Selective Catalytic Reduction of NO\textsubscript{x} from diesel engine exhaust using injection of urea

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Summary

The objective of this thesis is to contribute to the development of a catalytic aftertreatment device to remove NO\textsubscript{x} from diesel exhaust gases using the Selective Catalytic Reduction (SCR) technique employing injection of an aqueous urea solution. Lab scale catalyst testing has been performed and a urea injection system has been developed. Furthermore, preliminary tests with a small 0.4l direct injected diesel engine have been performed.

The NO\textsubscript{x} removal process to be developed should show an overall NO\textsubscript{x} removal efficiency of 70 percent. This percentage is needed to comply with future legal emission standards for heavy duty diesel engines (section 1.2). The amount of byproducts (N\textsubscript{2}O, NH\textsubscript{3}, urea condensation products, sulphate particles, see section 2.2) should be limited. Especially SO\textsubscript{2} oxidation should be limited as the resulting sulphates will contribute to the particulate emission (section 2.2.3).

Regarding application of SCR in transient (non steady state) devices (such as a truck diesel engine), some additional demands are stated. The amount of NO\textsubscript{x} produced by the engine depends on its load and speed, which vary rapidly. The urea injection should be adjusted accordingly as too much urea injected will lead to emission of urea decomposition products (mainly NH\textsubscript{3}). On the other hand, a shortage of urea will lead to inadequate NO\textsubscript{x} reduction. Another constrained on the NO\textsubscript{x} removal system is its size; the activity of the catalyst should be high in the temperature range of diesel exhaust gases.

These demands could not be met by using commercial vanadium type catalysts, which are applied in large scale deNO\textsubscript{x} units of power stations. The temperature window, 300-450°C, in which these catalysts are operated does not match the temperature range of diesel exhaust gases, 100-600°C. This range can be narrowed since temperatures above 550°C do rarely occur and temperatures below 300°C do not contribute much to the NO\textsubscript{x} output (section 2.2.1). The resulting temperature window has still a large high temperature region, which is not covered by commercial vanadium type catalysts. Therefore, catalyst testing of home-made zeolite and vanadium type catalysts has been performed as well (Chapter 3).

The development of the urea injection system has been undertaken simultaneously. This system has been tested on a small diesel engine (Chapter 4 and 5). Furthermore, process modelling and control of the system has been performed (Chapter 6). This thesis is concluded with some recommendations for future research to comply with the demands stated.

Catalyst development and testing

For catalyst testing two experimental setups have been built. The first one is a catalyst screening setup to test the activity of catalysts for the SCR reaction and SO\textsubscript{2} oxidation. The second one is a test bench to test the most promising catalysts with diesel exhaust gases. Home-made zeolite type catalysts and also commercial vanadium type catalysts have been tested. Catalysts that showed a high activity in diesel exhaust gases (Cu mordenite and \textit{V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}/WO\textsubscript{3}}), did show an undesirable SO\textsubscript{2} oxidation above 400°C. Furthermore, the deNO\textsubscript{x} activity drops at temperatures above 450°C due to ammonia oxidation.
It is shown that a newly developed Cerium mordenite catalyst has a high SCR activity above 400°C without oxidizing SO₂ to SO₃. Furthermore, the oxidation of NH₃ yields N₂ rather than NO. This allows the system to be operated with a small overdose of ammonia, thereby reducing the control problem considerably. However, its activity in the temperature region of 300-400°C is somewhat too low. Until now, this Cerium catalyst can only be used in high temperature applications or in combination with other compounds (e.g. copper).

Development of the urea injection system

In large scale SCR units ammonia is applied as the selective reacting component. The main reason for using urea in a small scale transient application is safety. Ammonia is a poisonous gas, which is stored under pressure.

A urea injection system has been developed and it is shown that urea reacts similar as ammonia. Prerequisite is that the temperature at the point of injection and urea decomposition is high enough (>300°C). No significant amount of byproducts has been detected (N₂O nor urea condensation products). However, before large scale application can be realized, some additional tests are recommended; the analytic procedures needed are described in Chapter four.

The urea injection system consists of an air blast nozzle equipped with an insulation cap to prevent byproduct formation on the cold nozzle surface. This nozzle is mounted on top of a reactor containing a static mixer and two catalytic monoliths (V₂O₅/TiO₂/WO₃ type). This setup has been tested behind a diesel engine successfully. Between 270-450°C the steady state SCR activity while using low sulphur (<10 ppm) diesel fuel or a 0.14 weight percent sulphur diesel fuel is comparable. A satisfactory NOₓ reduction performance, 70 percent at 300°C without ammonia slip, is obtained at a space velocity of 5000 h⁻¹. Higher space velocities, 15000 h⁻¹, lead at 270°C to insufficient NOₓ reduction and substantial ammonia slip. This 70% conversion level can be reached at higher temperatures; however some NH₃ slip remains. Therefore, space velocities which can be used for application of this process on a heavy duty diesel engine, are expected to be between 5000-15000h⁻¹.

Process modelling

The dynamic SCR reaction, of the V₂O₅/TiO₂/WO₃ catalyst used, has been modelled up to implementing the non steady state diffusion of NO and NH₃ in the porous catalyst layer (the washcoat, section 6.1.4). The dynamic behaviour depends mainly on the amount of ammonia adsorbed on the catalyst surface: the ammonia buffer. This buffer is a complex function of temperature, urea/NO inlet ratio, activity of the catalyst, exhaust gas flow and other adsorbing components. Therefore, the ammonia adsorption characteristics have been investigated (section 6.2.1) by measuring NH₃ breakthrough curves in air. There appear to be at least two adsorption sites for NH₃, one reversible and one irreversible. Literature review and additional measurements hinted at more complex processes in the presence of NO. More research is needed to unravel the precise role of these ammonia adsorption sites.

To interpret the dynamic measurements with diesel exhaust gases an additional simple model has been developed (section 6.1.2). It consists of only one ordinary differential equation. The main assumptions are ideal hydrodynamics (plug flow) and the kinetics are simplified to first order in NO and zero order in NH₃. As input parameters it needs the reaction rate constant and the ammonia buffer. This model predicts the dynamic behaviour qualitatively well and therefore might be used in future more complex control configurations. Of course, this is only valid at the operating conditions for which the input parameters (e.g. ammonia buffer) have been determined.
Process control

The most straightforward way to control this process is to measure the NO\textsubscript{x} output and adjust the urea injection rate accordingly. However, cheap, fast and accurate NO\textsubscript{x} analysers are not available (yet). In this study a chemiluminescence NO\textsubscript{x} analyser has been used (response time 10 seconds). Even with such an analyser timing problems occurred at high NO\textsubscript{x} conversions (using a PID control algorithm) with ammonia slip as a result.

In practice, the NO\textsubscript{x} output of the engine can be estimated on basis of other more easily measured variables (e.g. engine load and speed). If it is possible to predict this NO\textsubscript{x} output accurately, an open loop control system is the most appropriate control system. In such a control system, the urea dosage rate should be coupled to this prediction. For the diesel engine used in this study deviations of up to 30 percent occurred. Therefore, the conversions obtained with such a control system were limited (70 percent maximum). It is noted that this prediction might be improved by using more variables than the engine load and exhaust gas flow only.

As it was not possible (in this study) to predict the NO\textsubscript{x} output of the engine accurately, the NO\textsubscript{x} analyser has been employed also. By measuring the NO\textsubscript{x} concentration after the catalyst, the urea injection rate could be corrected for errors in this prediction. It is noted that in such a case the demands for an optional NO\textsubscript{x} sensor are less stringent as it is only used to correct for biases.

If (e.g. due to temperature transients) ammonia slip is unavoidable an oxidation catalyst can be applied to eliminate this slip. Furthermore, as there is no danger of ammonia slip, an open loop control system can be applied for the urea dosage. Such a configuration has been tested as well. A vanadium based catalyst was applied on top of a Pd oxidation catalyst. Eighty percent NO\textsubscript{x} reduction could be achieved easily (378°C, 7000 hr\textsuperscript{-1}) using an overdoses of 10-20 percent ammonia equivalents without NH\textsubscript{3} slip. Variations in the inlet NO\textsubscript{x} level of up to 100 ppm (25% relative) led to a change in NO\textsubscript{x} outlet of 10 ppm only (no NH\textsubscript{3} slip).

A drawback of using an oxidation catalyst might be the excessive sulphate production at higher temperatures. In the experiments conducted with the Pd oxidation catalyst this effect was not relevant as a very low (< 10 ppm) sulphur fuel was applied. This excessive sulphate production, when using a 0.05 weight percent sulphur diesel fuel, can be avoided using the newly developed cerium catalyst.

Summary
## Contents

### Summary

i

### Contents

iv

### Notation

vii

1 Introduction

1.1 Why diesel DeNO\textsubscript{X} ing?  
1.2 Legislation for heavy duty diesel engines  
1.3 Goal project and outline thesis  

2 Diesel exhaust NO\textsubscript{x} formation and abatement

2.1 Diesel DeNO\textsubscript{X} ing literature

2.1.1 Primary measures

2.1.1.1 NO\textsubscript{x} formation in diesel engines  
2.1.1.2 NO\textsubscript{x}/particulate and fuel consumption trade off  
2.1.1.3 Engine modifications  
2.1.1.4 Fuel modifications  

2.1.2 Secondary measures

2.1.2.1 Catalytic decomposition of NO  
2.1.2.2 Three way catalysis or N(S)CR  
2.1.2.3 Selective Non-Catalytic Reduction  
2.1.2.4 SCR catalysis with HC type reductant  
2.1.2.5 SCR catalysis with NH\textsubscript{3} type reductant  

2.1.3 SCR in diesel exhaust

2.1.3.1 Literature data of SCR in diesel exhaust  
2.1.3.2 Logistic aspects of using urea  

2.2 System considerations

2.2.1 Temperature range  
2.2.2 Space velocities  
2.2.3 Sulphur compounds in diesel fuel  
2.2.4 Byproduct formation and process safety

2.2.4.1 Urea decomposition products  
2.2.4.2 NH\textsubscript{3} slip  
2.2.4.3 N\textsubscript{2}O formation  
2.2.4.4 N-Nitroso compounds  

2.3 Summary

30
3 Catalyst testing
  3.1 Introduction 37
  3.2 Experimental facilities for testing catalysts 39
    3.2.1 Catalyst screening setup 39
      3.2.1.1 Equipment 39
      3.2.1.2 Catalysts tested 40
      3.2.1.3 Experimental procedures 42
    3.2.2 Test bench 45
      3.2.2.1 Equipment 45
      3.2.2.2 Catalysts tested 47
      3.2.2.3 Experimental procedures 48
  3.3 Transport phenomena in steady state fixed bed reactors 50
    3.3.1 Introduction 50
    3.3.2 Hydrodynamics of the reactor system 50
    3.3.3 External and internal mass transfer 54
  3.4 Catalyst testing 59
    3.4.1 Home made zeolite type catalysts 59
      3.4.1.1 Screening of zeolite type catalyst 59
      3.4.1.2 Testing with diesel exhaust 64
      3.4.1.3 Study on CeNa-Mordenite 65
    3.4.2 Vanadium type catalysts 71
      3.4.2.1 Lab scale study of DN32 & DN 110 71
      3.4.2.2 Testing with diesel exhaust 72
      3.4.2.3 Study on DN 32 and DN 110 72
    3.4.3 Comparison commercial/home made catalysts 75
  3.5 Summary 76

4 Development of a urea injection system 79
  4.1 Why injection 79
  4.2 Equipment 81
    4.2.1 Pilot-scale experimental setup 81
    4.2.2 HPLC analysis of urea decomposition byproducts 82
  4.3 Selection of nozzle type 83
  4.4 Reduction of byproduct formation 88
  4.5 Comparison urea and ammonia injection 90
  4.6 Concluding remarks 91
5 Diesel engine tests, urea injection on a 0.4l DI diesel engine
  5.1 Equipment
    5.1.1 The emissions of a Yanmar L90E diesel generator set
    5.1.2 Experimental setup
  5.2 Steady state experiments
    5.2.1 Stationary NO\textsubscript{x} production
    5.2.2 Injection of ammonia in the inlet air of the diesel engine
    5.2.3 NO\textsubscript{x} removal performance of the urea injection setup
  5.3 Dynamic experiments
    5.3.1 Response to changes in urea flow rate
    5.3.2 Response to changes in exhaust gas flow rate
    5.3.3 Response to changes in load
  5.4 Summary

6 Modelling of the SCR reaction and urea injection control
  6.1 Process modelling - theory
    6.1.1 Reaction mechanisms & kinetics of the SCR reaction
    6.1.2 Front model
    6.1.3 Tanks in Series model
      6.1.3.1 Basic equations TIS model
      6.1.3.2 Comparison of the TIS with front model
      6.1.3.3 Further modelling
    6.1.4 Diffusion models
    6.1.5 Summary
  6.2 Process modelling - validation
    6.2.1 Ammonia adsorption behaviour in model gases
    6.2.2 SCR reaction in model gases
    6.2.3 SCR reaction in diesel exhaust
    6.2.4 Summary
  6.3 Process control
    6.3.1 Introduction
    6.3.2 Control experiments
    6.3.3 The application of an oxidation catalyst
    6.3.4 Summary

7 Future outlook

Appendices
  1 DN32 structural and kinetic data
  2 Derivations
  3 Calculations with the extended TIS-models

Samenvatting
Dankwoord
Curriculum Vitae

Contents
Notation

Abbreviations

A-F  Air - Fuel
ACEA  Association des Constructeurs European d'Automobiles
AFR  Air to Fuel Ratio (by mass)
Cert  Certified
CSTR  Continuous-Stirred Tank Reactor
DI  Direct Injection
ECE 49  United Nations Economic Commission for Europe (regulation R49)
EGR  Exhaust Gas Recirculation
FBC  Fluidised Bed Combustor
FIE  Fuel Injection Equipment
FS  Full Scale
GC-ECD  Gas Chromatography-Electron Capture Detector
GHSV  Gas Hourly Space Velocity (at STP)
HC  Hydrocarbon
HD  Heavy Duty (ECE 49; gross vehicle weight over 3.5t)
HPLC  High Performance Liquid Chromatography
IDI  Indirect Injection
IRC  Injection Rate Control
MIPAN  Microwave Process Analyser
MOR  Mordenite
NA  Naturally Aspirated
NDIR  Non-Dispersive Infra-Red
NEO  National Environmental Outlook
NEPP  National Environmental Protection Plan
N(S)CR  Non-Selective Catalytic Reduction
PAN  PeroxyacetylNitrate
Part  Particulate
SCR  Selective Catalytic Reduction
SNCR  Selective Non-Catalytic Reduction
SS  Stainless Steel
STP  Standard Temperature and Pressure (0°C, 101325 Pa)
SV  Space Velocity (usually GHSV; exhaust gas flow (at STP) divided by catalyst volume)
TC  Turbo Charged
TNO-MEL  Dutch Institute for Industrial Research, section Motor Emission Laboratory
US FTP  United States Federal Test Procedure
UV  Ultra-Violet
VROM  Dutch Ministry of Housing, Physical Planning and the Environment
Symbols

\[ a_v \] volumetric interface surface area \[ \text{m}^2, \text{m}^{-3}\]
\[ A \] the area of the monolith channel \[ \text{m}^2, \text{m}^{-3}\]
\[ \text{Bo} \] Bodenstein number \[-\]
\[ C \] concentration \[ \text{mol m}^{-3}\]
\[ \text{Ca} \] Carberry number \[-\]
\[ C_i \] concentration at the interface \[ \text{mol m}^{-3}\]
\[ C_{\text{NH3/site}} \] concentration of amine sites \[ \text{mol/m}^3\]
\[ C_{\text{NH3}} \] ammonia concentration \[ \text{mol/m}^3\]
\[ C_{\text{NO}} \] NO concentration \[ \text{mol/m}^3\]
\[ C_{\text{site}} \] concentration of sites \[ \text{mol/m}^3_{\text{r or w}}\]
\[ C_{X,0} \] the concentration at the surface of the washcoat \[ \text{mol/m}^3\]
\[ d_c \text{ or } d_{\text{cell}} \] diameter channel \[ \text{m}\]
\[ d_{\text{chan}} \] diameter open area \[ \text{m}\]
\[ d_h \] hydraulic diameter \[ \text{m}\]
\[ d_p \] particle diameter \[ \text{m}_p\]
\[ D \] diameter droplet \[ \text{m}\]
\[ D_{\text{ax}} \] axial dispersion coefficient \[ \text{m}^3 \text{g}^{-1} \text{s}^{-1}\]
\[ D_e \text{ or } D_{\text{eff}} \] effective diffusion coefficient \[ \text{m}^3 \text{g}^{-1} \text{s}^{-1}\]
\[ D_g \] gas phase diffusion coefficient \[ \text{m}^2 \text{s}^{-1}\]
\[ D_{\text{knud}} \] Knudsen diffusion coefficient \[ \text{m}^2 \text{s}^{-1}\]
\[ E_a \] activation energy \[ \text{J/mol}\]
\[ h_{\text{cord}} \] average corderite wall thickness \[ \text{m}\]
\[ h_{\text{wash}} \] average washcoat thickness \[ \text{m}\]
\[ j_d \] j-factor for mass transfer \[-\]
\[ J \] the molar flux in the washcoat \[ \text{mol/m}^2 \text{s\} or [1/s}\]
\[ k \] reaction rate constant \[ \text{m}^3 \text{g}^{-1} \text{s}^{-1}\]
\[ k_0 \] pre exponential factor \[ \text{mol/m}^2 \text{s}\]
\[ k_{\text{ads}} \] adsorption rate constant \[ \text{1/s}\]
\[ k_{\text{des}} \] desorption rate constant \[ \text{mol/m}^2 \text{s}\]
\[ k_f \] mass transfer coefficient \[ \text{m}^2 \text{s}^{-1}\]
\[ k_m \] the mass transfer coefficient \[ \text{mol/m}^2 \text{s}\]
\[ k_{\text{NO}} \] reaction rate constant \[ \text{mol/m}^3\]
\[ K_{\text{NH3}} \] equilibrium constant ammonia \[ \text{mol/m}^3\]
\[ K_{\text{NO}} \] equilibrium constant NO \[ \text{mol/m}^3\]
\[ L \] length channel \[ \text{m}\]
\[ L_b \] length bed \[ \text{m}\]
\[ M \] molar mass \[ \text{kg mol}^{-1}\]
\[ N \] Number of Tanks in Series \[ \text{#}\]
\[ n \] reaction order \[-\]
\[ P_0 \] \[ \text{Pa}\]
\[ P_{\text{ex}} \] axial Peclet number \[-\]
\[ Q_i \] total concentration of sites \[ \text{mol/m}^3\]
\[ - \text{NH3} \] reaction rate ammonia \[ \text{mol/m}^3, \text{s}\]
\[ - \text{NO} \] reaction rate NO \[ \text{mol/m}^3, \text{s}\]
\[ r_{\text{N}} \] formation rate \[ \text{mol/m}^3, \text{s}\]
\[ r_{\text{obs, p}} \] observed reaction rate \[ \text{mol/m}^3, \text{s}\]
\[ r_{\text{pore}} \] average pore radius \[ \text{m}\]

Notation
- $r_{spe}$ reaction rate sites  
R gas constant  
$R_e_g$ particle Reynolds number  
$S_{BET}$ BET surface area  
Sc Schmidt number  
Sh Scherwood number  
t time  
t$_{c}$ life time droplet  
t$_{st}$ stoichiometric time  
T absolute temperature  
$T_0$ 273  
$T_d$ wet-bulb temperature droplet  
$T_g$ temperature gas phase  
u the linear gas phase velocity  
u$_g$ superficial gas velocity  
v$_c$ gas phase velocity in a channel  
v$_g$ interstitial gas velocity  
V volume reactor  
V$_{bed}$ volume of all tanks  
V$_g$ volume gas in one tank  
V$_{pore}$ pore volume  
V$_r$ total volume reactor  
V$_t$ volume of one tank  
x distance from the wall  
Y$_{NOin}$ dimensionless tank inlet NO concentration  
Y$_{NH3in}$ dimensionless tank inlet NH$_3$ concentration  
z position front (C6) or entrance region (C3)  

$\Delta H_{vap}$ latent heat  
$\Delta P$ the pressure drop  
$\epsilon_b$ porosity bed  
$\epsilon_{cord}$ porosity cordierite  
$\epsilon_{mono}$ porosity/void monolith  
$\epsilon_p$ porosity particle  
$\epsilon_{wash}$ porosity washcoat  
$\eta_e$ efficiency catalyst  
$\eta_g$ gas phase viscosity  
$\theta$ fraction of empty sites  
$\Theta$ dimensionless time  
$\lambda_e$ effective evaporation constant  
$\lambda_g$ thermal conductivity of the gas phase  
$\lambda_{st}$ steady state evaporation constant  
$\rho$ density droplet  
$\rho_g$ density gas phase  
$\sigma$ the perimeter length of the monolith channel  
$\xi$ conversion  
$\tau$ residence time  
$\tau_p$ tortuosity factor  
$\Phi$ Weisz modulus  

Notation
\( \phi \)  
Thiele modulus  
[-]

\( \varphi_v \)  
flow rate  
\( [\text{m}^3_{\text{g}} \text{ s}^{-1}] \)

Subscripts

\( \text{ax} \)  
axial

\( b \)  
bed volume

\( c \)  
channel

\( g \)  
gas phase

\( i \)  
interface

\( p \)  
particle

\( r \)  
reactor volume

\( \text{ref} \)  
reference

\( v \)  
volume

Note that the units of concentration, porosity, etc., vary in this thesis (e.g. a concentration might be in mol/m\(^3\)\(_{\text{reactor}}\) or mol/m\(^3\)\(_{\text{gas}}\)).
Chapter 1

Introduction

Mid 1990 the Delft project "Catalytic Removal of Soot and NOx from diesel exhaust gases" was started. This project was sponsored by VROM (the Dutch Ministry of Housing, Physical Planning and the Environment). The goal of this project is to contribute to the development of a catalytic aftertreatment device to remove Soot and NOx from diesel exhaust gases. This thesis is performed on the NOx removal part of the project.

1.1 Why diesel deNOx-ing?

This section will provide a short overview about the emission of nitrogen oxides in the Netherlands: its health and environmental effects, main emission sources, past and expected emission trends and air quality standards. Especially, the role of diesel engine sources will be highlighted. The problem of NOx emission is especially important in the Netherlands because of the high population density. This has led to one of the highest NOx emissions per square kilometre in western Europe\(^{1,2}\).

Nitrogen oxides have an effect on the ecosystem and on general health. Emission is generally over 90 percent in the form of NO. This is oxidized to NO\(_2\) by ozone (Table 1.1, reaction 4) or by photochemically generated peroxy radicals in the atmosphere (Table 1.1, reaction 8). The so formed nitrogen dioxide causes acid deposition, reacts to peroxyacetyl nitrates (PAN's) and can even form ozone photochemically (Table 1.1, reaction 3). This depletion and formation of ozone, see also Table 1.1, hints at the complex task of researchers trying to correlate health effects to concentration of this type of pollutants. In general, the combination of NOx and hydrocarbons leads to photochemical smog formation.

\textit{Table 1.1: Some of the reactions involved in photochemical smog formation}\(^{3,4}\).

\begin{verbatim}
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>Reagents</th>
<th>(\lambda) (\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(O_3 + hv)</td>
<td>(O_2 + O(3P))</td>
<td>(hv &lt; 610) (\lambda)</td>
<td></td>
</tr>
<tr>
<td>(O(3P) + O_2 + M)</td>
<td>(O_3 + M)</td>
<td>(1.2)</td>
<td></td>
</tr>
<tr>
<td>(NO_2 + hv)</td>
<td>(NO + O(3P))</td>
<td>(hv &lt; 430) (\lambda)</td>
<td></td>
</tr>
<tr>
<td>(NO + O_3)</td>
<td>(NO_2 + O_2)</td>
<td>(1.4)</td>
<td></td>
</tr>
</tbody>
</table>

Production of \(NO_2\) and \(O_3\) (reaction 3) by peroxy radicals

\(O_3 + hv\) | \(O_2 + O(1D)\) | \(hv < 310\) \(\lambda\) |
\(O(1D) + H_2O\) | \(2 OH\) | \(1.6\) |
\(OH + CO, organic\) | \(HO_2, RO_2, RCO_3\) | \(1.7\) |
\(HO_2, RO_2, RCO_3 + NO\) | \(NO_2 + OH, RO, RO_2\) | \(1.8\) |

Termination

\(OH + NO_2\) | \(HNO_3\) | \(1.9\) |
\end{verbatim}

Chapter 1
In the Netherlands, air quality standards for NO₂ (Table 1.2) are guidelines and do not have the power of law. NOₓ, especially NO₂, is strongly irritating and can damage cell structures, which may lead to lung afflictions. The photochemical pollution (ozone and PAN’s), is considered the main health hazard during summer smog periods. It is noted though, that reports are still being published in which health effects of NO₂ below the guidelines in Table 1.2 are suspected.

About 25 percent of the total acidification in the Netherlands is caused by NO₃ deposition. The main contributor to this NO₃ emission is traffic, for which values are reported of about 70 percent. This emission is divided in emission from cars (usually gasoline, for 1989 about 43%), trucks (34%, usually diesel engine) and other (23%). The past and expected trends and goals set by the government with respect to these emissions are shown in Table 1.3.

<table>
<thead>
<tr>
<th>NEPP</th>
<th>NEO</th>
<th>NEPP* objective</th>
<th>NEO* estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>cars</td>
<td>160</td>
<td>160</td>
<td>40</td>
</tr>
<tr>
<td>trucks</td>
<td>112</td>
<td>124</td>
<td>72</td>
</tr>
<tr>
<td>other</td>
<td>58</td>
<td>85</td>
<td>46</td>
</tr>
</tbody>
</table>

* NEO is the National Environmental Outlook, these are the predictions based on current measures and the NEPP is the National Environmental Protection Plan as stated by VROM.

These observations illustrate the need for further reduction of heavy duty diesel emissions (mainly trucks, see also section 1.2). Comparing diesel with otto engine emissions, Figure 1.1, the diesel is a relative clean engine concerning hydrocarbon, CO and NOₓ emission. However, particulate emission is much higher and so is NOₓ emission compared with otto engines equipped with three-way catalysts. It is expected that, by technical improvements, the NOₓ emission of a truck will be reduced significantly in 2010 (about 50%). However, the expected increase in transportation will almost negate this effect causing the goals for 2000 and 2010 to be not reachable without technological breakthroughs or changes in current policies. The main conclusion is that the relative contribution of the diesel engine to the total NOₓ emission is rising because of the increased availability of three-way catalysts for otto engines and the lack of similarly effective NOₓ-reduction measures for diesel engines.
1.2 Legislation for heavy duty diesel engines

In this paragraph the expected and current emission standards (of \( \text{NO}_x \), CO, HC and particulate) will be covered. These emission standards are to be met over a standardized test procedure, a test cycle. The most important test cycles for diesel engines, the European steady state 13 mode test and the US FTP transient cycle, will be discussed briefly. The purpose of this paragraph is to obtain an estimate about how much \( \text{NO}_x \) reduction is required by the de\( \text{NO}_x \)ing process to be developed.

The main contributor with respect to the diesel \( \text{NO}_x \) emission within the Netherlands and in Germany\(^5\) is the heavy duty engine (about 70%). Most of the literature published on lowering the \( \text{NO}_x \) output is aimed at the 95/96 Euro 2 limits of 7 g/kWh (Table 1.4). At the time of this literature, the diesel engines were running somewhere between 12 and 18 g/kWh. Limits of 5-6 g/kWh are in this stage under discussion yet, but it is anticipated that in a decade or so the direct injected heavy duty diesel engine has to run at 2-3 g/kWh\(^8\).

*Figure 1.1: Emissions of Otto engines with and without catalyst compared to Diesel\(^{23}\).*

Table 1.4: Current and expected emission trends for the European 13 Mode test\(^{13,14}\)

<table>
<thead>
<tr>
<th></th>
<th>Euro 1</th>
<th>Euro 2</th>
<th>Euro 3 under discussion</th>
<th>ACEA* proposed Euro 3</th>
<th>Euro 4 anticipated</th>
</tr>
</thead>
<tbody>
<tr>
<td>legislation</td>
<td>92/93</td>
<td>95/96</td>
<td>98/99</td>
<td>98/99</td>
<td>2003</td>
</tr>
<tr>
<td>tax incentive</td>
<td></td>
<td></td>
<td>95/96</td>
<td></td>
<td>end 90s</td>
</tr>
<tr>
<td>( \text{NO}_x ) (g/kWh)</td>
<td>8</td>
<td>7</td>
<td>4(^*)</td>
<td>5.5</td>
<td>2-3</td>
</tr>
<tr>
<td>( \text{HC} ) (g/kWh)</td>
<td>1.1</td>
<td>1.1</td>
<td>0.6</td>
<td>0.75</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>( \text{CO} ) (g/kWh)</td>
<td>4.5</td>
<td>4</td>
<td>2</td>
<td>2.3</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>PM(^{***} &gt; 80 ) kW (g/kWh)</td>
<td>0.36</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Representing the Industry

** sometimes the aim is 2.5 (Notably the Netherlands)

*** Particulate Matter

The European heavy duty exhaust emission test procedure (ECE 49) was developed for medium and heavy duty diesel engines operating in Europe. It is based on the obsolete US 13-mode procedure (1973-1984) corrected for the different European driving patterns. It is essentially a steady state test in which each of the 13 points is measured for about five minutes. In combination with some weighting factors the final output is calculated. For the original US test different weighting factors and distribution of loads were applied. The main
effect is a reduction of the measured hydrocarbons but an increase in the measured NOx and CO. The 13 test points and weighting factors are displayed in the load-speed diagram (Figure 1.2a).

![Load-Speed Diagram](image)

**Figure 1.2a: European 13 mode test**

The US transient test (Figure 1.2b) was introduced in 1984 and became mandatory in 1985, replacing the 13-mode steady state test. The reasons for moving to a transient cycle were to make the test more representative for urban and metropolitan conditions. The engine is tested over the full range of load and speed and run with a cold and a hot start. The emphasis of the test is on urban driving since the US air quality problem is most acute in major cities. The cycle is therefore not typical for average driving in either the US or Europe. As a result comparison between US (Table 1.5) and European limits is difficult. The concern for air quality in cities is reflected by the relatively enormous restriction on particulate emission from buses.

**Table 1.5: Expected emission trends measured over the US HD Transient cycle (g/kWh)**

<table>
<thead>
<tr>
<th>Year</th>
<th>NOx</th>
<th>HC</th>
<th>CO</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1994</td>
<td>6.7</td>
<td>1.75</td>
<td>20</td>
<td>1.35</td>
</tr>
<tr>
<td>1994 Bus</td>
<td>6.7</td>
<td>1.75</td>
<td>20</td>
<td>0.067</td>
</tr>
<tr>
<td>1998</td>
<td>5.3</td>
<td>1.75</td>
<td>20</td>
<td>1.35</td>
</tr>
<tr>
<td>1998 Bus</td>
<td>5.3</td>
<td>1.75</td>
<td>20</td>
<td>0.067</td>
</tr>
</tbody>
</table>

Latest engine technology allows heavy duty diesel trucks to run at 7 g/kWh. The long term objective for a catalytic aftertreatment device will be in the order of the 2-3 g/kWh. This means a reduction of about 70 percent.
1.3 Goal project and outline thesis

goal project

In the last decades the environmental awareness has led to several measures to lower emissions of harmful gases. One of the best known measures is the use of the three-way catalyst for automotive purposes. In the Netherlands, under influence of tax incentives on the national level and EC rule, many new cars have been equipped with catalysts and it is expected that over the years the share of the emissions caused by gasoline cars will decrease significantly.\(^7,16\)

With this decrease in emission of gasoline cars, the other major automotive source, the diesel engine, comes into focus. Unfortunately, due to the excess amount of \(O_2\) present, a three-way catalyst cannot be used in diesel exhaust gases (section 2.1.2.2). It is questionable, whether it will be possible to reach expected future legislation goals with engine modifications alone. It is anticipated that, like in the case of gasoline cars, further reductions obtained with engine modifications are minor compared to the use of an aftertreatment system.

The technical challenge is to develop a technology to remove the two major pollutants from diesel exhaust: Soot and \(NO_x\). (Soot and aldehydes are responsible for the negative image of the diesel engine; soot is also suspected to be carcinogenic and mutagenic\(^17\.)\) Mid 1990 a project "Catalytic Removal of Soot and \(NO_x\) from diesel exhaust gases" was started. The goal of this project is to contribute to the development of a catalytic aftertreatment technology to remove soot and \(NO_x\) from diesel exhaust gases.

The project is divided into two parts: Soot removal and \(NO_x\) removal. The reason is that the research fields are in an essentially different state of development; the soot research focuses on the development of entirely new catalysts that can bring down the most important parameter: the soot ignition temperature. This parameter is not only a function of the catalyst formulation, soot composition, heat transfer, etc., but probably more crucially depends strongly on the contact between soot and catalyst. This new insight can lead to the development of new and better soot removal devices\(^24\).

\(NO_x\) removal focuses on the use of an existing technique, the Selective Catalytic Reduction of \(NO_x\) using ammonia, on a new application. This technique is being used extensively in Japan and Germany to de\(NO_x\) off gases of coal fuelled power stations\(^1\). Ammonia is injected in the exhaust stream and the gases are subsequently passed over a catalyst. Water and nitrogen are the reaction products formed. Also, applications for marine diesel engines are in use\(^18\).

The main drawback for application on vehicles and small scale non stationary processes is the use of ammonia. Therefore the choice is made to work with urea, which is virtually harmless and does not need to be stored under pressure. The use of urea has been demonstrated on a gas engine in previous research\(^19\), where urea was used as prills in a fixed bed reactor. This had to be translated to an injection of an aqueous urea solution. One of the challenges is to match the urea dosage rate to the \(NO_x\) production rate, which in turn, depends mainly on the power output. Too much urea/ammonia added leads to emission of ammonia, the so-called \(NH_3\) slip, a shortage leads to inadequate \(NO_x\) reduction.
Another challenge, closely related to the previous one, is the temperature range in which the system needs to work (also called temperature window). In power plants this is more or less a design variable and can be controlled in a relative small range (about 50°C). In non steady state diesel exhaust the temperature varies between 200 and 600°C; a catalyst should work in this range without giving side reactions or deactivation. Catalysts used in power plants are not flexible enough to meet these requirements and therefore research in this field has been started as well. In the last few years, interesting commercial catalyst formulations for diesel engine application have been developed\textsuperscript{12}. One of these formulations has been used to demonstrate the urea injection system on a small diesel engine.

\textit{scope thesis}

The research has been performed on the NO\textsubscript{x} part of the project "Catalytic Removal of Soot and NO\textsubscript{x} from diesel exhaust gases". The aim of this thesis is to contribute to the development of a catalytic aftertreatment device to remove NO\textsubscript{x} from diesel exhaust gases using the Selective Catalytic Reduction technique employing an aqueous urea solution.

The thesis covers two main topics: catalyst testing (Chapter 3) and development of a urea injection system (Chapter 4-6). Catalyst testing reports on the test facilities and procedures used to evaluate home-made and commercial catalysts on laboratory scale. Furthermore, results obtained with promising home-made and commercial catalysts are described.

The development of the urea injection system includes the selection of the nozzle type (Chapter 4), preliminary tests on a simple 4 kW diesel engine with urea injection (Chapter 5) and process control (Chapter 6). The engine tests were carried out with a commercial catalyst as it was not practical to use home-made catalyst. This part of the thesis shows that it is possible to remove NO\textsubscript{x} with urea injection. Furthermore, recommendations to design a more compact system are given and the reader is provided with several options for process control. Durability considerations, especially in view of the presence of particles in the exhaust gases, were beside the scope of this thesis.

\textit{structure thesis}

Chapter 2 gives a literature review about deNO\textsubscript{x}ing methods, why urea injection was chosen and what the consequences of this choice are. It also explains why research was started to develop catalysts especially for diesel exhaust gases. Furthermore, some fundamental restrictions are described and boundary conditions stated. The chapter is concluded with a summary, which lists all demands of the system.

In Chapter 3 the results of the catalyst development are reported. Catalyst preparation, characterisation and initial screening will be reported by Ito\textsuperscript{31}. Commercial and home-made catalysts have been tested with model gases, and some more promising catalysts also with diesel exhaust. The behaviour of two catalysts, a home-made Cerium ion exchanged zeolite and a commercial vanadium type catalyst especially for diesel exhaust, is studied in detail. The cerium catalyst is the best home-made catalyst so far, the vanadium catalyst has been used for the development of the urea injection system.
The urea injection system to be used for the 4 kW diesel engine is described in Chapter 4. It focuses on the type of nozzle used and how to prevent byproduct formation. The goal is to show that urea is as good as ammonia for removing NO\textsubscript{x} (but only when treated properly).

Combining the knowledge in Chapter 2-4 gives a system to test on a small 4 kW diesel engine (Chapter 5). Similar work on urea injection for gas engines can be found in work of De Niet\textsuperscript{20}. A commercial catalyst has been used to study the steady state performance of this system, the transient behaviour and the influence of fuel sulphur.

The next Chapter, process modelling and control, reports on the efforts to match the urea dosage rate to the NO\textsubscript{x} production rate of this small diesel engine. Steps in engine load and exhaust gas flow are modelled to understand the transient behaviour of the catalyst. Different types of control systems are studied to keep the NO\textsubscript{x} conversion on an adequate level without ammonia slip.

This thesis is concluded with an outlook (Chapter 7) on the applicability of SCR type aftertreatment devices using urea. It describes some of the research to be undertaken before such a system is feasible on a truck diesel engine.

Literature

10 Frischer, T., Studnicka, M., Beer, E. and Neumann, M., *The Effects of Ambient NO\textsubscript{x} on Lung Function in Primary Schoolchildren*, Environmental research 62 (1993), 179-188.

Chapter 1


22 Engler, B. and Brand, R., *Katalysatoren fuer den Umweltschutz*, DEGUSSA AG.


Chapter 2
Diesel exhaust NO_x formation and abatement,
a literature review

2.1 Diesel deNO_x ing literature

This section presents a short literature review about the status of diesel deNO_x ing and the pros and cons of the method used in this study. For information about nitrogen oxides in general the reader is referred to Kolar and for NO_x removal in the presence of oxygen in particular to Bosch. When cleaning combustion off gases, there are essentially two different ways of coping with emissions: prevention or off gas cleaning. In other words pre- or post combustion control. Usually, it is desirable and most cost effective to prevent harmful emissions by modifying the fuel and/or optimizing the combustion process. These primary measures will be highlighted in the first part of this section.

2.1.1 Primary measures

The primary measures are fuel and engine modifications. Before going into detail a summary of the sources of NO_x formation in diesel exhaust will be given. Also, the major technical problem in designing low NO_x diesel engines will be highlighted. Subsequently engine modifications and alternative fuels will be described.

2.1.1.1 NO_x formation in diesel engines

Nitrogen oxides in combustion flue gases consist usually of NO and to a lesser extent NO_2. The amount of NO_x for otto engines is about 1-5 percent (a three-way catalyst reduces this below 1 percent). For diesel engines running at low loads values of 10-40 percent are reported, which decrease to 2-20 percent at high loads. This means that the amount of NO_2 in diesel exhaust may not be negligible (< 10%) at low loads, contrary to the gases produced in most stationary combustion processes.

The formation of NO_x follows the formation of NO and usually in the exhaust gas system according to the (global) Bodenstein reaction:

\[ 2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \]  \hspace{1cm} (2.1)

The homogeneous reaction has a very typical temperature dependency; the reaction rate decreases with increasing temperature. This reaction is catalysed by any high surface area. In case of combustion engines Lerner expects a maximal reaction rate at 200-300°C. An additional source of NO_2 is the reaction between NO and HO_2 radicals, which is important for gas turbines.

NO formation in combustion flue gases has three sources: fuel, thermal and prompt NO. 

Fuel NO is formed out of the nitrogen components present in the fuel, which are oxidized in the flame front (oxidation zone). The main dependencies are the concentration of nitrogen compounds in the fuel and the oxygen concentration. The reactions are relatively
quick and already proceed below 800°C. A conversion factor can be defined which is the amount of NO formed divided by the amount of fuel nitrogen. This factor is usually in the range of 0.1-1 meaning that generally less NOx is found in the exhaust gases than there are nitrogen compounds present. The reason is that NO can also be reduced to nitrogen. The mechanism is quite complex involving reactions with NH2 and CN type intermediates.

In case of distillate diesel fuel the concentration of fuel nitrogen is in the order of 100 to 300 ppm and therefore fuel NO can be neglected in most cases. Only when burning heavy fuel oil, e.g. marine diesel applications, fuel NO can be important due to the high nitrogen content of the fuel (range 0.05-0.5 wt%).

The most important mechanism of NO formation in most technical combustion processes is the thermal oxidation of atmospheric nitrogen. According to the Zeldovich the reaction proceeds:

\[ O_2 + M \rightleftharpoons 2 O + M \]  \hspace{1cm} (2.2)

\[ N_2 + O \rightleftharpoons NO + N \]  \hspace{1cm} (2.3)

\[ N + O_2 \rightleftharpoons NO + O \]  \hspace{1cm} (2.4)

The reaction of atomic oxygen with nitrogen, reaction 2.3, is rate determining. In case of oxygen deficiency, in fuel rich flame zones, one of the reactions to be considered also is:

\[ N + OH \rightleftharpoons NO + H \]  \hspace{1cm} (2.5)

The reactions 2.2-2.5 are also known as the extended Zeldovich mechanism. To predict a real combustion process the number of reactions and equations increases drastically while phenomena like turbulence and diffusion should be incorporated, especially for diesel engines. However, with aid of modern computers attempts are made to model NO formation in such complex systems.

The reactions occur behind the flame front at temperatures above 1300°C and depend on residence time and oxygen concentration. However, reaction 2.4 is not fast enough to follow the thermodynamic equilibrium of nitrogen and oxygen with NO. The temperature during combustion rises drastically so that not enough NO is formed to reach equilibrium. During the subsequent cooling down period the NO concentration reaches equilibrium at a certain temperature level. But this cooling down is too fast for the reaction to follow and this equilibrium will be 'frozen'. At room temperature the decomposition rate of NO is negligible.

Therefore, to control the NO emission of a diesel engine one can vary the oxygen concentration, temperature and residence time in the reaction zone. As the reaction occurs close to the flame front, the NO formation depends on the conditions in this region. This means that, for example, the NO emission depends on peak temperature rather than on the average temperature in the cylinder.

The last type NO formation is prompt NO; formation of cyanides by the reaction of atmospheric nitrogen with hydrocarbon radicals in reducing atmosphere (in the flame front). These cyanides are subsequently partly burned to NO (like the fuel nitrogen compounds).
2.1.1.2 NOx/particulate and fuel consumption trade off

When the combustion temperature and/or oxygen concentration is decreased to reduce NOx emissions, one should keep in mind that the combustion efficiency will be lowered as well. This results in an increased fuel consumption. Furthermore, the soot emission, caused by cracking of the hydrocarbon molecules, can rise dramatically. This is known as the NOx/particulate trade off and imposes limits on the current diesel engine technology; see Figure 2.1. It is expected that reduction of soot emission, independently of the NOx formation, can be obtained by minimizing hydrocarbon cracking. This is usually achieved by improving the fuel injection. The fuel composition can also be improved reducing soot formation; it is even possible to use a low soot producing fuel, e.g. methanol, followed by conventional techniques to lower NOx emissions.

2.1.1.3 Engine modifications

An efficient technology to lower NOx emissions is to modify the engine. The goal of such a technique is to improve mixture formation, increase speed of combustion and reduce the temperature and residence time in the reaction zone. This can be achieved by optimizing the fuel injection and combustion chamber. Examples are retarded injection timing, high pressure injection and exhaust gas recirculation. Trade offs between NOx output and particulate emission/fuel consumption are likely to occur.

Retarded injection timing could be used to reach the European 7 g NOx/kWh demand. This however, results in an increase in fuel consumption of 6 to 8 percent. Another disadvantage is that the particulate emission usually increases. The introduction of improved fuel injection and combustion systems allows retarded injection timing without this fuel penalty. High pressure fuel injection is such a technique; the combustion is improved considerably. A NOx reduction of 30 percent is reported with an even larger reduction in particulates. The effect of such a modification is shown in Figure 2.2.

