shifted signal is then linearly scaled to the upstream value for steady-state conditions. The parameters $p_2$ and $p_3$ do that independently for the lean and the rich phase.
AFR = 1 + \text{max}\left(0, \frac{\text{LSU} - p_1 - 1}{p_2}\right) + \text{min}\left(0, \frac{\text{LSU} - p_1 - 1}{p_3}\right) \tag{4.22}

The accuracy of the LSU sensor during the transients might be affected by the significantly changing exhaust composition, especially the existence of H$_2$. The downstream LSU sensor is used only for identification and validation purposes. Production applications rely on the downstream LSF sensor only.

### 4.2.4 Cylinder imbalance problem

The engine control unit uses the individual cylinder AFR controller developed by Schick et al. [58]. It ensures the homogenous exhaust gas composition that is required for TWC feedback control.

Figure 4.4 illustrates the problem that is encountered with a cylinder imbalanced engine. Two calibrated LSF sensors are placed opposite of each other in the exhaust tube after the catalyst. The system is placed in steady state such that $V_{\text{LSF1}} = 600 \text{ mV}$. The catalyst is then filled with oxygen. The AFR setpoint of 5% lean is overlaid with an sinusoidal excitation.
The sensor voltage of the second LSF sensor shows an offset with respect to the first LSF sensor under steady-state conditions. It also shows the switch to lean conditions well after the first LSF sensor. A feedback controller based on such a configuration would show a very poor performance.

### 4.2.5 Exhaust gas measurement

Exhaust gas concentration data are not needed as inputs to the controller, but they are used in Section 4.7 to validate the model and to test the derived controller. Table 4.4 lists the exhaust gas measurement devices available at the test bench. All of them are highly dynamic versions for transient measurements with short capillaries and small reaction chamber volumes for reduced response times. Möller [43] provides a more detailed description of the exhaust gas devices.
4 Three-Way Catalytic Converter

Table 4.4: Available exhaust gas measurement devices at the engine test bench.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Device Type (Manufacturer)</th>
<th>Measurement Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Cambustion fNOx 400 (CLD)</td>
<td>$t_{90} &lt; 10$ ms</td>
</tr>
<tr>
<td>HC</td>
<td>Cambustion HFR 400 (FID)</td>
<td>$t_{90} &lt; 10$ ms</td>
</tr>
<tr>
<td>CO, CO$_2$</td>
<td>Horiba MEXA 1300 FRI (NDIR)</td>
<td>$t_{90} &lt; 30$ ms</td>
</tr>
<tr>
<td>O$_2$, H$_2$, H$_2$O</td>
<td>Pfeiffer Omnistar (MS)</td>
<td>$t_{90} &lt; 75$ ms</td>
</tr>
</tbody>
</table>

4.3 Identification trajectories

The model is parameterized using test bench measurement data only. Expensive and time consuming model gas measurements as well as gas concentration measurements are not required.

The dynamometer runs in speed-controlled mode at constant speed while the engine is operated at a constant throttle plate angle. The catalyst is first preconditioned with rich exhaust gas in order to achieve highly repeatable results [53]. A very slow PI controller is then used to tune the offset of the upstream LSU sensor under stoichiometric conditions such that the downstream LSF sensor shows a value of 600 mV. This preparation can take up to several minutes, but it is very important because small deviations from stoichiometry lead to large changes in the steady-state ROL, as will be shown later. The resulting steady-state values for temperature and mass flow represent inputs to the model.

Figure 4.5 shows the identification trajectory derived that was measured for different operating points. The only variable input during identification measurements is the desired $\lambda$ setpoint. It is reached by adjusting the injected fuel mass.

The usual setpoint of $\lambda = 1$ is superposed by a sinusoidal signal with increasing period and amplitude over time. The values for the period and the amplitude are chosen such that the storage capacity of the catalyst compensates for the deviation from stoichiometry in the beginning. As time progresses, the catalyst is no longer able to compensate for the deviations and breakthroughs occur in the lean and rich directions. Subsequently, the identification procedure ends with steps between the lean and the rich phase. The breakthroughs are represented by NO in the lean case and by CO in the rich case.

Figure 4.6 shows the result of one of the identification measurements. The corrected LSU signal downstream of the catalyst can be well re-
produced by the model. Four different operating points are selected to completely parameterize the model.

The engine operating point shown in Figure 4.6 is kept constant resulting in a gas inlet temperature of 945 K and a residence time of the gas in the catalyst of 9.9 ms. The model proposed above very well predicts the time and the amplitude of the breakthroughs in the first phase and also the step from lean to rich. The step from rich to lean is less accurate. The model shows an instantaneous step response behavior of the downstream \( \lambda \) because it does not allow any CO to be stored on the catalyst’s surface. Nevertheless, an additional surface species PtCO is not an option since it would result in at least two additional reactions. The model complexity would increase significantly and the real-time capability would be lost.

The simulation of the identification measurement shown in Figure 4.6 takes about 0.6 s on a standard personal computer with a simulation step size of 1 ms. The ROL profile of the catalyst is initialized with the steady-state ROL profile of that operating point.

The very short gas residence time of 10 ms justifies the simplification of the quasi-static gas phase described in Section 2.4.1. If the catalyst is discretized in ten cells, the residence time of the gas in each cell is 1 ms,
which leads to a maximum step size in the order of 100 $\mu$s. Such a system cannot be computed on today’s engine control units.

### 4.4 Model validation

#### 4.4.1 Variable catalyst length

The model proposed is identified always using the same catalyst. For validation purposes, it is now tested against measurements taken with Catalyst 2 summarized in Table 4.3 with the same washcoat loading, but of a different volume. Its length is decreased to 67%, and the model parameters are changed accordingly. Figure 4.7 shows the result of the same engine operating point as in Figure 4.6, but with a slightly different $\lambda$ setpoint trajectory. The model still performs well.
4.4 Model validation

**Figure 4.7:** Validation of the model using a catalyst with the same washcoat but shorter by one-third

**Figure 4.8:** Catalyst recovery after rich phase to $\lambda_{LSU} = 1$ and $U_{LSF} = 600 \text{ mV}$ under stoichiometric conditions with smooth behavior of CO outlet concentration and downstream LSF
4 Three-Way Catalytic Converter

Figure 4.9: Catalyst recovery after lean phase to $\lambda_{\text{LSU}} = 1$ and $U_{\text{LSF}} = 600 \text{ mV}$ under stoichiometric conditions with NO breakthroughs and volatile LSF signal

4.4.2 ROL recovery under stoichiometric conditions

Simulations show that stoichiometric inlet conditions are sufficient for the catalyst to recover from any state to the stoichiometric steady state. This property is called asymptotic stability. This recovery is verified by test bench measurements.

Asymptotic stability is an important property for the desired control purposes. It makes the control system very robust since the underlying model recovers from any deviation with time. A simple tank model for the TWC fails at this experiment because the state of the catalyst does not change for stoichiometric inlet conditions.

Figures 4.8 and 4.9 show the procedure and the result of this experiment. Note the different time scale for the LSF signal. The inlet exhaust gas is kept at non-stoichiometric conditions until steady state is reached. The desired $\lambda$ setpoint is set back to stoichiometry at time $t = 0 \text{ s}$. The wide-range LSU sensor downstream of the catalyst recovers to stoichiometry within 3 s, which is well predicted by the model. The switch-type LSF sensor is more precise around stoichiometry and takes more than one
Figure 4.10: Model error and calculation time for two different approximations of the states in the gas phase

minute to recover to a value of 600 mV. Note that this is not a sensor drift, but a sign of a very slowly changing exhaust gas composition.

The LSF signal disturbance shown in Figure 4.9 is caused by the high sensitivity of the LSF sensor to NO \([4]\). The random NO breakthroughs in the first ten seconds are explained by the poor conversion rate of NO in slightly lean conditions, whereas the conversion of CO is good even under slightly rich conditions.

### 4.5 Number of cells

The number of axial cells is a design parameter of the model. Depending on the usage of the model, this value can be chosen from 2 to 50 or even higher. Figure 4.10 shows the development of the fitness function \(\Delta F\) for an increasing number of cells for the two different approximations of \(X\) according to Equations (2.37) and (2.38).

As expected, the approximation of the states with the mean value of the inlet and outlet concentrations performs better (red). For the TWC model, 20 cells are chosen since the accuracy of the model cannot be increased for more cells. The computational demand of the improved
approximation is only about 20% higher. The computational demand increases linearly with the number of cells; the computational overhead of the calculation is negligible.

Figure 4.11 shows the accuracy of the model depending on the number of cells. Even the two-cell model can represent the characteristic behavior of the TWC. However, the model overestimates the lean breakthroughs in the first phase and shows a pronounced plateau in the lean-to-rich step. In contrast, the 20-cell model predicts the breakthroughs more accurately and predicts a smooth downstream AFR.

### 4.6 Properties of the ROL profile

Simulations show that the steady-state relative oxygen level (ROL) profile is unique and attractive for each operating point. This is a desirable property of the model that lets the observer error go to zero over time, which increases the robustness of the control strategy. Therefore, the steady-state ROL profile is a good controller objective, as will be shown later.

The profiles can be derived by steady-state simulation or analytically by setting Equation (4.10) to zero. In combination with the equations
for the quasi-static gas phase in Equation (2.35), the following system of equations can be derived for steady-state conditions:

\[
\begin{align*}
0 &= 2 r_1 - r_2 \\
0 &= E_{O_2} - 2 r_1 \\
0 &= E_{CO} - r_2 
\end{align*}
\] (4.23)

The system of equations (4.23) is solved for the steady-state ROL and the outlet concentrations \([CO]_{out}\) and \([O_2]_{out}\) of each cell depending on the mass flow, the inlet concentrations, and the temperature of the solid. The outlet concentrations are further used as the inlet concentrations for the next cell.

Figure 4.12 shows the steady-state ROL profiles of a given operating point for several air-fuel ratios. The profile for stoichiometric conditions is indicated in black. The dashed line represents the corresponding mean ROL value. Small deviations from stoichiometric conditions lead to very different profiles and mean ROL values. More oxygen is stored on the surface for lean inlet conditions (blue) while less oxygen is stored for rich inlet conditions (red).

Deviations from stoichiometry only empty or fill the TWC to a certain level. As long as there is some CO and some O\(_2\) available at the inlet, the
catalyst is never completely full or empty. This is particularly the case in the front of the catalyst. The available $O_2$ in the gas phase only reacts with the empty surface, which results in an increased ROL also for rich conditions. The available CO in the gas phase is oxidized by continually taking $O_2$ from the surface. This leads to a decreased ROL even under lean conditions.

The sensitivity of the mean ROL is very high around stoichiometry as the dotted lines in Figure 4.12 clearly show. This insight stresses the importance of a calibrated upstream LSU sensor. Its offset can be as large as 1%.

### 4.6.1 Lean compensation capability of large TWCs

The cells of the model can be calculated one by one. The outlet of the first cells is the inlet of the next cell. This sequencing can be done because no diffusion process is modeled, as Figure 2.3 already illustrated. Additionally, if a catalyst is extended, the front part of the steady-state ROL profile does not change. Figure 4.12 indicates that the steady-state ROL profile increases all the way to the end of the catalyst.

The model predicts a bounded lean compensation capability of the catalyst. The amount of $O_2$ that a large catalyst can store on its surface is limited. It appears that an even larger catalyst cannot store any additional $O_2$. This claim has not been verified as yet, however.

### 4.7 Filling and depleting behavior

ROL profiles along the catalyst are necessary to understand the characteristic asymmetric filling and depleting behavior of three-way catalytic converters. However, since no measurements are available, the correctness of the ROL profiles cannot be validated. Nevertheless, the validity of the model presented indicates the validity of the profiles.

Figure 4.13 shows the upstream and downstream $\lambda$ trajectories of a sample pulse including measured concentrations for CO and NO (zoom from Figure 4.6). The downstream $\lambda$ shows a plateau at stoichiometry for the step from lean to rich, with the concentrations of CO and NO being zero. The step from rich to lean results in a strictly monotonic rise in
the downstream $\lambda$ with concentrations of CO and NO being non-zero for stoichiometry.

The reason for this difference is the extended reaction path of $O_2$. In the rich to lean step, $O_2$ first has to adsorb onto the surface before it can oxidize the CO, whereas in the lean to rich step, the $O_2$ already is on the surface. Figure 4.14 shows simulated ROL profiles along the catalyst for the same operating point as in Figure 4.6.

### 4.7.1 Depleting

Figure 4.14 (left) shows the switch of the inlet $\lambda$ from lean to rich at $t = 0 \text{ s}$, which leads to an excess of CO at the inlet.

$$\lambda_{ds} > 1 \quad \text{(i.e.} \ t = 0.2 \text{ s)}$$

The outlet $\lambda$ stays lean because some of the unequilibrated $O_2$ that is present even in the rich exhaust remains in the gas phase. The
Figure 4.14: Graphs of the asymmetric filling and depleting behavior of a three-way catalytic converter. Step from lean to rich (left). Step from rich to lean (right). Markers indicate time instances for profile plots.
oxidized surface first has to be reduced by the CO before new \( \text{O}_2 \) from the gas phase can adsorb on the surface.

\[ \lambda_{ds} = 1 \text{ (i.e. } t = 2.0 \text{s)} \]

The ROL in the first part of the catalyst is low and therefore \( \text{O}_2 \) from the gas phase is completely adsorbed on the surface. The oxidized surface depletes more and more as it compensates for the lack of oxygen in the rich inlet \( \lambda \). Neither CO nor \( \text{O}_2 \) are emitted.

\[ \lambda_{ds} < 1 \text{ (i.e. } t = 3.0 \text{s)} \]

CO is not completely oxidized anymore. The residence time of CO in the area of high ROL is decreased as a very low ROL is approached. More and more CO stays in the gas phase until steady state with an excess of CO is reached.

### 4.7.2 Filling

Figure 4.14 (right) shows the switch of the inlet \( \lambda \) from rich to lean at \( t = 0 \text{s} \) which leads to an excess of \( \text{O}_2 \) at the inlet.

\[ \lambda_{ds} < 1 \text{ (i.e. } t = 0.5 \text{s)} \]

The outlet \( \lambda \) stays rich because some CO remains in the gas phase. The excess of \( \text{O}_2 \) from the inlet first has to adsorb on the surface before it can be used to oxidize CO. As the \( \text{O}_2 \) is more and more adsorbed on the surface, the CO concentration in the gas phase is reduced.