Chapter 2
Exhaust gas recirculation (EGR) is a technique with which the long term NO\textsubscript{x} emission standard of 2.5 g/kWh might be achieved\textsuperscript{28}. The principle is that the exhaust gases are partly recirculated, thus lowering the O\textsubscript{2} content. Furthermore the increase in CO\textsubscript{2} concentration reduces the peak combustion temperature due to its higher heat capacity. The latter effect is considered especially effective if the recirculating gases are cooled. Disadvantages lie in the engine and valve wear caused by recirculating gases\textsuperscript{28}. This is especially a problem with low quality fuels.

2.1.1.4 Fuel modifications

Fuel modifications are additions to the air/fuel mixture; this includes water emulsion, fumigation, mixing of diesel with other fuels up to using other fuels instead of standard diesel oil.

*Modifying standard diesel oil*

As the nitrogen content of the diesel fuel is usually low hydrotreating to remove these compounds do not lower NO\textsubscript{x} emissions significantly. Differences in NO\textsubscript{x} emissions using normal diesel fuels, or ones treated with a hydrotreating step to obtain 0.05 weight percent sulphur content, are minor\textsuperscript{17,18}. Only when using the Swedish very low sulphur fuel ( < 0.001 weight percent), which is obtained by high pressure hydrogenation, a ten percent NO\textsubscript{x} reduction was observed\textsuperscript{18,100}. However, this is attributed to a change in hydrocarbon structure\textsuperscript{18-20} instead of to a further denitrification of the fuel.

*Fuel additives*

Fuel additives can be sprayed in the inlet air or mixed with the diesel fuel itself. For example, Wachter\textsuperscript{12} showed that by spraying 20 weight percent water in the air inlet a direct NO\textsubscript{x} reduction of about 20 percent can be obtained. When emulsifying water in the diesel fuel, comparable results are obtained\textsuperscript{21}. This is caused by a lowering of the combustion temperature. Another option is to add methanol or ethanol\textsuperscript{14}; 10 to 30 percent of the energy can be replaced this way. The result is a NO\textsubscript{x} reduction of 10 to 20 percent without increase of other undesirable emissions (except of a two to threefold increase in aldehydes).

It is expected that with this type of methods the maximum reduction to be obtained will be about 30 percent\textsuperscript{15}.

*Alternative fuels*

An alternative fuel should have a lower peak temperature during combustion and contain no nitrogen compounds. Also should be kept in mind that some of such fuels, e.g. rape seed oil\textsuperscript{1}, result in an increased particulate emission. One of the intensively researched fuels is methanol\textsuperscript{16,23,24}. It is easy to produce on a large scale, the existing diesel distribution system can be used, the particulate emission is very low and it is relatively cheap. The major drawbacks are the low cetane number, the hygroscopic and the poisonous nature, the high latent heat (giving cold start problems) and some additional aldehyde emission. Needham\textsuperscript{3} demonstrated a diesel engine using this fuel running at a NO\textsubscript{x} output level of 5.3 g/kWh. An oxidation catalyst is needed to remove any unburned methanol or aldehydes.
Mixtures of propane and butane have been investigated\textsuperscript{25} also because of their particulate reducing properties. A NO\textsubscript{x} reduction of 30 percent can be obtained, but the CO and HC emission increase at least tenfold. In the near future the use of alternative fuels is not expected to be chosen because of the relatively low reductions obtained and infrastructural problems involved. Only in case particulate emission must be very low, e.g. city buses subjected to US legislation, this can be an option.

\textbf{Summary primary measures}

The techniques employed to reach the future emission standards are the engine modifications. The emphasis lies on improvement of the fuel injection (timing, rate control and high pressure) and the combustion chamber. EGR may be a feasible technology when considering a possible long term standard of 2.5 g/kWh\textsuperscript{26,16,21,29-31}. The others give a high fuel penalty and/or additional particulate emission and usually only a limited NO\textsubscript{x} reduction. For infrastructural reasons the use of alternative fuels on a large scale, e.g. methanol, is not very likely.

\textbf{2.1.2 Secondary measures}

This paragraph will give a short overview of methods for catalytic exhaust gas deNO\textsubscript{x}ing\textsuperscript{6,8}. In the last few years research has intensified in this area, some progress has been made in the field of NO decomposition. Furthermore, some catalysts have been found which reduce NO\textsubscript{x} selectively in the presence of O\textsubscript{2} with hydrocarbon (HC) type compounds.

\textbf{2.1.2.1 Catalytic decomposition of NO}

Reaction:

\[ 2 \text{NO} \rightarrow \text{N}_2 + \text{O}_2 \quad (2.6) \]

This is the most desirable reaction because no additional reducing agents are required. The underlying principle is that NO is thermodynamically unstable at room temperatures. However, nobody has found a practical catalyst yet. The main problem is the tendency of NO to interact with catalysts so that the strength of the NO bond increases. Furthermore, the reaction with oxygen to NO\textsubscript{2} is highly favoured at low temperatures.

There are some developments in this field; Iwamoto\textsuperscript{32-35} showed that copper ion exchanged ZSM-5 decomposes NO in the presence of O\textsubscript{2} at 500\textdegree C. The pathway is supposed to be\textsuperscript{35}:

\[ 2 \text{Cu}^{2+} \rightarrow 2 \text{Cu}^{+} + \text{O}_2 \text{ (elevated temperature)} \quad (2.7a) \]
\[ 2 \text{Cu}^{+} + 2 \text{NO} \rightarrow 2 \text{Cu}^{2+}.\text{NO}^- \quad (2.7b) \]
\[ 2 \text{Cu}^{2+}.\text{NO}^- \rightarrow 2 \text{Cu}^{+} + \text{N}_2 + \text{O}_2 \quad (2.7c) \]
The Cu\(^{2+}\)-NO\(^{-}\) complex plays a central role\(^{36}\). As stated by Van den Bleek\(^{37}\) this type of complex (a negative charge on the NO molecule) weakens the NO bond. Furthermore, the desorption of O\(_2\) (reaction 2.7a) is essential for the decomposition to occur. The activity of this catalyst is not high enough for practical applications yet (furthermore inhibition by oxygen\(^{38,39}\), water\(^{33}\) and poisoning by SO\(_2\)\(^{33}\) is reported).

2.1.2.2 Three-way catalysis or N(S)CR

The reduction of NO can be performed with a reducing agent like CO or a hydrocarbon, which is also called N(S)CR; Non-Selective Catalytic Reduction. This technique works only in (near) stoichiometric exhaust gases such as produced by otto engines. In the presence of O\(_2\) one needs to add enough reductant to convert all the O\(_2\), only then NO\(_x\) can be reduced. In some cases, e.g. for gas engine heat generation, the increase in fuel usage is acceptable because the produced heat can be used as well. Three-way catalyst equipped cars are usually provided with a \(\lambda\)-sensor, an oxygen measuring device, which enables the engine to run near stoichiometry; the so called \(\lambda\)-window, see Figure 2.3.

![\(\lambda\)-window](image)

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \\
2 \text{HC} + \frac{5}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} + 2 \text{CO}_2 \\
\text{NO} + \text{CO} & \rightarrow \frac{1}{2} \text{N}_2 + \text{CO}_2 \\
\end{align*}
\]

**Figure 2.3:** Performance of a three-way catalyst as a function of the air-fuel ratio\(^{56}\).

The main reactions occurring over a three-way catalyst are given in Table 2.1. The name 'three-way' catalyst describes the three functions of the catalyst (oxidation of CO, oxidation of hydrocarbons and reduction of NO) rather than the actual number of reactions taking place.
Table 2.1: Main chemical reactions in three-way catalysis

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction</td>
<td></td>
</tr>
<tr>
<td>2 NO + 2 CO → N₂ + 2 CO₂</td>
<td>(2.8)</td>
</tr>
<tr>
<td>2 NO + 2 H₂ → N₂ + 2 H₂O</td>
<td>(2.9)</td>
</tr>
<tr>
<td>2(m+n/4) NO + CₘHₙ → (m+n/4) N₂ + n/2 H₂O + m CO₂</td>
<td>(2.10)</td>
</tr>
<tr>
<td>Oxidation</td>
<td></td>
</tr>
<tr>
<td>2 CO + O₂ → 2 CO₂</td>
<td>(2.11)</td>
</tr>
<tr>
<td>CO + H₂O → CO₂ + H₂</td>
<td>(2.12)</td>
</tr>
<tr>
<td>2 CₘHₙ + (2m+n/2) O₂ → 2m CO₂ + n H₂O</td>
<td>(2.13)</td>
</tr>
<tr>
<td>CHₙ + 2 H₂O → CO₂ + (2+n/2) H₂</td>
<td>(2.14)</td>
</tr>
<tr>
<td>2 H₂ + O₂ → 2 H₂O</td>
<td>(2.15)</td>
</tr>
</tbody>
</table>

The reason that a three-way catalyst cannot be applied on a diesel engine is that such an engine always runs with an O₂ excess (the right side of Figure 2.3). Using a three-way catalyst will result in a rapid oxidation of hydrocarbons and CO. After this oxidation no reducing agents are present any more to react with the NOₓ. It is noted that the three-way catalyst also possesses some undesirable side effects; e.g. N₂O emissions increase significantly.²⁶

2.1.2.3 Selective Non-Catalytic Reduction (SNCR)

The main reaction is:

6 NO + 4 NH₃ → 5 N₂ + 6 H₂O                                             (2.16)

It is possible to convert NOₓ with a selective agent without using a catalyst. This technique is applied in fluidized bed combustors (FBC); NH₃ or urea is injected just above the fluidized bed’s fire zone and reductions of 70-80% can be obtained with a relative low investment. The temperature level needed for this reaction is in the range of 700 to 1100°C.²⁰-⁴² Unfortunately, the temperature of diesel exhaust gases is too low to apply this technique. However, this temperature level is reached only inside the combustion chamber: Lausch²¹ showed a substantial NOₓ reduction (50 percent) when applying in-cylinder NH₃ injection.

2.1.2.4 SCR catalysis with HC type reductant

Main reaction:

NO + HC/CO + O₂ → N₂ + CO₂ + H₂O                                      (2.17)

In the last few years much attention has been paid to selective NOₓ reduction by hydrocarbons in the presence of O₂. This technique is sometimes also being categorized as NSCR, because the same reducing agents are used. The catalyst development in this area is
much more promising than with catalytic decomposition. Especially over Cu zeolite type catalysts several components (e.g. C₂H₄, C₃H₆, C₅H₁₀) are suitable for selective reduction⁴³,⁴⁵,⁴⁷,⁴⁹ and even selective NOₓ reduction with methane has been reported⁵⁰ (Co zeolite).

For this type of reactions the presence of oxygen has a positive influence⁴⁸ which is attributed to the formation of NO₂ and an enhanced reaction with carbon rich species formed on the zeolite originating from the hydrocarbons⁵¹,⁵². Another mechanism, proposed for Pt based catalysts, is the formation of reduced patches over which NO can dissociate⁵³. At higher O₂ concentrations and temperatures the selectivity drops because of hydrocarbon oxidation. The main drawback is that only conversions up to 30 percent have been shown in diesel exhaust at relative low temperatures, even when a large excess of hydrocarbons⁵⁴,⁵⁵ is used. Diesel engine exhausts generally do not contain enough hydrocarbons to reduce all NOₓ. Therefore, higher conversion can only be obtained dosing a large excess of hydrocarbons.

2.1.2.5 SCR catalysis with NH₃ type reductant

Main reactions:

\[ 4 \text{ NO } + 4 \text{ NH}_3 + \text{ O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O} \]  
(2.18)

\[ 6 \text{ NO}_2 + 8 \text{ NH}_3 \rightarrow 7 \text{ N}_2 + 12 \text{ H}_2\text{O} \]  
(2.19)

This technique has been used extensively for stationary NOₓ reduction⁵⁶ and as such is the only catalytic technique which has been proved to be effective in the presence of O₂. Bosch and Janssen⁸ have made an extensive literature survey about SCR with ammonia to which the reader is referred. More than thousand catalyst formulations have been tested for this reaction, including noble metals (e.g. Pt, Pd), base metal oxide catalysts (e.g. V, Fe, Cu, Mn, Cr, Co, Ni), zeolites, carbons and lanthanides. The vanadium type catalysts are among the most versatile due to their high activity and resistance against sulphur poisoning. The vanadium type catalysts are usually supported on TiO₂ or Al₂O₃ and occasionally on SiO₂.

It is not possible to give a general reaction mechanism for all the catalysts used. However, for vanadium type catalysts, there is some consensus; see Figure 2.4. Crucial is the strong adsorption of ammonia. The nitrogen oxide reaction with this adsorbed complex is rate determining. The result is that such a system has a large ammonia buffer; it reacts relatively slowly onto changes in ammonia dosage. This is valid for most vanadium type catalysts and also for most zeolites, the latter possessing even a larger ammonia storage capacity.

*Figure 2.4: Mechanism of the NO/NH₃/O₂ reaction*⁷⁷.
The ammonia dosage is important for the performance of an SCR system. An overdose will lead eventually to the emission of ammonia, the so-called NH₃ slip, which is even less desirable than NOₓ emission. On the other hand a shortage does lead to inadequate NOₓ reduction. The stoichiometry of the reaction is one (reaction 2.18), but sometimes larger amounts of ammonia are needed due to the presence of NO₂ (reaction 2.19) or due to NH₃ oxidation. This oxidation occurs at higher temperatures (typically above 450°C):

\[4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O}\] (2.20)

\[4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O}\] (2.21)

Together with catalyst stability, which also starts to give problems above 450°C, this ammonia oxidation is responsible for the upper temperature limit.

At low temperatures the reaction rate is rather low. Especially in coal fired applications an additional problem is the formation of ammonium sulphates which block the activity of the catalyst below 300°C:

\[2 \text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3\] (2.22)

\[\text{SO}_3 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4\] (2.23)

\[\text{SO}_3 + 2 \text{NH}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4\] (2.24)

At higher temperatures (> 350°C) the sulphates are desorbed and cause corrosion and fouling of downstream equipment. A method to reduce undesirable SO₂ oxidation is to add oxidation inhibitors to the catalyst (e.g. WO₃). The exact temperature at which the catalyst is deactivated depends on the SO₂/SO₃ levels in exhaust gases and on the pore size distribution of the catalyst. Due to capillary condensation ammonium sulphates are found in catalyst structures at temperatures much higher than their decomposition temperature. Zeolites pose a special problem due to their very small pores.

Therefore, the temperature range (or temperature window) in which vanadium type catalysts can be used is 250-450°C. The lower temperature limit being determined by catalyst activity and ammonium sulphate formation and the upper limit by ammonia oxidation, sulphate formation and catalyst stability.

More than 250 coal fired electricity plants and several hundreds of industrial utility units have been equipped with an SCR deNOₓ system. The reactor configuration chosen depends mainly on the type of flue gas cleaned; usually a low pressure drop is desirable so most configurations use monoliths, honeycombs or plate type structures. When catalyst pellets are used they are packed in such a way to prevent plugging and/or excessive pressure drop (e.g. Parallel Passage Reactor, Lateral Flow Reactor).
A typical reactor configuration for high dust coal fired applications is shown in Figure 2.5. Such a system is usually designed to give 80 percent NO\textsubscript{x} reduction in a temperature range of 300-450\degree C with an ammonia slip smaller than 5 ppm, with a space velocity in the range of 1000-5000 h\textsuperscript{-1}. The catalyst consists of several layers of monolith elements with a typical size 15*15 cm and a height of 100 cm. The pitch or channel diameter depends on dust load and is chosen between 4 and 10 mm. Usually one dummy layer of hard ceramic material is installed to prevent the catalyst from being sand blasted.

The main disadvantage of using monoliths is the absence of radial dispersion; i.e. a maldistribution at the entrance will be continued through the whole reactor. This is, apart from the more practical points, a reason for using more than one layer of catalyst elements. Usually an SCR system is equipped with a multiple point ammonia injection system and, optionally, static mixers to ensure an optimal radial dispersion of ammonia. The typical lifetime of a standard vanadium type catalyst is 2-5 years depending on dust load and operating conditions (temperature, space velocity).

In power plant applications NH\textsubscript{3} is generally used as the reducing agent. It has been shown by van den Bleek et al\textsuperscript{[3]} that it is possible to use a range of other nitrogen containing compounds; e.g. urea, melamine and even nitrogen containing wastes. These compounds decompose upon heating in NH\textsubscript{3} and other reducing agents (usually HCNO), which can subsequently react with NO\textsubscript{x} according to reaction 2.18 and 2.19. For example, urea decomposes upon heating above 100\degree C into (see also section 2.2.4.1):

\[
\text{CO(NH}_2\text{)}_2 \rightarrow \text{NH}_3 + \text{HCNO} \tag{2.25}
\]

The resulting iso-cyanic-acid may react with water vapour in the exhaust gases:

\[
\text{HCNO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \tag{2.26}
\]

In principle one urea molecule gives two ammonia equivalents.

The main reason for using other N-containing compounds is safety; NH\textsubscript{3} is a poisonous gas and is stored under pressure.

Summary of secondary measures

The only catalytic technique which can be applied in diesel exhaust gases is SCR with an ammonia type reductant. The other techniques do not give enough reduction. Although this technique, SCR with ammonia type reductant, is the most promising one, there are some drawbacks which need to be overcome. These drawbacks are the low space velocity, narrow temperature window and large response times. The latter can cause troubles with the
ammonia dosage control, which is more difficult yet because of the absence of cheap sensors. Furthermore, the use of pressurized NH₃ is not acceptable in automotive applications. Consequently, another reducing agent has to be used.

2.1.3 SCR in diesel exhaust

Since SCR has been used for years in the abatement of NOₓ in the presence of oxygen, several authors have already tested SCR systems in diesel exhaust. This section will begin with testing data obtained from literature and describe the newest developments (up to 1993). Furthermore, some logistic aspects of the use of urea as an alternative for ammonia will be discussed.

2.1.3.1 Literature data of SCR in diesel exhaust

Up to 1990 most literature reports on stationary diesel engines, usually for electricity generation. Such units can be treated as small power plants which run at a high load. To abate NOₓ, a commercial SCR catalyst and injection system is placed in the exhaust, where temperature levels of 350-400°C are encountered. The catalytic process is even easier than with coal fired power plants because the exhaust gases are much cleaner (e.g. less dust). Complications arise when the engine is subjected to rapid load fluctuations because then the temperature and NOₓ output levels will also fluctuate significantly.

Lepperhoff³⁹ (1988) tested three catalysts on their behaviour in diesel exhaust (one standard vanadium and two zeolite type catalysts). He concluded that the technique is principally suitable to reduce NOₓ emissions. It was found that a temperature level of at least 300-350°C was necessary to maintain performance (<500 ppm NOₓ). Furthermore, because of cold starts, deactivation was found. In case of the zeolite catalyst dead times of nearly 20 minutes were encountered. The zeolite catalysts also showed mechanical defects after 1300 hours of operation.

Held⁶⁴,⁶⁰ (1990) demonstrated catalytic NOₓ reduction in a diesel powered car using urea. Cu-ZSM5 was used on a 1.9 l naturally aspirated diesel engine resulting in more than 50 percent reduction starting at 320°C. This temperature corresponds to a driving velocity of about 80 km/h. He concluded also that SCR offers a possible path of development, but several problems remain unsolved: the urea dosage/volume control, minimum catalyst working temperature regarding partial loads and the possibility of side reactions.

Koebel⁶¹ (1990) used an SCR system with urea and a V₂O₅/TiO₂ catalyst on a stationary diesel engine. The system worked in the temperature region of 270-400°C; at higher temperatures ammonia oxidation was detected. He also investigated byproduct formation (N₂O, HCN and HCNO) and the urea decomposition itself. He concluded that when dosing slightly sub stoichiometric no HCNO and HCN were found. Furthermore, the N₂O emission, which originated mostly from the diesel engine itself, was reduced over the catalyst.

Gibson⁶₂ (1991) reported an SCR deNOₓ system for marine applications (8 MW MAN B&W two stroke diesel engine). The system used pressurized ammonia to reach NOₓ levels of 100-150 ppm in coastal waters (about 90 percent reduction). The catalyst was placed before the turbocharger because of the temperature level needed (320-400°C). An additional advantage was the pressure being above atmospheric, resulting in a smaller volume for the catalyst. As mechanism to control the ammonia injection, a combined feedforward-feedback control system was used. The feedforward control was based on the relationship NOₓ/engine load measured in test bench. The feedback control was based on NOₓ outlet signal. This

Chapter 2
method was employed rather than feedback only to secure a more accurate control of the ammonia dosage. The system was shut off if the flue gas temperature dropped beneath 310-320°C which corresponded to an engine load of 20-25 percent.

Götalmalm (1991) and HUG (1993) proposed another system to remove NOx from marine diesel engine exhaust; application of SCR with urea in combination with an oxidation catalyst to remove any undesirable NH3 slip. By using urea they claimed NOx reductions of at least 90 percent at an equivalent fuel penalty of 3-4 percent. Because of the use of an oxidation catalyst, the dosage control was based entirely on engine mapping; a λ-number (defined as the NH3/NO ratio) was kept close to one. Space velocities mentioned were 15 000 - 25 000 hr⁻¹ for the SCR catalyst and 90 000 - 110 000 hr⁻¹ for the oxidation catalyst.

An elegant way to prevent the presence of a large pressurized vessel with ammonia is to make it in situ. Takiguchi (1992) proposed an engine configuration with fuel reformer, ammonia synthesizer and SCR catalyst.

Walker (1992) described an NH3-SCR system for a heavy duty natural gas engine. An 80 percent NOx reduction with minimal ammonia slip (< 2 ppm) was obtained based on engine mapping only on a modified hot EPA transient cycle. Exhaust temperatures were in the range of 285-600°C and therefore a zeolite type SCR catalyst was used.

Leppenhoff (1992, 1993) had updated his tests (from 1988) with more and newer catalysts. The V2O5/TiO2 type catalysts could be used between 250-450°C (> 90 percent reduction), zeolites performed well in the high temperature range (> 350°C). The response time of the catalysts depended on the catalyst type and of the temperature. A temperature increase caused the adsorbed ammonia (the ammonia buffer) to desorb, resulting in a significant ammonia slip (> 100 ppm). An oxidation catalyst could remove this ammonia slip but gave extremely high sulphate production above 400°C. Furthermore, it was noted that all catalysts tested started to oxidize SO2 above 350-400°C.

2.1.3.2 Logistic aspects of using urea

The main reason for using urea is safety. Also, it may be cheaper in use because it does not require pressurized storage equipment. The feasibility depends not only on the technical possibility of the operation but also on logistic aspects such as the urea production capacity. From Table 1.3, representing the total NOx emissions in the Netherlands, it can be concluded that about 10-100 kT NOx has to be removed annually. This means that about 10-100 kT of urea should be produced additionally. As the typical urea plant size is 400 kT a year, the urea production capacity will not be a limiting factor.

The second logistic aspect is the amount of urea needed per kg diesel used. A modern diesel engine runs at 7 g NOx/kWh and with a fuel consumption of 220 g diesel/kWh. Assuming 70 percent reduction, see section 1.2, and using a 40 weight percent urea solution, the additional volume needed is about 50 ml per litre diesel. The raw material costs will be 1-2 cents per litre diesel (assuming a urea price of 250 fl/T). The overall system costs will be determined by the complexity of the system, the amount of catalyst used and probably crucial the sensors and electronics to control the process.

Summary diesel deNOx ing literature

SCR with urea is the option with the best perspective for NOx reduction in diesel exhaust. The precise configuration (SCR with or without oxidation catalyst), type of catalyst (vanadium or zeolite type) and control system (engine mapping and/or feedback) depends on the type of diesel engine and fuel used. The main factors are the temperature level, the
transients encountered and the SO₂ content of the exhaust gases. Furthermore, the size of the engine is important because of the costs of electronics and sensors (e.g. NOₓ measuring device) involved.

2.2 System considerations

This section gives the temperature range in which the system should work and also an overview of sulphur related problems. Furthermore, it goes into more detail about the consequences of using SCR with urea, regarding process safety (NH₃ slip and byproducts). This will determine the operating demands of the system.

2.2.1 Temperature range

To choose or develop a proper catalyst the operating conditions must be well known. The main condition is the temperature since most catalysts work only in a limited range. The operating temperature depends of course on the type of engine and the location of the catalyst in the exhaust pipe. It will be assumed here that the catalyst will be placed near, or will replace, the silencer.

![Figure 2.6a: NOₓ output of the DAF 268 kW TC DI diesel engine as a function of exhaust gas temperature](image1)

![Figure 2.6b: Relative contribution 13 Mode NOₓ output versus the exhaust gas temperature](image2)

In general, diesel exhaust gas temperatures vary between 150 and 600°C. However a more realistic estimate is needed; at TNO-MEL exhaust temperatures of two trucks have been measured on the road²¹. The amount of cargo was varied and also the type of journey (urban, sub-urban, slow and fast motorway). The differences in measured exhaust temperatures between the two trucks were mainly due to the length of the exhaust gas system. The truck with the short exhaust pipe showed temperatures in the range of 250-550°C with temperature excursions above 550°C being rare. The other truck showed temperatures 50-100°C lower, due to ambient cooling (see Figure 2.6).

Any catalytic after-treatment device has a certain temperature at which it will start to work; for three-way catalysts this is expressed in the so called light off temperature. At this temperature the reaction starts to run quite rapidly. Furthermore, it is known² that urea decomposition needs a minimum temperature of about 300°C to be byproduct free. Also the
fact that the SCR reaction itself needs a certain minimum temperature level, about 300°C in the presence of sulphur compounds, pinpoints the lower operating temperature at 300°C.

At temperatures below this 300°C, almost no NO\textsubscript{x} reduction can take place. The effect is a relatively low NO\textsubscript{x} penalty of about 10-20 percent of the total amount (for the DAF engine, see Figure 2.6). This low penalty is a result of the fact that diesel engines do not produce much NO\textsubscript{x} at lower loads and the fact that low load points are relatively less important in test cycle procedures. Considering the goal stated in section 1.2, 70 percent overall NO\textsubscript{x} reduction, this means that the actual reduction level in this limited temperature range (300-550°C) will have to be somewhat higher (80-90 percent).

Summary

The operating range of the catalyst is about 300-550°C with a NO\textsubscript{x} removal efficiency of 80-90 percent. At higher temperatures (>450°C) problems can be expected with the standard vanadium type catalysts because of NH\textsubscript{3} oxidation and stability. Of course one can try to modify the engine and prevent these high temperatures (e.g. cooling by using bypass air/valves).

2.2.2 Space velocities

There is no fundamental limitation on the amount of catalyst used. However, truck companies do want to transport cargo, not catalyst. Three-way catalysts usually operate with a space velocity of about 100 000 h\textsuperscript{-1}, so this might be the goal for a diesel catalyst also, which corresponds with a catalyst volume about equal to the cylinder volume. Standard space velocities for SCR processes range from 1000 - 3000 h\textsuperscript{-1} for high dust coal fired installations up to 5000 - 10 000 h\textsuperscript{-1} for fuel oil. The main differences being the pitch size (or the diameter of the channels in the monolith) used, which is related to the dust load. As diesel engine exhaust is not a high dust application space velocities of 5000 - 10 000 h\textsuperscript{-1} should be feasible. Although this is not too far away from the desired 100 000 h\textsuperscript{-1}, it is likely that a new catalyst formulation is necessary.

2.2.3 Sulphur compounds in diesel fuel

In this section attention is paid to an effect which is typical for diesel engine exhaust: the implications of the presence of sulphur in diesel fuel. These implications can be divided into the effect on the particulate emission and the effect on SCR activity. The sulphur in diesel fuel is mainly converted to SO\textsubscript{2}. An increased particulate emission is caused by catalytic oxidation of SO\textsubscript{2} to SO\textsubscript{3} over the SCR catalyst. Since SO\textsubscript{3} forms aerosols, this will be detected as particulates. The second effect is deactivation of the SCR catalyst by poisoning (e.g. ammonium sulphate formation).

Particulate emission

Standard diesel fuel contains up to 0.3 wt % sulphur. In the near future this will be limited to 0.05 wt %\textsuperscript{72}. More than 95% of this sulphur is converted to SO\textsubscript{2} (in a concentration range of 10-100 ppm), the remainder leaves the engine as SO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4} mist, or another oxide form. During the EPA transient test cycle about 1-3 percent is collected as H\textsubscript{2}SO\textsubscript{4} mist\textsuperscript{73}, independent of fuel sulphur content (range 0.1 to 0.5 %).
All oxidation catalysts tend to catalyse the oxidation of $\text{SO}_2$ to $\text{SO}_3$. Especially vanadium and platina type catalysts are well known $\text{SO}_2$ oxidation catalysts. For a commercial SCR catalyst, this is undesirable and this section serves to obtain an estimate of how much $\text{SO}_2$ conversion is allowed. Therefore, an estimation is needed of the particulate emission caused by $\text{SO}_3$ formation\textsuperscript{74,73}:

\[ \text{additional particulates} = \%	ext{ Sulphur} \times \% \text{ SO}_2 \text{ conversion} \times \text{fuel consumption} \times \text{constant} \]  \hspace{1cm} (2.27)

with:  
additional particulate emission [g/kWh];  
\% Sulphur [\%];  
SO\textsubscript{2} conversion [%];  
\text{constant} [\text{g part/g S}].

The fuel consumption is about 220 g/kWh. The constant takes care of the conversion of sulphur to sulphuric acid, a water and hydrocarbon absorption factor and the amount of sulphate collected during the test. The value of this constant is not well known: Ball\textsuperscript{74} states that 1 gram of oxidized $\text{SO}_2$ produces 3.7 grams of sulphuric acid particulate, Springer\textsuperscript{73} reports a value of about 6.1. The difference being the amount of water and hydrocarbons, which condenses along with the sulphuric acid. Here, the values were averaged. This gives the following simplified formula, which represents the additional emission of particulates caused by $\text{SO}_2$ oxidation:

\[ \text{additional particulates} = 0.1 \times \% \text{ Sulphur} \times \% \text{ SO}_2 \text{ conversion} \]  \hspace{1cm} (2.28)

It is proposed to limit the $\text{SO}_2$ conversion to 5 percent \textit{maximum}. It can be calculated that for an \textit{overall} 5 percent $\text{SO}_2$ oxidation rate using a low sulphur fuel (0.05 wt %), the resulting additional emission of particulates would be 0.03 g/kWh. This additional particulate emission is already quite high compared with the near future emission limit is 0.15 g/kWh (and engine manufacturers have already problems meeting this limit). The exact amount of additional particulate emission caused by this 5 percent maximum $\text{SO}_2$ oxidation depends of course on the weight factors applied for the high load points in the testing procedures.

In the literature\textsuperscript{74} another source of $\text{SO}_3$ emission is described: the sulphur stored on the catalyst support, which is released during a temperature transient. When oxidation catalysts (Pt on $\gamma$-Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2}) are subjected to aging (typically 300 hours) the amount of particulates during an EPA transient cycle increases drastically. A way to overcome this problem is using a support that does not store sulphur (SiO\textsubscript{2}).
The formation of ammonium sulphates

If SCR with ammonia or urea is applied in diesel exhaust ammonium sulphates can be formed. These salts can deposit on the catalyst surface, blocking the active sites and causing deactivation of the catalysts (see also reactions 2.22-24). At higher temperatures these salts decompose and the catalyst is partially regenerated. Based on the decomposition temperature, see Figure 2.7 (concentrations of SO₂ in diesel exhaust are in the range of 10-100 ppm), the temperature should be above 250°C. However, in practice, a temperature of 300°C or higher is recommended because of capillary condensation which causes the equilibrium lines in Figure 2.7 to shift to the right.

Summary

The temperature level needed should be high enough to prevent ammonium sulphate formation (generally > 300°C) but not too high to cause particulate formation (for vanadium catalysts 400-450°C).

2.2.4 Byproduct formation and process safety

Possible byproducts obtained in the SCR with urea process can be divided in several categories:

a) When injecting urea, byproducts can be formed because of incomplete decomposition. Some research has been performed regarding low temperature urea polymerisation reactions. Byproduct formation at high temperatures (>300°C) is not well known. Urea decomposition compounds are usually emitted as particulates and can cause plugging.

b) The ammonia formed can result in salt formation (e.g. ammonium sulphates, nitrates and carbamates). These salts can cause plugging and corrosion, they may be even explosive (e.g. ammonium nitrate).

c) Nitrous oxide, N₂O, can be formed by the SCR reaction, ammonium oxidation and possibly out of urea. Nitrous oxide is a greenhouse gas and destroys the ozone layer.

d) The possibility of formation of N-nitroso compounds has been studied. This type of compound can be formed when a nitrosating agent (e.g. NO₃) and amines or amides are present. The N-nitroso compounds are considered highly carcinogenic.

Figure 2.7: Decomposition temperatures of ammonium sulphates.

Diesel exhaust NOₓ formation and abatement
2.2.4.1 Urea decomposition products

Incomplete urea decomposition leads to urea polymerisation products, especially at lower temperatures. These products are not especially harmful to people. However, they are emitted as particulates and therefore this emission should be limited. The first experiments\(^6\) with the laboratory-scale experimental setup, using a capillary tube to inject a 2 wt % urea solution, indicate that the decomposition of urea is fast and complete above 330°C. Beneath 200°C deviations occur related to the formation of byproducts. In the range of 200 - 330°C the formation of byproducts could not be excluded.

This simple injection system had several non realistic features; the urea solution was very diluted (2 wt %, in practice a 40 wt % solution is more convenient). Furthermore, the reactor was operated at a low space velocity (\(< 10000\) h\(^{-1}\)) resulting in a large space time for the urea solution. Because of the lower temperature limit quoted (300°C, section 2.2.1) more attention will be paid to this subject.

In aqueous solution urea decomposition can occur at elevated temperatures:

\[
\begin{align*}
2\text{HN-CO-NH}_2 (\text{aq}) + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+2\text{HNCOO}^- (\text{aq}) \quad (2.29) \\
\text{NH}_4^+2\text{HNCOO}^- (\text{aq}) & \rightleftharpoons 2 \text{NH}_3 (\text{g}) + \text{CO}_2 (\text{g}) \quad (2.30)
\end{align*}
\]

In the solid state and in the urea melt:

\[
\begin{align*}
2\text{HN-CO-NH}_2 (\text{s}) & \rightarrow \text{NH}_4^+\text{NCO}^- (\text{s}) \quad (2.31) \\
\text{NH}_4^+\text{NCO}^- (\text{s}) & \rightarrow \text{NH}_3 (\text{g}) + \text{HNCO} (\text{g}) \quad (2.32)
\end{align*}
\]

Note that when water is present iso-cyanic acid (HNCO) can hydrolyse:

\[
\text{HNCO} (\text{g}) + \text{H}_2\text{O} (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{NH}_3 (\text{g}) \quad (2.33)
\]

During storage urea decomposition is unwanted. Experiments by Horsch\(^{25}\) have shown that hydrolysis of urea at normal storage conditions is negligible; for a 10 wt % urea solution at 20 °C 0.4 wt % of urea disappears in 150 days. The conclusion is that problems with urea storage are unlikely.

When injecting the urea solution a fast decomposition is desirable. The solution is relatively stable; even at elevated temperatures (100°C) it takes minutes to decompose urea. When injecting the solution, it is most likely that water vaporizes, leaving behind relatively pure urea. Urea melts at about 135°C and gradually starts decomposing in ammonia and isocyanic acid, which can also react with NO\(_2\). In exhaust gases, water vapour will enhance the decomposition rate.

Essentially two different pathways to urea condensation products are possible. The first is the cyanic acid intermediate path (T\(< 100°C\))\(^{26}\):

\[
\begin{align*}
\text{H}_2\text{N - CO - NH}_2 & \rightleftharpoons \text{HN - C = O + NH}_3 \rightarrow \text{N = C - OH + NH}_3 \\
\text{urea} & \quad \text{iso-cyanic acid} \quad \text{cyanic acid} \quad (2.34)
\end{align*}
\]
\[ N = C - OH + H_2O \rightarrow CO_2 + NH_3 \] (2.35)

\[ N = C - OH + H_2N - CO - NH_2 \rightarrow H_2N - CO - NH - CO - NH_2 \] (2.36)

urea

biuret

\[ N = C - OH + H_2N - CO - NH - CO - NH_2 \rightarrow H_2N - CO - NH - CO - NH - CO - NH_2 \] (2.37)

triuret

\[ H_2N - CO - NH - CO - NH - CO - NH_2 \rightarrow -NH_3 \] (2.38)

which leads to the first group of intermediates\textsuperscript{77,42,78,6}. These intermediates can also be used for the reaction but have higher decomposition temperatures: biuret 192°C, triuret 233°C and cyanuric acid 330°C. Of course, higher polymerisation products can not be excluded.

The second group are by-products formed through the cyanamide intermediate (≥ 300°C)\textsuperscript{79,77,80}.

\[ H_2N - CO - NH_2 \rightleftharpoons HN = C = O + NH_3 \rightleftharpoons H_2N - C \equiv N + H_2O \]
cyanamide (2.39)

\[ 2 \ H_2N - C \equiv N \rightarrow H_2N - C(NH) - NH - C \equiv N \] (2.40)
di-cyanic-diamide

\[ H_2N - C \equiv N + H_2N - CO - NH_2 \rightarrow H_2N - CO - NH - C \equiv N \] (2.41)

cyano-urea

\[ H_2N - C \equiv N + NH_3 \rightarrow H_2N - C(NH) - NH_2 \] (2.42)
guanidine

\[ H_2N - C(NH) - NH_2 \rightleftharpoons H_2N - C(NH) - NH - CO - NH_2 \] (2.43)

iso-cyanic acid

guani-urea

\textit{Diesel exhaust NO\textsubscript{x} formation and abatement}
3 H₂N – C ≡ N →
cyanamide

NH₃

→

melamine
+H₂O
-NH₃

ammeline

These products are formed at higher temperatures and suppressed by a high H₂O content of the exhaust gases. Melamine can again lose ammonia at high temperatures and low partial pressure, resulting in formation of polymerisation products (the polytriazines). An accumulation is possible because this type of product decomposes at higher temperatures (400°C). However, when heating up urea under atmospheric pressure, one normally finds a large formation of biuret, triuret and cyanuric acid. The amount of heavier products is limited and can be suppressed by a short residence time in the reactor. Therefore, the bulk of the urea condensation byproducts will be of the poly urea type but some cyano type emission can be also expected.

2.2.4.2 NH₃ slip

As the reaction stoichiometry (based on ammonia) is 1 an overdose of ammonia or urea (assuming one urea yields two ammonia) will lead to NH₃ emission at lower temperatures. Commercial vanadium type catalysts will oxidize this ammonia to NO, provided the temperature is high enough (reaction 2.20 and 21). The main problem here is to control the urea injection to such a degree that no NH₃ slip can occur. NH₃ is poisonous and strongly acidifying (even more than NO). Furthermore, it can give rise to formation of a number of ammonium salts which again cause various problems as will be discussed next.

*Ammonium sulphates*

The formation of ammonium sulphates has already been treated in section 2.2.3 and 2.1.2.5: at 300°C (NH₄)₂SO₄ and at 150°C NH₄HSO₄ are formed. The former causes catalyst deactivation problems (pore blocking) and the latter is a sticky compound which can cause severe corrosion problems.

*Ammonium nitrates*

NH₄NO₃ compounds can lead to plugging or even explosions. Ammonium nitrate can be formed beneath its melting point of 170°C:

\[
2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 \quad (2.45)
\]

\[
3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO} \quad (2.46)
\]

\[
\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3 \quad (2.47)
\]
Thermal decomposition occurs at 200 < T < 260°C:

\[ \text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2 \text{H}_2\text{O} \]  \hspace{1cm} (2.48)

Explosive decomposition occurs above 260°C:

\[ \text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O} + 0.5 \text{O}_2 \]  \hspace{1cm} (2.49)

In principle detonation can only occur at temperatures well above 210°C. As no ammonium nitrates are formed at these temperatures, explosions will not occur\(^6\): SCR units have run for years without problems of this type.

**Ammonium carbamate**

Formation of ammonium carbamate occurs at room temperature when leading NH\(_3\) over solid CO\(_2\). Actually it is the first step in the urea synthesis process\(^82\):

\[ 2 \text{NH}_3 + \text{CO}_2 \rightarrow _2\text{HN-CO-O-NH}_4 \]  \hspace{1cm} (2.50)

\[ _2\text{HN-CO-O-NH}_4 \rightarrow _2\text{HN-CO-NH}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (2.51)

The reactions run commercially under elevated temperature and pressure. The pressure at which ammonium carbamate dissociates has been researched extensively\(^83,84\), under atmospheric pressure it is unstable above 60°C.

**2.2.4.3 N\(_2\)O formation**

Nitrous oxide is a greenhouse gas and an O\(_3\) destroying agent but not dangerous for health in the concentrations encountered. It can be formed in the SCR reaction, especially over some type of catalysts\(^8,85\), but normally not in real scale applications\(^86\). The reactions proposed are\(^87\):

\[ 4 \text{NH}_3 + 4 \text{NO} + 3 \text{O}_2 \rightarrow 6 \text{H}_2\text{O} + 4 \text{N}_2\text{O} \]  \hspace{1cm} (2.52)

\[ 2 \text{NH}_3 + 2 \text{O}_2 \rightarrow 3 \text{H}_2\text{O} + \text{N}_2\text{O} \]  \hspace{1cm} (2.53)

N\(_2\)O formation is encountered in the NSCR with urea solution\(^40,41\), see also section 2.1.2.3. The temperature range researched is usually in the range of 700-1100°C. Beneath 800°C (temperatures in diesel exhaust are up to 600°C) no N\(_2\)O formation has been detected\(^40\) using a 45% aqueous urea solution. In case of urea injection and SCR in diesel exhaust\(^41\), only at temperatures above 400°C N\(_2\)O is detected (5-35 ppm), the concentration of the engine outlet generally being higher than the actual exhaust gases leaving the vanadium catalyst. Therefore, with standard catalysts N\(_2\)O formation is not a problem. However, for newly developed catalysts a check on N\(_2\)O is essential.
2.2.4.4 N-Nitroso compounds

The possibility of nitroso compound formation has been investigated. These compounds are considered highly carcinogenic and mutagenic.\textsuperscript{82,88} This type of compound can be formed by interaction of nitrogen containing organic compounds - amines and amides like urea, guanidine, urethane, cyramide - and a nitrosating agent, like NO\textsubscript{2}. The subdivision of nitroso compounds in nitrosamines and nitrosamides is because a nitrosamine compound usually needs metabolic activation to become carcinogenic in contrast to the nitrosamides. Examples are given in Figure 2.8.

The carcinogenic activity varies widely over the type of nitroso compounds researched\textsuperscript{89-95}. About 80 percent of the compounds tested on animals give tumours. There is no direct proof that humans react the same way, but it is generally believed they are not immune. Examples are NDMA (N-nitroso-dimethylamine) and NNN (N-nitroso nicotine) from smoking cigarettes. The formation of nitrosamines and amides proceeds according to:

\[ R'R-NH + X-NO \rightarrow R'R-N-NO +HX \]  \hspace{1cm} (2.54)

The reaction of amides with primary amine groups leads to the following reaction:

\[ RCONH_2 + NO^+ \rightarrow RCO_2H + N_2 + H^+ \]  \hspace{1cm} (2.55)

In the urea/deNO\textsubscript{2} system the formation of amides usually occurs in the form of urea, so the possible nitroso compounds would be of the form:

\[ R-NH-CO-NH_2 + HNO_2 \rightarrow R-N(NO)-CO-NH_2 + H_2O \]  \hspace{1cm} (2.56)

Urea itself does not possess a secondary amine group and the reaction will lead to carbon dioxide and water:

\[ NH_2-CO-NH_2 + 2HNO_2 \rightarrow CO_2 + 2N_2 + 3H_2O \]  \hspace{1cm} (2.57)

The nitroso amides are generally not very stable and decompose thermally (already between 25 and 100°C), photochemically and by an acid/base catalysed reaction. Groups with a R-CO-N(NO)-R' structure are generally among the more unstable compounds.\textsuperscript{89} Because of this unstable nature they can only be formed at relative low temperatures, meaning that they can only be formed after the exhaust gases have left the system. Furthermore, compounds with secondary amine groups must be present and the only likely candidates are the poly urea compounds (e.g. biuret, triuret).

Therefore, the result of this literature study is that nitroso compounds might result from a reaction with urea condensation products at low temperatures, so only when the off-gases have left the system. The theoretically resulting components were not found in literature and comparable compounds were quite unstable. The conclusion is that formation of nitrosamines is quite unlikely and prevention of urea condensation product formation will probably be sufficient.

\textit{Chapter 2}
Summary byproduct formation

To prevent byproduct formation, urea condensation products and ammonia salts, the temperature in the system should be higher than 300°C. For newly developed catalysts and NO\textsubscript{x} removal systems in general, checks on NH\textsubscript{3} slip and N\textsubscript{2}O formation are necessary. For the urea injection system a check on N-nitrosamide formation is desirable.

2.3 Summary

The urea injection device to be developed should:

- show an overall NO\textsubscript{x} removal efficiency of 70 percent;
- less than 5 % SO\textsubscript{2} oxidation regarding particulate emissions;
- give negligible amounts of secondary pollutants like ammonia slip and N\textsubscript{2}O formation;
- give negligible urea byproduct formation.

As for application in truck diesels the following additional demands are:

- a urea dosage control fast enough to prevent ammonia slip as a truck diesel engine is a non steady state device;
- a limited size of the system.

As stated in section 2.1 commercial catalysts, mainly vanadium type, are available for use in exhaust gases. They perform well in temperature range of 300-450°C. This temperature window does not match the temperature range of diesel exhaust gases, 100-600°C. This range can be narrowed by considering temperatures above 550°C do rarely occur and temperatures below 300°C do not contribute much to the NO\textsubscript{x} output.

The excess SO\textsubscript{2} and NH\textsubscript{3} oxidation and stability problems in the temperature range of 450-550°C has led to the development of new catalysts. The choice has been made to work with zeolite type catalysts. Medros\textsuperscript{86} showed activity of these catalysts in a broad temperature window. He used a high temperature catalyst, H-MOR, in series with a low temperature catalyst, Cu-MOR. The space velocities used (in the order of 100 000 h\textsuperscript{-1}), the temperature range (200-600°C) and the fact that flue gases were used (LNG-fired boiler), were further reasons to initiate research in this area (Chapter 3).

Parallel to this catalyst research the development of a urea injection system has been undertaken (Chapter 4). Research into urea dosage control and overall system dynamics has been performed with a vanadium type catalyst (Chapter 5 and 6). The reason for using such a catalyst is that catalyst development was a parallel project and catalyst material was not directly available. Furthermore, it is not easy to make a few litres on laboratory scale. Finally, zeolite synthesis usually yields a batch of zeolite crystals with a diameter of a few micrometers, which have to be coated on a low pressure drop carrier, which is not a trivial task.
Literature


Chapter 2


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Diesel exhaust NOx formation and abatement
Chapter 2


Chapter 3
Catalyst testing

3.1 Introduction

This chapter describes the catalyst testing for the SCR reaction at model and diesel exhaust gas conditions. As already mentioned in Chapter 2 a suitable catalyst for diesel exhaust gases was not available. Therefore, in cooperation with Mrs E. Ito of our group and the Department of Organic Chemistry and Catalysis, Delft University of Technology, development of a new catalyst has been undertaken. Home-made catalysts have been compared with commercially available ones. For this type of work the choice has been made to work with a standard fixed bed reactor. The experimental equipment has been designed to check if a catalyst works in the desired temperature range. For more accurate kinetic data a CSTR (e.g. a Berty reactor) is preferred. It is noted that no urea injection was used for the laboratory scale tests reported in this chapter. A bottle of NH₃ was used instead.

For this catalyst testing two setups are available:

- A catalyst screening setup; this setup uses typically 0.5 grams of catalyst and simulated gas mixtures to test the activity of the catalyst for the NO/NH₃ reaction and SO₂ oxidation. Data obtained from this setup should be regarded with some care because the gas mixtures used are generally too different from diesel exhaust to be extrapolated. The main advantage of this setup is that the amount of catalyst needed is quite small (no large quantities of catalyst have to be prepared) without introducing all kinds of catalyst inhomogeneity errors. The objective is to compare home-made catalysts with each other and with commercial SCR catalysts to isolate the promising ones, which will be studied with:

- A test bench. This is also a catalyst testing setup which can be connected to a side stream of the diesel engine to study the effect of using diesel exhaust gases and to determine which components in this gas mixture are detrimental for the activity of a certain catalyst. This setup uses about 15 grams material and is big enough to test structured catalysts (e.g. little pieces of monolith) but not too big to be unable to use simulated gas mixtures as well.

Summarizing, a catalyst which shows positive results on these setups is a promising catalyst for diesel engine service because it has already been tested with diesel exhaust gases.
Figure 3.1: Schematic drawing of the catalyst screening setup

Sketch Laboratory
Scale Equipment
R.J. Huitema
26 April 1991

Flow Number
Flow Temperature (°C)
Flow Pressure (bar)
P Pressure
I Inhibiting
C Controlling
A Alerting
T Temperature
F Flow

GAS CHROMATOGRAPH SAMPLE SYSTEM

C1
GC

C2
NO

ANALYSER

CALIBRATION GASES

MASS SPECTROMETER

CHOICE BETWEEN MS AND OFF-GAS ANALYSERS

TUBE OVEN OR REACTOR

MV1 MV2 MV3 MV4 MV5 MV6

MFC1 MFC2 MFC3 MFC4

P1

P2

P3

P4

P5

P6

MV1 MV2 MV3 MV4 MV5 MV6

not used

PREPARATION

HP

solution

wemed

needle

valve

washing
tank

vent

sample out

sample in

vent
3.2 Experimental facilities for testing catalysts

In this section a description of the catalyst testing setups is given. The catalysts are first screened on a small scale (section 3.2.1 catalyst screening setup) and the most promising ones on a somewhat larger scale with diesel exhaust gases (section 3.2.2 test bench). Both setups are essentially fixed bed reactors; the catalyst is put in a heated tube and gas mixtures are passed through this tube. The resulting changes in gas phase composition caused by the activity of the catalyst are measured with off-gas analysers.

3.2.1 Catalyst screening setup

3.2.1.1 Equipment

This setup, Figure 3.1, is used to screen catalysts. It consists of a gas feed section, a reactor section and an analysis section. The setup is fully automated with Transport System\textsuperscript{2} hardware and FIX\textsuperscript{3} software. Most catalyst tests are performed during the night without any operator interference.

*Gas feed section*

In the gas feed section a simplified exhaust gas is simulated. For catalyst activity tests a gas mixture consisting of NO, NH\textsubscript{3}, O\textsubscript{2} in balance Argon is used. For SO\textsubscript{2} oxidation tests SO\textsubscript{2} and O\textsubscript{2} in balance Argon are used. These gas mixtures are obtained by mixing gases from the following bottles:

- a) Ar 100 vol % Argon from Air Products
- b) O\textsubscript{2}/Ar 30 vol % Oxygen in Argon from Scott Specialty Gases
- c) NO/Ar 2 vol % nitric oxide in Argon from SSG
- d) NH\textsubscript{3}/Ar 2 vol % ammonium in Argon from SSG
- e) SO\textsubscript{2}/Ar 2 vol % sulphur dioxide in Argon from SSG

These gases are measured and controlled by Brooks 5850 Mass Flow Controllers (0-500 Nml/min Ar; 0-150 Nml/min O\textsubscript{2}/Ar; 0-150 Nml/min NO/Ar; 0-50 Nml/min NH\textsubscript{3}/Ar). The MFC’s are all heated up to 40°C. Since there are only four MFC’s the NH\textsubscript{3}/Ar bottle is changed for a SO\textsubscript{2}/Ar bottle in case of SO\textsubscript{2} oxidation experiments. Water or urea solution can be injected directly in the reactor using a Spectra Physics SP 8810 HPLC pump.

*Reactor section*

A tubular oven is used which contains an 8 mm internal diameter quartz tube which can be heated up to 600°C. The reactor material is quartz because stainless steel shows catalytic activity, NH\textsubscript{3} oxidation, above 400°C. The catalyst bed is isothermal ± 1°C and quarts wool is used to fix the catalyst particles. Catalyst temperature is measured directly by putting a K-type thermocouple in the catalyst bed.
Analysis section

The off-gases are passed at 100°C through a Signal 1000 UV NH₃ analyser (range 0-1000 ppm, accuracy 1% Full Scale) equipped with a heated cell (150°C). Water and NH₃ are subsequently removed with a washing bottle containing 75 wt % phosphoric acid and introduced into a Signal 4000 chemiluminescence NOₓ analyser (range 0-1000 ppm, accuracy 1% FS). Water is removed to avoid condensation problems and NH₃ will cause salt formation in the NOₓ analyser dropping the signal of the analyser irreversibly. The UV NH₃ analyser suffers interference from NO (5-6% relative), NO₂ (15% relative) and can be used as an SO₂ analyser as well (150% interference). These interferences have been determined with calibration gases.

During the experiments a VG Prima 600 Mass Spectrometer is used for analysis as well. The advantage is that all relevant nitrogen components are detected with a cycle time of one minute. Normally water is not added to the gas mixture because in that case it is not possible to measure NH₃. While it is possible to measure H₂O, O₂, NO, NO₂, N₂O, SO₂, NH₃ and N₂ only calibration gases for NO (572 ppm in Argon, Scott Specialty Gases, 2% accuracy), NO₂ (456 ppm in Argon, 5% accuracy), NH₃ (546 ppm in Argon, 5% accuracy), N₂ (2066 ppm in Argon, 5% accuracy) are used. All other components can only be measured qualitatively; water cannot be measured at all because it is difficult to obtain a stable signal with this MS.

3.2.1.2 Catalysts tested

Home-made metal ion exchanged zeolite type catalysts

A summary of the relevant catalysts for this thesis is given in Table 3.1. All catalysts have been prepared by Ito⁴⁻⁵ (a more extensive list of catalysts, preparation routes and characterization can be found in these references as well).

The zeolites were pressed with an IR tablet press, crushed and sieved in a range of 300-700 μm. No change in micro pore volume or micro pore structure caused by this procedure could be detected with N₂ adsorption experiments (BET method used).

DN 110: The Rhone-Poulec V₂O₅/Al₂O₃ catalyst

This is a commercially available catalyst also used by Wypkema⁶. This catalyst contains 10 wt % V₂O₅ on gamma alumina with a BET surface area of 100 m²/g. In practice it is used for off-gases from nitric acid plants⁷ and is delivered as 3 mm spheres. Before most catalyst tests these spheres were crushed to 300-700 μm.
Table 3.1: Summary of catalysts tested, the numbers in column one are the batch numbers used by Ito. The abbreviation Na-MOR means the Na form of mordenite obtained from PQ zeolite ($SiO_2/Al_2O_3=13.1$). The NaZ40 is the Na form of ZSM-5 from Uetikon AG ($SiO_2/Al_2O_3=40$), zeolite Y from AKZO ($SiO_2/Al_2O_3=5.2$).

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>ion exchange level (%)</th>
<th>metal load (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>H-MOR</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>37</td>
<td>H-MOR</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>47</td>
<td>CeNa-MOR</td>
<td>71</td>
<td>5.7</td>
</tr>
<tr>
<td>49</td>
<td>CuNa-MOR</td>
<td>69</td>
<td>3.7</td>
</tr>
<tr>
<td>53</td>
<td>CuNa-Z40</td>
<td>96</td>
<td>2.3</td>
</tr>
<tr>
<td>54</td>
<td>FeNa-Z40</td>
<td>94</td>
<td>1.4</td>
</tr>
<tr>
<td>55</td>
<td>CoNa-Z40</td>
<td>69</td>
<td>1.6</td>
</tr>
<tr>
<td>56</td>
<td>CuNa-MOR</td>
<td>85</td>
<td>4.8</td>
</tr>
<tr>
<td>60</td>
<td>CeNa-Z40</td>
<td>11</td>
<td>0.39</td>
</tr>
<tr>
<td>64</td>
<td>CeNa-MOR</td>
<td>41</td>
<td>3.2</td>
</tr>
<tr>
<td>66</td>
<td>CeNa-Z40</td>
<td>95</td>
<td>3.1</td>
</tr>
<tr>
<td>71</td>
<td>CeNa-Y</td>
<td>65</td>
<td>9.7</td>
</tr>
<tr>
<td>84</td>
<td>CeNa-MOR</td>
<td>45</td>
<td>3.8</td>
</tr>
</tbody>
</table>

DN 32: The Degussa AG $V_2O_5/TiO_2/WO_3$ catalyst washcoated on a monolith

The Degussa DN 32 is a structured catalyst (Table 3.2, see also Appendix 1); a monolith. It is delivered in pieces of 9.3 cm diameter and 15.2 cm length. To be able to test this catalyst in the catalyst screening setup a small part of this monolith is cut off. This means that only 12 channels are available with a length of 2.5 cm. The monolith is fitted into the quartz tube using quartz wool, so the outer wall will not be used for the reaction as the flow will go through the channels. Several remarks have to be made regarding interpretation of the results obtained with this configuration:

Table 3.2: Data on the 300 cpi Degussa DN 32 catalyst fitted in the catalyst screening setup

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>2.5 cm</td>
</tr>
<tr>
<td>Number of channels</td>
<td>12</td>
</tr>
<tr>
<td>Mass</td>
<td>0.717 g</td>
</tr>
<tr>
<td>washcoat mass</td>
<td>0.14 g</td>
</tr>
<tr>
<td>diameter wall</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>void</td>
<td>0.44</td>
</tr>
<tr>
<td>diameter channel</td>
<td>1 mm</td>
</tr>
<tr>
<td>washcoat thickness</td>
<td>0.08 mm</td>
</tr>
</tbody>
</table>

Chapter 3
the sample error will probably be quite large because the washcoat thickness is usually not really constant over the length of the original piece.

the exact catalyst load/washcoat thickness is not known; it is estimated on basis of the weight of such a monolith with and without the washcoat. Therefore, the exact weight of the catalyst nor its dimension (particle diameter/washcoat thickness) is well known.

All these points make comparing this catalyst with the other ones only qualitative.

3.2.1.3 Experimental procedures

**Type of experiments**

Most experiments were temperature programmed catalyst activity measurements. The experiments are programmed as follows: while the reactor is heated up to a certain set point the reactor feed composition is measured. As the oven reaches its desired set point 2 magnetic three-way valves are switched and the gas stream is passed through the reactor. When the gas phase composition is stable the steady state conversion can be calculated and a new (usually higher) temperature is chosen. This cycle is repeated and is executed at least once for each catalyst. On basis of the results this cycle can be repeated with a new catalyst batch to study reproducibility or with the same batch to study stability.

Standard conditions were chosen to be able to compare most of the catalysts without having to resort to calculations in which knowledge of mechanisms or kinetics is needed. As shown in Table 3.3 the reference base is the mass of the catalyst used; for most catalysts tested this results in a space velocity of about 30 000 h⁻¹. This space velocity is rather high compared with typical SCR installations used in practice (up to circa 5000 h⁻¹) but rather low compared with desired values (100 000 h⁻¹, see Chapter 2). The space velocity chosen is a compromise. The oxygen concentration of 5 percent is well above the region in which standard vanadium type catalysts are strongly dependent on this concentration and corresponds with a high load diesel exhaust (λambda close to 1). The particle diameter is a compromise between the dimensions of the catalyst bed (diameter bed/ length bed, diameter particle/ diameter bed) transport phenomena (mass transfer limitations decrease with decreasing particle diameter) and pressure drop (increase with decreasing particle diameter). Simply stated 0.5 mm is the smallest possible particle for this space velocity and bed configuration as to keep the pressure drop beneath 0.1 bar (for more detailed calculations see section 3.3).

Every temperature programmed experiment consisted of several steps in temperature. At every temperature level, zero values (the analyser signal using pure Argon), bypass values (the actual reactor feed composition) and reactor values (the reactor outlet composition) are measured. Sometimes more than one reaction mixture is used. The exact time table of the experiments (at a certain temperature level) is given in Table 3.4.

<table>
<thead>
<tr>
<th><strong>Table 3.3: Standard conditions.</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter catalyst</td>
</tr>
<tr>
<td>Mass catalyst</td>
</tr>
<tr>
<td>O₂ concentration</td>
</tr>
<tr>
<td>Flow rate</td>
</tr>
</tbody>
</table>
### Table 3.4: Time table experiments in hours.

<table>
<thead>
<tr>
<th>type of experiment</th>
<th>Zero (Ar)</th>
<th>Mixture number 1 bypass</th>
<th>Mixture number 1 reactor</th>
<th>Mixture number 2 bypass</th>
<th>Mixture number 2 reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO conversion (NO\textsubscript{2}-analyser)</td>
<td>1/2</td>
<td>1/2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO conversion (MS)</td>
<td>1/2</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{2}-oxidation (SO\textsubscript{2}-analyser)</td>
<td>1/2</td>
<td>1/2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{2}-oxidation (MS)</td>
<td>1/2</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO\textsubscript{2}-formation</td>
<td>1</td>
<td>1/2</td>
<td>5</td>
<td>2</td>
<td>1/2</td>
</tr>
<tr>
<td>NH\textsubscript{3}-adsorption</td>
<td>1/2</td>
<td></td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

### Table 3.5: Gas mixture composition for the experiments in Table 3.4.

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>mixture number</th>
<th>NO\textsubscript{x} (ppm)</th>
<th>NH\textsubscript{3} (ppm)</th>
<th>SO\textsubscript{2} (ppm)</th>
<th>Temperature program steps of 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO-conversion</td>
<td>1</td>
<td>1000</td>
<td>1000</td>
<td></td>
<td>200 - 600°C</td>
</tr>
<tr>
<td>SO\textsubscript{2}-oxidation</td>
<td>1</td>
<td>500</td>
<td></td>
<td></td>
<td>200 - 600°C</td>
</tr>
<tr>
<td>NO\textsubscript{2}-formation</td>
<td>1</td>
<td>1000</td>
<td></td>
<td></td>
<td>300 - 500°C</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1000</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH\textsubscript{3}-adsorption</td>
<td>1</td>
<td>1000</td>
<td></td>
<td></td>
<td>200 - 600°C</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The gas composition used during the bypass and reactor measurement is shown in Table 3.5. Typical concentrations of NO and NH\textsubscript{3} are 1000 ppm, which corresponds with normal diesel exhaust values. The SO\textsubscript{2} concentration used, 500 ppm, is rather high; diesel exhaust usually contains 10 - 50 ppm. The reason for this is the sensitivity of the MS in this range. Furthermore, steady state can be reached only after a very long time (because of adsorption phenomena at these low concentrations).
The time a certain reaction mixture needs to reach steady state is of course not constant. Experience showed that 2 hours is generally enough, but especially at low temperatures some catalysts are very slow, up to a conversion change of another 5 percent in 2 days. The experimental time table is made from a practical point of view; an experiment with this screening device should be done in one night.

Reactivity of the quartz reactor

Experiments with stainless steel 316 tubing showed substantial NH$_3$ oxidation above 400°C. Therefore the 'inertness' of the quartz reactor is checked for NH$_3$ oxidation, NO/NH$_3$ reaction and SO$_2$ oxidation. New tubing shows no detectable SO$_2$ oxidation or NO conversion and the NH$_3$ conversion is smaller then 4 percent at 600°C. After experiments with vanadium type catalysts, the tubing exhibits some catalytic activity; 6 percent SO$_2$ oxidation and even 23 percent NH$_3$ conversion. The conclusion is that the washing procedure, cleaning with water and acetone, is not sufficient. Therefore, tubing in which vanadium type catalysts is tested is not used for other catalysts.

Reproducibility

The reproducibility is defined as follows; a new catalyst sample of 0.5 grams is taken from the same batch number. This sample is subjected to the same experimental procedure as the original one; usually a temperature scan from 200 to 600°C. The calculated conversions are compared with each other. The average absolute standard deviation is defined as:

$$s = \sqrt{\frac{\sum_{i=1}^{N} \sum_{j=1}^{M} (\xi_{ij} - \bar{\xi})^2}{NM-N}}$$  \hspace{1cm} (3.1)

with
\begin{align*}
N &: \text{the number of settings;} \\
M &: \text{the number of points per setting;} \\
\xi &: \text{the measured respectively average conversion.}
\end{align*}

For a catalyst activity scan the standard deviation in NO conversion is 2 percent absolute. For SO$_2$ oxidation this is 3 percent.

N- and H-balance

When using the MS an N- and H-balance can be made. As already mentioned in section 3.2.1.1 calibration gases for N$_2$O and H$_2$O were not available. However, the N-balance is generally correct within 10 percent (total N present). The H-balance cannot be calculated always due to instabilities in the H$_2$O signal. Because of this and the absence of a calibration gas for water no useful data are obtained. Furthermore, this type of MS is not very suitable for measuring polar or 'sticky' compounds like H$_2$O (no heated cell).
3.2.2 Test bench

3.2.2.1 Equipment

This setup, see Figure 3.2, was used to test catalysts with simulated and diesel exhaust gases. Essentially it is the same type of equipment as in section 3.2.1. However it is bigger and it is also possible to use diesel exhaust gases. It also consists of a gas feed section, a reactor section and an analysis section. It is also automated with Transport System\textsuperscript{2} hardware and FIX\textsuperscript{3} software. This does not apply to the diesel engine, which is operated manually.

Gas feed section

In the gas feed section a simplified exhaust gas is generated or diesel exhaust can be used. Gas mixtures consisting of NO, NH\textsubscript{3}, O\textsubscript{2} and SO\textsubscript{2} in balance Nitrogen or air are used. These gases are obtained by mixing gases from the following bottles:

- a) Air Air Products or pressurized air
- b) N\textsubscript{2} Technical grade Air Products
- c) NO 99.0 % Air Products
- d) NH\textsubscript{3} 99.9 % Air Products
- e) SO\textsubscript{2}/N\textsubscript{2} 5 vol % sulphur dioxide in N\textsubscript{2} Scott Speciality Gases

These gases are measured and controlled by Sierra 840 Mass Flow Controllers (0-15 Nl/min Air, 0-15 Nl/min N\textsubscript{2}, 0-30 Nml/min NO, 0-30 Nml/min NH\textsubscript{3}; 0-150 Nml/min SO\textsubscript{2}/N\textsubscript{2}). Water and/or urea solution can be injected in the pre-heater or directly in the reactor with a Spectra Physics SP 8810 HPLC pump. In case of diesel exhaust one standard setting of the Yanmar diesel engine is used\textsuperscript{8}, see Table 3.6.

Reactor section

A fluidized bed oven is used to heat up the reactor, which has an internal diameter of 19 mm. This reactor is placed downstream and contains about 15 grams of catalyst. As the reactor material, stainless steel, exhibits NH\textsubscript{3} oxidation activity above 400\textdegree C, the amount of tubing in the fluidized bed has to be as short as possible. This of course without generating a large temperature profile over the catalyst bed (-\pm 2 °C). Catalyst temperature is measured directly by putting a thermocouple in the catalyst bed.

<table>
<thead>
<tr>
<th>Table 3.6: Standard diesel exhaust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel fuel</td>
</tr>
<tr>
<td>Power output</td>
</tr>
<tr>
<td>H\textsubscript{2}O concentration</td>
</tr>
<tr>
<td>CO\textsubscript{2} concentration</td>
</tr>
<tr>
<td>SO\textsubscript{2} concentration</td>
</tr>
<tr>
<td>O\textsubscript{2} concentration</td>
</tr>
<tr>
<td>NO concentration</td>
</tr>
<tr>
<td>NH\textsubscript{3} concentration</td>
</tr>
<tr>
<td>Flow rate</td>
</tr>
</tbody>
</table>
Analysis section

The off-gases are passed through a washing bottle containing 75 wt % phosphoric acid to remove water and NH\textsubscript{3}. The NO\textsubscript{x} concentration is subsequently measured with an Eco Physics chemiluminescence NO\textsubscript{x} analyser (range 0-1000 ppm, accuracy 1% Full Scale). Water causes condensation problems and NH\textsubscript{3} causes salt formation in the NO\textsubscript{x} analyser. In this case a high concentration of NH\textsubscript{3} gives also rise to interference.

NH\textsubscript{3} is measured with a Siemens MIPAN (Microwave Process ANalyser, range 0-2000 ppm, accuracy 1% FS). This analyser has its own heated sample line (200°C). When sulphur is present in the exhaust gases, it has to be removed first. In this case an additional SO\textsubscript{x} removal unit is used. This is a fixed bed at 350°C which has its own heated sample line (350°C). This is only necessary when using standard diesel exhaust or model gases that contain SO\textsubscript{2}. A lot of experiments are either performed with virtually sulphur free diesel or without this analyser (this analyser was not always available). In those cases only NO\textsubscript{x} conversions are measured. The main disadvantage of the SO\textsubscript{2} remover is the large dead time of 5 minutes.

In case of dry model gases SO\textsubscript{2} is measured with a Siemens Ultramat 5E NDIR (Non-Dispersive Infra-Red range 0-500 ppm, accuracy 1% FS) analyser. In case of diesel gases SO\textsubscript{3} is measured with a Severn Science Instruments automatic titration unit (used at range 0-50 ppm, accuracy 2% FS). In the former case the SO\textsubscript{2} oxidation is determined by how much SO\textsubscript{2} disappears, in the latter case how much SO\textsubscript{3} is formed. The infra red analyser cannot be used in diesel exhaust, so the SO\textsubscript{2} concentrations are calculated on basis of the fuel sulphur content.

Calibration gases from Scott Specialty Gases are used; 910 ppm NO in N\textsubscript{2} (1%), 901 ppm NH\textsubscript{3} in N\textsubscript{2} (5%) and 400 ppm SO\textsubscript{2} in N\textsubscript{2} (2%). The SO\textsubscript{3} analyser is calibrated using liquid sulphuric acid standard. One should keep in mind that at the SO\textsubscript{3} levels studied here (0-50 ppm), one generally detects 80-90% of the sulphates which are going in such a system.

In a few cases the N\textsubscript{2}O concentration in diesel exhaust gases has been measured with a GC-ECD (a 5890A Series II Gas Chromatograph from Hewlett Packard equipped with an Electron Capture detector). This analyser is very sensitive (the background concentration of N\textsubscript{2}O in ambient air of 300 ppb can be measured) but suffers from matrices effects\textsuperscript{9}. The effect is that the N\textsubscript{2}O concentration in diesel exhaust is overestimated with a factor of 1.7 compared to the calibration gas used (5.6 ppm N\textsubscript{2}O in N\textsubscript{2}, Scott Specialty Gases). Obviously, the results obtained with this analyser are qualitative only.

3.2.2.2 Catalysts tested

For detailed information on the catalysts tested see also section 3.2.1.2. Two promising home-made metal exchanged zeolite type catalysts were tested: CuNa-MOR 49 and CeNa-MOR 64. The only difference with the earlier tests (using the catalyst screening setup) is the particle diameter used, see Table 3.7, because of the higher pressure drop. The Rhone-Poulenc DN 110 (V\textsubscript{2}O\textsubscript{5}/γ-Al\textsubscript{2}O\textsubscript{3}) catalyst is used as delivered; spheres of about 3 mm. The Degussa DN 32 monolith is cut to five pieces with a length of 2.2 cm and a diameter of 1.95 cm which are fitted in the reactor.
Table 3.7: Catalysts tested (space velocity based on a flow of 15 NI/min).

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>CuNaMor 49</th>
<th>CeNaMor 64</th>
<th>DN 110</th>
<th>DN 32</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter catalyst</td>
<td>0.7-1.3 mm</td>
<td>1.3 - 2.0 mm</td>
<td>3 mm</td>
<td></td>
</tr>
<tr>
<td>Mass catalyst</td>
<td>15.0 g</td>
<td>15.0 g</td>
<td>15.0 g</td>
<td>24.8 g</td>
</tr>
<tr>
<td>Density</td>
<td>0.62 g/cm³</td>
<td>0.65 g/cm³</td>
<td>0.51 g/cm³</td>
<td>0.96 g/cm³</td>
</tr>
<tr>
<td>Space velocity</td>
<td>37 000 h⁻¹</td>
<td>39 000 h⁻¹</td>
<td>31 000 h⁻¹</td>
<td>35 000 h⁻¹</td>
</tr>
</tbody>
</table>

3.2.2.3 Experimental procedures

The experiments with the test bench are of the same type as performed with the screening setup. Some differences should be noted though; because of the much higher flow rate, 15 NI/min versus 0.5 NI/min, the main flow goes always through the reactor. When measuring the reactor feed composition, the reactor is subjected to the reactant gas mixture. In the case of the screening setup the whole flow was bypassed to measure the reactor feed composition. The effect is that for the screening setup steady state values were reached sooner.

The space velocities used for testing the catalysts are the same as in the screening setup. Pressurized air is used as a balance gas because of the high flow rates involved (see Table 3.8). The diesel engine exhaust is always filtered at 100°C before entering the setup. The gas phase composition of the diesel engine exhaust gases can be found in Table 3.6.

Most of the tests are of the same type as those for the catalyst screening setup; temperature activity tests. All tests with diesel exhaust are performed manually because the flow rate through the setup has to be checked regularly. The exact time table of the experiments (at one certain temperature level) is given in Table 3.9.

Table 3.8: Standard conditions.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx concentration</td>
<td>500 ppm</td>
</tr>
<tr>
<td>NH3 concentration</td>
<td>500 ppm</td>
</tr>
<tr>
<td>Flow rate</td>
<td>15 NI/min Air</td>
</tr>
</tbody>
</table>

Table 3.9: Time table experiments in hours.

<table>
<thead>
<tr>
<th>type of experiment</th>
<th>Zero (Air)</th>
<th>bypass</th>
<th>reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO conversion</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>SO2-oxidation</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>NH3-oxidation</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
</tr>
</tbody>
</table>

The gas composition used during the ‘bypass’ and ‘reactor’ measurements is shown in Table 3.10. Differences lie in the somewhat lower concentrations used (500 in stead of 1000 ppm) and smaller steps in temperature (50 instead of 100°C). Furthermore, the temperature maximum of the setup is 550°C.
Table 3.10: Gas mixture composition for the experiments in Table 3.9.

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>NO\textsubscript{x} (ppm)</th>
<th>NH\textsubscript{3} (ppm)</th>
<th>SO\textsubscript{2} (ppm)</th>
<th>Temperature program steps of 50\degree C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO-oxidation</td>
<td>500</td>
<td>500</td>
<td></td>
<td>200 - 550\degree C</td>
</tr>
<tr>
<td>SO\textsubscript{2}-oxidation</td>
<td>500</td>
<td></td>
<td>500</td>
<td>200 - 550\degree C</td>
</tr>
<tr>
<td>NH\textsubscript{3}-oxidation</td>
<td>500</td>
<td></td>
<td></td>
<td>200 - 550\degree C</td>
</tr>
</tbody>
</table>

Figure 3.3: NO\textsubscript{x} conversion on cerium mordenite as a function of temperature (15 g. 500 ppm NO&NH\textsubscript{3} in 15 Nl/min air).

Figure 3.4: Comparison results obtained with test bench and screening setup for NO conversion on CeNaMOR 64 as a function of temperature.

Reproducibility

The reproducibility is calculated for an experiment using a new catalyst batch. This gives the reproducibility of catalyst manufacture and testing. The average absolute standard deviation for cerium mordenite is about 3 percent, see Figure 3.3.

Comparison screening setup with test bench

The cerium catalyst is used to compare results obtained with the test bench and the screening setup. The concentrations used were not exactly the same: 500 ppm NO and NH\textsubscript{3} in air with the test bench versus 1000 ppm NO and NH\textsubscript{3} in Argon with 5 percent oxygen. However, the conversions are not very dependant on these concentrations because the SCR reaction is generally close to first order in NO and not very sensitive for oxygen above 1 percent. Therefore, the experiments can be compared and the absolute standard deviation is 4 percent, see Figure 3.4.
3.3 Transport phenomena in steady state fixed bed reactors

3.3.1 Introduction

In section 3.2 all the experimental procedures have been described. Before presenting the results some attention has to be given towards what is being measured; intrinsic kinetic data or a mass transfer limitation. In this thesis, measurements have also been performed with commercial catalysts in which mass transfer effects can occur (due to the larger particle diameter).

When performing catalyst testing in fixed bed reactors it is generally desirable to be able to describe the fixed bed with an ideal tubular reactor model. This means that the flow pattern through the bed is ideal; no channelling, back mixing, stagnant regions in the reactor or longitudinal dispersion. So when a pulse of an inert gas is put on the inlet of the catalyst bed, this pulse will be observed unchanged at the outlet. The time delay is called the residence time.

Furthermore, it is desirable that properties like temperature, composition and pressure are uniform throughout the reactor. Gradients can occur in the axial and radial direction of the reactor but also in the catalyst particle itself. When trying to design a fixed bed reactor an optimum has to be found between particle diameter, length and width of the bed. For example, decreasing the particle diameter decreases pore diffusion resistance but results in an increase in pressure drop. Trying to correct this by increasing the bed diameter (at a constant space velocity; bed length decreases) can cause channelling and longitudinal dispersion.

So, in this section the hydrodynamics of the reactor system, pore and film diffusion and heat transfer effects will be examined. This will be done for all the catalysts used, because pronounced differences exist between the zeolite and the vanadium type catalysts (pore structure) but also between particles (zeolite type catalysts and DN 110) and structured catalysts (DN 32).

3.3.2 Hydrodynamics of the reactor system

Consider the main reaction involved:

\[ 4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad -\Delta H_r = 407 \text{kJ/mol}^{10} \quad (2.18) \]

First of all the increase in number of molecules due to the reaction (9 to 10) has been neglected because of the low concentrations involved (0.1 volume percent maximum). The second point is the adiabatic temperature rise, which is about 0.14 °C per ppm NO converted. This means a maximum temperature rise of 14°C over the fixed bed for 100 percent conversion and 1000 ppm initial NO concentration. This is based only on the heat capacity of the gases. In a small fixed bed this temperature rise will be less. Therefore, this adiabatic temperature rise is neglected.
Axial gradients in packed beds

Axial dispersion depends on the ratio of particle diameter and bed length, fluid properties and fluid velocity. It means that the number of particles in the axial direction of the bed should be large enough and is expressed in the Bodenstein (Bo) number\textsuperscript{14, 12}:

\[
Bo = Pe_{ax} \frac{L_b}{d_p}
\]  

(3.2)

and:

\[
\frac{1}{Pe_{ax}} = \frac{0.5}{1 + \frac{3.8}{Re_p Sc}} + \frac{0.3}{Re_p Sc}
\]  

(3.3)

only when $0.008 < Re_p < 400$ $0.28 < Sc < 2.2$

where $Pe_{ax} = \frac{d_p v_g}{D_{ax}}$, $Re_p = \frac{\rho_g u_g d_p}{\eta_g}$, $Sc = \frac{\eta_g}{\rho_g D_g}$, $v_f = \frac{u_g}{\epsilon_b}$

(3.4)

with:

Bo : Bodenstein number [-];
$D_{ax}$ : axial dispersion coefficient [m$^3$ m$^{-1}$ s$^{-1}$];
$Pe_{ax}$ : axial Peclet number [-];
$Re_p$ : particle Reynolds number [-];
Sc : Schmidt number [-];
$v_g$ : interstitial gas velocity [m$^3$ s$^{-1}$];
$D_g$ : gas phase diffusion coefficient [m$^2$ s$^{-1}$];
$\eta_g$ : gas phase viscosity [Pa s];
$u_g$ : superficial gas velocity [m$^3$ m$^{-2}$ s$^{-1}$];
d$p$ : particle diameter [m$^3$];
$L_b$ : length bed [m$^3$];
$\rho_g$ : density gas phase [kg m$^{-3}$];
$\epsilon_b$ : porosity bed [m$^3$ m$^{-3}$];

and subscripts:

ax : axial;
b,r : reactor bed volume;
p : particle;
g : gas phase.

Chapter 3
In general axial dispersion does not occur, Bo > 20 see Table 3.11. When measuring very active catalysts, one uses a very small amount of material as to avoid 100 percent conversion. The height of the bed becomes very small leading to inhomogeneity in bed packing which gives channelling. Therefore, it is normally not advisable to have a bed length smaller than bed diameter without additional measures (e.g. dilution).

Table 3.11: Summary hydrodynamics of the fixed bed reactors used for a temperature of 300°C.

<table>
<thead>
<tr>
<th></th>
<th>Cu mordenite</th>
<th>Cu mordenite</th>
<th>Ce mordenite</th>
<th>DN 110</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Screening</td>
<td>Test bench</td>
<td>Test bench</td>
<td>Test bench</td>
</tr>
<tr>
<td>$D_p$ (mm)</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$Re_p$</td>
<td>4</td>
<td>38</td>
<td>63</td>
<td>115</td>
</tr>
<tr>
<td>$L_p/D_p$</td>
<td>32</td>
<td>85</td>
<td>49</td>
<td>34</td>
</tr>
<tr>
<td>Bo</td>
<td>100</td>
<td>187</td>
<td>104</td>
<td>71</td>
</tr>
<tr>
<td>$D_l/D_p$</td>
<td>16</td>
<td>19</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>$\Delta P$ (bar)</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Radial gradients in packed beds

Radial gradients in packed bed reactors stem from bad initial distribution and from channelling near the wall (local higher porosity). For laboratory units a good initial radial distribution can be obtained without extra measures (e.g. static mixers). The channelling at the wall can be neglected when sufficient particles are present on the tube diameter (at least 10 particles):\(^{13, 14}\):

$$\frac{d_b}{d_p} > 10$$  \hspace{1cm} (3.5)

The number of particles was usually between 10 and 20, Table 3.11, so a small influence of the resulting non-uniform velocity distribution can be expected (conversions for a first order reaction will be lowered due to the increase in residence time distribution). This should be kept in mind especially when testing large diameter particles in a small reactor; e.g. 3 mm DN 110 in an 8 mm reactor.
Axial and radial gradients in monoliths

Initial radial gradients across the reactor should be avoided especially in the case of monoliths because no exchange between the channels exists. For a laboratory scale setup this is generally not a problem but in larger scale units special designed multi point injector systems and static mixers are used. Furthermore, it is normal to use several layers of monoliths (about 3) to let the gases mix between.

Because of the laminar flow of the gases inside a monolithic channel, the velocity flow profile is parabolic. At the entrance of a channel this parabolic profile is not present yet. This entrance region should be small compared to the total length of the channel:\(^{15}\):\(^\text{(3.6)}\)

\[
\frac{z}{d_c} = 0.05 \, Re_c
\]

\[
Re_c = \frac{\rho_g \, v_c \, d_c}{\eta_g}
\]

with:

- \(z\) : entrance region [\(m_c\)];
- \(d_c\) : diameter channel [\(m_c\)];
- \(v_c\) : gas phase velocity in a channel [\(m^3_g \, m^{-2} \, s^{-1}\)];

and with subscript :

- \(c\) : channel.

The Peclet number can be calculated according to:\(^{15}\):\(^\text{(3.7)}\)

\[
Pe_{ax} = \frac{192}{Re \cdot Sc} \quad \text{for} \quad Re \cdot Sc > 1
\]

Also in this case axial dispersion is negligible, see Table 3.12. The entrance region is always less than 10 percent of the overall length of the monolith.
Table 3.12: Summary hydrodynamics monoliths used for a temperature of 300°C.

<table>
<thead>
<tr>
<th></th>
<th>Screening setup</th>
<th>Test bench</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of channels</td>
<td>12</td>
<td>133</td>
</tr>
<tr>
<td>Channel Length [mm]</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>Channel diameter [mm]</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Bo</td>
<td>551</td>
<td>136</td>
</tr>
<tr>
<td>Entrance region [%]</td>
<td>3</td>
<td>9</td>
</tr>
</tbody>
</table>

Pressure drop in packed beds

The pressure drop across a fixed bed reactor is usually the limitation for the particle diameter used (monoliths have a very small pressure drop). For 0.05 bar estimated (Ergun equation) pressure drop 0.5 mm particles were selected:

\[
\Delta P = \frac{u_s^2}{d_p} \frac{L_b}{e_b^3} \left( \frac{1-e_b}{e_b} \right)^2 \left( 170 \frac{1-e_b}{Re_p} + 1.75 \right)
\] (3.8)

with:

\( \Delta P \) : the pressure drop [Pa].

In practice this can be higher, because of the fact that a particle distribution has a higher pressure drop. For the Cu mordenite catalyst, see Table 3.11, the pressure drop exceeded 0.05 bars and therefore larger particles have been used.

Summary hydrodynamics

The hydrodynamics of the packed beds and monoliths used are such that an ideal tube reactor model can be applied to describe the results measured.

3.3.3 External and internal mass transfer

Mass and heat transfer from the bulk gas phase to a catalyst particle (external) and inside a porous catalyst particle (internal) can become the rate determining step as well. This phenomenon occurs especially at high reaction rates. Generally these types of limitations are expressed in observed reaction rate compared to physical transport parameters obtained from empirical correlations. The advantage is that no knowledge is required regarding kinetics (often only the reaction order). However, especially with the vanadium type catalysts, it is known that the order in NO is close to unity and in NH₃ is close to zero. When assuming this, one can calculate the minimum measured conversion for the reaction to be mass transfer limited.
The goal of this exercise is to establish a priori in which case influence by transport limitations can be expected. The exact values of the transport parameters involved, e.g. the mass transfer coefficient and effective diffusion coefficient, are to be evaluated experimentally. The correlations given in this paragraph are only an order of magnitude estimate. Furthermore, this evaluation holds only when ammonia slip is present: at high temperatures the NO conversion tends to drop with most catalysts while the ammonia conversion remains 100%. In that case it is not possible to predict the reaction rate any more.

**Internal mass transfer**

Pore diffusion limitation occurs generally at a lower temperature than film diffusion limitation. This is a result of the much lower diffusion coefficient in porous media. This lower diffusion coefficient rises from hindrance of diffusion in small pores expressed as Knudsen diffusion\(^{11, 12}\):

\[
D_{knu} = \frac{4r_{\text{pore}}}{3} \sqrt{\frac{2RT}{\pi M}}
\]

(3.9)

with:

- \(D_{knu}\) : Knudsen diffusion coefficient \(\text{[m}^2\text{g s}^{-1}]\);
- \(r_{\text{pore}}\) : average pore radius \(\text{[m]}\);
- \(R\) : gas constant \(\text{[8.314 J mol}^{-1}\text{K}^{-1}]\);
- \(T\) : absolute temperature \(\text{[K]}\);
- \(M\) : molar mass \(\text{[kg mol}^{-1}]\).

Averaging and considering the hindrance by the pores:

\[
D_e = \frac{\epsilon_p}{\tau_p} \frac{1}{\frac{1}{D_{knu}} + \frac{1}{D_g}}
\]

(3.10)

with:

- \(D_e\) : effective diffusion coefficient \(\text{[m}^2\text{g m}^{-1}\text{p s}^{-1}]\);
- \(\epsilon_p\) : porosity particle \(\text{[m}^3\text{m}^{-3}\text{p}]\);
- \(\tau_p\) : tortuosity factor \(\text{[m}^2\text{p m}^{-2}\text{g}]\).

To be able to calculate this effective diffusion coefficient some estimates are needed\(^{16}\); first of all the tortuosity factor (usually 2-5; 3.5 used) and the porosity (usually 0.3-0.6; 0.45 used). The other important parameter is the average pore diameter\(^{12, 14}\).

*Chapter 3*
\[ r_{pore} = \frac{2 \cdot V_{pore}}{S_{BET}} \]  \hspace{1cm} (3.11)

with:

- \( V_{pore} \): pore volume \([\text{m}^3\text{g}^{-1}]\);
- \( S_{BET} \): BET surface area \([\text{m}^2\text{g}^{-1}]\).