In areas with low ROL, CO\(_2\) oxidizes the surface while CO is produced. Both reactions in (4.1) can be reversed if the concentrations of the reactants are very low. In practice, CO is partly used in the water-gas shift reaction to generate significant amounts of \( \text{H}_2 \).

\[ \lambda_{ds} = 1 \text{ (t } \approx \text{ 2.2 s)} \]

The inlet CO is completely oxidized in areas of high ROL. In the last part of the catalyst, the ROL is still low and the surface is also oxidized by the reduction of CO\(_2\) to CO. Since the residence time of \( \text{O}_2 \) in these areas of low ROL is very short, both gas species are still available in the outlet even though the AFR is stoichiometric.
Three-Way Catalytic Converter

Figure 4.15: Complete AFR controller scheme for achieving stoichiometric conditions downstream of the catalyst

$\lambda_{ds} > 1$ (i.e. $t = 3.0 \text{s}$)

The reduction of CO$_2$ is inhibited with rising ROL until no more CO is formed. As the ROL reaches its steady-state value, more and more O$_2$ stays in the gas phase until steady state with an excess of O$_2$ is reached.

4.8 Optimal oxygen depletion after fuel cut-off

Figure 4.15 illustrates the substantial control action that is required to keep the air-fuel ratio (AFR) of the exhaust gas near stoichiometry. The AFR feedforward controller predicts the inducted air mass and compensates for wall-wetting effects and the dynamics in the inlet manifold [64]. Errors in the measurements, predictions, and actuators are corrected by the AFR feedback controller using the wide-range oxygen sensor (LSU) in the exhaust manifold [56]. The TWC feedback controller uses the switch-type oxygen sensor (LSF) downstream of the catalyst to compensate for the dynamic offset of the upstream LSU sensor. This offset is caused by changes in the composition of the engine out emissions and some leak current in the sensor.

Today’s most common TWC feedback control strategy basically uses a PI controller on the deviation of the LSF signal from stoichiometry without considering the oxygen storage dynamics of the catalyst. This lack can lead to undesired control actions after fuel cut-off phases resulting in NO$_x$ breakthroughs [43]. Therefore, the TWC feedback controller is
4.8 Optimal oxygen depletion after fuel cut-off
turned off during fuel cut-off phases and not turned on again until the
LSF signal has recovered to near stoichiometry. This recovery can take
up to 20 s during which time the TWC is not controlled. Therefore, a
TWC feedforward controller is needed (see Figure 4.15) that minimizes
the recovery time of the LSF signal by compensating the oxygen storage
dynamics of the catalyst. This controller might use the downstream LSF
signal to adapt the underlying TWC model to aging or poisoning.

4.8.1 Standard catalyst depletion

In order to avoid NO\textsubscript{x} breakthroughs after fuel cut-off phases, the oxygen
level of the TWC needs to be reduced with rich exhaust gas as soon
as fuel is injected again. Current TWC feedforward strategies recover
the catalyst with a rich phase of a certain duration depending on the
operating point. This strategy prevents any emissions from leaving the
catalyst. The drawback is the very long recovery time of the downstream
LSF sensor. The TWC feedback controller can only be turned on once
the LSF signal has recovered. Otherwise, the control input can lead to
NO\textsubscript{x} breakthroughs [43]. The actual amount of oxygen that is depleted is
not critical because the catalyst always recovers to the steady-state ROL
for stoichiometric conditions (see Section 4.4.2).

Möller stated in [43] that a better strategy is to deplete the catalyst
more than desired in a first phase and to refill it in a second phase. This
result is confirmed with the much simpler model proposed in this thesis.

4.8.2 Non-causal depletion strategy

An off-line TWC recovery strategy is now derived using the model de-
scribed. Since the downstream LSF sensor value is not observed by the
model, the recovery time of the ROL profile is taken as the cost function.
Measurements show that these values highly correlate.

Since a complete fuel cut-off causes additional side effects that are not
part of the problem, such as the wall film dynamics, the catalyst is ox-
idized using 10% lean exhaust gas, which sufficiently fills the catalyst with
oxygen (see Figure 4.12). The optimizer searches for a \( \lambda \) setpoint trajec-
tory in the band of \( \pm 2\% \) around stoichiometry except for the initial 5%
rich phase. Higher offsets can lead to unwanted breakthroughs on the rich or lean side.

Figure 4.16 shows the optimal $\lambda$ trajectory depending on the number of allowed switching events between lean and rich setpoints. The cost function $R$ is the Euclidean norm of the deviation of the current ROL profile from the steady-state ROL profile.

A bang-bang strategy with the switching between the boundaries of the search region was found to be optimal in any case. The recovery time of the ROL profile was reduced by more than 50% with respect to the conventional strategy. Table 4.5 lists the recovery time savings of the strategies relative to the conventional one-switch strategy.

**Table 4.5:** Recovery time savings depending on the number of switching events $s$

<table>
<thead>
<tr>
<th>$s$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>0.0%</td>
<td>40.1%</td>
<td>52.0%</td>
<td>56.9%</td>
<td>57.8%</td>
<td>58.7%</td>
</tr>
</tbody>
</table>
4.8 Optimal oxygen depletion after fuel cut-off

4.8.3 Comparison of one-switch and two-switch strategies

Table 4.5 shows only small improvements of the relative recovery time for more than two allowed switching events. Therefore, only the two-switch strategy is taken for further observations. Figure 4.17 illustrates the ROL profile over time for the two different strategies. The dashed lines in the lower plots of Figure 4.17 represent the initial position of the ROL profile for $\lambda = 1.1$. The behavior is the same until about 0.85 s (dashed blue) where the conventional strategy returns to stoichiometry.

The first depleting phase of the two-switch strategy lasts for 1.39 s until the oxidized surface of the last cells starts to reduce and the outlet concentration is stoichiometric. At this point, the first half of the catalyst is almost completely empty and the mean ROL is well below the desired level.

The next phase with lean exhaust gas compensates for the underdepletion during the first phase and refills the catalyst until $t = 2.93$ s. The conventional strategy takes almost 4 s until the ROL of the last cell starts
Figure 4.18: Comparison of the 1-switch and the 2-switch strategy in engine test bench measurements

to decrease. The recovery time saving of the two-switch strategy is greater than 40% with respect to the one-switch strategy.

Figure 4.18 shows the measured improvement of the downstream LSF signal including exhaust gas measurements using the two-switch strategy. The downstream LSF signal reaches steady state significantly faster than with the conventional strategy. The only drawback is a small CO peak during the first rich phase. However, the amount of additional CO is very small and well below the tolerated CO emissions of the legislation norms.

The depletion strategy derived is optimized for a specific operating point and needs a substantial amount of effort to be calibrated for the entire operating range. Therefore, it is not recommended for on-line applications.

4.8.4 Causal depletion strategy

The model is used to derive a causal catalyst depletion strategy after fuel cut-off phases with a performance similar to that of the off-line optimized
4.8 Optimal oxygen depletion after fuel cut-off

two-switch strategy. Since the current ROL profile is estimated during operation, it can be compared to the desired steady-state ROL profile that is calculated analytically according to Equation (4.23). The current deviation of the two profiles results in a control action.