The BET surface area and pore volume can be obtained from standard N\(_2\) adsorption techniques. For DN 110 the BET surface area is about 100 m\(^2\)/g and the pore volume is 0.45 ml/g giving an average pore diameter of 9 nm. The presence of pore diffusion limitation is expressed in terms of the Weisz modulus\(^{17}\):

\[ \Phi = \eta_e \phi^2 = \frac{(n+1)}{2} \frac{r_{v,p}^{obs} d_p^2}{D_e C_i 36} \]  \hspace{1cm} (3.12)

with:

- \( \Phi \): Weisz modulus [-];
- \( \eta_e \): efficiency catalyst [-];
- \( \phi \): Thiele modulus [-];
- \( n \): reaction order [-];
- \( r_{v,p}^{obs} \): observed reaction rate \([\text{mol m}^{-3}\text{s}^{-1}]\);
- \( D_e \): concentration at the interface \([\text{mol m}^{-3}\text{g}]\);

with the subscripts:

- \( i \): interface.

For a first order irreversible reaction and spherical particles, an efficiency of 95 percent corresponds with a Weisz modulus of 0.8. For DN 110 it can be shown that to fulfil this criterion the conversion on 0.5 mm particles should not exceed 80 percent, the 3 mm particles are already diffusion limited at 5 percent conversion, see Table 3.13. (Actually, due to the error in \( \epsilon_p \) and \( \tau_p \) this is a range of 2-12 percent.)
For the zeolite type catalysts a slightly different approach is taken. A zeolite pellet consists of zeolite crystals with a typical diameter of 1 μm. So the channels between those crystals will also be of this order of magnitude. The transport resistance through these channels is mainly caused by the (non) straightness and porosity, giving rise to a diffusion coefficient of about 0.1 times \((ε_p/τ_p)\) in equation 3.10) the bulk diffusion coefficient. The resulting diffusion limitation for the 0.5 mm particles can be neglected (the 1.7 mm particles can give problems over 80 percent conversion though).

Yet another diffusion limitation can be considered for zeolites; the diffusion in zeolite channels. The Knudsen approach cannot be used because the average diameter of the pores is on a molecular level. The average pore diameter is determined by the type of zeolite and can also be effected by the ion exchange procedure. The crystal size can be influenced by the preparation route. The ion exchange procedure was for each batch different (varying metal content and atoms) but generally the same zeolite batch was used (same crystal size). The order of magnitude\(^{18}\) of this type of diffusion coefficients is \(10^{-8}\) to \(10^{-12}\) m\(^2\)/s. Even with a diffusion coefficient of \(10^{-12}\) for 1 μm crystals the efficiency is still 95% at a measured conversion of 50%.

**External mass transfer**

External mass transfer limitation is usually expressed in Carberry numbers, which is the dimensionless concentration difference across the film\(^{17}\):

\[
Ca = \frac{r_{wp}^{obs}}{k_f a_v C} = \frac{C - C_i}{C}
\]  

(3.13)

with:

- \(Ca\) : Carberry number [-];
- \(k_f\) : mass transfer coefficient [m\(^3\)/g m\(^2\)/s];
- \(C\) : concentration [mol m\(^{-3}\)];
- \(a_v\) : volumetric interface surface area [m\(^2\)/m\(^3\)].

---

**Table 3.13: Summary internal diffusion DN110**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_p) [nm]</td>
<td>9</td>
</tr>
<tr>
<td>(ε_p) [m(^3)/g m(^3)]</td>
<td>0.45</td>
</tr>
<tr>
<td>(τ_p)</td>
<td>3.5</td>
</tr>
<tr>
<td>(D_p) [mm(^2)]</td>
<td>3</td>
</tr>
<tr>
<td>(D_e) [m(^3)/g m(^3) s]</td>
<td>(4.6 \times 10^{-7})</td>
</tr>
<tr>
<td>Conversion (Φ) = 0.8</td>
<td>5</td>
</tr>
</tbody>
</table>
The film transfer coefficient can be calculated from a standard Reynolds relation

\[ j_D = 1.66 \ Re_p^{-0.51} \]  \hspace{1cm} (3.14)

with:

\( j_D \) : j-factor for mass transfer [-].

When using 0.5 mm particles the maximum conversion to be measured without having film diffusion limitation is over 99.9 %. The most critical case is the measurement of DN 110 (3 mm spheres) in the test bench. It is estimated that above 80-90 percent measured conversion the Carberry number will exceed 0.05 and thus film diffusion limitation will occur. As to be expected all these values are lower for pore diffusion limitation meaning that pore diffusion occurs at an earlier stage.

**Internal and external mass transfer in monoliths**

The mass transfer problems in a washcoated monolith are somewhat different compared to the fixed bed case. A particle of 0.5 mm diameter has a maximum diffusion length of 0.25 mm whereas the space between the particles is even less. In the monolith case the washcoat thickness is about 0.05 mm and the diameter of the channel is 1 mm. Furthermore, the flow in the channels is usually laminar resulting in a low mass transfer coefficient.

Therefore, the presence of pore and film diffusion limitation has to be regarded simultaneously. The main problem is to estimate the effective diffusion coefficient, because the pore structure and average pore diameter are not known. Furthermore, the thickness of the washcoat is also not well known. Therefore, this parameter has to be estimated with experimental data. For the mass transfer coefficient literature data can be used:

\[ Sh = 2.976 \ (1 + 0.095 \ \frac{d_h}{L} \ Re \ Sc)^{0.45} \]  \hspace{1cm} (3.15)

with:

\( d_h \) : hydraulic diameter channel [m];
\( L \) : length channel [m];
\( Sh \) : Sherwood number [-].

It is noted that some differences exists in the prediction of Sherwood numbers, which can cause a factor of 3 or 4 deviation in calculated mass transfer coefficient. This observation only stresses the point made in the beginning of this paragraph that this type of correlation is an order of a magnitude estimate. The extra attention given here is because some empirical correlations give a Sherwood number, which is smaller than the analytic solution for laminar flow (2.976 for square channels). Using equation 3.15 gives Sherwood numbers close to three for both setups.

**Catalyst testing**
Film diffusion limitation will occur, equation 3.13, above conversions of about 60 percent. As pore diffusion limitation will probably occur at lower conversions, most of the experiments will be performed in a diffusion limited regime. More detailed information about mass transfer limitations in monoliths will be presented in Chapter 6.

Summary internal and external mass transfer

- All zeolite type catalysts are measured without film diffusion and inter zeolite crystal diffusion limitation
- Intra zeolite crystal diffusion limitation is not very likely even though reliable literature data and correlations for this type of diffusion coefficients are not available
- The DN 110 in original particle diameter is likely to be pore diffusion limited
- For DN 32 transport limitations have to be considered especially at higher conversions

These conclusions hold only for the standard configuration as described in section 3.2 and for conversions smaller than 90 percent.

3.4 Catalyst testing

The catalysts tested has been subdivided in home-made and commercial catalysts which will be described in section 3.4.1 (zeolite type catalysts) and 3.4.2 (vanadium type catalysts). Subsequently, in section 3.4.3, the most promising zeolite type catalysts will be compared with the commercial ones. The results described in section 3.4 have been published in a patent application\(^2\) and several articles\(^4,21,22\). The figures in this section represent the data points measured; the drawn lines only show the trend of the measurements.

3.4.1 Home-made zeolite type catalysts

This section describes the performance of the home-made zeolite type catalysts. In section 3.4.1.1 results of the catalyst screening are given and compared to results obtained with diesel exhaust gas (section 3.4.1.2). This section is concluded with a study on Ce mordenite (section 3.4.1.3).

3.4.1.1 Screening of zeolite type catalyst

To determine the influence of various types of zeolites and of exchanged metal ions, the catalysts were screened as a function of the temperature, keeping all the other variables constant. This screening was performed with the catalyst screening setup as described in section 3.2.1. The number of metal-ions to be screened is limited by previous research and literature\(^1,5\) to Fe, Cu, Co and Ce. The types of zeolites studied were zeolite Y, mordenite and ZSM-5 (instead of ZSM-5 the abbreviation Z40 will be used). The Si/Al ratio of these zeolites generally increases in this order. This means that the amount of metal ions which can be exchanged decreases, because this is proportional to the amount of alumina sites. On the other hand, zeolites tend to be more stable when having a high Si/Al ratio. In this way an optimum can be found regarding metal loading (activity) and stability.
The activity per metal atom will probably be dependent of the zeolite type; e.g. the acidity of the zeolites increases considerably with increasing Si/Al ratio. Furthermore, a higher metal loading does not always lead to a higher activity; the number of metal exchange sites in the zeolite cage may vary with loading or deposition on the outer surface of the zeolite crystals can occur. In literature, over 100% ion exchange is reported, especially for Cu-ions. In that case the Cu ion has been introduced in the 1 plus form allowing up to 200% ion-exchange when calculated on a 2 plus basis.

Promising catalysts are catalysts which show 1) a high activity for the NO/NH₃ reaction and 2) a low activity for the SO₂ oxidation in 3) a wide temperature range (200 to 600°C). A high activity for the NO/NH₃ reaction is defined as equal to or higher than 70% NO conversion (space velocity 30 000 h⁻¹), a low activity for the SO₂ oxidation is defined as less than 10% SO₂ conversion.

The influence of metal-ions on the activity of NaZ40

a) the SCR reaction

In Figure 3.5 the activity of Cu, Fe, Co and Ce exchanged Z40 is displayed as a function of temperature. At temperatures below 350°C the activity order is Cu > Fe > Ce > Co. However, above 350°C this changes to Fe = Ce > Cu > Co. The decrease in activity for CuNaZ40 can probably be attributed to a simultaneous NH₃ oxidation.

The activities of CuNaZ40 and FeNaZ40 are probably at their maximum for this Z40 since their ion-exchange rate is close to 100% (96% and 94% respectively). The loading of the Ce- and CoNaZ40 can be improved; they are 39 and 69 percent. CoNaZ40 will not be applicable in practice because of its low activity. CeNaZ40 however, is quite promising regarding its relative high activity between 300 and 600°C (in spite of its low loading).
b) SO$_2$ oxidation

The activity of Cu, Fe and CeNaZ40 for the SO$_2$ oxidation is shown in Figure 3.6 (CoNaZ40 has not been tested anymore). At 400°C Cu- and FeNaZ40 exhibited SO$_2$ oxidation whereas the CeNaZ40 showed only a small level of SO$_2$ oxidation at 600°C. From the point of view of SO$_2$ oxidation the CeNaZ40 shows the best performance.

The influence of metal-ions on the activity of NaMOR

a) the SCR reaction

This type of zeolite is less stable than Z40 but allows a higher metal load. The ion-exchanged mordenites show the same type of behaviour as the Z40, Figure 3.7. In this experiment a mass spectrometer was used to measure NH$_3$; at 200°C NH$_3$ slip was detected in case of Ce and H-MOR; CuNaMOR showed already 100 percent conversion. At higher temperatures (>300°C) no NH$_3$ slip was detected anymore for Ce- and CuNaMOR.
It has been attempted to raise the activity further by increasing the metal load for the Ce and Cu containing mordenite, Figure 3.8. For CuNaMOR one can expect not much effect because the NH$_3$ conversion is already 100%. However, the NH$_3$ oxidizing capacity might differ (in other words: the selectivity might change). As can be seen in Figure 3.8 the NO conversion is a little lower at high temperatures for the CuNaMOR 56 which has a higher metal load than CuNaMOR 49 (4.8 and 3.7 wt %). For CeNaMOR 47 (5.7 wt %) and CeNaMOR 64 (3.2 wt %) holds more or less the same; the NO conversion at 500 and 600°C is less. At 200°C the difference between the measurements is only 6 percent indicating a slight increase in reactivity. The conclusion is that the metal loading is sufficient for CeNaMOR; an increase does not lead to significant activity improvements anymore; on the contrary the selectivity decreases slightly.

b) SO$_2$ oxidation

In Figure 3.9 the SO$_2$ oxidation for Cu, Ce and H-MOR is displayed. As to be expected the base H-MOR did not show any SO$_2$ oxidation and like Z40, Cu did show a high activity and Ce a very low one.
The influence of the zeolite type on the activity of Ce

a) the SCR reaction

On basis of metal loading - CeNaZ40 60 0.37 wt%, CeNaMOR 3.2 wt% and CeY 9.7 wt% - the activity is expected to increase in this order. This is however not so; see Figure 3.10. The maximum is clearly found for CeNaMOR; so the influence of the zeolite is more important than a much higher metal load and thus, activity. The low activity for CeY can possibly be attributed to a low cerium atom utilisation (e.g. formation of CeO_x clusters in the large Y cages^4).

b) SO_2 oxidation

The SO_2 oxidative capacity is expected to be proportional to the Ce load; CeNaZ40 66 3.1 wt%, CeNaMOR 3.2 wt% and CeY 9.7 wt%, Figure 3.11. However, due to the low activity of the Ce catalysts the differences are not very significant meaning that from the point of view of SO_2 oxidation no preferences can be stated. Only CeY shows an SO_2 oxidation exceeding 10 percent at 600°C.
The influence of the zeolite type on the activity of Cu

The same type of experiment has been performed with Cu catalysts. Only CuNaZ40 53 (2.3 wt%) and CuNaMor 56 (4.8 wt %) were studied; the results of the activity towards the NO/NH₃ reaction and SO₂ oxidation are displayed in Figure 3.12. No significant differences can be seen regarding the activity for the SCR reaction up to 500°C, which is not surprising as the conversion for NH₃ is 100%. The only conclusion to be drawn is that the selectivity does not depend very much on whether Z40 or MOR is being used (except at 600°C). The SO₂ oxidizing capacity increases with a higher Cu load, but the onset of the reaction is in both cases about 400°C.

Concluding remarks on the catalyst screening

The best catalyst found in this catalyst screening is CeNaMor. This catalyst has the lowest SO₂ oxidation rate and still reaches 70 % conversion between 300 and 600°C. Therefore, this catalyst and CuNaMor have been used for further testing. The latter has been used also because it has a high activity at low temperatures; it is expected that the activity in diesel exhaust will be lower.

3.4.1.2 Testing with diesel exhaust

The CeNaMor 64 and CuNaMor 49 have been tested with diesel exhaust in the temperature range of 250-500°C, Figure 3.13. Evidently, the Cu catalyst has a satisfactory activity in this T range whereas the Ce catalyst only starts performing well above 400°C. This temperature can be lowered somewhat by decreasing space velocity but this Ce catalyst
cannot be expected to work far lower than 400°C. This low activity in the temperature range of 300-400°C is a serious drawback because 30 to 50 percent of the overall NO_x output of a diesel engine occurs in this range (Chapter 2).

One of the reasons for this low activity is the presence of SO_2 in the diesel exhaust; at 387°C a simulated diesel engine mixture (10% O_2 and 7% H_2O) has been treated with 50 ppm SO_2. The result is an activity drop; the conversion went down irreversibly from about 80 to 60 percent, Figure 3.14. This might be attributed to ammonium sulphate formation in the zeolite pores (see also Chapter 2).

The SO_3 formation is displayed in Figure 3.15; obviously also in diesel exhaust Cu mordenite oxidizes SO_2 excessively above 400°C whereas Ce mordenite does not.

![Figure 3.14: The influence of SO_2 on the NO conversion on CeNaMOR 64 (15 g, 500 ppm NO & NH_3, 10% O_2, 7% H_2O in 15 Nl/min N_2).](image)

![Figure 3.15: SO_3 formation as a function of temperature (15 g, 15 Nl/min diesel exhaust using 0.14% S fuel).](image)

3.4.1.3 Study on CeNa-Mordenite

The CeNa-Mordenite 64 has been subjected to further testing because it shows SCR activity without SO_2 oxidation. The stability of this type of catalyst has been investigated first. Subsequently attention has been paid to the selectivity and the influence of gas phase composition on the activity.
Stability of CeNaMOR 64

The stability of the catalyst has been studied with the catalyst screening setup first. In Figure 3.16 can be seen that an initial activity decline was observed at 200°C, when the catalyst had been subjected to one temperature programmed experiment. This means that the catalyst has been heated to 600°C for about 3 hours. Heating for 24 hours at 600°C showed only a small further activity drop. The activity at 300°C stayed almost at the same high level during this treatment. This deactivation is relatively minor compared to a sample taken from the same batch which has been exposed to diesel exhaust gases. Only at 500°C the activity was fully restored, and at 600°C the selectivity was less. The degree of degradation is quite severe, Figure 3.17, the Ce mordenite catalyst which has been treated with diesel exhaust has about the same activity as H-Mordenite.

![Graph](image.png)

**Figure 3.16:** The influence of aging on the NO conversion as a function of temperature for CeNaMOR 64 (0.5 g, 1000 ppm NO & NH₃, 5% O₂ in 500 Nml/min Ar).

**Figure 3.17:** Comparison of the activity of H-MOR with Ce-MOR 46 treated with diesel exhaust gases (0.5 g, 1000 ppm NO & NH₃, 5% O₂ in 500 Nml/min Ar).

This procedure has been repeated with the test bench using very low sulphur (< 0.001 weight percent) diesel fuel to exclude influence of SO₂ on the catalyst. The results, Figure 3.18, are essentially the same; exposure of the Ce mordenite to diesel exhaust leads to degradation. The reason for this is not yet clear; in the case of Cu zeolites degradation of the zeolite structure in the presence of water has been reported. Another explanation is that cerium forms CeOₓ clusters which are inactive for the SCR reaction. The third explanation would be the deposition of coke or other compounds on the catalyst.

The way to proceed is to test CeNaZ40 with diesel exhaust because it is supposed to be less sensitive to water vapour. Furthermore, it has a lower metal load and therefore less susceptible to CeOₓ formation. The activity of this catalyst in model gases is also reasonable, Figure 3.10.
Figure 3.18: Stability of CeNaMOR 84 in diesel exhaust (15 g, 500 ppm NO\textsubscript{x} and NH\textsubscript{3} in 15 Nl/min exhaust, low S diesel fuel used).

Figure 3.19: NH\textsubscript{3} conversion and NO formation as a function of temperature for CeNaMOR 64 (15 g, 500 ppm NH\textsubscript{3} in 15 Nl/min Air, ○, or 500 ppm NO & NH\textsubscript{3}, △).
Figure 3.20: NO & NH₃ conversion on CeNaMOR 84 as a function of NH₃ concentration at 440°C (△) and 530°C (○) (15 g in 15 Ni/min diesel exhaust using low sulphur fuel, 470 ppm NOₓ).

Ammonia slip

The main technical problem for application of SCR in transient operation lies in the control of the amount of ammonia/urea injected as explained in Chapter 2. Consequently, attention must be paid to the ammonia oxidative capacity of the catalysts. As shown in Figure 3.19, Ce-MOR does not produce any NO during SCR operation or ammonia oxidation (in contrast to Cu-MOR and vanadium type catalysts, see section 3.4.2).

The question is if it is possible to use an over stoichiometric amount of ammonia to reduce the NOₓ. The idea is that superfluous ammonia will be oxidized to nitrogen rather than NO. This would simplify the control problem considerably. As shown in Figure 3.20 this can be accomplished in a diesel exhaust gas at high temperatures. Of course, the amount of overdosing is limited because the onset of ammonia oxidation may also shift to a higher temperature in case of diesel exhaust. Furthermore, chances of ammonia slip caused by desorption due to temperature transients will increase because more ammonia will be stored on the catalyst.
Influence of gas phase composition

The influence of gas composition has been studied briefly to get an idea of the reaction order. Firstly the NO conversion as a function of NH$_3$/NO ratio rises linearly, Figure 3.21. The NO$_x$ conversion rises to 95 percent conversion and stays constant above this conversion level. This experiment has been repeated at lower NO$_x$ conversions showing the same trend; above a certain NH$_3$/NO inlet ratio the NO$_x$ conversion levels off. This means that the reaction order in ammonia is close to zero.

At a lower NO inlet concentration (keeping the NH$_3$/NO inlet ratio 1) the conversion increases, Figure 3.22. This means that the reaction order in NO is somewhat lower than one. The influence of O$_2$ at 250°C showed an order of about 1/4 indicating the presence of some sort of redox equilibrium constant, Figure 3.23. According to these experiments CeNaMOR 64 behaves at 250°C like a vanadium type catalyst$^7$; order in NO of about 1, an order in NH$_3$ close to zero and a low order in O$_2$. The same trends have also been observed for CuMOR and HMOR$^{24, 26}$. (This does not mean that the same reaction mechanism has to hold, see also Ito$^{21}$.)

Of course, more rigorous research is needed to obtain accurate kinetic data. Moreover, other gas phase components, e.g. water, have to be covered yet. In Figure 3.24 a simulated diesel exhaust gas (with the same water and O$_2$ concentrations as the diesel exhaust itself) is compared to the experiment with diesel exhaust gas. The agreement between the NO conversions is remarkable considering the stability of the catalyst and the fact that diesel exhaust gas contains a host of other components (hydrocarbons, CO, CO$_2$, etc).

![Graph](image1.png)

**Figure 3.21:** The influence of the NH$_3$/NO inlet ratio in the NO conversion on CeNaMOR 64 (0.5 g, 1000 ppm NO, 5% O$_2$ in 500 Nml/min Ar).

![Graph](image2.png)

**Figure 3.22:** The influence of NO inlet concentration on the NO conversion on CeNaMOR 64 (0.5 g, NH$_3$/NO=1, 5% O$_2$ in 500 Nml/min Ar).
$N_2O$ formation

The last check on the cerium mordenite catalyst is the amount of nitrous oxide produced. It has been reported\(^7\) that large amounts of $N_2O$ can be formed during the SCR reaction. Using a GC-ECD combination, the $N_2O$ output for the Ce-MOR catalyst using low sulphur diesel fuel has been measured. The diesel engine itself appears to produce $N_2O$, values in the range of 2 to 10 ppm are found. The catalyst produces up to 10 ppm $N_2O$ at 440°C during the SCR reaction. However, at 510°C it reduces the engine emission with up to 50 percent. The conclusion is that no significant effect of using a cerium catalyst for the SCR reaction on the $N_2O$ emission has been detected.

Applicability zeolite type catalysts in exhaust gases

Several authors\(^27\) do encounter problems when using zeolite type catalysts in exhaust gas application. The most serious one is the stability; especially Cu ion exchanged zeolites tend to be instable. In this work some catalyst activity decline has been encountered also. This does not mean that zeolites are unstable in exhaust gas application: Byrne\(^25\) reports a zeolite catalyst with unknown composition for use in high temperature SCR application. The catalyst had been tested in off gases from gas turbines and did not show the drastic deactivation from Cu zeolites. He also reports the selective oxidation of ammonia to nitrogen. Walker\(^28\) reports on the use of a 'zeolite catalyst without heavy metals' for use in high temperature (>400°C) application, for gas engines. This is consistent with the fact that Medros\(^26\) reports the H form of mordenite to be active at high temperatures as well (see also Figure 3.7). However, the activity at temperatures below 400°C is still low\(^29\).

Summary

It has been shown that a metal exchanged mordenite (Ce) can have a high SCR activity without oxidizing $SO_2$ to $SO_3$ and $NH_3$ to NO. The advantage of the Ce catalyst is that ammonia oxidation gives only nitrogen which is an advantage regarding process control. Furthermore, it should be noted that since most zeolites tend to absorb large amounts of $SO_2$, in practice some temperature transient related desorption effects can be expected.
3.4.2 Vanadium type catalysts

This type of catalyst is tested because of the proved activity in real exhaust gases. It will be shown that an optimized vanadium type commercial catalyst for diesel exhaust gases can work quite well. However, when using this catalyst it is especially important to prevent high temperatures (T > 450°C) in the exhaust gases.

![Graph showing NO conversion as a function of temperature (0.5 g DN110 or 0.6 g DN 32, 1000 ppm NO & NH₃, 5% O₂ in 500 Nml/min Ar).]

![Graph showing SO₂ conversion as a function of temperature (0.5 g DN110 or 0.7 g DN 32, 500 ppm SO₂, 5% O₂ in 500 Nml/min Ar).]

3.4.2.1 Lab scale study of DN32 and DN 110

The activity towards the NO/NH₃ reaction

A characteristic temperature plot for the vanadium type catalysts is shown in Figure 3.25. The activity starts at 200°C, goes through a maximum at 300°C and is zero above 500°C. Actually, at temperatures above 500°C more NO was coming out of the reactor then going in, pointing at a high ammonia oxidation. In such cases (negative conversion levels) the conversion has been put at zero in the figures.

The activity towards SO₂ oxidation

Vanadium type catalysts might be expected to oxidize SO₂ quite well: they are used in sulphuric acid plants. DN 32 is a V₂O₅/TiO₂ catalyst with WO₃ added to suppress this SO₂ oxidation. As shown in Figure 3.26 this has been quite successful compared with the DN 110. On basis of these results, excellent performance of DN 32 would be expected in diesel exhaust and only this commercial catalyst has been tested with diesel exhaust.
3.4.2.2 Testing with diesel exhaust

DN 32 shows an activity window which can be expected from a vanadium type catalyst (Figure 3.27); the activity starts at about 300°C, goes through a maximum at 400°C and drops off at 500°C due to ammonia oxidation. At the same time the SO₂ oxidation starts to rise at this 400°C. The conclusion is that DN 32 works quite well for the DeNOₓ reaction up to about 450°C, but some SO₃ formation should be considered.

Svachula⁶⁰ has performed an extensive study on the oxidation of SO₂ to SO₃ over vanadium type honeycomb catalysts. When performing the SCR reaction with low NH₃/NO ratios he found an increase in SO₃ output, when using high ratios (up to 0.8) the SO₃ output decreased compared to base level (no NH₃ or NOₓ). This was attributed to an inhibiting effect of ammonia and a promoting effect of NOₓ. Therefore, the base level activity is a good indication of the SO₃ output in practice. (All SO₃ formation measurements in diesel exhaust gases have been performed without NH₃ addition.)

3.4.2.3 Study on DN 32 and DN 110

Study on DN 110

As already mentioned in section 3.3 the DN 110 catalyst is probably internal diffusion limited. This has been checked by comparing the conversions of two different diameters, 0.5 and the original 3 mm, Figure 3.28 (without water). At low temperatures, low conversions, the conversion is for both particle diameters the same. However, an increased temperature gives rising conversions and larger particles show a significantly lower conversion.

The effect of adding water is to lower the reaction rate. However, the same trend can be observed: at about 20 percent conversion the particles of 0.5 mm start to exhibit higher activities than those of 3 mm. This means that at this conversion level of 20 percent the effect of pore diffusion starts to become visible. This was estimated to be between 2-12 percent conversion for an efficiency of 95 percent. The discrepancy can be explained by considering that 5 percent efficiency difference at 20 percent conversion level, results in only 1 percent change at that 20 percent conversion level. The experimental reproducibility of 2 percent is insufficient to detect such minor changes.

Catalyst testing
Figure 3.28: The NO conversion on DN110 as a function of temperature (0.5 g, 1000 ppm NO & NH₃, 5% O₂ in 500 Nml/min Ar with or without 15% water).

Figure 3.29: NH₃ conversion and NO formation as a function of temperature for DN 32 (25 g, 500 ppm NH₃ in 15 Nl/min Air, ○, or 500 ppm NH₃ & NO, △).
Study on DN 32

The decline in activity at higher temperatures is caused by NH$_3$ oxidation; see Figure 3.29. At lower temperatures, up to 300°C, the ammonia and NO conversion rise simultaneously. At the point that the NO conversion starts to drop, the ammonia conversion rises to 100 percent and the catalyst starts oxidizing NH$_3$.

Water has a larger influence on the SCR activity, see Figure 3.30. The influence of water on the activity of vanadium type catalysts is rather complex$^{31}$; besides competition with ammonia for reaction sites also inhibition due to irreversible adsorption is reported$^{32}$. However, the difference is not large enough to explain the activity of DN 32 in diesel exhaust. This is partly attributed to the presence of sulphur compounds which form sulphates at low temperatures (Chapter 2). These sulphates start to decompose at about 300°C.

![Diagram](image1)

Figure 3.30: The NO$_x$ conversion as a function of temperature for DN32 (25 g, 15 Nl/min diesel exhaust, air or 10% H$_2$O in air).

![Diagram](image2)

Figure 3.31: NO$_x$ conversion as a function of temperature using diesel exhaust gases (0.14 wt% S diesel fuel).
3.4.3 Comparison commercial/home-made catalysts

The catalysts will be compared primarily on basis of activity towards the DeNO$_x$ reaction and the activity for SO$_2$ oxidation. Furthermore attention will be given to the selectivity of the catalysts, NH$_3$ oxidation and N$_2$O formation.

Activity for the DeNO$_x$ reaction

As shown in Figure 3.31 the activity of CuMOR and DN 32 is satisfactory between 300 and 500°C. Above this temperature the NO conversion drops to unacceptable levels. The Ce mordenite starts exhibiting a satisfactory conversion from about 400°C. Therefore, when combining a Ce catalyst with CuMOR or DN 32 a system can be obtained which will probably show good performance at higher temperatures also. The main problem with such a solution is:

![Graph showing SO$_2$ production as a function of temperature using diesel exhaust (0.14 wt% S diesel fuel).]

Activity for SO$_2$ oxidation

Except Ce mordenite all catalysts studied exhibited SO$_2$ oxidation and SO$_3$ formation from about 400°C, Figure 3.32. Especially Cu catalysts are quite good at this. Therefore, when trying to use these catalysts in practice, it should be placed sufficiently down stream the exhaust pipe to avoid temperatures above 400°C. This can give rise to activity problems at lower temperatures.

Activity for NH$_3$ oxidation

The high temperature activity of a catalyst is mostly determined by its NH$_3$ oxidizing capacity. From these results one would expect the Ce catalyst to behave similarly, dropping NO conversion at higher temperatures. The difference is that all catalysts start producing NO (e.g. compare Figure 3.20 and 3.29), except Ce mordenite which produces only N$_2$ fortunately.

Activity for N$_2$O formation

N$_2$O formation is a rather undesirable phenomenon reported to occur with vanadium type catalysts\textsuperscript{7}. In model gases the vanadium type catalysts used, do indeed form N$_2$O. However, the presence of water inhibits N$_2$O formation substantially\textsuperscript{31} and this type of problems is reported\textsuperscript{33} not to occur in the steady state application of vanadium SCR catalysts. Indeed, the results for Ce mordenite, using model gases and diesel exhaust, show that no problems are to be expected regarding N$_2$O formation.

Chapter 3
3.5 Summary

For the catalyst testing two types of equipment have been built. The first one is a catalyst screening setup to test the activity of the catalyst for the SCR reaction and SO₂ oxidation. The second one is a test bench to test the most promising catalysts with diesel exhaust gases. Home-made zeolite type catalysts and commercial vanadium type catalysts have been tested. Cu mordenite and DN 32 showed a high activity in diesel exhaust, but did also show an undesirable SO₂ oxidation above 400°C. Furthermore, the deNOₓ activity tends to drop at temperatures above 450°C due to ammonia oxidation.

It has been shown that the home-made Ce mordenite catalyst can have a high temperature SCR activity (T > 400°C) without oxidizing SO₂ to SO₃ and NH₃ to NO. The problems with the control of the urea injection can be avoided when the dosing needs not to be very precise. Until now, ammonia slip is oxidized (in most cases to NO) by placing an oxidation catalyst behind the SCR system. This can be avoided in the case of this Ce catalyst; ammonia oxidation gives only nitrogen.

The activity of this Ce catalyst however, needs to be improved in the temperature region of 300-400°C before it can be applied to diesel exhaust gases. This might be achieved by using an additional compound (e.g. copper). Furthermore, the stability of the catalyst has not been evaluated extensively and some deactivation during use has been encountered.

Literature

1 Ito, E., *PhD thesis on the development of zeolite type catalysts for NOₓ removal in the presence of oxygen*, Delft University of Technology, Department of Chemical Engineering, The Netherlands, to be published in 1996.
8 Engler, B., Brand, R., *Katalysatoren fuer den Umweltschutz*, Degussa, AG.

Catalyst testing


24 Ham, S.W., Choi, H., Nam, I.S., Kim, Y.G., *Deactivation of copper-ion-exchanged hydrogen-mordenite-type zeolite catalyst by so2 for NO reduction by NH3*, Catalysis Today 11 (1992), 611-21.


Chapter 4

Development of a urea injection system,
selection of nozzle type and prevention of byproducts

The aim of this chapter is to describe the type of problem encountered and solutions proposed to inject a 10 to 40 weight percent aqueous urea solution in hot exhaust gases. At this stage no real exhaust gases were used but hot air with pure NO added. The emphasis lies on the reliability of such a system. The proposed solution consists of a stand alone unit which can be mounted behind an engine easily. The most critical part is the nozzle; evaporation of an aqueous urea solution can easily lead to plugging. Furthermore, methods to detect and of course prevent byproducts, resulting from incomplete urea decomposition, are described.

4.1 Why injection

There are several ways of using urea as an NH source needed for the selective removal of NOx. The choice was already taken in favour of injection of aqueous urea for application in diesel engine exhaust gases, because this seemed to be the most convenient way. However, several alternative methods can be considered also:

a) Wypkema\(^1\) employed a large fixed bed of urea prills for cleaning off gases of a natural gas engine. A small part of the exhaust gas stream is used to decompose this bed of solid urea at 100°C. Subsequently, this side stream is mixed up with the main stream and sent to a catalytic reactor in which the nitrogen oxides are converted. This system was developed for use in greenhouses to clean off gases from total energy installations. These installations are usually stationary and the presence of a large fixed bed is not a problem; it does not need to be transported and warm-up periods are less important.

b) At high temperatures (\(> 600°C\), see also section 2.1.2.3) direct injection of solid urea can be applied. At these temperatures urea can react directly, without catalyst, with NO\(_x\). Unfortunately, temperatures in diesel exhaust gases are too low for this technique. The advantage of using solid urea injection would be the absence of large quantities of water and no freezing problems at winter temperatures (below -10°C). However, processing solids is almost always more difficult than processing liquids, especially hygroscopic solids like urea.

c) Another option is to decompose the urea solution into ammonia before injection by an additional vaporizer. This is the only way to avoid byproduct formation when the exhaust gas stream has a low temperature (\(< 300°C\)). However, vaporizing requires energy and is somewhat more complex than direct injection. The alternative would be the use of an aqueous ammonia solution for which the process can be easily adapted. However, a safety problem arises with the storage of such a solution.

The choice has been made in favour of direct injection of a urea solution because of the ease of handling liquids, the simplicity of the overall process, process safety and the controllability.
Figure 4.1: Pilot-scale equipment for the development of the urea injection system.
4.2 Equipment

In this section the equipment used for the development of the urea injection system will be described. During the experiments urea decomposition products were formed at cold spots in the system. Therefore, a method to determine the amount and chemical nature of these compounds will be described.

4.2.1 Pilot-scale experimental setup

A pilot-scale experimental setup has been used to develop the urea injection system. This experimental setup has a capacity of 20 Nm$^3$/h air to which 0-1000 ppm NO is added (at this stage no vehicle/diesel engine was used). The urea solution can be injected using different types of nozzles. Figure 4.1 shows a sketch of the experimental setup. The main points of interest are the influence of the method of injection, the type of nozzle, the overall NOx reduction, the ammonia slip and the formation of byproducts. For off-gas analysis a chemiluminescence NOx analyser (Signal 4000 series) and a NH$_3$ analyser (Signal 1000 series) have been used (see section 3.2.1).

The reactor in Figure 4.1 is an adapted version of an earlier setup (Wypkema$^1$). A flexible unit has been made which can be placed behind an engine easily. Essentially, the reactor is an externally heated SS pipe, internal diameter 10 cm, length 0.5m. In this pipe catalytic monoliths can be mounted using insulation blankets. Alternatively catalyst pellets can be loaded at the bottom of the reactor. On top of this reactor the urea injection nozzle is mounted. A metal deflection ring is installed to prevent the spray to be blown against the reactor wall. Furthermore, the nozzle can be removed easily for maintenance. In the course of the experiments the following reactor configurations were used:

a) For initial test work 550 grams of DN 110 (3 mm V$_2$O$_5$/γ-Al$_2$O$_3$ pellets, see also Chapter 3) were loaded on the bottom of the reactor. Several nozzle types were used.

b) As the DN 110 pellet type catalyst configuration was deemed to have an excessive pressure drop a monolith was applied. One or two 400 cpi DN32 elements (V$_2$O$_5$/TiO$_2$/WO$_3$ was coated on a cordierite monolith, see also Chapter 3 and appendix 1) were applied. Van der Eijk$^2$ studied the performance of this system. During the experiments it appeared advantageous to apply 'Raschig rings' on top of the monoliths to improve the radial dispersion of urea decomposition products.

c) De Niet$^3$ extended the setup to include a Sulzer SMV100 static mixer instead of Raschig rings. Furthermore, one DN 32 element and an oxidation catalyst (a Hereaus D30 Pt-Rh monolith) were applied in series. This configuration was tested behind a natural gas engine. The oxidation catalyst was necessary to remove unburned hydrocarbons as the cleaned off-gases will be used in greenhouses for crop growth stimulation (CO$_2$ fertilization, see also Lugt$^4$). A positive side effect is that any NH$_3$ slip was oxidized as well.

In this Chapter only the experiments relevant for the development of the urea injection system for diesel exhaust gases will be reported. These experiments were carried out with configurations A and B, so no oxidation catalyst was applied. All experiments were carried out using a simulated exhaust gas (NO in air).
4.2.2 HPLC analysis of urea decomposition byproducts

Equipment

High Performance Liquid Chromatography with weak acid anion exchange-column and UV-detector made it possible to determine byproducts from the urea decomposition\(^4\). Advice from DSM (Mr Andrien, section FA-CP, Geleen) led to the equipment described in Table 4.1. With this configuration it was possible to determine six urea decomposition products, see Table 4.2. The nature of these byproducts is described in Chapter 2 of this thesis. The minimum concentration which can be detected is determined by the sensitivity of the apparatus. The maximum concentration is determined by the solubility of the products and the linear range of the equipment. The analysis time is short, about 30 minutes, and the separation is good, see Figure 4.2. The drift is 5 percent per day and reproducibility is less than 2 percent.

Table 4.1: HPLC equipment used for the determination of urea condensations products\(^4\).

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
<td>HP 1050 gradient</td>
</tr>
<tr>
<td>Detector</td>
<td>HP 1050 UV/VIS at 220 nm</td>
</tr>
<tr>
<td>Column</td>
<td>Dionex AS10</td>
</tr>
<tr>
<td>Injection system</td>
<td>Rheodyne 7125 (Tefzel rotor seal)</td>
</tr>
<tr>
<td>Injection volume</td>
<td>20 μl</td>
</tr>
<tr>
<td>Pressure</td>
<td>2000 psi</td>
</tr>
<tr>
<td>Flow</td>
<td>1 ml/min</td>
</tr>
<tr>
<td>Solvent</td>
<td>pH=11.5, NaOH + 450 mg/l Na(_2)SO(_4)</td>
</tr>
</tbody>
</table>

Table 4.2: Detection limits of urea byproducts\(^4\) (see also Chapter 2)

<table>
<thead>
<tr>
<th>Byproduct</th>
<th>(C_{\text{max}}) (mg/l)</th>
<th>(C_{\text{min}}) (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>biuret</td>
<td>493</td>
<td>5.9</td>
</tr>
<tr>
<td>ammonelene</td>
<td>45</td>
<td>0.41</td>
</tr>
<tr>
<td>ammellide</td>
<td>50</td>
<td>0.25</td>
</tr>
<tr>
<td>triuret</td>
<td>44</td>
<td>1.39</td>
</tr>
<tr>
<td>cyano-urea</td>
<td>200</td>
<td>0.61</td>
</tr>
<tr>
<td>cyanic acid</td>
<td>146</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 4.2: Sample HPLC chromatogram from urea byproducts calibration standard.

Pretreatment

The equipment was used to determine the composition of urea condensation products formed at cold spots and for condensation products in the cleaned off-gases. The solid urea condensation products are solved ultrasonically in the NaOH/Na₂SO₄ solution (see Table 4.1, concentration in the order of 25-50 mg/l per component). Subsequently, this solution can be injected.

The emission of urea byproducts has been determined when using catalyst configuration C, section 4.2.1, on a natural gas engine exhaust gas³⁴. The exhaust gases, 2.5 NI/min, were passed over a heated quartz wool filter (0.5-1 g) for about 30 hours. Subsequently, this quartz wool was dried at 70°C for 3 days. The difference in mass of the quartz wool, 30-60 mg, equals the particulate emission of the system. The dried quartz wool was put in 15 ml solvent (20 minutes ultrasonic). The quartz wool is filtered off and rinsed three times obtaining 25 ml solution. Subsequently, this solution can be injected. It is noted that more reliable results can be obtained using standard exhaust gas filters (e.g. Gelman glass fiber filter type A/E with 99.98 percent collecting efficiency for 0.3 μm particles).

4.3 Selection of nozzle type

Droplet size

When injecting a urea solution one will want to make a very large contacting area of the solution with the surrounding exhaust gases for better heat and mass transfer. This is normally achieved by making small droplets. The rate of decomposition is strongly temperature dependent. Small droplets will be vaporized quickly; in this way the decomposition will be rate determining. If the droplets are too large, the temperature will be not high enough for decomposition to occur. These droplets will be captured on the catalyst or leave the system.
To determine the required size of the droplets, the type of equipment to be used, an estimate of the droplet life time is needed. Since the urea decomposition rate is not known, it is assumed that this decomposition is fast and that the evaporation of the droplet is rate determining. (Of course, this is certainly not correct at exhaust gas temperatures below 200°C.) As most of the experiments were carried out with 10 weight percent urea solution, 90 percent water, this seemed a reasonable initial approach. Anyway, the droplet has to vaporize before NH₃ production can occur.

When a spherical droplet of pure water is suddenly immersed in gas at high temperature its temperature will rise. As the temperature of the droplet is raised the amount of vapour formed will also increase. As this evaporation requires energy, the latent heat of vaporization, the droplet temperature will increase more slowly. Eventually the droplet temperature will stabilize at its wet-bulb temperature. As this is essentially a heat transfer problem, the lifetime of a droplet of water is approximately proportional to its diameter squared⁸:

\[ t_e = \frac{D^2}{\lambda_e} \]  \hspace{1cm} (4.1)

with \( t_e \) : life time droplet [s];
\( D \) : diameter droplet [m];
\( \lambda_e \) : effective evaporation constant \([\text{m}^2/\text{s}]\).

This effective evaporation 'constant' is a complicated function of droplet composition, size, surrounding temperature and relative velocity. In a non flowing environment and a steady state situation (droplet at wet-bulb temperature), it can be estimated by:

\[ \lambda_{se} = \frac{8 \lambda_g (T_g - T_d)}{\rho \Delta H_{vap}} \] \hspace{1cm} (4.2)

with \( \rho \) : density droplet \([\text{kg}/\text{m}^3]\);
\( \lambda_{se} \) : steady state evaporation constant \([\text{m}^2/\text{s}]\).
\( \Delta H_{vap} \) : latent heat \([\text{J/kg}]\);
\( \lambda_g \) : thermal conductivity of the gas phase \([\text{J/mK}]\);
\( T_g \) : temperature gas phase \([\text{K}]\);
\( T_d \) : wet-bulb temperature droplet \([\text{K}]\).

This wet bulb temperature increases with higher gas phase temperatures but will not exceed the boiling point of the liquid phase. Lefebvre⁵ describes methods to calculate this wet-bulb temperature. Furthermore, a more thorough method to calculate the droplet life time is given (incorporating effects of the droplet heat-up period and of convection).
Figure 4.3: Droplet life time in a non flowing environment as a function of the gas phase temperature\(^5\).

The life time of a spherical drop of water in a non flowing environment as a function of the droplet diameter and the surrounding temperature is shown in Figure 4.3. Convection, due to the injection, will decrease the life time significantly; a 10 m/s velocity difference will half the life time.

As most SCR installations are used at space velocities of 1000-10000 h\(^{-1}\) a droplet life time in the order of 0.1 seconds is desirable. While droplets of the appropriate size (50 \(\mu\)m, Figure 4.3) can be produced by standard atomizers occasionally large droplets will hit the catalyst or leave the system. Furthermore, this process will become more critical as more active catalyst formulations become available (e.g. a space velocity of 100 000 h\(^{-1}\) at 300°C means a residence time of 0.017 seconds). In such cases it is advantageous to inject urea as close as possible to the cylinder outlet.