Figure 4.19 illustrates the TWC controller scheme developed. The current ROL profile $x$ from the on-line observation is compared to the steady-state ROL profile $r$ that is a function of the mass flow $\dot{m}$ and the exhaust gas temperature $T_g$. The differential profile is multiplied by the weighting vector $w$ and summed up. The resulting controller input $e$ is then multiplied by the controller gain $K_P$. The controller output $u$ is saturated with $-5\%$ and $+2\%$ and overlaid with the $\lambda$ setpoint from the AFR controller.

The weighting vector $w$ is chosen to be linearly increasing along the catalyst which results in the desired high sensitivity to the deviation from the current ROL to the steady-state ROL of the last cells. A higher weight at the back results in the desired underdepletion of the catalyst. Figure 4.20 illustrates this behavior. Again, the dashed lines in the right-hand plots of Figure 4.20 represent the initial position of the ROL profile for $\lambda = 1.1$.

At the time $t = 1.17$ s the desired $\lambda$ setpoint switches from rich to lean. The catalyst is well underdepleted at that time. In the next phase, the catalyst is refilled to the desired level until $t = 1.91$ s. Only small corrections are then made while the ROL profile approaches the steady-state ROL profile for stoichiometric inputs. The “integrating” behavior of the model prevents steady-state errors even though a simple P controller is used.

Figure 4.21 shows the measurement trace of the causal depletion strategy compared with that of the optimal non-causal two-switch strategy. The $\lambda$ setpoint trajectory generated on-line with the causal strategy is

![Figure 4.19: Scheme of the feedforward TWC controller used for the causal strategy](image)
Figure 4.20: Error and control output trajectories for the causal depletion strategy comparable to the trajectory optimized off-line with the two-switch strategy. The measured upstream $\lambda$ trajectories are even more similar because the switching of the $\lambda$ setpoint from rich to lean or vice versa takes time. The measured LSF signal and also the measured exhaust concentrations (not shown) of the causal method are almost identical to those of the two-switch strategy.

The calibration effort for the controller is very small. The weighting vector $w$ and the controller gain $K_P$ are the only parameters. This strategy works for all operating points where the TWC model is valid.
4.8 Optimal oxygen depletion after fuel cut-off

Figure 4.21: Performance of the causal depletion strategy compared to the optimal non-causal two-switch depletion strategy
5 Selective Catalytic Reduction

The selective catalytic reduction (SCR) with ammonia (NH$_3$) has already been presented in the Introduction. Many kinetic studies have been published and meanwhile many models have been derived. A short literature overview is given about the modeling and control of the NH$_3$-SCR.

Tronconi et al. [16, 17, 66] and Schär et al. [59, 60] described models for the vanadium-based SCR catalyst, with the standard SCR being the only NO$_x$ reducing reaction. Rahkamaa-Tolonen et al. [55] showed that the presence of NO$_2$ in the inlet flow significantly enhances the catalytic activity of fresh and aged zeolite catalysts. Therefore, models for zeolite-based SCR catalysts usually not only include the standard SCR reaction but also the fast and the slow SCR reaction. Schuler et al. [39, 62] and Devadas et al. [19] presented models for the Fe-zeolite SCR catalyst. Olsson et al. [50] described a very similar model for the Cu-zeolite SCR catalyst. All presented models are not real-time capable, which disqualifies them for model-based control.

The control objective of an SCR system is to maximize the NO$_x$ reduction efficiency while minimizing the urea consumption and the downstream NH$_3$ slip. Willems et al. [69] stated that closed-loop control is needed to make the SCR system robust against urea dosage inaccuracy, catalyst aging, and NO$_x$ engine-out variations. Seher et al. [63] presented a stationary approach which is corrected by the output of the dynamic model that compensates for the storage behavior of the catalyst and its NO conversion efficiency. Devarakonda et al. [20] extended that approach with NO$_2$ and the fast and slow SCR reaction. Ericson et al. [23] developed a simplified model of a heavy duty SCR catalyst, primarily intended for use in combination with an engine-out emissions model to perform model based offline optimizations of the complete system.

Schär [59] developed several model-based control strategies with static, feedforward, and feedback components. Schuler et al. [62] showed that
Schär’s feedforward control with surface coverage estimator ($S_2$) dosing controller is possible on a model gas test bench.

Schär’s feedforward controller for constant ammonia slip ($S_3$) shows promise as well. This strategy is therefore applied to the SCR model derived here. The first part of the chapter introduces the control-oriented SCR model that is then identified for two different catalysts with several measurements from an engine test bench. The second part of the chapter is about optimal NH$_3$ dosing strategies derived from the model.

## 5.1 Control-oriented model

An SCR model was to be developed that accurately predicts the NO$_x$ reduction efficiency and the ammonia storage dynamics of the catalyst. The complexity of the model should be as low as possible in order to keep the computational demand low and thus allow its operation on the ECU with a sample rate of 100 Hz or more.

The model inputs are total mass flow through the catalyst, exhaust gas temperature, and concentrations of NO$_x$ and NH$_3$. The model outputs are the downstream temperature, gas concentrations, and the relative ammonia level (RAL) profile along the catalyst.

Only the chemical model is described here. The derivation of the complete model including the physical part is explained in detail in Chapter 2.

### 5.1.1 Reaction scheme

Control-oriented modeling starts from the most simple reaction scheme and increases the complexity of the model only if the results are unsatisfactory. Therefore, the SCR reaction scheme 1.4 shown in the Introduction has been simplified to only the standard SCR reaction and the NH$_3$ oxidation in addition to the NH$_3$ adsorption. This simplification works well for exhaust compositions with small amounts of NO$_2$, which is then treated as NO. This is the case especially on vanadium-based SCR catalysts since they are usually operated without an oxidation catalyst. Nevertheless, the reaction scheme is also applied to a Fe-zeolite catalyst. The restrictions are mentioned.
Busca et al. [12] found no evidence for the storage of NO or NO$_2$ on any SCR catalyst’s surface. Therefore, they suggest the use of an Eley-Rideal mechanism, with NH$_3$ being the only species to be stored on the surface. The NH$_3$ from the gas phase first adsorbs onto the empty surface V. The occupied surface VNH$_3$ is then used to reduce the NO. This results in the following reaction scheme that is then applied to the framework described in Chapter 2:

\[
\begin{align*}
V + \text{NH}_3 & \leftrightarrow \text{VNH}_3 \\
4 \text{VNH}_3 + 4 \text{NO} + \text{O}_2 & \leftrightarrow 4 \text{V} + 4 \text{N}_2 + 6 \text{H}_2\text{O} \\
4 \text{VNH}_3 + 3 \text{O}_2 & \leftrightarrow 4 \text{V} + 2 \text{N}_2 + 6 \text{H}_2\text{O}
\end{align*}
\] (5.1)

5.1.2 Reaction kinetics

The reaction species vector $q$ is derived directly from reaction scheme (5.1).

\[
q = \begin{pmatrix}
\text{H}_2\text{O} \\
\text{N}_2 \\
\text{NH}_3 \\
\text{NO} \\
\text{O}_2 \\
\text{V} \\
\text{VNH}_3
\end{pmatrix}
\] (5.2)

The matrix of the stoichiometric coefficients $V$ is derived from the reaction scheme and the species vector $q$.

\[
V = \begin{pmatrix}
0 & 0 & 1 & 0 & 0 & 1 & -1 \\
-6 & -4 & 0 & 4 & 1 & -4 & 4 \\
-6 & -2 & 0 & 0 & 3 & -4 & 4
\end{pmatrix}
\] (5.3)

The complexity of the reaction scheme requires the order coefficient matrix $W$ to be set to the default value $W = \text{sign}(V)$. Otherwise, the derived system of equations might not be solvable.

\[
W = \begin{pmatrix}
0 & 0 & 1 & 0 & 0 & 1 & -1 \\
-1 & -1 & 0 & 1 & 1 & -1 & 1 \\
-1 & -1 & 0 & 0 & 1 & -1 & 1
\end{pmatrix}
\] (5.4)

The reaction rates $r$ are then calculated according to Equation (2.8).

\[
\begin{align*}
 r_1 &= k_1^f \cdot [V] \cdot [\text{NH}_3] - k_1^b \cdot [\text{VNH}_3] \\
 r_2 &= k_2^f \cdot [\text{VNH}_3] \cdot [\text{NO}] \cdot [\text{O}_2] - k_2^b \cdot [V] \cdot [\text{N}_2] \cdot [\text{H}_2\text{O}] \\
 r_3 &= k_3^f \cdot [\text{VNH}_3] \cdot [\text{O}_2] - k_3^b \cdot [V] \cdot [\text{N}_2] \cdot [\text{H}_2\text{O}]
\end{align*}
\] (5.5) (5.6) (5.7)
The empty site V can be represented as the storage capacity \(SC_{NH_3}\) minus the occupied site. The changes in the concentrations of \(N_2\), \(H_2O\), and \(O_2\) due to the reaction rates are negligible. They are therefore defined as static gases with fixed concentrations.

\[
[V] = SC_{NH_3} - [VNH_3] \tag{5.8}
\]

\[
[N_2] = 70 \% \cdot c_0 \tag{5.9}
\]

\[
[H_2O] = 10 \% \cdot c_0 \tag{5.10}
\]

\[
[O_2] = 10 \% \cdot c_0 \tag{5.11}
\]

The backward reaction rate constants \(k_i^b\) are determined using the chemical equilibrium constant with a correction for the mole balance according to Equation (2.12). Reaction (5.6) does conserve the mole balance, but Reactions (5.5) and (5.7) do not.

\[
k_1^b = \frac{k_1^f}{K_1} \cdot c_0 \quad k_2^b = \frac{k_2^f}{K_2} \quad k_3^b = \frac{k_3^f}{K_3} \cdot \frac{1}{c_0} \tag{5.12}
\]

The resulting net reactions for the dynamic species considered are:

\[
R_{VNH_3} = r_1 - 4 r_2 - 4 r_3 \tag{5.13}
\]

\[
R_{NH_3} = -r_1 \tag{5.14}
\]

\[
R_{NO} = -4 r_2 \tag{5.15}
\]

### 5.1.3 Gibbs energy constraints

The chemical equilibrium constants \(K_i\) depend on the change in the scaled Gibbs energies for each reaction in (5.1) that is calculated according to Equation (2.15).

\[
\Delta \Gamma_1 = \Gamma_{VNH_3} - \Gamma_V - \Gamma_{NH_3} \tag{5.16}
\]

\[
\Delta \Gamma_2 = \Gamma_V + \Gamma_{N_2} + \Gamma_{H_2O} - \Gamma_{VNH_3} - \Gamma_{NO} - \Gamma_{O_2} \tag{5.17}
\]

\[
\Delta \Gamma_3 = \Gamma_V + \Gamma_{N_2} + \Gamma_{H_2O} - \Gamma_{VNH_3} - \Gamma_{O_2} \tag{5.18}
\]
The scaled Gibbs energy for the empty surface V is zero, while the one for the occupied surface VNH$_3$ is a parameter of the system. The chemical equilibrium of all reactions is expected to lie on the right-hand side because the catalyst is known to work well in the desired operating conditions. This information can be used to define a feasible region for $\Gamma_{VNH_3}$ by setting Equations (5.16–5.18) smaller than zero. This results in three inequalities for the unknown scaled Gibbs energy of the occupied surface $\Gamma_{VNH_3}$.

\[
\begin{align*}
\Gamma_{VNH_3} &< \Gamma_{NH_3} \quad (5.19) \\
\Gamma_{VNH_3} &> \Gamma_N + \Gamma_{H_2O} - \Gamma_{NO} - \Gamma_{O_2} \quad (5.20) \\
\Gamma_{VNH_3} &> \Gamma_N + \Gamma_{H_2O} - \Gamma_{O_2} \quad (5.21)
\end{align*}
\]

Figure 5.1 shows the calculated boundaries that limit the feasible region for $\Gamma_{VNH_3}$. The lower boundaries cross at around 450 K because the scaled Gibbs energy of NO changes signs at that temperature (see Fig. 2.2).

The identification procedure finds for both catalysts that the three nodes $g^1$, $g^2$, $g^3$ of the scaled Gibbs energies described in Section 3.3.3 lie in the feasible region. The resultant scaled Gibbs energy of the occupied surface $\Gamma_{VNH_3}$ leaves that feasible region for low temperatures. This was
not further investigated since the light-off temperature of an SCR catalyst is close to 450 K. The models are thus not valid for temperatures below the light-off temperature.

5.1.4 Irreversible reactions

Figure 5.1 shows that the derived values of the scaled Gibbs energy for the occupied surface $\Gamma_{\text{VNH}_3}$ of the Fe-zeolite catalyst is far from the lower boundary in the region after the light-off temperature. Hence, the chemical equilibrium of reactions 2 and 3 lie clearly on the right-hand side.

Simulations show that the standard SCR and the NH$_3$ oxidation can be modeled irreversibly. The simulation error is well below 1% but the calculation time is reduced by 40%. Since no evidence was found in the literature that nitrogen and water can fill an SCR catalyst with NH$_3$, the backward reactions 2 and 3 were not included in the model.

This simplification was done based on the available measurement data. It has to be reconsidered once further identification measurements have been taken.

5.1.5 Number of parameters

The simple reaction scheme (5.1) keeps the number of parameters small. This is beneficial for the parameter identification process. The physical model parameters $\alpha$ (heat transfer coefficient) and $c_{ps}$ (specific heat capacity of the solid) are identified separately in advance. Table 5.1 lists the chemical parameters for the SCR model derived. The parameters for the scaled Gibbs energy and for the reaction kinetics are the transformed values according to Section 3.3.2.

<table>
<thead>
<tr>
<th>parameter</th>
<th>quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen storage capacity</td>
<td>1 $(\text{SC}_{\text{NH}_3})$</td>
</tr>
<tr>
<td>scaled Gibbs energy of VNH$_3$</td>
<td>3 $(g^1, g^2, g^3)$</td>
</tr>
<tr>
<td>reaction kinetics</td>
<td>6 $(u^1_1, u^2_1, u^1_2, u^2_2, u^1_3, u^2_3)$</td>
</tr>
</tbody>
</table>
The number of parameters is independent of the simplification made in the previous section. The backward reaction of the standard SCR and the NH$_3$ oxidation was neglected for computational reasons only.

## 5.2 Test bench

The measurements described in this chapter were taken on a test bench with a production type Liebherr D946 diesel engine. Table 5.2 summarizes the specifications of the engine.