Type of atomizer

To develop the urea injection system the pilot-scale experimental setup has been used (see section 4.2). The research has been focused on the urea injector, meeting the following requirements:

A. a yield of about 1 ml/min (10 wt% urea solution)
B. a fine spray is preferred as the droplets have to evaporate
C. temperatures up to 600°C
D. no/less sensitive to corrosion; urea in solution can be corrosive at high temperatures
E. reliability: e.g. protection against clogging.
Sprays may be produced in various ways. All that is needed is a high velocity difference between the liquid to be atomized and the surrounding air or gas. Some atomizers accomplish this by discharging the liquid at high velocity into a relative slow-moving stream of air or gas. Notable examples include the various forms of pressure atomizers and rotary atomizers. An alternative approach is to expose the relative slow-moving liquid to a high-velocity air stream. The latter method is generally known as twin-fluid, air-assist, or air blast atomization.

Another distinction in injector type can be made; continuous or discontinuous injection. Most injectors tested are based on continuous flow; for optimal atomization this flow can only be varied in a relatively small range. By using a pump in the liquid feed, the desired flow rate is forced through the injector. Discontinuous injection has the advantage of ranging the flow rate from zero to maximum continuous throughput of the injector accurately. From the viewpoint of the exact urea dosage control to remove the nitrogen oxides, discontinuous injection is therefore a very attractive technique. However, for laboratory scale research this fact is less important.

The injectors tested are summarized in Table 4.3. It was difficult to find continuous working atomizers for use in the bench scale equipment. In this setup 1 ml/min 10 wt % urea solution needs to be atomized (for our diesel engine about the same flow rate is needed). Most industrial atomizers are not suitable for this low flow rate (except somewhat exotic types of atomizers like electrostatic or sonic).

<table>
<thead>
<tr>
<th>Table 4.3: The material type and atomizing force of the injectors tested.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand 'Le Cock Duiker'</td>
</tr>
<tr>
<td>Stainless steel liquid pressurised nozzle</td>
</tr>
<tr>
<td>Brand 'Bete SR050A'</td>
</tr>
<tr>
<td>Stainless steel air blast nozzle</td>
</tr>
<tr>
<td>V-groove</td>
</tr>
<tr>
<td>Kelf (plastic) air blast nebuliser</td>
</tr>
<tr>
<td>LPG car injectors</td>
</tr>
<tr>
<td>Aluminium liquid pressurised</td>
</tr>
</tbody>
</table>

A pressure atomizer, brand "Le Cock Duiker" with a capacity of 1.5 l/h, has been tested. It was necessary to cool the atomizer externally but it remained very sensitive to clogging. Installing an air blast nozzle (brand Bete, type 1/4 XA SR050A) gave better results. The capacity was 0.4 l/h using 1 m³/h 1.5 bar pressurized air. This atomizer works even at very low liquid loads because the atomizing agent is air. The atomizer is relatively insensitive to clogging when air is flowing. Furthermore, the spray of this type of atomizers is usually somewhat finer than of the liquid pressurized nozzle. This droplet size is relatively independent of the liquid flow rate.

On the basis of this result another type of nozzle has been tested which also uses air for atomization: the "V-groove atomizer" (developed by DUT®). This type of atomizer is even better plug resistant. The "V-groove" atomizer is made of Kelf-polymer (the type of material has a large influence on the spray quality) and because of its low melting point (160°C) this injector is externally cooled.

For results obtained with this atomizer see Figure 4.4. An 80-90 percent reduction can be reached without NH₃ slip. The NOₓ signal is not very stable which could be attributed to droplet formation on this V groove nozzle. Instead of a continuous fine spray large droplets (> 200 μm) were formed also.
Figure 4.4: Sample experiment with the V-groove atomizer (550 g DN110, 300 °C, 1000 ppm NO in 9 Nm³/h using 10 weight percent urea solution at NO/urea = 2).

GENTEC bv (Son, developer of injection based LPG systems in motor-cars) participated in this project by means of an engineering contribution. A standard LPG injection system was adjusted to our specific requirements. Using a standard housing on top of the reactor, it was possible to test different types of commonly used LPG car-injectors. A discontinuous injection is obtained by using a pulse generator (frequency range 1-100 Hz, pulse width of 1-100 ms) to switch a magnetic valve.

The expected advantage of this type of injection system (controlling the flow with a high accuracy by means of a pulse generator) could not be accomplished. It appeared that for an optimal atomization the liquid flow can only be varied in small ranges at a frequency of approximately 10 Hertz and an injector opening time of 1.3 to 1.5 milliseconds. This leads to an injector liquid capacity of 0.5 ml/min of urea solution, which is just adequate for pilot scale experiments, but will not be suitable in scaling up this process. Increasing the injector opening time lead to large droplet formation (instead of atomization), the same effect occurred when higher frequencies were chosen.

For all further experiments the choice has been made to work with the Bete SR050A Air blast nozzle. The main reason was the reliability of this nozzle. Regarding plug formation it was superior to the pressurized nozzle tested and because it is made of SS the corrosion characteristics will be superior to the other two nozzles (V-groove and LPG). Furthermore, most comparable literature references\textsuperscript{6,7} use this type of twin fluid nozzle.
4.4 Reduction of byproduct formation

Condensation products can be formed when the temperature is too low for urea decomposition in ammonia type products to be complete. This can be caused by low exhaust gas temperatures or cold spots. The former is trivial; the system should not be used at these conditions. This section describes what to do about cold spots. Furthermore, the results of a check on byproduct emission are presented.

Cold spots

Initially, the biggest cold spot was the wall of the reactor between the nozzle and the top of the catalyst bed (no static mixer had been installed yet, configuration A section 4.2.1). And indeed, some white products were formed on this wall. Insulation and external heating solved this problem. The external heating was applied because of the relative small flow through this system, which resulted in strongly non-adiabatic conditions. It is expected that in practice a well insulated reactor will not give this type of problems. In a later stage a stainless steel static mixer has been installed (configuration C section 4.2.1) and no byproducts have been seen on its surface.

So essentially one cold spot remains: the nozzle. A cake of urea byproducts was formed which dropped on the catalyst bed periodically. A practical solution to prevent this was proposed by Heaton (TNO-Motor Emission Laboratory, Delft). The same type of problems arise with the injection of diesel into the pre-combustion chamber of diesel engines (soot formation). For urea injection with the air blast nozzle, formation of solid material can be prevented by placing an isolating 'hat' between the injector and the reactor, see Figure 4.5.

Several 'hats' were built by TNO and tested during experiments over 5 hours with the injection of 2 g/min of 10wt% urea solution. Figure 4.6 shows some of the results. Without the 'hat' the build up of by-products almost blocks the atomizer spay, whereas in the case of an installed isolating hat, hardly any by-products were formed at all. More extensive tests behind a natural gas engine² (50 hours 300-330°C, catalyst configuration C) shows no fouling of the nozzle surface, static mixer nor plugging of the catalytic monoliths.

HPLC was used to determine byproduct composition. The white cake formed on the nozzle (without cap) consisted of biuret (0-32 wt%), triuret (0-35 wt%) and cyanuric acid (43-89 wt%)¹⁰, traces of ammeline (0-1 wt%) and ammelide (0-10 wt%) were detected also.

Figure 4.5: Schematic drawing of the isolating 'hat': A. top reactor shell (hot); B. atomizer (cold); C. 'hat'; D. isolating air gap between atomizer and reactor shell; E. atomizing spray.
Byproduct emission

To check if the urea decomposition was complete, a part of the off-gases has been filtered and subjected to analysis (section 4.2.2). In this case the off-gases of a natural gas engine were treated with the setup described in section 4.2 (configuration C) using one SCR catalyst (space velocity 5000 h⁻¹) and an oxidation catalyst (space velocity 10000⁻¹) for about 30 hours at 300-330°C. The amount of byproducts detected was minor, 0.001 weight percent based on the amount of urea injected and 0.1 weight percent based on the particulates measured. The main components were biuret (45-98 wt%), ammelide (1-20 wt%) and cyanuric acid (1-34 wt%), traces of ammeline (<2 wt%) and cyano-urea (<0.4 wt%) were detected also. Because of the small amount of byproducts found no check on nitroso compounds has been performed.

During the experiments with the gas engine a check on formation of the following components was performed: formaldehyde, acetone and hydro cyanic acid. Only 5-10 ppm cyanic acid could be detected after the DN 32 catalyst. No hydro cyanic acid could be detected in the engine exhaust, after the urea injector but before the catalyst, and after the oxidation catalyst. It appears that some hydro cyanic acid is formed over DN 32 but this is removed by the oxidation catalyst.

![Figure 4.6 (a)](image1)

![Figure 4.6 (b)](image2)

Figure 4.6 shows the injector (with the nozzle-opening in the centre of the picture) from a viewpoint inside the reactor (top). Figure 4.6 (a) is without and Figure 4.6 (b) with a 'hat' after 5 hours of injecting urea solution into the reactor (Reactor temperature 330°C; GHSV 10 000 h⁻¹; NO inlet conc. 1000 ppm; urea dosage 2 g/min 10wt% solution). In the right figure hardly any formation of by-products can be seen, in the left figure a layer of by-products has been formed (approximately 2 mm thick), which nearly covers the spraying nozzle.
4.5 Comparison urea and ammonia injection

The DN 32 catalytic monolith is designed for application in NO\textsubscript{x} removal from exhaust gases from stationary diesel engines with the use of ammonia as reactant. As described before, the DN 32 catalytic monolith is used for testing the injection system. With this catalyst, urea was never used before and one of the first experiments, Figure 4.7, was started with ammonia as a reactant. After 85 minutes the feed was switched from NH\textsubscript{3} to injection of urea instantaneously. This experiment was satisfactory; the difference between the conversion with ammonia or urea is hardly visible.

![Graph showing NO concentration over time](image)

*Figure 4.7 Application of monoliths, progress during experiment:*

A: 480 ppm NO feed in air, 300°C, one 400 cpi DN 32 element at GHSV=10000 h\textsuperscript{-1};
B: dosage of ammonia, NH\textsubscript{3}/NO = 0.90 (mol/mol);
C: dosage of ammonia, NH\textsubscript{3}/NO = 0.45;
D: switched to dosage of urea solution (10wt% in water), "NH\textsubscript{3}\textsubscript{2}/NO = 0.471;"
E: dosage of urea, "NH\textsubscript{3}\textsubscript{2}/NO = 0.94."

Several steady state experiments have been performed to quantify this observation, Table 4.4. The NO\textsubscript{x} conversion has been measured as a function of NH\textsubscript{3}/NO inlet ratio (range 0.2-1). The conditions were such (low space velocity) that ammonia slip only occurs when the NH\textsubscript{3}/NO inlet ratio is very close to or exceeds 1. When assuming that one urea molecule yields 2 ammonia molecules (NH\textsubscript{3} equivalents) the stoichiometry of the reaction is one. The use of pure ammonia, NH\textsubscript{3}(g), an injection of aqueous ammonia, NH\textsubscript{3}(aq), and of the 10 or 40 weight percent urea solution all yield comparable results.

These experiments show that the Delft NO\textsubscript{x}/Urea-Process can successfully be applied to catalytic monoliths. It shows also that one molecule urea reduces two molecules of NO. Therefore, one urea molecule produces two ammonia equivalents. Also note that the stability of the NO signal is only slightly less than using ammonia but superior to the injection using the V-groove nozzle (Figure 4.4).
Table 4.4: The stoichiometry of the SCR reaction over DN 32 (1 400 cpi element, 1000 ppm NO inlet, 10 Nm³/h air, resulting in a space velocity of 12500 h⁻¹ at 327°C).

<table>
<thead>
<tr>
<th>Inlet ratio (NH₃ equivalents)</th>
<th>Temperature (°C)</th>
<th>Concentration (weight percent)</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>urea/NO</td>
<td>327</td>
<td>10</td>
<td>1.04</td>
</tr>
<tr>
<td>urea/NO</td>
<td>327</td>
<td>40</td>
<td>0.99</td>
</tr>
<tr>
<td>NH₃(aq)/NO</td>
<td>327</td>
<td>5</td>
<td>0.98</td>
</tr>
<tr>
<td>NH₃(g)/NO</td>
<td>327</td>
<td>-</td>
<td>1.01</td>
</tr>
<tr>
<td>urea/NO</td>
<td>352</td>
<td>10</td>
<td>1.02</td>
</tr>
<tr>
<td>urea/NO</td>
<td>377</td>
<td>10</td>
<td>1.02</td>
</tr>
<tr>
<td>NH₃(g)/NO</td>
<td>377</td>
<td>-</td>
<td>0.99</td>
</tr>
</tbody>
</table>

4.6 Concluding remarks

A urea injection system has been developed which consists of a Bete SR050 Air Blast nozzle equipped with an insulation cap to prevent byproduct formation on the cold nozzle surface. This nozzle is mounted on top of the reactor containing a static mixer and two DN 32 catalytic monoliths (optional one DN 32 element and one oxidation catalyst). Essentially, this is a stand alone unit which can be mounted on an engine easily. Results of such a configuration mounted on a 4 kW diesel engine will be presented in Chapter 5. Future improvements can be established by integration of this unit with the engine; i.e. placing the urea injection and static mixer close to the cylinder outlet and mounting the optional oxidation catalyst sufficiently downstream to prevent excessive sulphate production.

Before this process can be applied on a large scale additional research on the urea decomposition is desirable. The amount of byproducts detected is small, but some components (e.g. HCN) are quite poisonous. Furthermore, the sampling procedure described in section 4.2.2 can be improved.

Literature


11 Lugt, P.M., Bleek, C.M. van, Het delfse NOx/Ureum proces. W/K-uitlaatgas reiniging t.b.v. CO2-dosering in de glastuinbouw, Eindrapportage fase IV novem contract 248.401-005.4, Delft University of Technology, Department of Chemical Engineering, The Netherlands, Delft (1994), 63p.

Development of a urea injection system
Chapter 5

Diesel engine tests, urea injection on a 0.4l DI diesel engine

The urea injection system developed in Chapter 4 is tested behind a 0.4 litre one cylinder DI (direct injection) diesel engine. The exhaust gases are treated using the Degussa DN 32 V₂O₅/WO₃/TiO₂ washcoated monolith with 300 cells per square inch. The space velocities used are 5000-15000 h⁻¹ and the temperatures vary from 250 to 450°C. This system is tested on its steady state performance. Moreover, the response on steps and pulses in load, exhaust gas flow rate and urea flow rate is determined. The type of fuel is also varied. The performance of the deNOₓ system using a certified fuel, which contains 0.14 weight percent sulphur, and a low sulphur (less than 0.001 weight percent) fuel is compared. The variables studied are the NOₓ reduction performance and NH₃ slip.

5.1 Equipment

The experiments in this chapter are performed with a Yanmar L90E diesel engine in combination with an SDMO NX6000E generator set. The exhaust emission characteristics of this combination are described and compared to a heavy duty DAF engine in section 5.1.1. The urea injection system used to inject the urea solution has been described extensively in Chapter 4. Section 5.1.2 goes into more detail about testing procedures and the experimental setup.

5.1.1 The emissions of a Yanmar L90E diesel generator set

The Yanmar DI diesel engine used in this study is not representative for an HD diesel engine used for road transport. For example, the Yanmar engine is designed to run at one speed only (3000 rev/min for power generation). Furthermore, it is designed to be a cheap engine and is as such not very fuel efficient. In this section the Yanmar emissions will be compared to those of a DAF WS268G turbo charged and intercooled DI truck diesel engine. This engine, 11.63 l swept volume and 268 kW power output at 2000 rev/min, is thought to be typical of the modern truck diesel engine for the European markets. All this work has been carried out by TNO-MEL (Heaton¹).

Table 5.1: Specifications of the Yanmar L90E single cylinder vertical DI diesel engine

<table>
<thead>
<tr>
<th>Cylinder bore</th>
<th>84 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine stroke</td>
<td>70 mm</td>
</tr>
<tr>
<td>Operating speed</td>
<td>3000 rev/min</td>
</tr>
<tr>
<td>Max. continuous output</td>
<td>5.1 kW</td>
</tr>
</tbody>
</table>
The combination of the Yanmar diesel engine, see Table 5.1, and an SDMO NX6000E generator set gives a combination capable of generating about 4 kW electric power output. The engine mapping was tested at seven loads: 0, 0.5, 1, 2, 3, 4 and 4.5 kW. The actual load was applied by switching resistors as required. The effect of the engine load on the exhaust emissions is shown in Figure 5.1. The point at 4.5 kW is not representative for real engine operating conditions; the exhaust composition changes drastically and the actual power output remains the same. Therefore, the point at 4 kW nominal power output is denoted as 100 percent load. The gross exhaust emission follows the expected trends with increasing power output; an increasing NO\textsubscript{x} emission when more diesel fuel is being burned, dropping HC and CO emission because of the higher combustion temperature which levels off and even increases at higher load because of the dropping combustion efficiency (lower oxygen content). The particulate emission also rises very strongly when the engine is overloaded.

Figure 5.1: Engine mapping Yanmar diesel engine and generator set

![Graph showing exhaust emissions vs. nominal engine load](image)

Figure 5.2a: Influence of the air fuel ratio on the hydrocarbon emission

![Graph showing HC ppm vs. AFR](image)

Figure 5.2b: Influence of the air fuel ratio on the CO emission

![Graph showing CO ppm vs. AFR](image)

The differences in application of the DAF and Yanmar engine can be seen in their Hydrocarbon, CO and particulate emission figures (Figure 5.2abc). In these Figures the exhaust gas composition is plotted against the air fuel ratio (mass based), note that the power output of the engine increases with decreasing air fuel ratio. The DAF engine has a much higher combustion efficiency resulting in a lower emission of unburned compounds. This causes the NO\textsubscript{x} emission to rise (5.2d) again. This is an example of the so called NO\textsubscript{x} / particulate trade off; engine designers have to count on an increase in NO\textsubscript{x} emission when decreasing the soot emission if this is achieved by higher combustion efficiencies. Finally, the exhaust temperature of the Yanmar match those of the DAF engine closely, see Figure 5.2e.

Diesel engine tests
Although the combustion and emission characteristics of the Yanmar and the DAF engine differ considerably, the fact that the temperature levels bulk concentrations CO₂, H₂O and O₂ of both engines are similar indicate that the former can be used as a test engine. For SCR application the Yanmar engine is more difficult because of the much higher soot concentration (up to 10 times).

5.1.2 Experimental setup

The urea injection system described in Chapter 4 has been tested on the Yanmar diesel engine, see Figure 5.3. As the engine is used to generate electricity it should always run at 3000 rev/min (50 Hz). This causes the variation in engine speed to be small as compared to a heavy duty truck engine. A bypass valve has been installed, which is operated manually, to simulate the variation in the exhaust gas flow rate (at constant load). The actual flow rate is measured with an orifice at the reactor outlet. The silencer has been removed to avoid temperature losses. This, in combination with the fact that this diesel engine has only one cylinder, causes the flow to become rather pulsating.
Figure 5.3: Schematic sketch of the experimental setup

This setup is also connected to the data acquisition system 'the FIX' as described in Chapter 3. The temperature of the inlet air, the engine oil, the outlet exhaust gas, the orifice and reactor temperatures, the orifice pressure drop and fuel consumption are monitored continuously. In steady state experiments the urea solution, 10 weight percent urea in water, is injected using a 'Spectra Physics 8810' HPLC pump. To remove all the nitrogen oxides from the exhaust gases a urea solution flow rate of up to 5 ml/min is needed (depending on engine load).

In dynamic experiments a 'Gibson minipuls3' peristaltic pump is used. The nozzle is, see also Chapter 4, the '1/4 XA-SR050 Bete' air blast nozzle, operated with one bar pressurized air (0.5 Nm⁻³/h air usage).

The reactor, described extensively in Chapter 4, contains two DN 32 300 cpi V₂O₅/TiO₂/WO₃ washcoated corderite monoliths with a diameter of 9.3 and length of 15.2 cm (1025 grams per element). A 'Sulzer Katapak MK' static mixer is installed above the monolithic elements and the catalyst. The distance between the nozzle opening and this Sulzer mixer, 5 cm, is too small for urea decomposition to be complete. As already stated in Chapter 4 the life time of a droplet is a few tenths of a second and the corresponding distance is consequently somewhere between 10 cm and 1 metre. Therefore some urea droplets will hit the mixer and decompose on its surface. This is preferred above hitting the catalyst itself as it reduces the danger of damaging the washcoat (thermal shock) and ammonia slip (the channels are open and straight).

The analytic equipment used is essentially the same as in Chapter 3. The most important components are the chemiluminescence NOₓ analyser, the microwave NH₃ analyser and the GC-ECD N₂O analyser. The NOₓ concentrations used in this Chapter refer to a dry gas, so a correction must be applied for the amount water in the gases, see also Table 5.2. This table includes the correction factor for the MIPAN NH₃ analyser caused by matrix effects of CO₂.
Table 5.2: The NO\textsubscript{x} and NH\textsubscript{3} correction factors as a function of engine load

<table>
<thead>
<tr>
<th>Power (kW)</th>
<th>NO\textsubscript{x}</th>
<th>NH\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.951</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>0.956</td>
</tr>
<tr>
<td>1</td>
<td>0.994</td>
<td>0.963</td>
</tr>
<tr>
<td>2</td>
<td>0.979</td>
<td>0.978</td>
</tr>
<tr>
<td>3</td>
<td>0.964</td>
<td>0.994</td>
</tr>
<tr>
<td>4</td>
<td>0.941</td>
<td>1.017</td>
</tr>
<tr>
<td>4.5</td>
<td>0.925</td>
<td>1.034</td>
</tr>
</tbody>
</table>

and O\textsubscript{2}. In steady state experiments the NO\textsubscript{x} concentration is measured with the aid of washing bottles containing 85 weight percent H\textsubscript{3}PO\textsubscript{4} acid to remove NH\textsubscript{3}. In case of the dynamic experiments this is not possible because of the large dead time (approximately one minute); tube heating is applied and the off-gases are fed to the analyzer directly. Ammonia slip (> 10 ppm) has to be avoided because it interferes and fouls the NO\textsubscript{x} analyzer. The sample lines are equipped with 2 \(\mu\)m stainless steel filters to remove soot and are heated to about 100°C to avoid condensation. Cleaning is performed regularly (every 8 h) because of the large amount of soot trapped.

Before an experiment is started, the reactor is allowed to heat up to its operating temperature. Because of the large amount of piping used, compared to a real engine, heat up times are in the order of one or two hours. The reactor is operated quasi adiabatically, no additional external heating is applied. This results in a temperature drop over the reactor of about 60°C, the reactor temperature reported is the temperature between the two monoliths. The reactor entrance is about 30°C higher, the exit about 30°C lower. Furthermore, all dynamic experiments are conducted almost isothermally in time: the average reactor temperature changes only a few centigrades during this type of experiments.

The exhaust gas composition is monitored just after the reactor; the NO\textsubscript{x} inlet concentration is evaluated by switching off the urea injection. In that case the NO\textsubscript{x} concentration does not change in the reactor, only some NO\textsubscript{2} is formed (at normal operating conditions of the reactor and at 3 kW the NO\textsubscript{2} percentage rises from 3 to 6 percent in the reactor, see also Table 5.3).

Table 5.3: Influence of the catalyst on the NO\textsubscript{2} percentage of the NO\textsubscript{x} concentrations in the exhaust gases

<table>
<thead>
<tr>
<th>Power (kW)</th>
<th>% NO\textsubscript{2} before reactor</th>
<th>% NO\textsubscript{2} after reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>0.5</td>
<td>41</td>
<td>44</td>
</tr>
<tr>
<td>1</td>
<td>23</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>8.9</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>2.6</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>4.5</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* When the system is applied to a HD truck engine the temperature variations will be quite large. However, due to the more massive piping of the setup the changes in temperature are quite slow. This has however the advantage that temperature effects are excluded thereby providing the response of the system on a step in one variable only. The effects of larger temperature changes will be discussed in Chapter six.

Chapter 5
Steady state conversions are determined after each change of the urea flow rate by monitoring the outlet concentrations during 15 to 30 minutes for NOX conversions and up to 60 minutes for NH3 slip. N2O production is measured with a sample rate of one per 6 minutes. The N2O outlet levels never exceeded 10 ppm and are therefore not reported. Dynamic experiments are performed by changing the desired input (urea flow rate, exhaust gas flow or engine power) momentarily and monitoring the NOX signal with a data sampling rate of one measurement per two seconds.

The experimental accuracy is determined mainly by the measurement of the exhaust gas flow rate. This flow rate can be measured between 10-30 Nm3/h with a relative standard deviation of approx 6 percent. At lower flow rates (<10 Nm3/h) the error is larger (more than 10 percent) due to the low pressure drop over the orifice in combination with the pressure variations of the one cylinder diesel engine without silencer. Other error sources are the NOX analyser (10 ppm maximum), the ammonia analyser (10 ppm maximum) and the urea flow rate (on mass basis, less than 1 percent relative). Normally, the error in NO/NH3 ratio is within 10 percent, if the exhaust gas flow is larger than 10 Nm3/h.

5.2 Steady state experiments

5.2.1 Stationary NOX production

In the day to day use the NOX emission of the Yanmar diesel engine is far from constant. Variations in the order of 10 to 20 percent in NOX emission do occur. This can cause considerable problems when trying to use a control system based on engine mapping (predicting the NOX output based on easily measured variables, e.g. temperatures and power output, and adjusting the urea injection rate accordingly). When using a low sulphur fuel, the standard deviation of the difference between predicted and measured NOX output is about 40 ppm (the NOX output level is between 100 and 600 ppm).

Reasons for this deviation in the NOX production are changes in air inlet temperature, air moisture content, general maintenance status of the engine, etc. During the experiments the air inlet and outlet temperature, the oil temperature and fuel consumption are monitored continuously. When using these variables a better correlation is obtained with a standard deviation of about 20 ppm; see Figure 5.4. (The correlation is of the type NOX predicted = a*variable_1+b*variable_2+.. etc.)

Figure 5.4: Prediction of NOX output on basis of a linear correlation of power production, inlet & outlet air temperature and oil temperature using low sulfur fuel. Data points are collected over a period of three months.

Diesel engine tests
When taking into account the variation in fuel consumption, the prediction of the NO$_x$ output does not improve significantly compared to the prediction based on power production alone. This in contrast with changes in inlet and outlet air temperatures. It is noted that the temperatures are coupled because the diesel engine is placed in an enclosed room which rises in temperature (15-20°C) during the experiments.

Using the certified diesel fuel the NO$_x$ output is about 50 ppm higher. Although most diesel engines are rather insensitive to the type of diesel fuel used this difference in NO$_x$ output might be caused by the fact that the low sulphur fuel is strongly hydrogenated (see also section 2.1.1.4). When comparing the output levels with those previously measured by TNO$^1$ a decrease of up to 30 percent is observed. This is attributed to the fact that the engine has been under repair repeatedly.

As the predicted NO$_x$ output of this diesel engine can deviate up to 30 percent from reality, using an SCR process based on engine mapping alone must be restricted to less than 70 percent NO$_x$ reduction because of the danger of ammonia slip. Of course, such a feedback control should, in practice, be able to account for many more variables than in the present study.

### 5.2.2 Injection of ammonia in the inlet air of the diesel engine

This section (5.2.2 only) is not part of the scope of the research but has been added because it reports on a somewhat unusual idea for diesel deNO$_x$ing. As explained in section 2.1.2, there are several alternative catalytic processes for the SCR process currently under investigation. A technique is the Selective Non-Catalytic Removal of NO$_x$ with ammonia or urea. The problem is that the temperature window for this reaction is 800-1100°C, which is only available inside the combustion chamber. Tree$^2$ showed up to 30 percent NO$_x$ reduction by adding five weight percent cyanuric acid derivative to the fuel. Alternatively, Lausch$^3$ showed a NO$_x$ reduction of up to 50 percent by applying ammonia injection into the cylinder (after the bulk of the fuel had been burned).

![Figure 5.5: The influence of ammonia injection in the air inlet on overall NO$_x$ emission (an ammonia equivalent is the ammonia concentration obtained when mixing pure ammonia with the exhaust gases).](image)

Since urea does not dissolve in diesel fuel (<0.1 grams per litre) and in-cylinder injection of an urea solution was not possible for technical reasons, pure ammonia has been injected into the air inlet. (A urea solution cannot be used because the temperature of the air inlet is too low for its decomposition.) This approach however leads to additional NO$_x$ production, see Figure 5.5. At one kW (25 percent load) about 30 percent of the ammonia injected was converted to NO$_x$ and at four kW this was about 20 percent. Of course this was to be expected because ammonia is combustible, on the other hand the same holds for fuel additives.
5.2.3 NO\textsubscript{x} removal performance of the urea injection setup in diesel exhaust

The steady state NO\textsubscript{x} conversion and ammonia slip performance of the urea injection setup is tested using two diesel fuels, two exhaust gas flow rates and three load points. The results of the experiments performed with the low sulphur fuel and with maximum flow rate as a function of engine load are plotted in Figure 5.6 and 7. The main differences between the load points (2, 3 and 4 kW) are the inlet NO\textsubscript{x} concentration (321, 442 and 558 ppm NO\textsubscript{x}), the flow rate (space velocity 15 000, 14 400 and 12 900 h\textsuperscript{-1}) and most important of all the reactor temperature, which rises from about 271°C (2 kW), 350°C (3 kW) to 465°C at 4 kW.

As shown in the NO\textsubscript{x} conversion versus NH\textsubscript{3}/NO inlet ratio plot, Figure 5.6, the NO\textsubscript{x} conversion performance of 3 and 4 kW almost coincides whereas at 2 kW the conversion is definitely lower. Most likely the temperature level at 2 kW is too low for sufficient conversion at this space velocity, which is illustrated by the fact that ammonia slip, Figure 5.7, occurs even at low NH\textsubscript{3}/NO ratios. This ammonia slip is less manifest in the 3 and 4 kW conversion curves in Figure 5.7. Under these conditions the slip increases only drastically when the stoichiometric ratio of 1 is exceeded.

![Figure 5.6: The NO\textsubscript{x} conversion as a function of the NH\textsubscript{3}/NO inlet ratio at 2 kW (271°C, 321 ppm NO\textsubscript{x}), 3 kW (350°C, 442 ppm NO\textsubscript{x}) and 4 kW (465°C, 558 ppm NO\textsubscript{x}) using low sulphur diesel fuel.](image)

![Figure 5.7: The NH\textsubscript{3} slip as a function of the NH\textsubscript{3}/NO inlet ratio, conditions as in figure 5.6 (due to analyser problems absolute value NH\textsubscript{3} inaccurate; figure serves to determine the onset of NH\textsubscript{3} slip).](image)

It will be clear that the activity of this system is somewhat too low (space velocity too high for the setup and catalysts used). This can be illustrated best by looking at the results at a lower space velocity of approx 5350h\textsuperscript{-1}, Figure 5.8. In this situation the NO\textsubscript{x} output decreases linearly to almost zero at NH\textsubscript{3}/NO=1. This is equivalent to a linear increase of the conversion to 100 percent in Figure 5.6. Now ammonia slip only occurs at NH\textsubscript{3}/NO ratios close or more than one. Because of the lower flow rate the temperatures (276 and 372°C) were lower also; the temperature at 2 kW was too low for the urea decomposition to be complete (<250°C).

100

*Diesel engine tests*
Figure 5.8: The $\text{NO}_x$ output and ammonia slip of the urea injection setup in diesel exhaust gases at 3 kW (276°C, 5200 h⁻¹) and 4 kW (372°C, 5500 h⁻¹) using low sulphur fuel (due to analyser problems $\text{NH}_3$ signal inaccurate; figure serves to determine onset $\text{NH}_3$ slip only).

The same experiments are performed using the certified diesel fuel containing 0.14 weight percent sulphur, see Figure 5.9 (resulting SO₂ level calculated on basis of fuel sulphur content: 34 ppm at 2 kW, 44 ppm at 3 kW and 58 ppm at 4 kW). The NOₓ conversion versus $\text{NH}_3$/NO inlet plots are roughly the same as those in Figure 5.6, even for 2 kW. Probably the temperature at this low load (270°C) is too high for ammonium sulphates to become a serious problem for the catalyst. In Chapter 2 it is stated that SO₂ can be a problem, however the temperatures mentioned are for systems burning coal (up to 1 percent sulphur) or heavy fuel oil (more than 1 percent sulphur). Furthermore, those systems are running at a higher NOₓ inlet level (about 1000 ppm) and subsequently higher $\text{NH}_3$ level. The combination of a lower sulphur level and a lower $\text{NH}_3$ level might explain why no deactivation due to deposition of ammonium sulphates is found.

Figure 5.9: The NOₓ conversion as a function of the $\text{NH}_3$/NO inlet ratio at 2 kW (277°C, 385 ppm NOₓ), 3 kW (358°C, 576 ppm NOₓ), 4 kW (466°C, 613 ppm NOₓ) using certified diesel fuel.
Figure 5.10: The NO\textsubscript{x} conversion and ammonia slip is a function of the NH\textsubscript{3}/NO inlet ratio for urea and ammonia injection in diesel exhaust gases using low sulphur fuel (300°C, 5000 h\textsuperscript{-1}).

To check if urea reacts in the same way as pure NH\textsubscript{3}, as measured in section 4.4, experiments with aqueous ammonia solution have been performed. In Figure 5.10 the NO\textsubscript{x} conversion and the NH\textsubscript{3} slip are plotted when using both urea and ammonia injection. The figure shows that both reactants behave similarly. One molecule of urea reduces two molecules of NO and yields two molecules of ammonia upon decomposition. During this type of steady state experiments with urea injection the N\textsubscript{2}O emission was always lower than 10 ppm. Therefore, it is likely that the amount of nitrogen containing urea condensation products will be limited.

The results obtained with the urea injection setup are compared with those obtained with the test bench (a catalyst testing setup, see also Chapter 3). The results obtained with this test bench can be summarized by the following equation (for numerical data see Appendix 1):

\[
\xi = 1 - e^{-k\tau}
\]  

(5.1)

with \( k \): reaction rate constant [1/s];
\( \xi \): NO\textsubscript{x} conversion [-];
\( \tau \): residence time [s].

In Table 5.4 the NO\textsubscript{x} conversions in the urea setup at NH\textsubscript{3}/NO=1 are compared with those calculated on basis of equation 5.1. The conversions measured with the test bench are always higher, as expected, because in the test bench no soot is present and the radial flow and ammonia distribution is perfect. (See Chapter four why this is probably not so for the urea injection setup.) To reach the same conversion levels about twice the amount of catalyst is needed.
Note that this equation assumes that the reaction order of ammonia is zero. However, results using the urea injection setup show that the conversion does not rise linearly to the maximum conversion and do not remain constant above an NH$_3$/NO ratio of one. This can be attributed partly to a slightly positive order in ammonia although the non-uniform distribution of urea is probably more important.

Table 5.4: The NO$_x$ conversions in the urea injection setup compared to those calculated with equation 5.1 (results test bench) at NH$_3$/NO=1.

<table>
<thead>
<tr>
<th>Power (kW)</th>
<th>Temperature (°C)</th>
<th>Space velocity (h$^{-1}$)</th>
<th>Conversion measured</th>
<th>Conversion calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>271</td>
<td>15000</td>
<td>40</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>350</td>
<td>14400</td>
<td>70</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>276</td>
<td>5200</td>
<td>92</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>372</td>
<td>5500</td>
<td>93</td>
<td>100</td>
</tr>
</tbody>
</table>

5.3 Dynamic experiments

The main problem regarding application of SCR to a transient diesel engine is the control of the ammonia/urea flow rate. The amount of NO$_x$ produced varies rapidly, changes can occur in the order of seconds and even faster, corresponding to engine load and speed. The flow rate of ammonia/urea has to be adjusted; in case of an overdose ammonia slip will occur, when injecting too little insufficient NO$_x$ reduction is the result. If the diesel engine NO$_x$ output could be predicted or measured fast and accurate and if the catalyst system could also react fast and accurate, the urea flow could easily be coupled to this NO$_x$ output signal under transient conditions. However, since this is not the case, some attention has to be given to the dynamic behaviour of the DeNO$_x$ system to determine what type of control system is needed. Actual control systems will be implemented in section 6.3.

The dynamic experiments consist of steps and pulses in the exhaust gas flow rate, the urea flow rate and the load of the engine. This is equivalent to changes in speed (exhaust gas flow) and power output of the engine, which result in a variable NO$_x$ output. All system signals are monitored with a data acquisition rate of one point per two seconds. It will be shown that the dead time of some components (e.g. analysers) is considerably larger. In this section a response is called fast if it reacts in two or less than two seconds (one data point) while a slow response takes more than one minute (thirty data points).

The most straightforward dead time is the residence time in the reactor and the piping; the time it takes for an NO molecule to travel from the cylinder outlet to the sample point. This depends on flow rate and temperature and is in the range of 0.2 seconds (25 Nm$^3$/h, 400°C) to 2 seconds (5 Nm$^3$/h, 200°C). The NO$_x$ analyser and sample line have a dead time of about ten seconds. Furthermore, the NO$_x$ signal does not rise immediately to the final value; this takes another four seconds (90 percent of final value, T$_{90}$). The ammonia analyser has a larger dead time, 20 seconds, and the subsequent T$_{90}$ value takes another 100 seconds. A difference with the NO$_x$ signal is the very strong ‘tailing’; when the inlet of the analyser is switched from ammonia to air, the ammonia signal drops to 10 percent of the beginning value according to the T$_{90}$ time, but several minutes are required for the signal to drop below 1 percent. Therefore, this analyser is not suitable for dynamic experiments and serves only

Chapter 5
to check whether ammonia slip is present or not.

The diesel engine response is fast; changes in load take effect within one or two seconds. The same holds for the pressure drop sensor to measure the exhaust gas flow rate. The urea flow is determined by a pump. The time it takes between activating the pump and actual injection is usually 2 to 6 seconds. This can be observed by studying the atomizer spray in open air.

The last important time constant is that of the adsorption-desorption process on the catalyst itself. In Chapter six these effects will be described quantitatively. In this Chapter only a qualitative explanation is given. It is expected that ammonia adsorbs strongly on the catalyst, creating an ammonia buffer. Nitrogen oxides can only react with the adsorbed ammonia. Since in practice always an underdose of ammonia is injected, the time constant for changes in ammonia concentration will be large. As the catalyst needs to be covered with adsorbed ammonia before ammonia slip occurs, such slip will only occur when dosing more than stoichiometric amounts for prolonged periods.

The NO\textsubscript{X} outlet signal will respond much faster because it does not adsorb on the catalyst. However the NO\textsubscript{X} outlet changes will be smaller than the inlet changes due to reaction with this ammonia buffer.

The experiments are conducted at 3 kW, 300°C, a space velocity of about 5000 h\textsuperscript{-1} and steps around 70 percent NO\textsubscript{X} reduction at an inlet level of 400 ppm. This working point is chosen because it is a point at the low temperature end of the catalyst system to be applied (see Chapter 2). Problems caused by a slow response are to be encountered in this situation because at low temperatures the amount of adsorbed ammonia is large and the catalyst activity is low.

5.3.1 Response to changes in urea flow rate

The response of the system to steps in urea flow, at constant load and exhaust gas flow, determines how fast a control action can possibly be. Changes in the pump setting lead to a change in the amount of solution injected between 2 and 6 seconds later. Two responses are plotted in Figure 5.11 and 5.12. Generally the dead time is between 15 and 25 seconds whereas the analyser dead time is ten seconds. So there exists some additional dead time (<< 10 s) which can not be ascribed to the pump or sampling system. This means that the time between the control action and the NO\textsubscript{X} response is at least 10 seconds.

The responses vary; it usually takes longer for the system to go to a higher NO\textsubscript{X} reduction level (is equal to a lower NO\textsubscript{X} output level) than to a lower. This can be attributed to the effect that the amount of catalyst covered with ammonia needs to be exponentially larger to reach the same additional 10 percent conversion. Due to the same effect, the conversion for a first order reaction in an ideal tube reactor, rises exponentially with the amount of catalyst used (see also equation 5.1; the residence time is proportional to the amount of catalyst used).

In Figure 5.13 the response to a step in urea and ammonia flow rate is plotted. The response for an injection of an ammonia solution is comparable to the response with urea injection. Therefore, no time delay due to the decomposition of urea could be detected.
Figure 5.11: The response of the urea injection setup on a step in urea injection rate (3 kW, 300°C, 5200 h⁻¹ using low sulphur fuel).

Figure 5.12: The response of the urea injection setup on a step in urea injection rate (3 kW, 300°C, 5200 h⁻¹ using low sulphur fuel).

Figure 5.13: Comparison of the response on a step in urea with a step in ammonia injection rate (3 kW, 300°C, 5200 h⁻¹ using low sulphur fuel).

Figure 5.14: The response of the urea injection setup on a pulse in exhaust gas flow (3 kW, 300°C, 5200 h⁻¹ using low sulphur fuel).
5.3.2 Response to changes in exhaust gas flow rate at constant load

The diesel exhaust gas flow rate is varied manually and the flow rate is measured online. The result of a pulse of one minute from 12 to 28 Nm³/h is plotted in Figure 5.14. The NOₓ signal rises after about eight seconds, the analyser dead time, to its final value, which corresponds to the NOₓ output level expected on basis of the one on one reaction stoichiometry, within a few seconds.

The pulse to lower flow rates, Figure 5.15, shows that the NOₓ inlet signal changes significantly slower and does not reach its final value (which is about zero). Here, the pulse to a lower flow rate causes temporarily relatively much more NH₃ to be injected. If the system would react infinitely fast this would result in a very low NOₓ level and an ammonia slip. The fact that no ammonia slip is present shows that the excess ammonia is stored on the catalyst.

Therefore, in case of an inappropriate control action on changes in flow the effect will be insufficient NOₓ reduction at higher flow rates but not a direct ammonia slip at lower flow rates (this takes at least a minute).

Repeating the experiments with a proportional urea flow rate gives Figure 5.16. Clearly, the effect of urea injection is too slow to keep the NOₓ signal at the same level. This delay cannot be explained by a time lag in the urea flow rate because the time scale of this type of phenomena is seconds rather than minutes. It takes an additional minute for the signal in Figure 5.16 to reach its steady state value, which is at the same level as before the step in flow.

![Figure 5.15: The response of the urea injection setup on a pulse in exhaust gas flow (3 kW, 300°C, 5200 h⁻¹ using low sulphur fuel).](image1)

![Figure 5.16: The response of the urea injection setup on a pulse in exhaust gas flow with proportional urea injection (3 kW, 300°C, 5200 h⁻¹ using low sulphur fuel).](image2)

Diesel engine tests
5.3.3 Response to changes in load

As the heat capacity of this setup is very high the experiments are performed practically isothermally. Therefore, changes in load are changes in exhaust gas composition only. The type of response is comparable to the response on changes in exhaust gas flow Figure 5.17 and 5.18. From Figure 5.17 the dead time of the NO\textsubscript{x} analyser can be derived again, ten seconds, and it also clear that the NO\textsubscript{x} production by the engine changes quickly with a load change. However, some tailing effects are also present as the engine needs to adjust itself to the new operating point (e.g. engine temperature).

In Figure 5.18 the same trends can be observed as with a step to lower flow rates, Figure 5.15. The changes in inlet NO\textsubscript{x} concentration are flattened off; the inlet NO\textsubscript{x} concentration drops about 100 ppm while the outlet drops initially about 30 to 40 ppm. The differences are even more pronounced when switching back to higher loads; whereas the engine NO\textsubscript{x} output level changes almost momentarily to a higher value the NO\textsubscript{x} outlet level rises far more smoothly.