### Table 5.2: Engine specifications of the SCR test bench

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>Liebherr</td>
</tr>
<tr>
<td>Model</td>
<td>D946</td>
</tr>
<tr>
<td>Injection system</td>
<td>direct</td>
</tr>
<tr>
<td>Number of cylinders</td>
<td>6</td>
</tr>
<tr>
<td>Displacement volume</td>
<td>11.9 l</td>
</tr>
<tr>
<td>Maximum output power</td>
<td>340 kW</td>
</tr>
</tbody>
</table>

### 5.2.1 Catalysts

Commercial SCR catalysts are used throughout the project. Table 5.3 summarizes the data sheet for the Fe-zeolite and the vanadium-based catalyst.

### Table 5.3: Characteristics of the SCR catalysts

<table>
<thead>
<tr>
<th>Specification</th>
<th>Fe-zeolite</th>
<th>Vanadium-based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>$V_{cat}$</td>
<td>401</td>
</tr>
<tr>
<td>Length</td>
<td>$L_{cat}$</td>
<td>550 mm</td>
</tr>
<tr>
<td>Mass</td>
<td>$M_{cat}$</td>
<td>50 kg</td>
</tr>
<tr>
<td>Cell density</td>
<td>cpsi</td>
<td>300</td>
</tr>
<tr>
<td>Open area</td>
<td>$\epsilon$</td>
<td>0.8225</td>
</tr>
</tbody>
</table>
5.2.2 Dosing ratio $\alpha$

Reaction scheme (5.1) clearly shows that each NO molecule requires one \( \text{NH}_3 \) molecule in order to be reduced by the standard SCR reaction. Hence, the stoichiometric \( \text{NH}_3 \) dosing is a good approximation under steady-state conditions. The desired amount of \( \text{NH}_3 \) is therefore normalized with the upstream \( \text{NO}_x \) concentration, which results in the scaled ammonia dosing ratio $\alpha$:

$$
\alpha = \frac{[\text{NH}_3]_{us}}{[\text{NO}_x]_{us}} \quad (5.22)
$$

The stoichiometric dosing ratio is therefore $\alpha_{st} = 1$. In this thesis, the optimal dosing ratio $\alpha_{opt}$ is defined to be reached if under steady-state conditions the downstream \( \text{NH}_3 \) slip is at 10 ppm.

The optimal dosing ratio $\alpha_{opt}$ is lower than $\alpha_{st}$ if the reaction rates are low and if not all \( \text{NO}_x \) can be converted. It is higher if a large amount of \( \text{NH}_3 \) oxidizes and is thus no longer is available for the \( \text{NO}_x \) reduction.

5.3 Identification trajectories

The models are parameterized using test bench measurement data only. Expensive and time-consuming model gas measurements as well as gas concentration measurements are not required.

The dynamometer runs in speed-controlled mode at constant speed while the engine’s injected fuel mass is constant. The resulting steady-state values for temperature and mass flow represent inputs to the model. The catalyst is preconditioned with large amounts of \( \text{NH}_3 \) until \( \text{NH}_3 \) breakthroughs occur. Then the \( \text{NH}_3 \) dosing is turned off until \( \text{NO}_x \) conversion is stopped completely. This test helps to put the catalyst in a predefined state and to check the operation of the test bench.

Figure 5.2 shows identification trajectories that have been found useful. The only variable input is the \( \text{NH}_3 \) dosing ratio. The reaction rates are best determined with the \( \text{NH}_3 \) screening test, while a basic filling and depleting test identifies the \( \text{NH}_3 \) storage capacity. The upstream as well as the downstream exhaust gas composition need to be measured for both tests.
5.3 Identification trajectories

Figure 5.2: Trajectories of $\alpha$ used for identification measurements. NH$_3$ Screening (top). Storage dynamics (bottom).
5 Selective Catalytic Reduction

The NH$_3$ screening identifies the NO$_x$ conversion rate for various ratios of NH$_3$ dosing for steady-state conditions. The dosing ratios need to vary from zero to clearly higher than $\alpha_{opt}$. It is crucial that the system is in steady-state before changing the operating point. This can be a very time-consuming measurement.

The measurement for the storage dynamics starts with a preconditioned and empty catalyst. The NH$_3$ dosing ratio is set above the optimal dosing ratio, which leads to a filled catalyst with clearly measurable NH$_3$ slip downstream of the catalyst. Once steady-state is reached, the NH$_3$ dosing ratio is dropped below the optimal dosing ratio. The downstream NO$_x$ concentration rises and no more NH$_3$ slip is expected. The NH$_3$ dosing ratio is raised above the optimal dosing ratio again before it is set back to zero.

Note that the NO$_x$ conversion ratio should be below 100% during the whole measurement. Otherwise, the reaction rates cannot be correctly identified. The catalyst’s volume can be reduced to achieve that even under overdosing phases.

5.3.1 Fe-zeolite catalyst

Figure 5.3 shows the results from the NH$_3$ screening test for the Fe-zeolite catalyst. Unfortunately, the NO$_x$ conversion rate of the measurement is 100% for the overdosing phase. Therefore, the reaction kinetics are difficult to identify. Note that the x-axis does not show the time, but the independent steady-state operating points. The calculation of the steady-state behavior for all operating points takes just about 5 ms. It can be done analytically, as will be shown later.

The model is able to predict the steady-state behavior of the catalyst for temperatures above the light-off temperature. The model is even valid in the phases where the amount of NO$_2$ is higher than the amount of NO, which was not expected. One exception is the overestimated NO$_x$ conversion efficiency for low temperatures and high NH$_3$ dosing levels (OPs: 42 and 98). This a drawback of the simplified reaction scheme by disregarding the fast and slow SCR reactions. The model is not valid for temperatures below light-off.
5.3 Identification trajectories

Figure 5.3: Identification of the steady-state behavior of the Fe-zeolite catalyst
Figure 5.4 shows the result of a dynamic identification measurement for the Fe-zeolite catalyst. The engine operating point is kept constant, which results in a constant gas inlet temperature of 650 K.

The step from overdosing to underdosing NH$_3$ results in a delayed increase in the downstream NO$_x$ concentration. This is to be expected since the catalyst is still full of NH$_3$ that is used to reduce the NO$_x$. What is not expected is the constant NH$_3$ slip for about 10 s until it starts to drop and finally reaches zero. The parameterized model is going to help explaining this phenomenon in Section 5.5.

The step from underdosing to overdosing shows a delayed increase of the downstream NH$_3$ concentration because the catalyst is being filled with NH$_3$. The downstream NO$_x$ concentration shows an immediate reaction to the step by going to zero. The reduction of the NO$_x$ starts as soon as NH$_3$ is available on the surface.

The model proposed above very well predicts the complete identification measurement. This includes the downstream gas concentrations during steady state and the immediate or delayed response of the downstream
concentrations to the steps. The domain of the model is restricted to low NO\textsubscript{2} levels, which generally is not the case on Fe-zeolite catalysts. Nevertheless, this model was used for further investigations.

The simulation of the identification measurement shown in Figure 5.4 takes about 0.5 s on a standard personal computer with a simulation step size of 10 ms. The RAL profile of the catalyst is initialized with the steady-state RAL profile of that operating point.

5.3.2 Vanadium-based catalyst

Figure 5.5 shows the NH\textsubscript{3} screening test for the vanadium-based catalyst. The engine is operated at constant speed and load while the NH\textsubscript{3} dosing is varied. The NH\textsubscript{3} dosing is turned off completely between two levels. Unfortunately, the NO\textsubscript{x} measurement devices were turned off during these phases, which results in a discontinuous NO\textsubscript{x} measurement downstream of the catalyst. Additionally, the system was not always in steady state before the operating point was changed.

The model very accurately predicts the NH\textsubscript{3} slip downstream of the catalyst. A steady-state offset is observed for the NO\textsubscript{x} conversion efficiency, but the dynamics of the storage capacity is well observed. The available identification measurements did not suffice to completely parameterize the model. The requirement of the limiting reaction kinetics, which was stated in Section 3.2, is not fulfilled. The vanadium-based model therefore cannot be used for further investigations. However, the controller derived later in this chapter will still be valid even for this model.

5.4 Model validation

Figure 5.6 illustrates the validation of the model of the Fe-zeolite SCR catalyst against a driving cycle measurement. The concentrations are scaled to the maximum NO\textsubscript{x} level upstream of the catalyst.

Even though the fast and the slow SCR reactions are neglected, the qualitative trend of the downstream NO\textsubscript{x} is reproduced. The simulation observes some breakthroughs in NH\textsubscript{3} concentration downstream of the catalyst, which is not the case in the measurement. More identification measurements are required to identify the NH\textsubscript{3} breakthroughs more ac-
Figure 5.5: Trajectory of $\alpha$ used for identification measurements of vanadium-based catalysts
5.4 Model validation

Figure 5.6: Validation of SCR model
curately. Nevertheless, the model is used for the design of an optimal model-based NH$_3$ dosing strategy. This strategy is independent from the parameters identified since it is also a function of these parameters.

### 5.5 Properties of the RAL profile

Simulations show that the steady-state relative ammonia level (RAL) profile is unique and attractive for each operating point. The profiles can be derived by steady-state simulation or analytically by setting Equation (5.13) to zero. In combination with the equations for the quasi-static gas phase in Equation (2.35), the following system of equations can be derived for the steady state:

\[
\begin{align*}
0 &= r_1 - 4r_2 - 4r_3 \\
0 &= E_{\text{NH}_3} - r_1 \\
0 &= E_{\text{NO}} - 4r_2
\end{align*}
\]  

(5.23)

This system of equations is solved for the steady-state RAL and the outlet concentrations [NH$_3$]$_{\text{out}}$ and [NO]$_{\text{out}}$ of each cell depending on the mass flow, the inlet concentrations, and the temperature of the solid. The outlet concentrations are further used as the inlet concentrations for the next cell.

Figure 5.7 shows the steady-state RAL profile for several dosing ratios $\alpha$. The higher the NH$_3$ dosing ratio is, the higher the mean RAL value becomes. The stoichiometric dosing ratio $\alpha_{\text{st}}$ is indicated in black, lower ratios are shown in red, and higher ratios in blue.

Even though the RAL profile is in steady state, NH$_3$ continuously interacts with the surface. Adsorption and desorption are just balanced. The falling RAL profile at the end of the catalyst for overdosed conditions is caused by the NH$_3$ oxidation.

### 5.6 Filling and depleting behavior

Figure 5.4 already showed the characteristic filling and depleting behavior of the SCR catalyst during pulse measurements. Figure 5.8 helps to understand the different time responses for the changes in the concentrations.
The NO reduction is faster than the adsorption of NH\textsubscript{3} onto the surface. This can be seen in the wavelike depleting of the catalyst, while the filling of the catalyst occurs more evenly. One consequence is the shorter settling time of the system during the depletion of the catalyst compared to when the catalyst is filled.

### 5.6.1 Depleting

Figure 5.8 (left) shows the depleting of the SCR catalyst from an overfilled to a completely depleted state. Before the switch, the RAL profile is high but decreasing to the end because of the NH\textsubscript{3} oxidation. The NO reduction is completed after about one-fifth of the catalyst length. The NH\textsubscript{3} concentration in the gas phase is high but also decreasing to the end because of the NH\textsubscript{3} oxidation.

At time \( t = 0 \) s, the NH\textsubscript{3} dosing is switched off. In the first phase, the downstream concentrations remain constant. The NO reduction is very fast and can be completed in a small region of the catalyst. Therefore,
Figure 5.8: Graphs of the filling and depleting behavior of an SCR catalyst. Depleting (left) and filling (right). Markers indicate time instances for profile plots.
the RAL decreases quickly, resulting in a wavelike movement of the RAL profile through the catalyst. In the back part of the catalyst, the RAL is still high, and NH$_3$ desorbs into the gas phase keeping the NH$_3$ at its level.

As the wave approaches the end of the catalyst, the NH$_3$ slip starts decreasing while the NO conversion is still complete. The residence time of the NO in the regions of high RAL becomes shorter and shorter and the NO starts breaking through. In that phase, both NO and NH$_3$ are non-zero in the gas phase downstream of the catalyst.

At the end, the RAL is completely depleted causing all reactions to stop because NH$_3$ is available neither on the catalyst’s surface nor in the upstream gas composition.

### 5.6.2 Filling

Figure 5.8 (right) shows the filling of the SCR catalyst starting from a completely depleted state. Before the switch, the RAL is zero and no NO is converted.

As soon as the NH$_3$ dosing is switched on, the RAL in the front of the catalyst starts rising and the NO reduction begins. The NO concentration downstream of the catalyst starts to decrease. The residence time of the NO in the region with high RAL becomes longer and longer until a conversion efficiency of 100% is reached.

Even though the NH$_3$ is overdosed, no NH$_3$ slip occurs because the excessive NH$_3$ is stored on the catalyst’s surface. This evenly fills the catalyst until a first NH$_3$ breakthrough can be seen that slowly increases to the steady-state value. This value is well below the difference of the concentrations in the upstream composition (500 ppm) because NH$_3$ is also directly oxidized.

### 5.7 Optimal steady-state NH$_3$ dosing

Many NH$_3$ dosing controllers presented in literature are based on steady-state NH$_3$ dosing maps that maximize a certain objective [20, 62, 63]. Usually, a dosing ratio is desired that results in a predefined NH$_3$ slip of around 10 ppm, which maximizes the NO$_x$ conversion efficiency. The val-
ues are determined through steady-state simulations that are then stored in lookup tables.

Since this strategy is valid only under steady-state conditions, the system of equations (5.23) can be used to calculate the optimal dosing ratio $\alpha_{\text{opt}}$. The downstream NH$_3$ concentration is defined as the desired NH$_3$ slip of 10 ppm. Even though the computational demand is very low, this strategy was not further investigated, since a more promising control strategy is presented in the next section.

### 5.8 Optimal NH$_3$ slip control

Steady-state NH$_3$ dosing is not possible for the transient operation of the engine. The storage dynamics of the catalysts have to be taken into account. This can be done with model-based control strategies for which the SCR model presented can be used.

Schär [59] presented several different model-based approaches for NH$_3$ dosing strategies. His NH$_3$ slip controller (S$_3$) is applied to the model derived. Its objective is to inject a certain amount of urea into the system such that the NH$_3$ slip at the outlet reaches a predefined concentration. This state controller requires a partly inverted model to determine the optimal dosing amount of NH$_3$.

#### 5.8.1 Controller scheme

Figure 5.9 shows the basic procedure of the NH$_3$ slip controller. The NH$_3$ dosing amount can be explicitly calculated if the state of the catalyst is known. The observations of the RAL profile and the temperature profile $T_s$ are received from the SCR model, which is updated on-line. The NH$_3$ setpoint is then calculated analytically.