![Figure 5.17: The response of the urea injection setup on a pulse in load without urea injection (3 kW, 300°C, 5200 h\textsuperscript{-1} using low sulphur fuel).](image1)

![Figure 5.18: The response of the urea injection setup on a pulse in load with urea injection (3 kW, 300°C, 5200 h\textsuperscript{-1} using low sulphur fuel).](image2)

5.4 Summary

The urea injection setup developed in Chapter 4 has been tested behind a diesel engine successfully. Two 300 cpi DN 32 V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}/WO\textsubscript{3} catalytic monoliths have been used. Between 270-450°C no differences in steady state SCR activity is detected between using low sulphur diesel and 0.14 weight percent diesel. A satisfactory NO\textsubscript{x} reduction performance, 70 percent at 300°C without ammonia slip, is obtained at a space velocity of 5000 h\textsuperscript{-1}. Higher space velocities, 15000 h\textsuperscript{-1} at 270°C, lead to insufficient NO\textsubscript{x} reduction and substantial ammonia slip. The catalyst activity decline caused by deposition of soot and non radial distribution of urea is estimated to be equivalent to requiring twice the amount of catalyst as expected on basis of measurements in a laboratory test reactor. Therefore, the space
velocities that can be used for application of this process on a heavy duty diesel engine are expected to be in the range of 5000-15000h\(^{-1}\). Higher space velocities can be obtained by using alternative catalysts, e.g. V\(_2\)O\(_5\)/TiO\(_2\) catalysts without the WO\(_3\) oxidation suppressor. In such a case the SO\(_2\) oxidation may rise considerably when using normal diesel fuel with 0.05 weight percent sulphur. The upper temperature limit of the catalyst will then probably shift to lower temperature values due to ammonia oxidation (see also Chapter 2 and 3).

When injecting an aqueous urea solution in diesel exhaust gases one molecule of urea produces two molecules of NH\(_3\). Injection of aqueous ammonia gives the same NO\(_x\) reduction performance at 300\(^\circ\)C. Also in the dynamic experiments no differences have been detected in using urea or ammonia.

The urea injection setup has been tested on steps and pulses in urea flow rate, exhaust gas flow and engine load. The NO\(_x\) response of the engine (before catalyst) on changes in load is fast (< 2 seconds), especially when compared to the analyser dead time of ten seconds. The initial response of NO\(_x\) outlet signal (after the catalyst) on steps in engine load and exhaust gas flow rate is fast. After the analyser dead time the NO\(_x\) outlet signal starts to change immediately. The rate depends upon whether the step is in the high or in the low NO\(_x\) conversion range. Usually steps at high NO\(_x\) conversions are more slowly, which can be explained by assuming that the catalyst needs to be covered with ammonia before NO\(_x\) can react. This fill-up process takes longer for high conversions, but is generally complete in about a minute. The catalyst offers a buffer capacity for a temporarily overdose of ammonia, but for changes in NO\(_x\) output no buffer capacity is available and only a damping effect at higher conversions can be observed.

So, the stationary and transient behaviour of the urea injection setup in combination with the DN 32 vanadium catalyst has been evaluated on a 4 kW DI diesel engine. As most of the experiments have been conducted around 300\(^\circ\)C (the lower temperature limit of the system, see also section 2.2.1) responses and activities are expected to be relatively slow, respectively low. Further evaluation of these responses and implementation of control algorithms will be performed in Chapter 6.

Literature

Chapter 6
Modelling of the SCR reaction
and urea injection control

In the first section of this Chapter several models for the dynamic processes, resulting from the diesel engine transients, taking place in the catalytic monoliths are described. Validation is performed with the setups described in Chapters 4 and 5. The goal is to achieve a better understanding of these processes to enable design of a urea injection control configuration. For control purposes models are needed which are not too complex. Here a model is developed with minimal complexity and calculation time. To evaluate the influence of the assumptions made in this model two more complex models are developed.

6.1 Process modelling - theory

A heterogeneous catalytic process such as the SCR reaction usually consists of the following steps (see also section 3.3); transport of the reaction components from the gas phase to the catalyst wall/particle, diffusion in the porous catalyst, adsorption on the active sites, reaction, desorption of the reaction products and transport to the bulk gas phase. In a monolith additional gradients are created in the axial (reactant concentrations decrease along the reactor axis) and the radial (different channels) direction of the reactor. The following assumptions hold for all models presented in this Chapter:

1) Ideal hydrodynamics of the flow in monoliths: plug flow in all channels and no changes of concentrations, flow rates and temperatures over the various channels of the monolith.
2) The pressure drop is very small and can be neglected.
3) The increase in the number of molecules (the reaction generates ten molecules from nine) is neglected.
4) The (exo)thermal effects of the reaction are neglected.
5) The ideal gas law can be used to calculate concentrations and densities.
6) The presence of NO₂ is not taken into account.

Assumptions 2-6 are reasonable, see section 3.3, assumption one is somewhat dubious, see Chapter 4 and 5. Three types of dynamic models have been developed. They differ mainly in the number of place coordinates which are considered. In the first model, the 'front' model (section 6.1.2), a sharp boundary between empty catalytic sites and sites occupied by ammonia is assumed. Up to this front sites are occupied by ammonia which can react with NO and behind this front no ammonia is present and NO will not react. This leads to one differential equation describing the location of this front as a function of time and an analytic expression for the NO conversion. Therefore, the NO conversion depends on a scalar variable, the position of the front.

The second model, the tanks in series model (section 6.1.3), allows for the axial concentration profiles of the various concentrations as a function of time. This leads to one partial differential equation for each component considered. A way to solve the resulting equations is to describe the monolith with a finite number of tanks in series (or numerically by a first order discretisation in the place coordinate).
The third model, the 'diffusion' model (section 6.1.4), takes into account the concentration profiles in the washcoat. The resulting partial differential equations are discretized and solved numerically.

Considering radial distribution across the channel inlets as well yields another space coordinate. The paper by Zygourakis\textsuperscript{1}, who studied the effects of radial nonuniform flow distributions on the transient behaviour of a monolithic three-way catalyst, shows that the resulting equations are far more complex.

6.1.1 Reaction mechanism and kinetics of the SCR reaction

As stated in Chapter 2 the adsorption processes taking place on the catalyst surface will influence the dynamic behaviour significantly. The reason is that the number of molecules adsorbed on the catalyst surface exceeds the number of molecules in the gas phase by several magnitudes. The concentration of ammonia in the gas phase is in the order of 0.002-0.02 mol/m\textsuperscript{3}, whereas the amount of ammonia on the catalyst is in the order of 2-20 mol/m\textsuperscript{3}. These values are valid for the temperature range of 200-350°C and the catalyst configuration described in Chapter 4. For significant changes in the catalyst surface concentration to occur, many cubic metres of gas phase need to be passed over one cubic metre of catalyst. Changes in processes on the catalytic surface tend to take several residence times. It is therefore essential to know which species adsorb on the catalyst and the reaction mechanism.

It will be shown that, as a first approximation, the SCR reaction over vanadium/titanium type catalysts can be described as zero order in NH\textsubscript{3} and first order in NO with a large amount of NH\textsubscript{3} adsorbed on the catalyst.

Kinetic studies\textsuperscript{2-5} usually reveal a slightly smaller order in NO, typically 0.5 to 1, orders in ammonia close to zero, orders in oxygen ranging from 0 to 1 and low negative orders in water. It appears that the type of support (e.g. TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}), the presence of additives (e.g. WO\textsubscript{3}), the gas phase composition (e.g. amount of O\textsubscript{2} and H\textsubscript{2}O) and the temperature influence the catalyst significantly. As it is not the scope of this thesis to unravel the exact reaction mechanism of the catalyst used in this study (over which scientists discuss more than two decades) it is assumed that the mechanism described in Chapter two is 'correct'. The mechanism proposed by Myamoto\textsuperscript{6} gives a qualitative explanation for the reaction orders mentioned and is described in more detail. Most of the mechanisms proposed later\textsuperscript{3, 7-10} are derived from this mechanism incorporating ammonia oxidation, N\textsubscript{2}O formation and the reaction in absence of O\textsubscript{2}. The overall reaction is (see also Chapter 2):

\[
4\text{NO}(g) + 4\text{NH}_3(g) + \text{O}_2(g) \rightarrow 4\text{N}_2(g) + 6\text{H}_2\text{O}(g)
\]  

(6.1)

Step 1: adsorption of ammonia on a site

\[
\text{NH}_3(g) + \text{site} = \text{NH}_3\text{site}
\]  

(6.2)

Modelling of the SCR reaction and urea injection control
This step is a common feature in almost all mechanisms proposed for the SCR reaction. The differences in mechanisms proposed are the nature of the adsorption (simple physical or dissociative chemisorption\textsuperscript{8, 10, 11}) and the adsorption site itself. E.g. Otto\textsuperscript{12, 13} supposes that a NH\textsubscript{3} dissociation is the rate determining step (he used noble metal catalysts though). Recently\textsuperscript{14} this idea revived and a mechanism was proposed in which this dissociation was replaced by the term 'activation'.

Step 2: reaction of NO

\[
\text{NH}_3/\text{site} + \text{NO(g)} \rightarrow \text{NO}/\text{NH}_3/\text{site} \tag{6.3}
\]

Step 3: decomposition of the activated complex

\[
\text{NO}/\text{NH}_3/\text{site} \rightarrow \text{site}/\text{H} + \text{N}_2 + 1/2 \text{H}_2\text{O} \tag{6.4}
\]

The second step, reaction of NO with the adsorbed ammonia to form a surface nitrosocomplex is somewhat dubious. Several authors\textsuperscript{15-17} prefer to suppose the formation of a surface nitrate compound which reacts with ammonia while even additional steps via a N\textsubscript{2}O\textsubscript{3} compound are proposed\textsuperscript{11}. The original paper of Miyamoto suggests the formation of a transition complex (therefore step two might be rate determining). Another proposal\textsuperscript{9} is that the formation of this complex is in equilibrium and the decomposition of this complex is rate determining. Other authors assume NO is weakly adsorbed on the catalyst. In case of some type of NO adsorption a NO buffer will be formed. Of course, if the equilibrium constant is small, this buffer will be small.

Step 4: oxidation of the reduced site

\[
\text{site}/\text{H} + 1/4 \text{O}_2 = \text{site} + 1/2 \text{H}_2\text{O} \tag{6.5}
\]

The last step, the oxidation equilibrium of the reduced sites is assumed to be fast. However, also on this last step the opinions differ considerably\textsuperscript{18}.

These four steps do generate a relative complex kinetic expression and some simplifications must be made to develop a dynamic model. The following equilibrium constants can be defined:

\(K_{\text{NH}_3}\): adsorption of ammonia on a site

\[
K_{\text{NH}_3} = \frac{C_{\text{site}/\text{NH}_3}}{C_{\text{site}} \cdot C_{\text{NH}_3}} \tag{6.6}
\]
\[ K_{NO} = \frac{C_{siteNH_3NO}}{C_{siteNH_3} \cdot C_{NO}} \] (6.7)

\[ K_{ox} = \frac{C_{H_2O}^{\frac{1}{4}} \cdot C_{site}}{C_{siteH} \cdot C_{O_2}^{\frac{1}{4}}} \] (6.8)

The total number of sites is fixed:

\[ C_{site\text{total}} = C_{site} + C_{siteNH_3} + C_{siteNH_3NO} + C_{siteH} \] (6.9)

Assuming equilibrium for steps 1, 2 and 4 and step 3 to be rate determining gives the following rate expression of NO removal (see Appendix 2 for the derivation):

\[ -r_{NO} = k C_{siteNH_3NO} \]

\[ -r_{NO} = \frac{k K_{NO} C_{NO} K_{NH_3} C_{NH_3} K_{ex} C_{site\text{total}}^{\frac{1}{4}}}{C_{H_2O}^{\frac{1}{4}} + K_{ex} C_{O_2}^{\frac{1}{4}} + K_{NH_3} C_{NH_3} K_{ex} C_{O_2}^{\frac{1}{4}} + K_{NO} C_{NO} K_{NH_3} C_{NH_3} K_{ex} C_{O_2}^{\frac{1}{4}}} \] (6.10)

Various simplifications lead to the kinetic models mentioned in the literature. E.g. assuming \( K_{NO} C_{NO} \ll 1 \) leads to the equation proposed by Hofmann, alternatively assuming the reoxidation unimportant the 'nitrosamidic intermediate' models of Tufano are obtained. For engineering purposes usually both assumptions are made, resulting in:

\[ -r_{NO} = k K_{NO} C_{NO} \frac{K_{NH_3} C_{NH_3}}{1 + K_{NH_3} C_{NH_3}} \] (6.11)

Modelling of the SCR reaction and urea injection control
Or, when the ammonia adsorption is very strong \((K_{\text{NH}_3C_{\text{NH}_3}} > > 1)\):

\[-r_{\text{NO}} = k \ C_{\text{NO}} \tag{6.12}\]

So, the most rigorous simplification is that the catalyst adsorbs ammonia strongly and NO reacts with this adsorbed NH\(_3\) via a first order reaction. This model was already used by Miyamoto in his pulse experiments\(^{20}\) and is the basis upon which all dynamic models described here are developed.

The influence of components which interfere with the SCR reaction is not fully explained. Especially water is a components upon which several authors disagree significantly. The most simple approach is to assume that water competes with ammonia for the reaction site which results in a \(K_{\text{H}_2\text{O}C_{\text{H}_2\text{O}}}\) term in the denominator of equation 6.11. However, it is generally believed that \(\text{H}_2\text{O}\) also increases the selectivity towards \(\text{N}_2\) formation\(^{21}\). Turco\(^{22}\) proposes irreversible adsorption of water on energetically not equivalent sites, which suggests a more complex mechanism.

6.1.2 Front model

The NO balance for the front model is in principle the same as used for a plug flow reactor model (for the actual reactor see Figure 5.1). A steady state molar balance is set up for an infinitesimal small piece of the reactor d\(V\):

\[
\varphi_v \ C_{\text{NO}} \left|_{\nu dv} \right. \ = \ \varphi_v \ C_{\text{NO}} \left|_{\nu} \right. \ - \ (-r_{\text{NO}}) \ \epsilon \ dV \tag{6.13}
\]

With:
- \(\varphi_v\) : flow rate \([\text{m}^3 \text{g}^{-1} \text{s}^{-1}]\);
- \(C_{\text{NO}}\) : NO concentration \([\text{mol m}^{-3} \text{g}]\);
- \(V\) : volume reactor \([\text{m}^3\text{g}]\);
- \(\epsilon\) : bed porosity \([\text{m}^3/\text{m}^3]\);
- \(-r_{\text{NO}}\) : reaction rate \([\text{mol m}^{-3} \text{g}^{-1} \text{s}^{-1}]\).

The reaction rate of NO can be solved by integrating equation 13 over the part of the reactor where the sites are occupied with ammonia. This means integrating \(V\) not from zero to one but from zero to the position of the front or to the amount of occupied sites (note that the numerical value for \(z\) cannot exceed 1);

\[
\int_{C_{\text{NO,init}}}^{C_{\text{NO,max}}} \frac{dC_{\text{NO}}}{-r_{\text{NO}}} = -\frac{V_r}{\varphi_v} \ \epsilon \ \int_0^z dz \tag{6.14}
\]

With:
- \(V_r\) : total volume reactor \([\text{m}^3\text{g}]\);
- \(z\) : dimensionless position of the front \([-]\).

Substituting a suitable expression for the reaction rate, e.g. equation 12 into 14, leads to an analytic solution for the NO conversion:

\[
\xi_{\text{NO}} = 1 - e^{-kt\tau} \tag{6.15}
\]

\[
\tau = \frac{V_r}{\varphi_v} \ \epsilon
\]

Chapter 6
with: \( \tau \) : residence time \([s]\);
\( \xi_{NO} \) : NO conversion [-];
\( k \) : reaction rate constant \([1/s]\).

The location of the front* follows from the dynamic molar balance of ammonia over the reactor:

\[
\frac{d(z, V, Q_z)}{dt} - \varphi V C_{NH3,inlet} - 0 - \varphi V C_{NO,inlet} \xi_{NO}
\]

with: \( Q_t \) : total concentration of sites \([\text{mol/m}^3]_t\).

Note that the amount of ammonia which leaves the reactor is supposed to be zero. Ammonia slip only occurs when the position of the front exceeds one. It is assumed that the solid phase ammonia consumption equals the steady state NO\(_x\) conversion and that the stoichiometry is one. Furthermore, the gas phase accumulation is neglected. Substitution of 15 in 16 yields:

\[
\frac{dz}{dt} = \varphi V C_{NH3,inlet} - \varphi V C_{NO,inlet} (1 - e^{-k\tau})
\]

\[
\frac{V_r Q_t}{V_r Q_t}
\]

Hence, to calculate the position of the front from the steady state NO removal performance, the inlet NO and the ammonia concentration one needs to know the adsorption capacity of the catalyst. This can be determined using standard adsorption methods and is a function of temperature: equation 17 can only be used for isothermal operation. In all other cases the left side of equation 16 needs to be evaluated in more detail:

\[
\frac{d(z, V, Q_z)}{dt} = V_r (Q_t \frac{dz}{dt} + z \frac{dQ_t}{dt})
\]

\[
\frac{dQ_t}{dt} = \frac{dQ_t}{dT} \frac{dT}{dt}
\]

\[
\frac{dz}{dt} = \varphi V C_{NH3,inlet} - \varphi V C_{NO,inlet} (1 - e^{-k\tau})
\]

\[
\frac{V_r Q_t}{Q_t} \frac{dQ_t}{dT} \frac{dT}{dt}
\]

* Actually, the assumption that a sharp front is present is not necessary to describe the transient NO signal. The variable \( z \) is also the fraction of sites which are covered with ammonia and as the SCR reaction is first order and plug flow is assumed the physical position of the occupied sites is not relevant.
The concentration profiles of NO and ammonia for a typical steady state situation are plotted in Figure 6.1. Both profiles decrease exponentially (equation 6.15) until they reach the position of the front. After the front the sites are empty and NO will not react any more. It is assumed that ammonia reacts infinitely fast with empty sites and therefore the ammonia concentration will always be zero after the front. The only way for ammonia to be emitted is in the situation that the position of the front is at the end of the reactor.

An increase in ammonia inlet concentration will cause the front to shift to the right. Because of the exponential shape of the lines such an increase causes a larger change in front position than the same decrease. This means that the NO\textsubscript{X} conversion is less sensitive to changes in NH\textsubscript{3}/urea at high conversions and/or front positions close to one.

Ammonia will only be emitted when the front position is at the end of the reactor. Clearly, this happens when an overdoses of urea/ammonia is injected. However, there is another possibility; e.g. when the ammonia buffer itself becomes smaller by a rapid increase in catalyst temperature. The amount of ammonia on the catalyst and number of active sites decrease if the temperature rises (dQ/dT is negative in equation 6.19). This decrease in number of sites causes the position of the front to shift towards the end of the reactor when the temperature is raised, see also Figure 6.2. When the temperature rise is over the front will shift back into the reactor and attain a new steady state more towards the entrance of the reactor than before. In the mean time a large amount of ammonia can be emitted. This effect has been reported by Lepperhof\textsuperscript{23} using SCR on diesel exhaust and switching from a low to high engine load.

### 6.1.3 Tanks in Series model

A Tanks in Series (TIS) model describes the axial concentration profile of the components NO, NH\textsubscript{3} and sites. The molar balances for components as a function of time yield three partial differential equations with respect to place and time. Rather than direct discretisation of these equations, the plug flow reactor is simulated by using a number of tank reactors in series. Essentially this is the same as a first order backwards discretisation in place and subsequently using an ordinary differential equation (ODE) solver to obtain numerical results.

*Chapter 6*
The reasons for using this tanks in series approach is that the molar balances can be made over simple chemical engineering units, ideal tank reactors, and that implementing a deviation in the hydrodynamics in the form of axial dispersion is relatively easy. Furthermore, this type of model has been applied successfully for the transient behaviour of a packed bed reactor (with the SCR catalyst DN 110). For an ideal plug flow reactor an infinite number of tanks in series is needed. In practice the numerical solution does not change significantly above twenty.

6.1.3.1 Basic equations TIS model

In the TIS model the reaction mechanism is simplified by assuming an adsorption of ammonia on an empty site followed by a first order reaction with NO (for the derivation see Appendix 2):

\[ \text{NH}_3 \text{ + site} \rightarrow \text{NH}_3/\text{site} \]  \hspace{1cm} (6.20)
\[ \text{NH}_3/\text{site} + \text{NO} + 1/4 \text{O}_2 \rightarrow \text{N}_2 + 3/2 \text{H}_2\text{O} + \text{site} \]  \hspace{1cm} (6.21)

The reaction rates of the gas and solid phase compounds and all site types are:

\[ -r_{\text{NH}_3} = k_{\text{ads}} C_{\text{NH}_3} C_{\text{site}} - k_{\text{des}} C_{\text{NH}_3/\text{site}} \]  \hspace{1cm} (6.22)
\[ -r_{\text{NO}} = k C_{\text{NO}} C_{\text{NH}_3/\text{site}} \]  \hspace{1cm} (6.23)
\[ -r_{\text{site}} = (-r_{\text{NH}_3}) - (-r_{\text{NO}}) \]  \hspace{1cm} (6.24)
\[ C_{\text{site, total}} = C_{\text{Site}} + C_{\text{NH}_3/\text{site}} \]  \hspace{1cm} (6.25)

with:

\[ -r_{\text{NH}_3} \] : reaction rate ammonia [mol/m$^3$ r s];
\[ k_{\text{ads}} \] : adsorption rate constant of ammonia [m$^3$/mol s];
\[ C_{\text{NH}_3} \] : concentration of ammonia [mol/m$^3$ g];
\[ C_{\text{site}} \] : concentration of sites [mol/m$^3$ r];
\[ k_{\text{des}} \] : desorption rate constant [1/s];
\[ C_{\text{NH}_3/\text{site}} \] : concentration of amine sites [mol/m$^3$ r];
\[ -r_{\text{NO}} \] : reaction rate NO [mol/m$^3$ r s];
\[ C_{\text{NO}} \] : concentration of NO [mol/m$^3$ g];
\[ k \] : reaction rate constant [m$^3$/mol s];
\[ -r_{\text{site}} \] : reaction rate sites [mol/m$^3$ r];
\[ C_{\text{site, total}} \] : overall sites concentration [mol/site/m$^3$ r].

The following dimensionless and additional variables are introduced:

\[ Y_{\text{NO}} = \frac{C_{\text{NO}}}{C_{\text{NO, ref}}} \quad Y_{\text{NH}_3} = \frac{C_{\text{NH}_3}}{C_{\text{NO, ref}}} \quad Y_s = \frac{C_{\text{site}}}{C_{\text{site, ref}}} \quad Y_{\text{SN}} = \frac{C_{\text{NH}_3/\text{site}}}{C_{\text{site, ref}}} \]
\[ e = \frac{V_g}{V_t} \quad \tau = \frac{V_t}{\phi_v} \quad t_{st} = \frac{V_{bed}}{\phi_{v,ref}} \quad (e + \frac{C_{site,ref}}{C_{NO,ref}}) \quad \Theta = \frac{t}{t_{st}} \]

with:
- \( V_g \): volume gas in one tank [m^3];
- \( \phi_v \): flow rate [m^3/s];
- \( V_t \): volume of one tank [m^3];
- \( C_{NO,ref} \): reference NO concentration [mol/m^3];
- \( C_{site,ref} \): reference site concentration [mol/m^3];
- \( \epsilon \): porosity [m^3/m^3];
- \( \phi_{v,ref} \): reference flow rate [m^3/s];
- \( \tau \): residence time [s];
- \( t_{st} \): stoichiometric time [s];
- \( V_{bed} \): volume of all tanks [m^3];
- \( \Theta \): dimensionless time.

The molar balances for one tank are:

\[ \frac{1}{t_{st}} \frac{dY_{NO}}{d\theta} = \frac{Y_{NO_{in}} - Y_{NO}}{\tau} - \frac{(-r_{NO})}{e C_{NO,ref}} \]  

(6.26)

\[ \frac{1}{t_{st}} \frac{dY_{NH3}}{d\theta} = \frac{Y_{NH3_{in}} - Y_{NH3}}{\tau} - \frac{(-r_{NH3})}{e C_{NO,ref}} \]  

(6.27)

\[ \frac{1}{t_{st}} \frac{dY_{S}}{d\theta} = \frac{(-r_{site})}{C_{site,ref}} \]  

(6.28)

with:
- \( Y_{NO_{in}} \): dimensionless tank inlet NO concentration;
- \( Y_{NH3_{in}} \): dimensionless tank inlet NH3 concentration.

### 6.1.3.2 Comparison of the TIS with front model

It is expected that for large values of the adsorption- and small values for the desorption rate constants \((k_{ads} \text{ and } k_{des} \text{ in equation 6.22})\) the front and the TIS model will give almost the same NO\(_x\) conversions. Differences are the gas phase accumulation, which is taken into account by the TIS model and not by the front model. However, this is a small difference (compare \( e \) with \( C_{sites, total} / C_{NH3_{in}} \) in the definition of \( t_{st} \)). Therefore a typical response of switching on the ammonia yields virtually the same NO outlet signal, Figure 6.3. The profile of the sites concentration is also sharp, Figure 6.4, the concentration in sites changes from zero to one in one or two tanks.
Differences do exist in dynamic responses, however only in the site concentration profile and not in the NO outlet signal. In case of an increase in ammonia inlet level additional tanks are filled one by one, which corresponds to a gradual shifting of the front towards the reactor exit. However, decreasing the ammonia inlet level does not mean that the tanks will be emptied starting at the full tank closest to the reactor exit. All tanks between the position of the new and the old front are emptied gradually with about the same rate, see also Figure 6.5. This means that during a transient, sites can be covered with ammonia closer to the reactor exit than expected on basis of the front model. This means that the chance of ammonia slip increases; when designing/controlling with the front model care should be taken to keep the front at a save distance from the reactor outlet.

Figure 6.5: The response of the empty sites concentration along the axial reactor coordinate (Z) on a step in ammonia inlet concentration. The ammonia inlet is lowered from 800 (steady state figures 6.3 and 6.4) to 0.6 at t=0 s.
Until now the comparison of the front and TIS models was performed by assuming the ammonia adsorption equilibrium constant is infinitely large. This constant $K_{\text{NH}_3}$, also equal to $k_{\text{ads}}/k_{\text{des}}$, of course has a finite value. The influence of the adsorption and desorption rate constants is twofold. First, when possessing a finite value they will slow the overall process. Secondly, a finite value for the desorption coefficient allows ammonia to desorb again. The first effect is probably not very important since this type process is usually fast. The second effect causes an incomplete occupation of the sites up to equilibrium:

$$\frac{C_{\text{site/NH}_3}}{C_{\text{site, total}}} = \frac{K_{\text{NH}_3}C_{\text{NH}_3}}{1 + K_{\text{NH}_3}C_{\text{NH}_3}}$$  \hspace{1cm} (6.29)

This has a direct impact on the reactivity; the reaction rate for NO is now equation 6.11. Under the same conditions the amount of catalyst needed is larger and the front is closer to the reactor outlet.

The effect of introducing a finite equilibrium constant is illustrated in Figure 6.6. The term $K_{\text{NH}_3}C_{\text{NH}_3, inlet}$ is varied: a value of 1 means that, at reactor inlet conditions, the activity of the catalyst is reduced by a factor of two (equation 6.11). As the amount of ammonia in the gas phase decreases along the reactor length, the activity of the catalyst, in terms of number of sites which are occupied with ammonia and can react, decreases. If the $K_{\text{NH}_3}C_{\text{NH}_3}$ is unity a substantial ammonia slip (65 ppm at 1000 ppm inlet value) is present. This means that the term $K_{\text{NH}_3}C_{\text{NH}_3, inlet}$ should be large for the front model to be applied. Here a criterion of $K_{\text{NH}_3}C_{\text{NH}_3, inlet} > 10$ is proposed.

**6.1.3.3 Further modelling**

As stated before the kinetics were simplified here to a first order in NO. Usually orders of 0.5-1 are found and DN 32 exhibits an order in NO of about 0.7-0.8. Therefore equation 6.3, formation of a nitrosocomplex, is taken into account. This results in an order in NO smaller than one and a certain amount of NO to be adsorbed. It is expected that this model will have a different transient behaviour. If assumed that the adsorption and desorption processes are in equilibrium the following set of equations describing the dynamic behaviour of one tank (for derivations see Appendix 2) are obtained:
\[
\begin{align*}
\frac{1}{t_{\text{st}}} \frac{dY_{\text{NO}}}{d\theta} &= \frac{Y_{\text{NOin}} - Y_{\text{NO}} - r_{\text{N2}}}{\tau \frac{Y_{\text{NO}}}{Y_{\text{NO}}} \frac{Y_{\text{NO}}}{C_{\text{NO,0}}}} \\
\frac{1}{t_{\text{st}}} \frac{dY_{\text{NH3}}}{d\theta} &= \frac{Y_{\text{NH3in}} - Y_{\text{NH3}} - r_{\text{N2}}}{\tau \frac{Y_{\text{NH3}}}{Y_{\text{NH3}}} \frac{Y_{\text{NH3}}}{C_{\text{NO,0}}} - \frac{dY_{\text{SNH}}}{dY_{\text{NH3}}} \frac{Y_{\text{NH3}}}{C_{\text{NO,0}}}}
\end{align*}
\]

With:

\[
r_{\text{N2}} = k \frac{K_{\text{NH3}} Y_{\text{NH3}} K_{\text{NO}} Y_{\text{NO}} C_{\text{site, total}} C_{\text{NO,0}}^2}{1 + K_{\text{NH3}} Y_{\text{NH3}} C_{\text{NO,0}} + K_{\text{NH3}} Y_{\text{NH3}} K_{\text{NO}} Y_{\text{NO}} C_{\text{NO,0}}^2}
\]

\[
\frac{dY_{\text{SNH}}}{dY_{\text{NH3}}} = \frac{(K_{\text{NH3}} + K_{\text{NO}} Y_{\text{NO}} K_{\text{NH3}} C_{\text{NO,0}}) C_{\text{NO,0}}}{(1 + K_{\text{NH3}} Y_{\text{NH3}} C_{\text{NO,0}} + K_{\text{NH3}} Y_{\text{NH3}} K_{\text{NO}} Y_{\text{NO}} C_{\text{NO,0}}^2)^2}
\]

\[
\frac{dY_{\text{SNH}}}{dY_{\text{NO}}} = \frac{(1 + K_{\text{NH3}} Y_{\text{NH3}} C_{\text{NO,0}} + K_{\text{NH3}} Y_{\text{NH3}} K_{\text{NO}} Y_{\text{NO}} C_{\text{NO,0}}^2)}{(1 + K_{\text{NH3}} Y_{\text{NH3}} C_{\text{NO,0}} + K_{\text{NH3}} Y_{\text{NH3}} K_{\text{NO}} Y_{\text{NO}} C_{\text{NO,0}}^2)^2}
\]

The major difference with the previous models is that NO is also stored on the catalyst in the form of a nitrosocomplex. This causes the NO signal to respond more slowly as a NO buffer is formed. However, this buffer will be smaller than the ammonia buffer as the equilibrium constant is much smaller and NO can only adsorb on reduced sites.

Another effect which can (and at high temperatures should) be implemented is ammonia oxidation. However, the knowledge on the mechanism and kinetics is even more limited especially for diesel exhaust gases.
6.1.4 Diffusion models of the transport of reactants in and to the washcoat

The goal of this section is to evaluate the effects of mass transport on the transient behaviour of SCR catalysts. To take mass transfer into account a model has been derived including the diffusion of reactants into the washcoat. This diffusion transport can be subdivided in diffusion from the bulk gas phase to the wall (film diffusion) and diffusion through the porous washcoat to the catalytic site (pore diffusion). The spatial coordinates are defined in Figure 6.7; transport in the axial direction (dimensionless \( Z \)); the actual position divided by the length of the monolith) and into the washcoat (dimensionless \( X \); the actual position in the washcoat divided by the washcoat thickness).

![Diagram showing spatial coordinates Z and X](image)

*Figure 6.7: Definition of the spatial coordinates Z and X. The gas flows through the monolith from \( Z = 0 \) to \( 1 \), NO and \( \text{NH}_3 \) diffuse from the bulk gas phase to the washcoat (\( x = 0 \)) and diffuse through the washcoat from \( X = 0 \) to \( 1 \) reacting with the sites.*

The transport from the bulk gas phase to the wall is modelled according to the film model (for the complete derivation see Lugt\textsuperscript{26}):

\[
J = k_m \left( C_b - C_{X=0} \right)
\]  

(6.35)

with:
- \( C_b \): bulk gas phase concentration [mol/m\(^3\)\(_g\)];
- \( J \): the molar flux in the washcoat [mol/m\(^2\)\(_w\)s];
- \( C_{X=0} \): the concentration at the surface of the washcoat [mol/m\(^3\)\(_g\)];
- \( k_m \): the mass transfer coefficient [m\(^3\)\(_g\)/m\(^2\)\(_w\)s].
The mass transfer coefficient can be obtained using a standard 'Sherwood' type relation. In this case the Hawthorn\textsuperscript{27} correlation has been used (equation 3.15). Several correlations can be found in literature\textsuperscript{28, 29}. However, they are not consistent with the analytic solution for laminar flow as Reynolds approaches zero\textsuperscript{30}. The conditions in which this type of monolith is used are indeed close to this analytic solution (3 < Sh < 4, see also section 3.3).

The ammonia adsorption and NO reaction are modelled as first order reactions (equation 6.20 and 21). Desorption of ammonia is not taken into account, the adsorption rate constant \( k_{ads} \) is assumed to be infinitely large. The mass transfer in the porous washcoat can be described as a standard diffusion process yielding\textsuperscript{26}:

\begin{equation}
\frac{\partial C_{NH3}}{\partial t} = \frac{D_e}{\varepsilon_w} \frac{\partial^2 C_{NH3}}{\partial x^2} - k_{ads} C_{NH3} \Theta \tag{6.36}
\end{equation}

\begin{equation}
\frac{\partial C_{NO}}{\partial t} = \frac{D_e}{\varepsilon_w} \frac{\partial^2 C_{NO}}{\partial x^2} - k_{NO} C_{NO} (1-\Theta) \tag{6.37}
\end{equation}

\begin{equation}
\frac{\partial C_{\text{site,empty}}}{\partial t} = -k_{ads} C_{NH3} \Theta \varepsilon_w + k_{NO} C_{NO} (1-\Theta) \varepsilon_w \tag{6.38}
\end{equation}

with:
- \( C_{NH3} \) : ammonia concentration [mol/m\textsuperscript{3}_g];
- \( C_{NO} \) : NO concentration [mol/m\textsuperscript{3}_g];
- \( C_{\text{site,empty}} \) : concentration empty sites [mol/m\textsuperscript{3}_w];
- \( x \) : distance from the wall [m\textsubscript{w}];
- \( \varepsilon_w \) : porosity washcoat [m\textsuperscript{3}_g/m\textsuperscript{3}_w];
- \( D_e \) : effective diffusion coefficient [m\textsuperscript{3}_g/m\textsuperscript{3}_w s];
- \( t \) : time [s];
- \( k_{ads} \) : adsorption rate constant [1/s];
- \( k_{NO} \) : reaction rate constant [1/s];
- \( \Theta \) : fraction of empty sites [-].

The boundary conditions at the wall of the washcoat are found by setting the film diffusion towards the washcoat (equation 6.35) equal to the flux inside the washcoat at \( x=0 \) (the diffusion coefficients of NH\textsubscript{3} and NO are assumed to be identical):

\begin{align*}
\quad k_m & \left( C_{NH3,\text{bulk}} - C_{NH3,x=0} \right) = -D_e \left| \frac{dC_{NH3}}{dx} \right|_{x=0} \\
\quad k_m & \left( C_{NO,\text{bulk}} - C_{NO,x=0} \right) = -D_e \left| \frac{dC_{NO}}{dx} \right|_{x=0} \tag{6.39}
\end{align*}
The boundary conditions at the inner side of the washcoat, \( x=0 \), read:

\[
\frac{dC_{NH_3}}{dx} = 0
\]

\[
\frac{dC_{NO}}{dx} = 0
\]  \hspace{1cm} (6.40)

The convectional transport in the axial direction, Figure 6.7, can be described as:

\[
\frac{dC_{\text{bulk}}}{dz} = - \frac{k_m \sigma}{uA} (C_{\text{bulk}} - C_{x=0})
\]  \hspace{1cm} (6.41)

With:  
- \( u \) : the linear gas phase velocity, \([\text{m/s}]\);
- \( A \) : the area of the monolith channel \([\text{m}^2]\);
- \( \sigma \) : the perimeter length of the monolith channel \([\text{m}]\).

The resulting equations are made dimensionless, discretized and solved numerically\(^{26}\). The influence of mass transfer limitation on reactor performance has been investigated for the 400 cpi DN 32 monolith in model gases at 250°C. The variables calculated are the NO outlet signal as a function of time when switching the NO and ammonia feed on. Furthermore, the steady state NO/NH\(_3\) and sites profiles have been calculated.

**Chemical reaction is rate controlling**

This is achieved by putting the values of the mass transfer coefficient \( k_m \) and effective diffusion coefficient \( D_e \) at a sufficiently high value (10 \( \text{m}^3/\text{m}^2\cdot\text{s} \) and \( 1\times10^{-4} \text{m}^3/\text{m}^2\cdot\text{s} \) respectively). Due to these large values no gradients in the \( x \) direction will occur. The NO outlet signal as a function of time and the NO/NH\(_3\) steady state concentration profile in the axial \( (Z) \) direction are plotted in Figure 6.8 and 9. As in case of the TIS model, section 6.1.3.2, comparison with the front model shows minor deviations.

![Figure 6.8: Comparison front model and diffusion model chemical rate controlling](image1)

![Figure 6.9: Concentration profile of NH\(_3\) and NO, diffusion model, chemical rate controlling (front at \( z=0.21 \))](image2)
Influence of film diffusion

Substituting a realistic value of the mass transfer coefficient $k_m$ (0.2 m$^3$/m$^2$.s) yields Figure 6.10. Obviously the influence of film diffusion is very small; the concentration profile in the axial direction hardly changes. Furthermore, the concentration at the wall is not significantly lower compared to the previous case. As a result the NO$_x$ outlet signal will be the same.

![Graph showing NO and NH$_3$ concentration profiles](image)

*Figure 6.10: Influence film diffusion*

![Graph showing NO concentration profiles with and without diffusion limitation](image)

*Figure 6.11: Influence pore diffusion*

Film diffusion limitation occurs only at lower values of $k_m$. In such cases the steady state concentration profile of NO in the axial direction will be shifted to the reactor exit. The amount of sites in use will be larger and it will take longer for the NO outlet signal to reach its steady state level.

![Graph showing influence of pore diffusion on NH$_3$ and NO concentration profiles](image)

*Figure 6.12: Influence pore diffusion on concentration profiles of NH$_3$ and NO*
**Influence of pore diffusion**

Decreasing the effective diffusion coefficient to realistic values \(5 \times 10^{-7} \text{ m}^3/\text{m}^2\text{s}\), Appendix 1) leads to slower responses, Figure 6.11. The concentration profiles of NO and NH\(_3\) in the Z direction shift to the reactor exit, Figure 6.12. Profiles of NO and NH\(_3\) in the washcoat are formed, Figure 6.13. Note that the sites are completely \(C_{\text{sites, empty}}=0\) occupied when the ammonia concentration is above zero.

**Formation of concentration profiles in the washcoat**

Until now, only the NO outlet signal as a function of time and the resulting steady state NO/NH\(_3\)/sites profiles in the washcoat has been displayed. These evolving concentration profiles in the washcoat are calculated at certain time intervals when the NO outlet signal, Figure 6.11, is not constant yet. The concentration profiles in the washcoat at Z=0 as a function of time is plotted in Figure 6.14. Figure 6.14a shows that the sites in the X direction are filled like in the Z direction predicted by the front model. Relative sharp fronts of occupied sites move from the wall, X=0, into the washcoat.

The evolving ammonia concentration profiles in the washcoat, Figure 6.14b, penetrate in the washcoat and eventually reach a steady state level dictated by the reaction rate of NO with the sites occupied with ammonia. Comparing Figure 6.14a with 6.14b yields that the ammonia concentration is almost zero when the sites are empty. This is a consequence of putting the adsorption coefficient of ammonia at a very large value.

The NO concentration profiles in the washcoat, Figure 6.14c, drop slowly as sites are being filled with ammonia. In contrast with the ammonia concentration profiles, the NO profiles do not become zero when the sites are empty, Figure 6.14a, but level off as NO does not react with empty sites.

The profiles plotted in Figure 6.14 are valid for any Z coordinate. The difference is only that the NO and NH\(_3\) concentration at the wall are lower. Furthermore, some time lag is present since the process occurs downstream.

**Remarks**

For DN 32 the influence of film- and pore diffusion limitation at 250°C is not very large. Effectivities are in the range of 0.5 to 1 depending on the value of \(D_e\). Larger influences can be expected at higher temperatures and thicker washcoats (e.g. the 300 cpi version or using full catalyst monoliths). The buffer capacity is not affected seriously; sites are occupied throughout the washcoat. It is noted that at lower \(K_{\text{NH3}}\) values deviations will occur since the ammonia concentration may decrease strongly in the washcoat. This will typically occur at higher temperatures where the reaction rate increases and the \(K_{\text{NH3}}\) value decreases.
Figure 6.13: The concentration profiles of NO, NH$_3$ & empty sites in the porous washcoat (X) as a function of the reactor length (Z).

Figure 6.13a

Figure 6.13b

Figure 6.13c

Figure 6.14: The concentration profiles of NO, NH$_3$ & empty sites in the porous washcoat (X) at Z=0 as a function of time.

Figure 6.14a

Figure 6.14b

Figure 6.14c
6.1.5 Summary process modelling - theory

In section 6.1 three models are presented to describe the dynamic behaviour of the SCR reaction. The difference between the models is the number of spatial coordinates taken into account.

The front model assumes a sharp boundary between sites occupied by ammonia and empty sites. This model is therefore only useful at high $K_{NH3}$ values. No concentration profiles in or to the washcoat are described. These phenomena are lumped into the kinetic data used. The model consists of one ODE as a function of time for the ammonia adsorption and an analytic expression for the NO conversion.

The tanks in series models allows the effect of finite $K_{NH3}$ values to be taken into account. Furthermore, it is relatively easy to implement more complex reaction mechanisms. As with the front model transport phenomena are lumped in the kinetic data used. The model consists of one PDE for each component. Hence, it describes the process as a one-dimensional time dependant problem. The tanks in series approach allows to rewrite these PDE’s to a set of ODE’s which can be solved using a standard numerical package.

The diffusion model studies the effect of concentration profiles in the washcoat. It yields two PDE’s for each component. It describes the process as a two-dimensional time dependant problem. Solutions are obtained by home written routines (Lugt\textsuperscript{26}).

Depending on the situation and values of the parameters ($K_{NH3}$, $D_e$, $k_{NO}$, etc) one of the models can be chosen. The diffusion model can, in principle, be extended to describe all other models in section 6.1. However, the amount of work is much larger, in terms of programming efforts as well as calculation time. The latter can be important when using online model predictions for process control purposes.

6.2 Process modelling - validation

The validation of deNO$_x$ models concentrates on two phenomena; the ammonia adsorption characteristics and the SCR reaction itself. The most important parameters of the models developed in section 6.1 and in literature\textsuperscript{31} are the adsorption capacity (in terms of mol NH$_3$/m$^3$ and/or equilibrium values) and the activity of the catalyst itself (in terms of reaction rate constants).

6.2.1 Ammonia adsorption behaviour in model gases

Figure 6.15: NH$_3$ adsorption capacity of DN 32 as a function of temperature (457 g 400 cpi DN 32, 63 & 500 ppm NH$_3$, 5 Nm$^3$/h air).

The ammonia adsorption capacity has been determined using the experimental setup as described in Chapter 4. The catalyst is oxidized in air (and/or NO) at higher temperatures to remove all ammonia. Subsequently,
the breakthrough curve is determined by switching on the ammonia feed and by monitoring the ammonia outlet signal. The overall adsorption capacity is equal to the integral of the difference between the inlet and outlet ammonia signal (correcting for equipment dead time). The results for the 400 cpi DN 32 monolith, used in Chapter 4, are plotted in Figure 6.15. Due to ammonia oxidation it was not possible to measure the ammonia adsorption above circa 300°C. It should be noted that by using this technique all adsorbed ammonia is determined. However, not all adsorbed ammonia does necessarily contribute to the deNO_x reaction.

The data points in Figure 6.15 (500 ppm NH_3 only) are used to obtain a relationship between the total number of sites and temperature for the 400 cpi DN 32 version:

\[ C_{\text{site,total}} = 126 - 0.34 T \text{ \( \mu \text{mol/g} \) } \quad (6.42) \]

\[ 200 < T < 330^\degree \text{C} \]

In this temperature region the adsorption capacity is a weak function of the concentration; at a lower concentration the amount of adsorbed NH_3 should be lower which is only observed above 280°C. This means that the equilibrium constant, K_{NH_3}, is large and the sites are almost completely covered with ammonia. The decrease in adsorption capacity with increasing temperature cannot be explained by a decreasing K_{NH_3} only. The adsorption capacity should become constant (the total number of sites) below a certain temperature in case of such a K_{NH_3} effect. Therefore, the overall site concentration probably also changes.

When inspecting the breakthrough curves measured with 63 ppm NH_3, Figure 6.16, two phenomena can be observed. First, the high-temperature breakthrough curve does not reach the ammonia inlet level any more. This can be explained by NH_3 oxidation which starts at about 250°C. In those cases the ammonia storage capacity is calculated by integrating the difference between the ammonia outlet signal and the steady state outlet signal.

![Figure 6.16: Response of switching on the NH_3 feed as a function of temperature (457 g 400 cpi DN 32, 63 ppm NH_3 in 5 Nm^3/h air).](image)

![Figure 6.17: Adsorption and desorption curves of DN 32 at 100°C (457 g 400 cpi DN 32, 63 ppm NH_3 in 5 Nm^3/h air).](image)
The second phenomenon is that it takes quite long for the ammonia outlet concentration to become constant and to become equal to the inlet level. This cannot be explained by a simple Langmuir adsorption of NH$_3$ (equation 6.6). Furthermore, upon desorption (switching off the ammonia feed), not all adsorbed ammonia is retrieved (Figure 6.17). If a new breakthrough curve is measured after desorption the adsorption capacity is lower; about the same amount as which was desorbed. The gap between original adsorption and subsequent adsorption curves can be explained by assuming the presence of two adsorption sites. The first type is reversible and fast, the other type irreversible and slow. The fraction (and the formation rate) of the two types of sites can be determined from the adsorption and desorption curves (Appendix 3) and appears to be about 50 percent of the total number of sites.

This second type of sites is not likely to be very important in the reaction with NO because its formation rate is too low (see Appendix 3). Since this site (when covered with ammonia) can react with NO, the amount of this type of sites will probably be small when an overdose of NO is present. Therefore, the actual ammonia buffer capacity of the catalyst in situations of NO$_x$ surplus may be overestimated by a factor of at least two.

6.2.2 SCR reaction in model gases

Experiments with the setup described in Chapter 4 have been performed to validate the front model described in section 6.1. The equations used are 6.15 and 6.19. The temperature at which the experiments were performed is 250°C. This temperature was chosen to exclude NH$_3$ oxidation. For kinetic data see Appendix 1 equation A1.11 (note that the reaction rate is extrapolated somewhat).

![Figure 6.18: Model and experimental response of the NO$_x$ signal after switching the NH$_3$ feed off (457 g 400 cpi DN 32, 310 ppm NO inlet at NH$_3$/NO=0.86, 250°C in 12.8 Nm$^3$/h air).](image)

![Figure 6.19: Modified model and experimental response of NO$_x$ signal after switching the NH$_3$ feed off (457 g 400 cpi DN 32, 310 ppm NO inlet at NH$_3$/NO=0.86, 250°C in 12.8 Nm$^3$/h air).](image)

Firstly, the transient behaviour of switching off the ammonia feed is studied and compared with the model prediction. The model prediction of the NO response is too slow, Figure 6.18. This can be explained by assuming that the ammonia buffer is less than according to equation 6.42. The reasons for this have already been explained in section 6.2.1; about 50 percent of the adsorption sites are filled with NH$_3$ rather slowly and might not be present when sub stoichiometric amounts of ammonia are used. In this case 0.29 times the buffer capacity is sufficient to match the model and experimental curve; Figure 6.19. Therefore this value has been used to determine the actual amount of NH$_3$ on the catalyst in the presence of NO for the remainder of section 6.2.2.
The next step was changing the NO and NH$_3$ concentration simultaneously, Figure 6.20, by decreasing the air flow. This means that the steady state NO output should rise (about 130 ppm) because the NH$_3$/NO ratio remains constant. However, this does not occur initially (experiment and model) because the residence time decreases and thus the conversion increases; equation 6.15. This increase in conversion is temporarily because the front position (z in equation 6.15) will decrease to the same conversion as before the increase in air flow. The NO outlet concentration does not reach the corresponding steady state level because the flow is increased after one minute.

Subsequently a pulse in NO concentration is studied and compared with the model responses, Figure 6.21 and 6.22. The sharp peaks at the beginning and the end are caused by equipment over/undershoots which are not taken into account by the model. The major deviations between experiment and model occur if an overdoses of NH$_3$ is present which allows site type two to be formed. This might be the case when switching off the NO feed, Figure 6.22. It takes much longer than expected for NO to be found again in the reactor exit. Another explanation is that NO adsorbs on sites covered with ammonia, see also section 6.1.3.3. In such a case a relative sharp breakthrough of NO is expected comparable to the ammonia breakthrough curves described in section 6.2.1. However, no clear mathematical justification of these explanations could be given (Appendix 3).

Figure 6.20: Model and experimental response of the NO$_x$ signal on a pulse in air flow rate to 4.4 Nm$^3$/h (457 g 400 cpi DN 32, 250°C, 310 ppm NO inlet at NH$_3$/NO=0.86 in 12.8 Nm$^3$/h air).

Figure 6.21: Model and experimental response on doubling the NO feed for 60 seconds (457 g 400 cpi DN 32, 250°C, 310 ppm NO inlet at NH$_3$/NO=0.86 in 12.8 Nm$^3$/h air).

Figure 6.22: Model and experimental response of the NO$_x$ signal on switching off the NO feed for 60 seconds (457 g 400 cpi DN 32, 250°C, 310 ppm NO inlet at NH$_3$/NO=0.86 in 12.8 Nm$^3$/h air).
The response on a change in temperature is plotted in Figure 6.23. The change in temperature is rather slow because it was not possible to keep the reactor temperature homogeneous at a higher temperature change rate. Subsequently, the \( \frac{dT}{dt} \) term in equation 6.19 is very small in this case. Therefore, it was not possible to validate this term in the front model.

![Graph showing NO\(_x\) and temperature response over time](image)

**Figure 6.23:** Model and experimental response of NO\(_x\) signal on a change in temperature (457 g 400 cpi DN 32, 310 ppm NO inlet at NH\(_3\)/NO = 0.86 in 12.8 Nm\(^3\)/h air).

The results show that the front model can predict the dynamic behaviour of the catalyst qualitatively. It should be noted that the NH\(_3\) or urea dosage must be sub stoichiometric. The buffering capacity determined by the ammonia breakthrough curves only gives an upper bound in the presence of NO. A more complete knowledge about the reaction mechanism of the SCR reaction and the adsorption processes is needed to extent these limitations.

### 6.2.3 SCR reaction in diesel exhaust

The setup used for the experiments with diesel exhaust gases has been described in Chapter 5. An NH\(_3\) breakthrough curve in diesel exhaust gases has been determined by injecting a large (almost 100 percent) overdose 10 weight percent aqueous urea solution. This curve, Figure 6.24, resembles the curves determined with model gases, Figure 6.16. Whether this is due to the same phenomenon (two different sites) is unknown (yet) because desorption curves were difficult to determine. Note that such a curve can also be ascribed to maldistribution at the inlet.

![Graph showing ammonia breakthrough over time](image)

**Figure 6.24:** Ammonia breakthrough curve using 2 g/min ten weight percent urea solution in diesel exhaust gases (2045 g 300 cpi DN 32, 305°C, 400 ppm NO\(_x\) inlet, 13 Nm\(^3\)/h).
The estimated adsorption capacity is 21 μmol/g 300 cpi DN 32 catalyst at 305°C, which is about the same as determined for model gases (24 μmol/g 400 cpi DN 32, see section 6.1). As a first estimate, the adsorption capacity as determined by equation 6.42 has been used. The kinetic data have been determined from the results in Chapter 3 (see also Appendix 1). Like in section 6.2.2 the model response was much slower than the actual experimental response. Again these two have been matched by decreasing the adsorption capacity in the model. In this case the capacity had to be reduced to 0.1 of the original value. Obiously the relationship between the maximum adsorbed amount of ammonia and the amount present at sub stoichiometric conditions differs considerably. This means that the danger of ammonia slip will be less than expected on basis of the front model. It should be noted that the kinetic data used is less reliable because of the temperature profile in the reactor, the presence of soot, maldistribution at the inlet, etc.

![Figure 6.25: Model and experimental response on steps in urea dosage rate (2045 g 300 cpi DN 32, 300°C, 10 weight percent urea solution, 12.7 Nm³/h diesel exhaust using low sulphur diesel fuel).](image1)

![Figure 6.26: Model and experimental response on pulses in flow rate (2045 g 300 cpi DN 32, 300°C, 1 g/min 10 weight percent urea solution at 400 ppm NO₅ inlet using low sulphur diesel fuel).](image2)

The model predictions were compared with experimental data in which the urea flow rate was changed. The NOₓ inlet level is assumed to be constant. The experimental NOₓ output signal is compared with the model prediction, equations 6.15 and 6.17, which are corrected for analyser lag. NOₓ variations caused by steps in urea dosage rate can be predicted well, Figure 6.25. Pulses in gas flow rate, at a constant urea dosage rate, can also be described well, Figure 6.26. With an increase in exhaust gas flow rate at constant urea dosage rate the NH₃/NO ratio decreases. The NOₓ output rises and reaches almost its steady state output value at the end of the pulse.

132 Modelling of the SCR reaction and urea injection control
Figure 6.27: Model and experimental response on pulses in engine load (2045 g 300 cpi DN 32, 300°C, 10 Nm³/h exhaust gases, 1 g/min 10 weight percent urea solution at 400 ppm NOₓ inlet using low sulphur diesel fuel).

The comparison with a model response on a pulse in load also at a constant urea dosage rate, is plotted in Figure 6.27. Due to the change in engine load the NOₓ inlet level drops about 100 ppm which causes the NH₃/NO ratio to increase and the NOₓ output to decrease. The figure shows that the NOₓ outlet signal has not reached its steady state level yet when the load is switched up again. The model prediction is good considering the change in gas phase composition due to the load variation of the engine. Especially changes in water concentration influence the reactivity of the catalyst considerably. Furthermore, a deviation in NH₃ adsorption capacity can be expected due to competitive adsorption of water.

The front model can predict the dynamic response qualitatively only. More precise results would require at least the use of TIS model developed in section 6.1.2. However, to apply this model successfully more knowledge is needed about the different adsorption sites (e.g. NH₃, H₂O and NO). This means that at all combinations of engine load and exhaust gas flow the relevant kinetic data and adsorption capacities should be measured as a function of temperature. For the experimental setup used in this study, the usefulness of such an approach is severely limited by the accuracy of the measurements and stability of the equipment.
6.2.4 Summary process modelling - validation

The front model has been validated for predicting the dynamic response of SCR catalysts at low temperature (< 350°C; no NH₃ oxidation). Dynamic responses can be predicted qualitatively at sub-stoichiometric NH₃/NO ratios. The NH₃ adsorption capacity of the catalyst plays a crucial role. The upper bound of this capacity is determined by the total adsorption capacity measured with ammonia breakthrough curves. The actual amount of ammonia on the catalyst at sub-stoichiometric NH₃/NO ratio is smaller, 10 - 30 percent, than expected on basis of this overall value. This can be explained partially by the presence of several types of adsorption sites. The actual value should be measured by switching the ammonia feed on and off and integrating the difference between the actual and the steady state NOₓ outlet signal.

To obtain better model predictions the nature of the ammonia adsorption sites needs to be investigated. Furthermore, the possibility of an additional NO adsorption process should be evaluated. But even if the actual reaction mechanism and all adsorption processes are known additional work remains to be performed, such as the influence of water and other components which are present in diesel exhaust gases. Furthermore the temperature profile, the ammonia inlet distribution and the urea decomposition have to be investigated which will probably n'tl vary with exhaust gas flow, composition and temperature.

All in all, the front model is a useful tool due to its simplicity for describing and understanding system responses if the limitations are taken into account.

6.3 Process control

This section describes the implementation of a control system on the urea injection setup described in Chapter five. It starts with an introduction, section 6.3.1, on control configurations found in the literature. In the next section, section 6.3.2, the performance of such control systems at one specific operating condition (300°C and 6000 h⁻¹ GHSV) is described. This operating condition is at the low temperature limit. At this temperature the catalyst activity is very low. Hence, the responses will be the slowest encountered in practice. Therefore, large deviations in urea injection are likely to result in undesirable ammonia slip. In section 6.3.3 another catalyst configuration is used. Here, an oxidation catalyst is added to eliminate all ammonia slip problems.

6.3.1 Introduction

In a transient diesel engine exhaust the NOₓ output varies rapidly with a time constant of less than a few seconds. As explained in Chapter two excess urea will lead to ammonia slip and a shortage to inadequate NOₓ reduction. Therefore, the urea dosage rate should be adjusted according to this NOₓ output. As with three-way catalyst control systems two approaches can be applied; e.g. an open loop (feedforward) or a closed loop (feedback) control system.

In the closed loop control system of a three-way catalyst an oxygen measuring device is used to adjust the fuel injection rate. Analogously a NOₓ measuring device can be used to adjust the urea injection rate. However, fast and cheap NOₓ measuring devices are still under development. Here, a standard NOₓ chemiluminescence apparatus, is utilized. Until a fast sensor is developed the measurement of NOₓ will be much slower than the changes in NOₓ output of the engine. Therefore, the applicability of this approach depends on the
buffering capacity of the catalyst. This means that the catalyst should maintain an adequate NO\textsubscript{x} reduction level at temporarily NH\textsubscript{3} shortage and even more important, store NH\textsubscript{3} in case of an overdoses.

An open loop (feedforward) control strategy can be applied to avoid this timing problem. The NO\textsubscript{x} production depends mainly on engine speed and torque; both can be measured very fast. Walker\textsuperscript{33} describes how to implement a strategy using these variables for SCR application on a heavy duty natural gas engine. Basically, at a number of engine torque/speed combinations the steady state ammonia delivery to reach the desired reduction is determined. Subsequently, a look up table is generated which is used to determine the ammonia injection rate in a transient situation.

The effectiveness of this open loop strategy depends mainly on the accuracy of the relationship between the predicting variables (e.g. engine speed and torque) and the actual NO\textsubscript{x} output. This relationship is usually measured on a test bench and does not necessarily remain constant during practical operation. As already shown in Chapter 5 the relationship between the exhaust gas flow (engine speed) and power output (torque) of the diesel engine used in this study, does not permit an accurate estimate of the NO\textsubscript{x} output. It is expected that the maximum NO\textsubscript{x} reduction cannot exceed 70 percent (for our diesel engine) due to the danger of ammonia slip (see also Chapter 5). It is noted that the diesel engine used in this study is not representative for a heavy duty diesel. Therefore, application of this open loop strategy is not excluded in practice.

Two solutions for the ammonia slip problem are reported in the literature. The first is to combine feedforward and feedback control. This is done by using a NO\textsubscript{x} measuring device to determine the actual NO\textsubscript{x} output\textsuperscript{34, 35}. Such a NO\textsubscript{x} measurement introduces a time lag because of the analyser/sensor dead time. Furthermore, an additional time lag is caused by the catalyst itself (SCR catalysts are noted for their large response times). However, a large response time of the system is less important as the NO\textsubscript{x} measurement is only used to correct feedforward biases.

The second solution is to convert excess ammonia to N\textsubscript{2} by installing an additional oxidation catalyst\textsuperscript{23, 36}. A drawback will be sulphate production at temperatures above 400°C.

Note that the urea injection system is not able to respond on a millisecond scale (about 2 seconds minimal, see also Chapter 5). However, it is probably not really necessary to respond that fast on changes in engine performance. As shown in Chapter five and section 6.2 some time lag can be overcome by the inertia of the catalyst itself. A possible route to a much faster injection system has been described in Chapter 4, the Gentec injection system.

6.3.2 Control experiments

The effects of implementing open and closed loop control configurations are studied in this section (see also Figure 6.28). All experiments are conducted with the setup described in Chapter 5 (Figure 5.1). In case of feedback (closed loop) control the NO\textsubscript{x} analyser is used to measure the NO\textsubscript{x} outlet signal. This NO\textsubscript{x} signal is compared to the setpoint. Subsequently, the difference between setpoint and actual value is entered in a PID control algorithm which calculates the new urea dosage rate. A standard PID control configuration was used as it was readily available in the process control software. More advanced algorithms will yield somewhat better results.
Feedforward (open loop) control is a combination of an engine map and the measured exhaust gas flow (Nm³/h). The engine map is determined by measuring the NOₓ output without urea injection at certain engine loads and exhaust gas flows. The amount of urea needed to obtain the desired reduction can be calculated assuming one molecule of urea yields two NH₃ equivalents and NH₃ reacts 1:1 with NOₓ. The results are expressed in ml urea/Nm³ exhaust gas at a certain power production. The multiplication of the exhaust gas flow rate with the engine map yields the desired urea dosage (in ml urea/min).

The performance of feedforward control depends on the stability of the engine map and accuracy of the flow measurement. As described in Chapter 5 errors can occur up to 30 percent. This is in contrast to the model experiments of Chapter 4 where 90 percent reduction can be achieved easily with feedforward alone. As the aim is to achieve 70-90 percent NOₓ removal (overall 70 percent; in the temperature range of 300-550°C 80-90 percent) a feedback component must be added.

Figure 6.29 shows a typical result of using feedback control to obtain a NOₓ output of 100 ppm (70 percent conversion). The PID control parameters have been determined by a standard controller tuning technique (the Cohen and Coon method). It takes a few minutes for the signal to stabilize and the NOₓ conversion is already acceptable (70-80 percent) within 2-3 times the dead time of the setup. Any change in PID parameter settings to improve this leads to a typical under damped signal, Figure 6.30.
The front model developed in section 6.1.1 can be used as a design test tool; the dotted line in Figure 6.30 is a model prediction. The experimental and model responses have been compared and the buffer capacity is adjusted until both yield comparable results. Subsequently, the controller parameters have been adjusted to improve the controller performance (model prediction only). The values obtained with the standard controller tuning technique are quite optimal. A minimal sum of square deviation approach on the model prediction yields only marginal improvement. Therefore, the PID constants are optimal (for this disturbance at these operating conditions).

![Figure 6.29: Response of the NO\textsubscript{x} signal on switching on the urea injection using feedback control (optimal PID constants, setpoint 100 ppm, DN 32, 311°C, flow 13.7 Nm\textsuperscript{3}/h, load 3 kW).](image1)

![Figure 6.30: Response of the NO\textsubscript{x} signal on switching on the urea injection using feedback control (PID gain too strong, setpoint 100 ppm, DN 32, 311°C, 13.7 Nm\textsuperscript{3}/h flow, 3 kW load).](image2)

![Figure 6.31: Response of NO\textsubscript{x} outlet signal on a pulse in engine load using feedback control (setpoint 100 ppm, DN 32, 298°C, 13.7 Nm\textsuperscript{3}/h flow, 3 kW load).](image3)

The inherent problem with this type of feedback control is the inertia of the system. Figure 6.31 shows the response on a disturbance; a step in load which causes the NO\textsubscript{x} \textit{inlet} to drop from 350 to 150 ppm. The NO\textsubscript{x} \textit{outlet} signal drops to low values and stays there quite long. No ammonia slip results because the load is switched back again after 180 seconds. Repeating this procedure will lead to ammonia slip; Figure 6.32. Obviously the feedback action is too slow to avoid this slip. This does not mean that this feedback control configuration does not work; at a somewhat higher setpoint, Figure 6.33, the NO\textsubscript{x} variation does not give ammonia slip although an overdose of 100 percent exists during the analyser dead time. The NO\textsubscript{x} variation at the outlet is still 100 ppm. Compared to the 250 ppm NO\textsubscript{x} variation at the inlet, the damping effect is only about 50 percent.

Chapter 6

137
Figure 6.32: Response of NO$_x$ and NH$_3$ signals on pulses in engine load using feedback control (setpoint 50 ppm, DN 32, 315°C, 13.6 Nm$_3$/h flow).

Figure 6.33: Response of NO$_x$ and NH$_3$ signals on pulses in engine load using feedback control (setpoint 100 ppm, DN 32, 298°C, 13.7 Nm$_3$/h flow).

These experiments show that the control system does not react very fast; in such cases the NO$_x$ output would be zero immediately after switching to low loads until the urea dosage rate is adjusted. As the analyser dead time is about ten seconds this does not happen. Therefore, it is not really necessary to measure the NO$_x$ concentration and adjust the urea dosage rate on a millisecond scale.
Feedback control problems can occur because of the inertness of the system (catalyst and analyser), see Figure 6.32. This can be avoided by application of feedforward control since the actual NO\textsubscript{x} outlet response to changes in NO\textsubscript{x} inlet does not have taken place before the control action. This feedforward is implemented as a simple ratio control; if the NO\textsubscript{x} output changes due to engine load or exhaust gas variations the urea dosage rate is changed so that the NH\textsubscript{3}/NO ratio is kept constant. (System responses on pulses in flow and engine load at constant NH\textsubscript{3}/NO ratio have also been reported in section 5.3.)

![Graph showing NO\textsubscript{x} and Flow response to pulses in exhaust gas flow (setpoint 100 ppm, DN 32, 306°C, 3 kW load).](image)

*Figure 6.34: Response of NO\textsubscript{x} and NH\textsubscript{3} signals on pulses in exhaust gas flow (setpoint 100 ppm, DN 32, 306°C, 3 kW load).*

As explained in section 6.3.1 the accuracy of the relationship between NO\textsubscript{x} production and engine variables, the so-called engine map, is the bottleneck for this type of control. For the diesel engine used in this study some type of feedback component is needed to reach sufficient conversion. This is illustrated by the experiment plotted in Figure 6.34. The response of a feedforward control system is plotted on pulses in exhaust gas flow. In this case the flow measurement was biased considerably. Especially in the case of a pulse to lower flow rates the NO\textsubscript{x} outlet signal drops to dangerously low values (no ammonia slip yet).

Adding the feedback component draws the NO\textsubscript{x} signal away from these low values easily. The usefulness of this feedback component lies in the fact that large errors due to engine map deviations can be corrected. This will be illustrated further by the following experiments in which a feedforward control system designed to yield an engine output of about 50 ppm (85 percent conversion) is used. A dynamic situation is simulated by switching the load from 50 to 100 percent and back every minute. The urea output is adjusted accordingly. However, at the 50 percent load point a large error is introduced; the urea output is now twice the desired output.
In Figure 6.35 the response of the feedforward system alone is plotted. The NO\textsubscript{x} output variation slowly goes to lower values and after 10 minutes NH\textsubscript{3} slip appears. At the onset of ammonia slip the load was switched to 75 percent and the urea injection rate again sub stoichiometric. The NH\textsubscript{3} slip appeared to be still rising; even switching off the urea dosage pump after 30 minutes does not have an immediate effect on NH\textsubscript{3} slip. This delay is caused by the strong adsorption behaviour of ammonia on the catalyst and will make control systems based on ammonia measurement fraud with a very large dead time. Furthermore, it is noted that it takes rather long for ammonia slip to become manifest, so running temporarily over stoichiometric does not automatically lead to ammonia slip. On the average the urea doses should be sub stoichiometric tough. A combination of this feedforward component with an additional feedback system, Figure 6.36, leads to a slow adjustment of the overall injection rate thereby preventing ammonia slip.

Figure 6.35: Response of NO\textsubscript{x} and NH\textsubscript{3} signals on pulses in engine load using feedforward control (setpoint 50 ppm, DN 32, 289° C, 12.1 Nm\textsuperscript{3}/h flow).

Figure 6.36: Response of NO\textsubscript{x} and NH\textsubscript{3} signals on pulses in engine load using feedforward and feedback control (setpoint 50 ppm, DN 32, 293° C, 12.2 Nm\textsuperscript{3}/h flow).
6.3.3 The application of an oxidation catalyst

The BASF R-025 catalyst** has been installed to illustrate the possibility of using oxidation catalysts in SCR application. The experimental setup described in Chapter five was filled with 1 l SCR catalys (V-based) and 1 l oxidation catalyst (Pd based). In principle the ammonia reacts with NO as with the DN 32 catalyst. Any unreacted ammonia is oxidized by the oxidation catalyst. The urea dosage rate can be stoichiometric or even slightly over stoichiometric. The advantages of this configuration are that no ammonia slip will be present and the SCR catalyist will be fully used.

![Diagram](image)

**NH₃/NO

Figure 6.37: The NOₓ signal as a function of the NH₃/NO inlet ratio (R-025, 370°C, 13.5 Nm³/h flow, 3 kW load).

The steady state performance of this approach is illustrated in Figure 6.37. A conversion of 90 percent is reached at a NH₃/NO inlet ratio of about one and this level is sustained even up to NH₃/NO inlet ratios of two without ammonia slip. The DN 32 catalyst alone would yield a large NH₃ slip at these conditions, section 5.2. At this temperature the oxidation of ammonia yields mainly N₂. The N₂O levels displayed in the figure do increase when the NH₃/NO ratio exceeds one. The actual amount of N₂O stays below 10 ppm so the selectivity towards N₂ exceeds 90 percent. Furthermore, it can be expected that at higher temperatures the ammonia oxidation will also yield NO. Therefore, the NH₃/NO inlet ratio should be kept close to one.

** This catalyst is a pellet type catalyst (6 mm cylinders) and originally designed as an NH₃ oxidation catalyst. It is a mixture of a SCR and an oxidation catalyst, which were separated into two layers with the SCR catalysist on top.

Chapter 6

141
Figure 6.38: Response of NO\textsubscript{x} and NH\textsubscript{3} signals on pulses in load (R-025, 378°C, 13.6 Nm\textsuperscript{3}/h, inlet 466 ppm NH\textsubscript{3} equivalents).

This concept, applying an oxidation catalyst, also works in a transient situation. Changes in load, Figure 6.38, at a constant urea dosage rate do lead to minor changes in NO\textsubscript{x} outlet level. Actually, when switching from 75 to 50 percent load, a 100 ppm NO\textsubscript{x} inlet level difference, the change in NO\textsubscript{x} outlet is only about 10 ppm. This can be explained by the first order nature of the SCR reaction. Since the system operates at a 90 percent conversion level, changes in NO\textsubscript{x} concentration will also be damped 90 percent.

Figure 6.39: Response of NO\textsubscript{x} and NH\textsubscript{3} signals on pulses in exhaust gas flow (R-025, 384°C, NH\textsubscript{3}/NO = 1.1 above 15 Nm\textsuperscript{3}/h, else 1.25 due to pump limitation, 3 kW load).

Another example is the response on changes in exhaust gas flow, Figure 6.39. The urea flow rate is proportional to this exhaust gas flow rate and the NH\textsubscript{3}/NO ratio was kept over stoichiometric (1.1-1.25). The NO\textsubscript{x} outlet level now changes more than a few ppm but the conversion remains above 70 percent. The reason for this variation, is that with increasing gas flow the residence time decreases which leads to a lower conversion.
No sulphur related problems were encountered because the low sulphur diesel (\(<\ 10\ ppm\)) was used so no substantial amounts of sulphates could be formed.

6.3.4 Summary process control

The SCR control system to be applied depends on the stability of the engine map compared to the amount of reduction required. With this engine map it should be possible to estimate the NO\(_x\) output of the engine as a function of its operating parameters (e.g. engine load and speed). If it is possible to determine an accurate engine map open loop control is the most appropriate control system. In such cases, the urea injection rate can be coupled to the predicted NO\(_x\) output of the engine. However, ammonia slip due to desorption as a result of temperature changes can occur (section 6.1). This depends on the engine itself (temperature exhaust versus load), the catalyst (NH\(_3\) adsorption and heat capacity) and the actual amount of reduction required (the fraction of adsorption sites utilized). Due to the high heat capacity of the experimental setup used no such effects were encountered in this study.

If the engine map is not stable enough, the predicted NO\(_x\) output will be inaccurate, causing insufficient urea injection (resulting in inadequate NO\(_x\) reduction) or superfluous urea injection (resulting in ammonia slip). Some type of NO\(_x\) sensor can be used to correct these biases. However, these sensors are rather slow and not very cheap. If (e.g. due to temperature transients) ammonia slip is unavoidable an oxidation catalyst can be applied to eliminate this slip. In combination with open loop control on NH\(_3\)/NO equals one this system solves most of the control problems. The only drawback is excessive sulphate production at higher temperatures.

For the diesel engine used in this study some type of feedback component is necessary because the prediction of the NO\(_x\) output was found to be inaccurate (deviations of up to 30 percent occurred). In practice, this prediction might be improved by using more variables than the engine load and exhaust gas flow only.

Literature


15 Tagaki, M., Kawai, T., Soma, M., Onishi, T., Tamaru, K., *The mechanism of the reaction between NOx and NH3 on V2O5 in the presence of oxygen*, Journal of Catalysis 50 (1977), 441-6.


*Modelling of the SCR reaction and urea injection control*


33 Walker, J., Speronello, B.K., *Development of an Ammonia/SCR NOx reduction system For A Heavy Duty Natural Gas Engine*, SAE 921673, 171-81.


Chapter 7
Future outlook

This thesis was divided into three main sections: catalyst testing with lab scale flow equipment in Chapter three (A), urea injection system development in Chapter four and five (B), and process modelling and control in Chapter six (C). The aim of this Chapter is to connect these separate parts and to give recommendations for future research.

A. The catalyst development has resulted in a new and promising catalyst: cerium mordenite. The key properties of this catalyst are its low SO\textsubscript{2} oxidation activity, a high selectivity to N\textsubscript{2} in case of NH\textsubscript{3} oxidation, and high NO\textsubscript{x} conversions up to 550°C. Still there are some hurdles to be taken before this zeolite type catalyst can be applied in an engine exhaust gas in practice. The most obvious one is that synthesis yields zeolite powder which must be applied on a low pressure drop carrier. Usually the catalyst is applied on or in a monolith by washcoating or extrusion techniques\textsuperscript{1,2}. Also direct synthesis on a metal carrier, which is currently researched at Delft University\textsuperscript{7}, is possible. Therefore, this seems to be a solvable problem.

A somewhat higher hurdle is the low activity of zeolite type catalysts at temperatures below 400°C in diesel exhaust. The space velocities at which these catalysts can be applied are still an order of a magnitude too low. Therefore, it can be expected that the catalyst formulation should be improved\textsuperscript{3}.

The main hurdle is the stability of zeolite type catalysts. This is not limited to SCR with urea/NH\textsubscript{3} but holds for almost all zeolites used as catalyst in engine exhaust gases. Several authors\textsuperscript{4,5} do find deactivation during use. Also during this work some decline in activity has been encountered, which is most pronounced at lower temperatures.

B. A urea injection system has been developed and it has been shown that urea decomposes into components which, with respect to SCR, react similarly as ammonia. Prerequisite is that the temperature at the point of injection, is high enough (T > 300°C) as this determines the urea decomposition. No significant amount of byproducts has been detected (N\textsubscript{2}O nor urea condensation products). However, some additional tests are recommended; the analytical procedures needed are described in Chapter four. Optimization of the urea injection setup is possible, especially regarding the injection timing and the radial distribution of the urea decomposition products. The extent of the modifications/improvements needed depend on the required accuracy of the injection rate and the type of control system that has to be applied.

C. The dynamic behaviour of the catalyst studied in this thesis (a vanadium type) is determined by the amount of ammonia adsorbed on its surface. Since this amount can be large, especially for zeolite type catalysts, response times can be very large. This gives rise to difficulties with respect to process control. Fast, accurate and cheap NO\textsubscript{x}/NH\textsubscript{3} sensors were not available at the start of this study. Application of a slow/inaccurate sensor inevitable leads to ammonia slip in transient situations. Furthermore, predicting the NO\textsubscript{x} output on basis of an engine map and adjusting the urea injection rate accordingly was found too inaccurate for the diesel engine used in this study. If new sensors become available\textsuperscript{8}, a process control system based on a combination of predicting/measuring the NO\textsubscript{x}/NH\textsubscript{3} output is possible.
Furthermore, information on the stability and accuracy of engine maps on diesel engines in practical use, is desirable.

At this moment, the only option for avoiding ammonia slip while maintaining adequate NO\textsubscript{x} reduction, is the use of an oxidation catalyst\textsuperscript{5}. A drawback is the excessive sulphate production above circa 400°C\textsuperscript{6}. This is the reason the cerium catalyst is most interesting. In principle, it oxidizes ammonia selectively to N\textsubscript{2} whereas SO\textsubscript{2} does not react. This catalyst is still under development. If on a short notice a catalytic system is needed an oxidation catalyst seems inevitable. To avoid sulphate emissions an option would be to keep the temperatures below 400°C in which case activity problems can be expected. Another option is to use a very low sulphur fuel.

With regard to model development the main issue is the nature, amount and reactivity of the different sites for ammonia adsorption. A better understanding of how NO interacts with these sites will lead to more accurate model predictions. The simple front model developed in this thesis, is probably sufficient for control purposes. Its prediction of a step in engine load might be used to adjust the urea injection rate. Model biases can be corrected with a NO\textsubscript{x} sensor.

Literature

8 Regulations are getting stricter. *Diagnostics with toxic gas sensors*, Roth-Technik GMBH & Co., Gaggenau, Germany.
Figure A1.1: Magnification of the 300 cpi monolith after several months of use.

Figure A1.2: Magnification of the 400 cpi monolith after several months of use.

Figure A1.3: Magnification of a fresh 300 cpi monolith.

Figure A1.4: Arrhenius plot of DN 32 (24.8 grams of 300 cpi DN32, 500 ppm NO & NH$_3$ in 7.5-15 Nl air/min)
Appendix 1: DN32 structural and kinetic data

In this thesis two versions of the Degussa DN 32 catalytic monolith have been used; the 400 cpi (cells per square inch) in Chapter four and the 300 cpi in Chapter three and five. The objective of this appendix is to provide the reader with all catalyst parameters and to show how they are estimated, calculated or which have been found in literature. Furthermore, the two versions (300 and 400 cpi) of the DeNO\textsubscript{x} catalyst are compared in terms of activity.

**Bulk dimensions of the monolithic elements**

The monolithic elements are fitted in the reactor using an insulation blanket. This caused some channels of the 400 cpi elements to be blocked. The dimensions in Table A1.1 are thus effective values. In case of the two 300 cpi elements no blocking occurred.

### Table A1.1: bulk dimensions of the DN 32 catalytic monoliths (one element)

<table>
<thead>
<tr>
<th>cpi (#/inch\textsuperscript{2})</th>
<th>300</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>diameter (mm)</td>
<td>93</td>
<td>82.5</td>
</tr>
<tr>
<td>length (mm)</td>
<td>152.4</td>
<td>152.5</td>
</tr>
<tr>
<td>mass (g)</td>
<td>1025</td>
<td>457.3</td>
</tr>
<tr>
<td>volume (l)</td>
<td>1.035</td>
<td>0.815</td>
</tr>
</tbody>
</table>

**Diameter and shape of the channels**

Obviously, the diameters of the 300 and 400 cpi monolith channels are different; see Figure A1.1 and 2, and also Table A1.2. Not only the diameter of the open area is different but also the wall thickness is twice as big for the 300 cpi monolith as for the 400 cpi. Furthermore, the shape of a 400 cpi channel resembles a square whereas the 300 cpi channels are more circular. The latter is also a function of time; the fresh monolith has almost circular channels, see Figure A1.3.

The monolith channel is assumed to be square shaped with a uniform washcoat. For modelling purposes this washcoat layer is considered to have flat plane geometry. The washcoat thickness is chosen so that the overall catalyst volume is almost equal to that of Figures A1.1 and 2. Note that in case of diffusion limitation, the corners of the catalyst (diffusion lengths of up to 250 \(\mu\)m) are utilized badly. Furthermore, the amount of catalyst shown in the Figures A1.1 and 2 will be less than in the experiments because the photographs have been taken after use. For the difference with a fresh catalyst compare Figure A1.1 with 3. In case of the 400 cpi catalyst a few grams of washcoat material were found at the bottom of the reactor after several months of use.
Table A1.2: Dimensions of the monolith cells

<table>
<thead>
<tr>
<th>cpi (#/inch²)</th>
<th>300</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{cell} (mm)</td>
<td>1.47</td>
<td>1.27</td>
</tr>
<tr>
<td>h_{cord} (mm)</td>
<td>0.33</td>
<td>0.16</td>
</tr>
<tr>
<td>h_{wash} (µm)</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>d_{chan} (mm)</td>
<td>0.976</td>
<td>1.03</td>
</tr>
<tr>
<td>void (m³/m³)</td>
<td>0.443</td>
<td>0.658</td>
</tr>
<tr>
<td>σ (m²_wash/m³)</td>
<td>1816</td>
<td>2554</td>
</tr>
</tbody>
</table>

Definitions

d_{cell} : The pitch of the monolith, calculated on basis of the number of cells per square inch.

\[
d_{cell} = \sqrt{\frac{0.0254^2}{\text{cpi}}} \quad (A1.1)
\]

h_{cord} : The average thickness of the corderite wall, estimated with a microscope.

h_{wash} : The average thickness of the washcoat, estimated with a microscope.

d_{chan} : The edge of the open area of a cell, calculated on basis of the other diameters. Note that the channel diameter of the 400 cpi monolith is larger than the 300 cpi channel, this is due to the thicker wall of the 300 cpi monolith.

\[
d_{chan} = d_{cell} - h_{cord} - 2 \cdot h_{wash} \quad (A1.2)
\]

voidage (or ε): The open area through which the gases can flow compared to the overall volume of the monolith.

\[
ε = \frac{d_{chan}^2}{d_{cell}^2} \quad (A1.3)
\]

σ : specific area, the external surface area of the catalyst per volume area. This area is the interchange area between the gases and the washcoat and not the internal surface area of the porous washcoat.

*DN32 structural and kinetic data*
\[ \sigma = \frac{4 \frac{d_{\text{chan}}}{d_{\text{cell}}}} \] (A1.4)

Internal surface area

N₂ adsorption measurements were performed with a 'quantachrome autosorb 6 automated gas sorption' apparatus. After a few months of experiment with the setup described in Chapter four, a few grams of material were found at the bottom of the reactor. XRD revealed that this material contained a mixture of Ti/W/V oxides only. It is assumed that the sorption measurements on this material give more reliable data on the washcoat than the data obtained by grinding a piece of monolith itself (300 cpi).

Table A1.3: Results of N₂ sorption measurements

<table>
<thead>
<tr>
<th></th>
<th>S_{BET} (m²/g)</th>
<th>V (ml/g)</th>
<th>2*V/S (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 cpi washcoat only</td>
<td>76</td>
<td>0.33</td>
<td>8.7</td>
</tr>
<tr>
<td>300 cpi washcoat and wall</td>
<td>14</td>
<td>0.084</td>
<td>12</td>
</tr>
</tbody>
</table>

Porosity/void

For a structured catalyst such as a monolith, several porosities can be defined:

\[ \epsilon_{\text{cord}} \]: the porosity of the basic construction material;
\[ \epsilon_{\text{wash}} \]: the porosity of the washcoat layer;
\[ \epsilon_{\text{mono}} \]: the porosity/void of the monolith, this is the volume of the channels defined by the overall volume of the monolith (equation 4).

In this thesis \( \epsilon_{\text{mono}} \) is used (the subscript is dropped) predominantly. It is used to calculate velocities in the channels since the flow through the porous washcoat is negligible. Only when considering pore diffusion in the washcoat \( \epsilon_{\text{wash}} \) is used. Values of \( \epsilon_{\text{wash}} \) are in the order of 0.4-0.5; in the literature a value of 0.43 is encountered usually².

Effective diffusion coefficient

Buzanowski and Yang¹ (see also §3.3) estimated the effective diffusion coefficients (\( D_{\text{eff}} \)) based on Bosanquet/Knudsen diffusivities with a tortuosity of 6. However, in their case the efficiencies of the catalyst used, were typically higher than 0.45 resulting in a relatively small influence of \( D_{\text{eff}} \).
Table A1.4: Buzanowski data

<table>
<thead>
<tr>
<th>Temperature</th>
<th>D_{eff} (m^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.64e-7</td>
</tr>
<tr>
<td>200</td>
<td>5.45e-7</td>
</tr>
<tr>
<td>300</td>
<td>6.15e-7</td>
</tr>
</tbody>
</table>

In the temperature range of 320-380°C different effective diffusion coefficients of ammonia and NO are found by Tronconi:

\[ D_{\text{eff,NO}} = 2.2 - 2.3 \times 10^{-6} \, \text{m}^2/\text{s} \]
\[ D_{\text{eff,NH}_3} = 2.6 - 2.8 \times 10^{-6} \, \text{m}^2/\text{s} \]

Also differences in effective diffusion coefficients are mentioned; a monomodal 7nm mean pore diameter catalyst has a \( D_{\text{eff,NO}} \) of 6.17e-7 m²/s whereas a bimodal catalyst with additional 70nm pores has a \( D_{\text{eff,NO}} \) of 2.66e-6 m²/s. The values for the catalyst with a monomodel pore distribution agree well with the data of Buzanowski and Yang.

Using the approach described in Chapter three, equations 3.9-3.11, and the data in Table A1.3 yields effective diffusion coefficients of 4e-7/5e-7 in the temperature region of 200-400°C. This agrees well with Table A1.4. Therefore, the \( D_{\text{eff,NO}} \) used in the diffusion model described in §6.1.4 is estimated to be 5e-7 m²/s at 250°C.

Ammonia adsorption capacity

The ammonia adsorption capacity of the 400 cpi monolith has been determined:

Table A1.5: Adsorption capacity of DN 32 (400 cpi, one element using 530 ppm NH₃ in 9.8 Nm³/h air)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>adsorption capacity (µ mol NH₃/gDN32)</th>
</tr>
</thead>
<tbody>
<tr>
<td>202</td>
<td>55</td>
</tr>
<tr>
<td>227</td>
<td>47.3</td>
</tr>
<tr>
<td>252</td>
<td>45.4</td>
</tr>
<tr>
<td>277</td>
<td>30.8</td>
</tr>
<tr>
<td>302</td>
<td>23.6</td>
</tr>
<tr>
<td>327</td>
<td>12.6</td>
</tr>
</tbody>
</table>

These data points are fitted for modelling purposes with a straight line:

\[ C_{\text{site,total}} = 125.77 - 0.3402 \, T \]

\[ 200 < T < 330 \, ^\circ \text{C} \]

(A1.5)
Kinetics of the DN 32 catalyst

It was not the goal of this thesis to investigate the kinetics of vanadium or any other SCR catalysts. However, it was necessary to have at least an estimate of the activity of the catalyst as a function of temperature and space velocity to be able to compare the experiments using the various setups. Furthermore, the results presented here are used for modelling of the dynamic behaviour of the DN 32 catalyst.

Formulae used:

Flow rate:

\[ \phi_v = \phi_{v,0} \frac{T}{T_0} \frac{P_0}{P} \]  \hspace{1cm} (A1.6)

with: \( \phi_{v,0} \) : flow rate at 0°C and 1 atm \([\text{Nm}^3/\text{s}]\); 
\( \phi_v \) : flow rate at reactor temperature and pressure \([\text{m}^3/\text{s}]\); 
\( T_0 \) : 273.15 [K]; 
\( P_0 \) : 101325 [Pa].

Space time:

\[ \tau = \frac{V_r}{\phi_v} \epsilon \]  \hspace{1cm} (A1.7)

with: \( \tau \) : space time \([\text{s}]\); 
\( V_r \) : volume reactor (catalyst bed) \([\text{m}^3]\); 
\( \epsilon \) : porosity catalyst bed \([\text{m}^3/\text{m}^3]\).