#### 5.8.2 Explicit NH$_3$ calculation

The NH$_3$ adsorption is the only reaction that interacts with the NH$_3$ from the gas phase. The amount of NH$_3$ that is transferred from the gas phase to the surface (or vice versa) depends on the current RAL and the current temperature of the solid. Therefore, it is sufficient to solve the quasi-static
5.8 Optimal $\text{NH}_3$ slip control

The gas concentration of $\text{NH}_3$ in the equation for its net reaction (5.14) is replaced by the mean values of the inlet and outlet $\text{NH}_3$ concentrations. The concentration of the empty site $[V]$ is replaced by $1 - [\text{VNH}_3]$.

\[
R_{\text{NH}_3} = -r_1 = k^b_1 \cdot [\text{VNH}_3] - k^f_1 \cdot [\text{NH}_3] \cdot [V] \quad (5.25)
\]

\[
= k^b_1 \cdot [\text{VNH}_3] - k^f_1 \cdot \frac{[\text{NH}_3]_{\text{in}} + [\text{NH}_3]_{\text{out}}}{2} \cdot (1 - [\text{VNH}_3]) \quad (5.26)
\]

Equation (5.24) can be solved for the inlet concentration $[\text{NH}_3]_{\text{in}}$ depending on the desired outlet concentration $[\text{NH}_3]_{\text{out}}$ and the state of the catalyst (RAL, $T_s$).

The calculation of the upstream $\text{NH}_3$ setpoint starts from the last cell. The $[\text{NH}_3]_{\text{out}}$ concentration here is the desired $\text{NH}_3$ slip. The desired inlet of the cell is the desired outlet of the previous cell. The inlet $\text{NH}_3$ concentration of the first cell is the desired $\text{NH}_3$ setpoint.

The method presented works without limitation even if the fast or slow SCR reactions are included. The additional reactions only influence the model update step and thus the RAL profile passed to the controller.

5.8.3 Simulation

The state controller derived is tested in simulation where it is expected to work perfectly because it is based on the the same model.
Figure 5.10 illustrates the behavior of the NH$_3$ slip controller for the driving cycle measurement shown in Figure 5.6. The upstream exhaust composition is taken from the measurement. The downstream composition consists of the simulated values. The controller works perfectly under certain conditions.

For the first 150 s, the light-off temperature has not been reached and the injected amount of NH$_3$ is very low. The target NH$_3$ slip of 10 ppm is perfectly met in this phase, and only small amounts of NH$_3$ adsorb onto the surface.

After 150 s the NO$_x$ conversion suddenly begins. At that time the light-off temperature has been reached, but more importantly, the mass flow through the catalyst drops significantly. The NH$_3$ slip drops below the desired value of 10 ppm. The catalyst is now able to adsorb large amounts of NH$_3$, but the NH$_3$ dosing is limited.

At around 280 s the NH$_3$ slip is greater than 10 ppm even though no NH$_3$ is injected. The amount of NH$_3$ released from the surface exceeds the need for the reduction of the NO$_x$. The mean RAL value is very high during that phase. This phenomenon exceeds after sudden changes in the mass flow, temperature, or NO$_x$ inlet concentrations.

The state controller derived works perfectly in simulation if the desired NH$_3$ concentration stays between zero and the boundary given by the hardware. In the application, the controller highly depends on the accuracy of the model.
5.8 Optimal NH$_3$ slip control

![Graph showing NH$_3$ slip control in simulation](image)

**Figure 5.10:** NH$_3$ slip controller in simulation
6 Conclusions

The catalyst model presented in this thesis is derived from physical and chemical principles. Mass and energy balances are maintained. The forward and backward reaction rates are coupled through the change in Gibbs energies of each reaction which ensures compliance with the chemical equilibrium at all times. A good approximation for the well-known Gibbs energies of gases is presented, and feasible regions of the unknown Gibbs energy of the occupied surface can be defined.

In combination with the slow storage dynamics of the catalyst, the large gradients in the gas phase lead to a numerically stiff system. Nevertheless, the system needs to be solved by explicit solvers that are required for real-time applications. The problem is solved by assuming steady-state conditions in the gas phase. A method is introduced that limits the possibly large reaction rates in order to keep the gas concentrations non-negative while still maintaining the mass balances.

The framework presented has been implemented in the auto-code generator called camgen that is made freely available for download. This code generator builds complete, executable models from an XML description of the desired catalyst. The advantages are not only the fast one-click generation of new models, but also the optimized C or MATLAB code that results in fast execution times. The standardized workflow also prevents typing errors.

The framework is first applied to the three-way catalytic converter (TWC). The model of the TWC is identified and validated using measurement data from an engine test bench. It accurately predicts the downstream air-fuel ratio even though the reaction mechanism is simplified to the oxidation of CO with O$_2$ over the catalyst’s surface. The asymmetric filling and depleting behavior of the TWC is explained using the simulated relative oxygen level (ROL) profiles. A method is introduced that completely defines the inlet gas composition using just the upstream
wide-range oxygen sensor. This is the only information required about
the composition of the exhaust gas entering the TWC in gasoline engines.

The model is further used to derive an optimal TWC depletion strategy
after fuel cut-off phases. Since the steady-state ROL profiles are unique
and attractive, they can be used as the setpoints for the depletion con-
troller. These target profiles can be calculated on-line using an analytic
function. This strategy significantly reduces the recovery time of the
downstream switch-type oxygen sensor, which is crucial for the operation
of an additional feedback TWC controller. This non-causal strategy can
be replaced by the proposed causal depletion strategy that shows a similar
performance, but requires a significantly smaller calibration effort. The
causal strategy requires an on-line observation of the relative oxygen level
profile and a determination of the steady-state profile. For both purposes,
the proposed model provides an ideal solution.

The framework is further applied to the catalysts of the selective cata-
lytic reduction (SCR). These models are also identified and validated
using measurements from an engine test bench. The model for the Fe-
zeolite SCR catalyst accurately predicts the steady-state NO\textsubscript{x} conversion
efficiency and the transient behavior of the Fe-zeolite catalyst, even though
the reaction mechanism of the NO\textsubscript{x} reduction is simplified to the standard
SCR reaction only. While the available identification measurements of the
vanadium-based SCR catalyst were not sufficient to completely parame-
terize the dynamics of the model, it allows the steady-state behavior to
be well observed.

An optimal NH\textsubscript{3} dosing controller is derived using the models. The state
controller uses the inverted reaction of NH\textsubscript{3} adsorption to determine the
optimal NH\textsubscript{3} dosing setpoint based on the state of the catalyst. This leads
to the predefined amount of NH\textsubscript{3} slip downstream of the catalyst. The
controller works perfectly in simulation as long as the hardware boundaries
of the injector are met. The performance of the state controller in the
application highly depends on the quality of the models.

Future emission standards will require better control strategies for ex-
haust gas aftertreatment catalysts. This thesis shows that first principle
modeling and control-oriented modeling are not mutually exclusive. It
provides the basis for model-based control strategies for chemical reac-
tors.
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[31] Y.-W. Kim, J. Sun, I. Kolmanovsky, and J. Koncsol. A phenomenological control oriented lean NO\textsubscript{x} trap model.


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