First order solution for ideal tube reactor:

\[ \xi = 1 - e^{-k \tau} \]  \hspace{1cm} (A1.8)

with: \( \xi \) : NO conversion \([-]\); 
\( k \) : reaction rate constant \([1/\text{s}]\);

\[ k = k_0 e^{-\frac{E_a}{RT}} \]  \hspace{1cm} (A1.9)

with: \( k_0 \) : pre-exponential factor \([1/\text{s}]\); 
\( E_a \) : activation energy \([\text{J/mol}]\).
Actually for fitting the $k_0$ and $E_a$ the following equation is used to reduce the strong and undesirable correlation between these two parameters:

$$
k = k_0' e^{-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}
$$

(A1.10)

with $T_{ref}$: arbitrary reference temperature [K].

**Data 400 cpi monolith - model gas experiments**

The setup described in Chapter 4 has a maximum air flow rate of about 15 Nm$^3$/h. This causes the conversion to be above 95 percent at 200°C. Therefore some care must be taken when using equation A1.10 at higher temperatures; typically above 250°C ammonia oxidation starts to become important and the equation will become unreliable.

$$
k_0' = 9.5 < 11.2 < 13.7 \ \text{1/s} \ \ E_a = 28 < 49 < 72 \ \text{E3 J/mol}
$$

$$
T_{ref} = 445.15 \ \text{425 < T < 465 K}
$$

(A1.11)

The value of the activation energy, 49 kJ/mol, is in the same range as those reported by Wypkema$^3$ (48 kJ/mol; 140-250°C) and Bosch$^4$ (44 kJ/mol; 190-225°C). It should be noted that the assumption that the reaction is first order in NO is not valid; orders in NO of 0.79 to 0.87 are found (172-192°C; 100-1000 ppm NO). However, since this deviation is not very large it is neglected. The large 95 percent confidence regions are due to the low number of measurements (5 data points) used for the fit, which was actually quite good (2.2 percent standard deviation). More extensive measurements can be found in the work by van der Eijk$^5$.

**Data 300 cpi monolith - model gas experiments**

In Chapter 3 it was shown that the conversion rises with increasing temperature to a maximum of 0.8 to 1 at 300°C. At higher temperatures the conversion decreases due to ammonia oxidation. This ammonia oxidation starts at 300°C, and is complete at 450°C. It should be noted that the reactor wall (stainless steel) is also active for oxidation of NH$_3$ starting at 350°C up to 50 percent at 480°C. Furthermore, significant amounts of N$_2$O can be formed, up to 30 percent at 400-500°C.

To compare results obtained with this 300 cpi monolith with the 400 cpi used in Chapter 4, it is necessary to have an estimate of the reaction rate constant of the SCR reaction. Only data points below circa 320°C have been taken into account. In Figure A1.4 the reaction rate constant is plotted for all experiments. The large variation is due to ageing of the catalyst which can be seen most clearly at low temperature NO conversion (Table A1.5).
The data points in Figure A1.4 result in:

\[ k_0' = 55 < 64 < 76 \, \text{s}^{-1} \quad E_a = 34 < 39 < 44 \, \text{kJ/mol} \]

\[ T_{ref} = 540 \quad 425 < T < 595 \, \text{K} \]  \hspace{1cm} (A1.12)

When studying this fit, equation A1.12, it appears that the activation energy is lower than for the 400 cpi monolith. Obviously, this is not significant studying the 95 percent confidence region of equation A1.11. Furthermore, the temperatures are on average higher so an explanation might be the presence of diffusion limitations which have a lowering effect on the activation energy. When calculating reaction rate constants, the difference with equation 11 is small, on average 10 percent in the temperature region in which equation 11 is valid. This difference increases rapidly with temperature and is already 50 percent at 250°C.

The conclusion is that the 300 and 400 cpi catalysts poses activities in the same order of magnitude as was to be expected for the same type of catalyst.

*Table A1.6: Catalyst ageing; conversions at temperatures beneath 200°C as a function of time (24.8 g 300 cpi DN 32, 500 ppm NO & NH₃ in 15 Nl/min air)*

<table>
<thead>
<tr>
<th>Date</th>
<th>Temperature</th>
<th>NO conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 14</td>
<td>173</td>
<td>0.357</td>
</tr>
<tr>
<td>May 18</td>
<td>176</td>
<td>0.316</td>
</tr>
<tr>
<td>May 30</td>
<td>173</td>
<td>0.248</td>
</tr>
<tr>
<td>June 2</td>
<td>175</td>
<td>0.251</td>
</tr>
<tr>
<td>June 5</td>
<td>174</td>
<td>0.238</td>
</tr>
<tr>
<td>June 5</td>
<td>173</td>
<td>0.238</td>
</tr>
<tr>
<td>July 12</td>
<td>166</td>
<td>0.199</td>
</tr>
<tr>
<td>August</td>
<td>164</td>
<td>0.191</td>
</tr>
</tbody>
</table>

Apparently, there is an initial activity drop at May 14-18 and an activity drop which may be related to the use of diesel exhaust at May 28. The duplo experiment at June 5 shows that the reproducibility is acceptable and the experiments at July 12 - August 5 indicate a stabilisation in activity level. The aging is probably due to the fact that the catalyst has been heated up repeatedly to 550°C which is probably too high for vanadium type catalysts. The result is that the fit, equation A1.12, is less accurate (48 data points, standard deviation 6.8 percent) than equation A1.11 (5 datapoints, standard deviation 2.2 percent).
A typical experiment carried out with diesel exhaust has been plotted in Chapter three, Figure 3.27. The catalyst starts to work at about 270°C where the conversion rises quite suddenly; this may be caused by the presence of sulphur compounds which have adsorbed at low temperatures and must desorb before the catalyst can attain its activity. This restricts ways to obtain kinetic parameters severely. To have a crude estimate the same activation energy has been used as in the case with model gases adjusting the pre-exponential factor to have a fit in the region of 270-370°C; equation A1.13.

\[ k_0 = 90 \ E^3 \ \text{l/s} \ E_a = 39 \ E^3 \ \text{J/mol} \]

\[ 540 < T < 640 \]

(A1.13)

Literature


5 Eijk, J.P. van der, Karakterisering van monolietkatalysator DN32 ten behoeve van de opschaling van het Delfse NO2/Ureumproces, MsC thesis, Delft University of Technology, Department of Chemical Engineering, Delft (1993).
Appendix 2 - Derivations

A) The kinetic expression 6.10 and simplifications to 6.11 and 6.12:

Rewrite equations 6.6-6.8 to:

\[ C_{\text{site|NH}_3} = K_{\text{NH}_3} C_{\text{site}} C_{\text{NH}_3} \]  \hspace{1cm} (A2.1)

\[ C_{\text{site|NH}_3\text{NO}} = K_{\text{NO}} C_{\text{site|NH}_3} C_{\text{NO}} \]  \hspace{1cm} (A2.2)

\[ C_{\text{site|H}_2\text{O}} = \frac{C_{\text{H}_2\text{O}}^{0.5} \cdot C_{\text{site}}}{K_{\text{ox}} \cdot C_{\text{O}_2}^{0.25}} \]  \hspace{1cm} (A2.3)

Substitution of 1 in 2 gives:

\[ C_{\text{site|NH}_3\text{NO}} = K_{\text{NO}} K_{\text{NH}_3} C_{\text{NH}_3} C_{\text{site}} C_{\text{NO}} \]  \hspace{1cm} (A2.4)

Substitution of 1, 3 and 4 in 6.9 gives:

\[ C_{\text{site|total}} = C_{\text{site}} + K_{\text{NH}_3} C_{\text{NH}_3} C_{\text{site}} + K_{\text{NO}} K_{\text{NH}_3} C_{\text{NH}_3} C_{\text{site}} C_{\text{NO}} + \frac{C_{\text{H}_2\text{O}}^{0.5} C_{\text{site}}}{K_{\text{ox}} C_{\text{O}_2}^{0.25}} \]  \hspace{1cm} (A2.5)

Rearrangement of 5:

\[ C_{\text{site}} = \frac{C_{\text{site|total}} K_{\text{ox}} C_{\text{O}_2}^{0.25}}{K_{\text{NH}_3} C_{\text{NH}_3} K_{\text{ox}} C_{\text{O}_2}^{0.25} + K_{\text{NO}} K_{\text{NH}_3} C_{\text{NH}_3} C_{\text{NO}} K_{\text{ox}} C_{\text{O}_2}^{0.25} + C_{\text{H}_2\text{O}}^{0.5} + K_{\text{ox}} C_{\text{O}_2}^{0.25}} \]  \hspace{1cm} (A2.6)

The rate expression for NO removal is:

\[ -r_{\text{NO}} = k C_{\text{site|NH}_3\text{NO}} \]  \hspace{1cm} (A2.7)
Substituting 6 in 4 and the result in 7 yields equation 6.10:

\[-r_{NO} = \frac{k \cdot K_{NO} \cdot C_{NO} \cdot K_{NH_3} \cdot C_{NH_3} \cdot K_{ox} \cdot C_{O_2}^{0.25} \cdot C_{site/total}}{C_{H_2O}^{0.5} + K_{ox} \cdot C_{O_2}^{0.25} + K_{NH_3} \cdot C_{NH_3} + K_{ox} \cdot C_{O_2}^{0.25} + K_{NO} \cdot C_{NO} \cdot K_{NH_3} \cdot C_{NH_3} \cdot K_{ox} \cdot C_{O_2}^{0.25}}\]  

(A2.8)

\[B) \ Derivation \ of \ the \ TIS \ model\]

Internal and external diffusion limitations are not taken into account by any TIS model.

Reaction mechanism:

Step 1: adsorption of ammonia on a site

\[\text{NH}_3 + \text{site} \rightleftharpoons \text{NH}_3/\text{site}\]  

(A2.9)

Step 2: formation of the nitroso amine complex

\[\text{NH}_3/\text{site} + \text{NO} \rightarrow \text{NO/NH}_3/\text{site}\]  

(A2.10)

Step 3: decomposition of the nitroso amine complex

\[\text{NO/NH}_3/\text{site} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{site/HH}\]  

(A2.11)

Step 4: oxidation of the reduced site

\[\text{site/HH} + 1/4 \text{O}_2 \rightarrow \text{site} + 1/2 \text{H}_2\text{O}\]  

(A2.12)

Overall reaction:

4 NO + 4 NH_3 + O_2 → 4 N_2 + 6 H_2O  

(A2.13)

For the implementation of these reactions the following additional assumptions are made:

a) Step 1, the adsorption of NH_3 on an empty site, is not in equilibrium.
b) Step 2, the formation of the nitroso complex, is rate determining and irreversible
c) Step 3, the dissociation of the nitroso complex, is fast
d) Step 4, the reoxidation of the reduced site formed after the dissociation, is fast.

For modelling purposes it can be assumed that reaction 2 yields an empty site directly. The equations of the Tanks In Series concept are derived directly, without writing down the partial differential equations. The reaction rates of the gas and solid phase compounds and all site types are (subscript r is for reactor and g is for gas):

\[-r_{NH_3} = k_{a1} C_{NH_3} C_{site} - k_{d1} C_{NH_3/site}\]  

(A2.14)
with: 
- \( r_{\text{NH}_3} \): reaction rate ammonia [mol/m^3 s];
- \( k_{a1} \): adsorption rate constant of ammonia [m^3/g mol s];
- \( C_{\text{NH}_3} \): concentration of ammonia [mol/m^3];
- \( C_{\text{site}} \): concentration of sites [mol/m^3];
- \( k_{d1} \): desorption rate constant of the amine complex [1/s];
- \( C_{\text{NH}_3/site}} \): concentration of amine sites [mol/m^3].

Dimensions:

\[
\frac{\text{mol}}{m^3 \ s} = \frac{m^3_g}{\text{mol \ s}} \cdot \frac{\text{mol}}{m^3_g} \cdot \frac{\text{mol}}{m^3_r} - \frac{1}{s} \cdot \frac{\text{mol}}{m^3_r}
\]

\(-r_{\text{NO}} = k \ C_{\text{NO}} \ C_{\text{NH}_3/site}} \) \hspace{1cm} (A2.15)

with:
- \( r_{\text{NO}} \): reaction rate NO [mol/m^3 s];
- \( C_{\text{NO}} \): concentration of NO [mol/m^3 g];
- \( k \): reaction rate constant [m^3/g mol s].

Dimensions:

\[
\frac{\text{mol}}{m^3 \ s} = \frac{m^3_g}{\text{mol \ s}} \cdot \frac{\text{mol}}{m^3_g} \cdot \frac{\text{mol}}{m^3_r}
\]

\(-r_{\text{site}} = (-r_{\text{NH}_3}) - (-r_{\text{NO}}) \) \hspace{1cm} (A2.16)

with:
- \( r_{\text{site}} \): reaction rate sites [mol/m^3 s].

Finally the concentration of nitroso amine sites can be obtained by the balance:

\[ C_{\text{site, total}} = C_{\text{site}} + C_{\text{NH}_3/site}} \] \hspace{1cm} (A2.17)

with:
- \( C_{\text{site, total}} \): overall sites concentration [mol/site/m^3].

Basic balance for one tank:

accumulation = in - out - conversion \hspace{1cm} (A2.18)

Balance for NO:

\[
\frac{d(C_{\text{NO}, V_i})}{dt} = \phi_{i} C_{\text{NO, in}} - \phi_{i} C_{\text{NO}} - (-r_{\text{NO}}) V_{i}
\] \hspace{1cm} (A2.19)
with:  
\( C_{\text{NOin}} \): inlet NO concentration \([\text{mol/m}^3] \);  
\( V_g \): volume gas in one tank \([\text{m}^3] \);  
\( \phi_v \): flow rate \([\text{m}^3/\text{s}] \);  
\( V_t \): volume of one tank \([\text{m}^3] \).

Dimensions:

\[
\frac{\text{mol}}{\text{m}^3} \times \frac{\text{m}^3}{\text{s}} \times \frac{1}{\text{s}} = \frac{\text{m}^3}{\text{s}} \times \frac{\text{mol}}{\text{m}^3} - \frac{\text{m}^3}{\text{s}} \times \frac{\text{mol}}{\text{m}^3} - \frac{\text{mol}}{\text{m}^3} \times \frac{\text{m}^3}{\text{s}}.
\]

Balance for \( \text{NH}_3 \):

\[
\frac{d(C_{\text{NH3}}V_g)}{dt} = \phi_v C_{\text{NH3in}} - \phi_v C_{\text{NH3}} - (-r_{\text{NH3}})V_t \quad (A2.20)
\]

with:  
\( C_{\text{NH3in}} \): inlet \( \text{NH}_3 \) concentration \([\text{mol/m}^3] \).

Dimensions:

\[
\frac{\text{mol}}{\text{m}^3} \times \frac{\text{m}^3}{\text{s}} \times \frac{1}{\text{s}} = \frac{\text{m}^3}{\text{s}} \times \frac{\text{mol}}{\text{m}^3} - \frac{\text{m}^3}{\text{s}} \times \frac{\text{mol}}{\text{m}^3} - \frac{\text{mol}}{\text{m}^3} \times \frac{\text{m}^3}{\text{s}}.
\]

Balance for the sites:

\[
\frac{d(C_{\text{site}}V_t)}{dt} = -(-r_{\text{site}})V_t \quad (A2.21)
\]

Dimensions:

\[
\frac{\text{mol}}{\text{m}^3} \times \frac{\text{m}^3}{\text{s}} \times \frac{1}{\text{s}} = \frac{\text{mol}}{\text{m}^3} \times \frac{\text{m}^3}{\text{s}}.
\]
Introducing the following dimensionless variables:

\[ Y_{NO} = \frac{C_{NO}}{C_{NO,ref}}, \quad Y_{NH3} = \frac{C_{NH3}}{C_{NO,ref}}, \quad Y_s = \frac{C_{site}}{C_{site,ref}}, \quad Y_SN = \frac{C_{NH3,site}}{C_{site,ref}} \]

with:
- \( C_{NO,ref} \) : reference NO concentration [mol/m\(^3\)];
- \( C_{site,ref} \) : reference site concentration [mol/m\(^3\)].

results in the following set of equations for the reaction rates:

\[ Y_{SN} = 1 - Y_s \quad (A2.22) \]

\[ (-r_{NH3}) = k_1 Y_{NH3} Y_s C_{site,ref} C_{NO,ref} - k_2 Y_{SN} C_{site,ref} \quad (A2.23) \]

\[ (-r_{NO}) = k Y_{NO} Y_{SN} C_{site,ref} C_{NO,ref} \quad (A2.24) \]

\[ (-r_{site}) = (-r_{NH3}) - (-r_{NO}) \quad (A2.25) \]

The reference concentrations are usually equal to the inlet NO concentration and total site concentration. However, these variables can change during transient operation; e.g. a step in NO concentration or in temperature. This would lead to mathematical complications in the differential equations.

Introduction of the following additional constants:

\[ \epsilon = \frac{V_s}{V_i}, \quad \tau = \frac{V_t}{\phi_v}, \quad t_{st} = \frac{V_{bed}}{\phi_v,ref} \left( \epsilon + \frac{C_{site,ref}}{C_{NO,ref}} \right), \quad \theta = \frac{t}{t_{st}} \]

with:
- \( \epsilon \) : porosity [m\(^3\)/m\(^3\)];
- \( \phi_v,ref \) : reference flow rate [m\(^3\)/s];
- \( \tau \) : residence time [s];
- \( t_{st} \) : stoichiometric time [s];
- \( V_{bed} \) : volume of all tanks [m\(^3\)];
- \( \Theta \) : dimension less time.

The stoichiometric time is the time it will take for ammonia (at \( Y_{NH3} = 1, Y_{NO} = 0 \)) to occupy all sites (which were empty at \( \Theta = 0 \)) in case of a large equilibrium constant (see also Rodrigues\(^1\)).

results in the balances:

\[ \frac{1}{t_{st}} \frac{dY_{NO}}{d\theta} = \frac{Y_{NO,in} - Y_{NO}}{\tau} - \frac{-r_{NO}}{\epsilon C_{NO,ref}} \quad (A2.26) \]

Appendix 2
\[ \frac{1}{\tau_s} \frac{dY_{NH3}}{d\theta} = \frac{Y_{NH3,end} - Y_{NH3}}{\tau} - \frac{(-r_{NH3})}{C_{NO,ref}} \]  \hspace{1cm} (A2.27)

\[ \frac{1}{\tau_s} \frac{dY_s}{d\theta} = -\frac{(-r_{site})}{C_{site,ref}} \]  \hspace{1cm} (A2.28)

C) Derivation of the two sites model

Mechanism:

Step 1: adsorption of ammonia on site1

\[ \text{NH}_3 + \text{site1} \rightarrow \text{NH}_3/\text{site1} \]  \hspace{1cm} (A2.29)

Step 2: adsorption of ammonia on site2

\[ \text{NH}_3 + \text{site2} \rightarrow \text{NH}_3/\text{site2} \]  \hspace{1cm} (A2.30)

The following alternative NO reaction mechanism has been investigated:

\[ \text{NH}_3/\text{site2} + \text{NO} + \frac{1}{4} \text{O}_2 \rightarrow \text{N}_2 + \text{site2} + \frac{3}{2} \text{H}_2\text{O} \]  \hspace{1cm} (A2.31)

For the implementation of these reactions the following additional assumptions are made:

a) Step 1, reversible adsorption of NH3 on an empty site1
b) Step 2, slow and irreversible adsorption of NH3 on an empty site2
c) Step 3, reaction of NO with adsorbed ammonia on site2

The reaction rates of the gas and solid phase compounds and of all site types are (subscript r is for reactor, g is for gas, 1 is for site1 and 2 is for site2):

\[ -r_{NH3} = k_{s1} C_{NH3} C_{\text{site1}} - k_{d1} C_{NH3/site1} + k_{s2} C_{NH3} C_{\text{site2}} \]  \hspace{1cm} (A2.32)

with:
- \( C_{\text{site1}} \): concentration of sites type one [mol/m^3];
- \( C_{\text{site2}} \): concentration of sites type two [mol/m^3];
- \( k_{s2} \): adsorption rate constant of ammonia on site type two [m^3/g/mol s];
- \( C_{NH3/site1} \): concentration of amine sites type one [mol/m^3].

Dimensions:

\[ \frac{\text{mol}}{m^3} = \frac{m^3}{\text{mol}} \frac{m^3}{\text{mol}} \frac{m^3}{s} \frac{1}{\text{mol}} + \frac{m^3}{\text{mol}} \frac{m^3}{\text{mol}} \frac{m^3}{\text{mol}} \]

162 Derivations
\[-r_{\text{NO}} = k \ C_{\text{NO} \cdot \text{NH}_3/\text{site2}} \]  \hspace{1cm} (A2.33)

with: \(C_{\text{NH}_3/\text{site2}}\) : concentration of amine sites type two \([\text{mol/m}^3]\).
\(k\) : reaction rate constant \([\text{m}^3/\text{mol s}]\).

Dimensions:
\[
\frac{\text{mol}}{m^3 \cdot s} = \frac{m^3}{\text{mol s}} \cdot \frac{\text{mol}}{m^3} \cdot \frac{\text{mol}}{m^3} = \frac{\text{mol}}{m^3 \cdot s}
\]

\[-r_{\text{site1}} = k_{a1} C_{\text{NH}_3} C_{\text{site1}} - k_{d1} C_{\text{NH}_3/\text{site1}} \]  \hspace{1cm} (A2.34)

\[-r_{\text{site2}} = k_{a2} C_{\text{NH}_3} C_{\text{site2}} - k C_{\text{NO} \cdot \text{NH}_3/\text{site2}} \]  \hspace{1cm} (A2.35)

with: \(-r_{\text{site}}\) : reaction rate sites \([\text{mol/m}^3 \cdot s]\);

Finally the concentration of amine sites can be obtained by the balance:

\[C_{\text{site1, total}} = C_{\text{site1}} + C_{\text{NH}_3/\text{site1}} \]  \hspace{1cm} (A2.36)

\[C_{\text{site2, total}} = C_{\text{site2}} + C_{\text{NH}_3/\text{site2}} \]  \hspace{1cm} (A2.37)

with: \(C_{\text{site, total}}\) : overall sites concentration \([\text{mol/site/m}^3]\);

The basic balances of NO and NH\(_3\) for one tank are the same as in derivation B, equations 18 to 20. The mass balances for the two types of sites are analogous to equation 21:

\[
\frac{d(C_{\text{site1}} V_p)}{dt} = -(-r_{\text{site1}}) V_t
\]  \hspace{1cm} (A2.38)

\[
\frac{d(C_{\text{site2}} V_p)}{dt} = -(-r_{\text{site2}}) V_t
\]  \hspace{1cm} (A2.39)

Dimensions:
\[
\frac{\text{mol}}{m^3 \cdot r} \cdot \frac{m^3}{s} \cdot \frac{1}{s} = \frac{\text{mol}}{m^3 \cdot r} \cdot \frac{m^3}{s}
\]

Appendix 2
Introducing the following additional dimensionless variables:

\[ Y_{S1} = \frac{C_{\text{site}1}}{C_{\text{site.ref}}}, \quad Y_{S2} = \frac{C_{\text{site}2}}{C_{\text{site.ref}}}, \quad Y_{S1,0} = \frac{C_{\text{site}1,0}}{C_{\text{site.ref}}}, \quad Y_{S2,0} = \frac{C_{\text{site}2,0}}{C_{\text{site.ref}}} \]

results in the following set of equations for the reaction rates:

\[
(-\tau_{\text{NH3}}) = k_{a1} Y_{\text{NH3}} Y_{S1} C_{\text{site.ref}} C_{\text{NO.ref}} - k_{d1}(Y_{S1,0} Y_{S1}) C_{\text{site.ref}} \quad \text{(A2.40)}
\]

\[
(-\tau_{\text{NO}}) = k Y_{\text{NO}} (Y_{S2,0} Y_{S2}) C_{\text{site.ref}} C_{\text{NO.ref}} \quad \text{(A2.41)}
\]

\[
(-\tau_{\text{site}1}) = k_{a1} Y_{\text{NH3}} Y_{S1} C_{\text{site.ref}} C_{\text{NO.ref}} - k_{d1}(Y_{S1,0} Y_{S1}) C_{\text{site.ref}} \quad \text{(A2.42)}
\]

\[
(-\tau_{\text{site}2}) = k_{a2} Y_{\text{NH3}} Y_{S2} C_{\text{site.ref}} C_{\text{NO.ref}} - k Y_{\text{NO}} (Y_{S2,0} Y_{S2}) C_{\text{site.ref}} C_{\text{NO.ref}} \quad \text{(A2.43)}
\]

Substituting the dimensionless groups results in the balances:

\[
\frac{1}{t_{st}} \frac{dY_{\text{NO}}}{d\theta} = \frac{Y_{\text{NO}0a} - Y_{\text{NO}}}{\tau} - \frac{-\tau_{\text{NO}}}{C_{\text{NO.ref}}} \quad \text{(A2.44)}
\]

\[
\frac{1}{t_{st}} \frac{dY_{\text{NH3}}}{d\theta} = \frac{Y_{\text{NH3}0a} - Y_{\text{NH3}}}{\tau} - \frac{(-\tau_{\text{NH3}})}{C_{\text{NO.ref}}} \quad \text{(A2.45)}
\]

\[
\frac{1}{t_{st}} \frac{dY_{S1}}{d\theta} = -\frac{(-\tau_{\text{site}1})}{C_{\text{site.ref}}} \quad \text{(A2.46)}
\]

\[
\frac{1}{t_{st}} \frac{dY_{S2}}{d\theta} = -\frac{(-\tau_{\text{site}2})}{C_{\text{site.ref}}} \quad \text{(A2.47)}
\]

Note that equations 44 and 45 are the same as 26 and 27. Furthermore, equations 46&47 are analogous to equation 28.
D) Derivation of the nitroso complex model

Reaction mechanism:

Step 1: adsorption of ammonia on a site
\[ \text{NH}_3 + \text{site} \rightleftharpoons \text{NH}_3/\text{site} \quad (A2.9) \]

Step 2: formation of the nitroso amine complex
\[ \text{NH}_3/\text{site} + \text{NO} \rightleftharpoons \text{NO/NH}_3/\text{site} \quad (A2.48) \]

Step 3: decomposition of the nitroso amine complex
\[ \text{NO/NH}_3/\text{site} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{site}/\text{H} \quad (A2.11) \]

Step 4: oxidation of the reduced site
\[ \text{site}/\text{H} + 1/4 \text{O}_2 \rightarrow \text{site} + 1/2 \text{H}_2\text{O} \quad (A2.12) \]

Overall reaction:
\[ 4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad (A2.13) \]

For the implementation of the nitroso complex formation in the Tanks In Series formulation of the transient SCR model the following additional assumptions are made:

a) Step 1, the adsorption of \( \text{NH}_3 \) on an empty site, is in equilibrium.

b) Step 2, the formation of the nitroso complex, is also in equilibrium; NO adsorbs on the site occupied by ammonia.

c) Step 3, the dissociation of the nitroso complex, is the rate determining step.

d) Step 4, the reoxidation of the reduced site formed after the dissociation, is fast. For modelling purposes it can be assumed that reaction 4 (Step c) yields a 'Site' directly.

The number of unknown constants has been limited by assuming that the ad- and desorption processes are in equilibrium. Now 'only' three constants are unknown (the reaction rate constant and the two equilibrium constants) instead of five (reaction rate constant and the ad- and desorption rate constants of the two adsorption processes). The equilibrium constants are defined as:

\[ K_{\text{NH}_3} = \frac{C_{\text{NH}_3/\text{site}}}{C_{\text{NH}_3} \cdot C_{\text{site}}} \quad (6.6) \]

with: \( K_{\text{NH}_3} \) : equilibrium constant ammonia \([\text{m}^3/\text{mol}]\).
\[ K_{NO} = \frac{C_{NO/NH3/site}}{C_{NO} C_{NH3/site}} \]  
(6.7)

with: \( K_{NO} \) : equilibrium constant NO \([m^3/g\, mol]\).

And the reaction rate (11) and (12):

\[ \text{NO/NH}_3/\text{site} + 1/4 \text{O}_2 \rightarrow \text{N}_2 + \text{site} + 3/2 \text{H}_2\text{O} \]  
(A2.49)

\[ +r_{N2} = k C_{NO/NH3/site} \]  
(A2.50)

with: \( +r_{N2} \) : formation rate \( \text{N}_2 \) \([\text{mol}/\text{m}^3\, \text{s}]\);
\( k \) : reaction rate constant \([1/\text{s}]\).

The overall sites balance is:

\[ C_{site,\text{total}} = C_{site} + C_{NH3/site} + C_{NO/NH3/site} \]  
(A2.51)

or the derivative with respect to time:

\[ 0 = dC_{site}/dt + dC_{NH3/site}/dt + dC_{NO/NH3/site}/dt \]  
(A2.52)

The balances of \( \text{NH}_3 \) and NO over one tank are becoming somewhat more complicated:

Accumulation\(_{\text{gas phase}}\) + accumulation\(_{\text{solid phase}}\) = in - out - consumption  
(A2.53)

The accumulation in the gas phase and the in and out terms of equation 53 are trivial, see equations 18-20. The second term, the accumulation in the solid phase equals the derivatives of the solid phase complexes with respect to time. The consumption equals the nitrogen production. This ammonia solid phase accumulation is (use also equation 52 and assuming that \( V_i \) is constant):

\[ \text{accumulation}_{\text{NH}_3 \text{ solid phase}} = d(V_i C_{NH3/site})/dt + d(V_i C_{NO/NH3/site})/dt = -d(V_i C_{site})/dt \]  
(A2.54)

Accordingly for NO:

\[ \text{accumulation}_{\text{NO solid phase}} = d(V_i C_{NO/NH3/site})/dt \]  
(A2.55)

The problem is now to evaluate an expression for the derivative of the solid phase concentration with respect to time. At this point the equilibrium assumption has to be introduced. Substitution of equation 1 and 2 in 51 leads to:

\[ C_{site} = \frac{C_{site,\text{total}}}{1 + K_{NH3} C_{NH3} + K_{NH3} C_{NH3} K_{NO} C_{NO}} \]  
(A2.56)
\[ C_{\text{NO(NH3)\_site}} = \frac{K_{\text{NH3}} C_{\text{NH3}} K_{\text{NO}} C_{\text{NO}} C_{\text{site\_total}}}{1 + K_{\text{NH3}} C_{\text{NH3}} + K_{\text{NH3}} C_{\text{NH3}} K_{\text{NO}} C_{\text{NO}}} \]  \hspace{1cm} (A2.57)

Now, as the relations \( C_{\text{solid}} = f(C_{\text{gas}}) \) are established the derivatives of the solid concentration can be rewritten:

\[ \frac{dC_{\text{site}}}{dt} = \frac{dC_{\text{site}}}{dC_{\text{NH3}}} \frac{dC_{\text{NH3}}}{dt} \frac{dC_{\text{NO(NH3)\_site}}}{dt} = \frac{dC_{\text{NO(NH3)\_site}}}{dC_{\text{NO}}} \frac{dC_{\text{NO}}}{dt} \]  \hspace{1cm} (A2.58)

With:

\[ \frac{dC_{\text{site}}}{dC_{\text{NH3}}} = - \frac{(K_{\text{NH3}} + K_{\text{NO}} C_{\text{NO}} K_{\text{NH3}}) C_{\text{site\_total}}}{(1 + K_{\text{NH3}} C_{\text{NH3}} + K_{\text{NH3}} C_{\text{NH3}} K_{\text{NO}} C_{\text{NO}})^2} \]  \hspace{1cm} (A2.59)

\[ \frac{dC_{\text{NO(NH3)\_site}}}{dC_{\text{NO}}} = \frac{(1 + K_{\text{NH3}} C_{\text{NH3}} K_{\text{NO}} K_{\text{NH3}} C_{\text{NH3}} C_{\text{site\_total}}}{(1 + K_{\text{NH3}} C_{\text{NH3}} + K_{\text{NH3}} C_{\text{NH3}} K_{\text{NO}} C_{\text{NO}})^2} \]  \hspace{1cm} (A2.60)

The overall accumulation of NO, the left hand side of equation 55, is derived by substitution of 58 in 52:

\[ \text{accumulation}_{\text{NO}} = V_g \frac{dC_{\text{NO}}}{dt} + V_t \frac{dC_{\text{NO(NH3)\_site}}}{dC_{\text{NO}}} \frac{dC_{\text{NO}}}{dt} \]  \hspace{1cm} (A2.61)

Substitution of 61 in the balance for one tank (19) leads to:

\[ \frac{dC_{\text{NO}}}{dt} = \frac{\phi_t}{V_g} (C_{\text{NO}} - C_{\text{NO}}) - (r_{\text{NO}}) \frac{V_t}{V_g} \]

\[ 1 + \frac{V_t}{V_g} \frac{dC_{\text{NO(NH3)\_site}}}{dC_{\text{NO}}} \]  \hspace{1cm} (A2.62)
Dimensions:

\[
\frac{\text{mol}}{m_g^3 s} = \frac{\frac{\text{mol}}{m_g^3} - \frac{\text{mol}}{m_g^3}}{s} \cdot \frac{1}{m_s^3} - \frac{\frac{\text{mol}}{m_s^3}}{m_r^3} \cdot \frac{\text{mol}}{m_r^3} \
1 + \frac{m_r^3}{m_s^3} \cdot \frac{\text{mol}}{m_s^3}
\]

The overall accumulation of NH₃, the left side of equation 54, is derived by substitution of 58 in 51:

\[
\text{accumulation}_{NH_3} = V_g \frac{dC_{NH_3}}{dt} - V_i \frac{dC_{site}}{dC_{NH_3}} \frac{dC_{NH_3}}{dt} 
\]

(A2.63)

Substitution of 63 in the balance for one tank (20) leads to:

\[
\frac{dC_{NH_3}}{dt} = \frac{\phi_v}{V_g} \left( C_{NH_3,\text{in}} - C_{NH_3} \right) - \left( r_{NO} \right) \frac{V_i}{V_g} \\
1 - \frac{V_i}{V_g} \frac{dC_{site}}{dC_{NH_3}}
\]

(A2.64)

Introduction of the dimensionless variables leads to:

\[
\frac{1}{t_{st}} \frac{dY_{NO}}{d\theta} = \frac{Y_{NO,\text{in}} - Y_{NO}}{\tau} - \frac{r_{NO}}{C_{NO,0} \epsilon} \\
1 + \frac{1}{\epsilon} \frac{dY_{NN}}{dY_{NO}} \left( \frac{C_{site,\text{total}}}{C_{NO,0}} \right)
\]

(A2.65)

\[
\frac{1}{t_{st}} \frac{dY_{NH_3}}{d\theta} = \frac{Y_{NH_3,\text{in}} - Y_{NH_3}}{\tau} - \frac{r_{NO}}{C_{NO,0} \epsilon} \\
1 - \frac{1}{\epsilon} \frac{dY_{OS}}{dY_{NH_3}} \left( \frac{C_{site,\text{total}}}{C_{NO,0}} \right)
\]

(A2.66)
With:

\[ r_{N2} = k \frac{K_{NH3} Y_{NH3} K_{NO} Y_{NO} C_{site,total} C_{NO,0}^2}{1 + K_{NH3} Y_{NH3} C_{NO,0} + K_{NH3} Y_{NH3} K_{NO} Y_{NO} C_{NO,0}^2} \]  

(A2.67)

\[ \frac{dY_S}{dY_{NH3}} = -\frac{(K_{NH3} + K_{NO} Y_{NO} K_{NH3} C_{NO,0}) C_{NO,0}}{(1 + K_{NH3} Y_{NH3} C_{NO,0} + K_{NH3} Y_{NH3} K_{NO} Y_{NO} C_{NO,0}^2)^2} \]  

(A2.68)

\[ \frac{dY_{SNH}}{dY_{NO}} = \frac{(1 + K_{NH3} Y_{NH3} C_{NO,0}) K_{NO} K_{NH3} Y_{NH3} C_{NO,0}^2}{(1 + K_{NH3} Y_{NH3} C_{NO,0} + K_{NH3} Y_{NH3} K_{NO} Y_{NO} C_{NO,0}^2)^2} \]  

(A2.69)

Not only the number of unknown constants has decreased but the model has now only two ODE’s per tank. If the adsorption and desorption processes would have been taken into account four ODE’s could be derived.

Literature

Appendix 3: Calculations with the extended TIS-models

The two sites model for ammonia breakthrough curves

To predict the ammonia breakthrough curves (no NOx present; no reaction) the two sites model has been developed. The derivation of this model is given in appendix 2C, equations A2.45-47. For each tank these three ODE’s were integrated with the SIMUSOLV\textsuperscript{1} package. It uses Gear’s BDF implicit method for integration and Nelder Mead’s method for optimization of the likely hood function in case of parameter estimation. In principle 5 parameters are unknown and have to be estimated; the adsorption and desorption coefficient of the reversible site (\(k_{a1}\) and \(k_{d1}\)), the adsorption rate coefficient of the irreversible site (\(k_{a2}\)), the overall number of sites (\(S\)) and the fraction of reversible sites (\(F_{rev}\)). The last two parameters can also be obtained by determining the area above and under the ad- and desorption curves. The results are presented in the Figures A3.1-3 and Table A3.1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>100</th>
<th>200</th>
<th>277</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{a1}) (m(^3)/mols)</td>
<td>7.5E2</td>
<td>5.1E2</td>
<td>1.8E3</td>
</tr>
<tr>
<td>(k_{d1}) (1/s)</td>
<td>0.081</td>
<td>0.10</td>
<td>0.71</td>
</tr>
<tr>
<td>(k_{a2}) (m(^3)/mols)</td>
<td>0.059</td>
<td>0.17</td>
<td>0.90</td>
</tr>
<tr>
<td>(F_{rev})</td>
<td>0.44</td>
<td>0.48</td>
<td>0.67</td>
</tr>
<tr>
<td>(S) (mol/m(^3))</td>
<td>82</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>standard deviation (ppm)</td>
<td>1.3</td>
<td>0.61</td>
<td>0.98</td>
</tr>
<tr>
<td>(K_{NH3}) (m(^3)/mol)</td>
<td>9.2E3</td>
<td>5.0E3</td>
<td>2.5E3</td>
</tr>
</tbody>
</table>

The breakthrough curves of ammonia can be described fairly well up to 200°C. At 277°C the curves are less easy to describe due to ammonia oxidation. The values of the ad- and desorption coefficients are very likely not the chemical rate constants because of diffusion limitations (section 6.1.4). Also the values of the equilibrium constants (\(K_{NH3}=k_{a2}/k_{d1}\)) should be treated with some care as all kinds of non idealities will be lumped into this constant. However, these values are large and therefore the reversible sites will be occupied almost completely with ammonia. At 277°C the value of \(K_{NH3}C_{NH3, inal}\) is about 27 at 500 ppm ammonia inlet level which is enough for the front model to be applied (§6.1.3). Furthermore, this value is large enough for the sites to be covered with ammonia almost completely (equation 6.29). Therefore, the overall amount of ammonia on the catalyst decreases with increasing temperature mainly due to the decrease of the overall number of sites and not because of the decreasing \(K_{NH3}\). The latter effect will even become important at higher temperatures.

The adsorption of ammonia on the irreversible sites is a very slow process (compare the values of \(k_{a1}\) with \(k_{a2}\)). The nature of these sites remains unclear; wether it is a strong chemisorption or even reduction of some sites (N\(_2\) should evolve) was not investigated.
Figure A3.1: Model and experimental Adsorption and desorption curve of DN 32 at 100°C (457 g 400 cpsi DN 32, 63 ppm NH₃ in 5 Nm³/h air).

Figure A3.2: Model and experimental Adsorption and desorption curve of DN 32 at 200°C (457 g 400 cpsi DN 32, 63 ppm NH₃ in 5 Nm³/h air).
Figure A3.3: Model and experimentalAdsorption curve of DN 32 at 277°C (457 g 400 cpi DN 32, 63 ppm NH₃ in 5 Nm³/h air).

Figure A3.4: Prediction of the NO outlet signal as a function of the preexponential factor for the reaction of NO with the second type of adsorbed ammonia at 200°C (457 g 400 cpi DN 32, 500 ppm NH₃&NO in 10 Nm³/h air).
The two sites model for predicting the NO reaction rate

One of the unanswered questions is the nature of the second type of sites, or from a practical point of view, how much it contributes to the NO/\text{NH}_3 reaction. It was observed that ammonia adsorbed on this second type of sites could be removed and thus react with NO. Therefore, the two sites model has been used with the assumption that NO reacts with site type two (appendix 2C equations A2.44-47). At 200°C the conversion obtained with a fitted first order approach (appendix 1, equation A1.11) would be 90 percent whereas the conversion for reaction with the second type of site does not exceed 40 percent even when making the reaction with NO infinitely fast, Figure A3.4. The latter is of course a strange idea because in such a case the reaction rate would be first order in ammonia instead of first order in NO.

When assuming the first type of site is in fact reacting with NO (some trivial changes in appendix 2, equations A2.41-43 are sufficient, alternatively equations A2.26-28 can also be used) the conversion does indeed reach the value of 90 percent. (It is noted that these values are obtained after correcting the reaction rate constant in the TIS model for dimensions and number of sites, \(k(\text{TIS}) = k(\text{equation A1.11}) \times (\text{F}_{\text{rev}} \times S_0)\), which only holds for large values of \(k_{\text{aq}}\) and \(K_{\text{NH}_3}\)).

These observations and calculations are not prove that there are only two types of sites. It is only likely that the second type of site (if this is indeed one type only and if it reacts with first order kinetics, etc) does not contribute significantly to the NO conversion in the SCR reaction. However, it does contribute to the ammonia breakthrough curve. Therefore, knowledge about this type of site is essential when modelling ammonia slip.

The two sites model for predicting the response on a pulse in NO

The front model prediction of the response of the NO signal on switching the NO feed off during one minute while keeping the ammonia feed rate constant is plotted in Figure 6.22. The fit was poor; the NO outlet signal remained zero for a much longer period than predicted by the front model. A possible explanation would be that while the NO feed was switched off a considerable amount of sites of the irreversible type would be covered with ammonia. If the reaction rate with this second type of site is large an effect as observed (NO signal remaining zero for a prolonged period) can be expected. When implementing this assumption in the two sites model, Figure A3.5 and Table A3.2, the difference between the model and experimental response is still large. Therefore, the experimental response cannot be explained by the presence of this second type of site only.

| Table A3.2: Parameters used for the two sites model at 250°C (interpolation Table A3.1, for \(\text{F}_{\text{rev}}\), the correction factor from §6.2.2 is used). |
|---------------------------------|------------------|
| \(k_{\text{aq}}\) (m\(^3\)/mol s) | 1.3E3            |
| \(k_{\text{aq}}\) (1/s)          | 0.5              |
| \(k_{\text{aq}}\) (m\(^3\)/mol s) | 0.64             |
| \(\text{F}_{\text{rev}}\)        | 0.29             |

Appendix 3
Figure A3.5: Model (two sites and one site) and experimental response of the NO$_x$ signal on switching off the NO feed at time = 1000s for 60 seconds (457 g 400 cpi DN 32, 250°C, 310 ppm NO inlet at NH$_3$/NO = 0.86 in 9.2 Nm$^3$/h air).

Figure A3.6: Model (nitroso complex and one site) and experimental response of the NO$_x$ signal on switching off the NO feed at time = 1000s for 60 seconds (457 g 400 cpi DN 32, 250°C, 310 ppm NO inlet at NH$_3$/NO = 0.86 in 9.2 Nm$^3$/h air).
The nitroso amine model for predicting the response on a pulse in NO

Studying the response on the pulse NO feed, the NO outlet signal resembles some type of breakthrough curve. This led to the idea that NO could also be adsorbed on the catalyst in some way. In this case the approach of Tufano\(^2\) has been followed assuming NO adsorbs on a site covered with ammonia or alternatively forms a surface complex (§6.1.1). The resulting equations are derived in appendix 2D, A2.65-67. The number of ODE’s has been limited considerably by the assumption that the gas phase adsorption processes are in equilibrium with the solid phase. This can only be true if the reaction rate is much slower than the ad- and desorption processes.

![Graph](image)

*Figure A3.7: Model (nitroso complex) and experimental response of the NO\(_x\) signal on switching off the NO feed at time = 1000s for 60 seconds (457 g 400 cpi DN 32, 250°C, 310 ppm NO inlet at NH\(_3\)/NO=0.86 in 9.2 Nm\(^3\)/h air).*

The equilibrium constant for ammonia adsorption, K\(_{\text{NH3}}\), is calculated from Table A3.2 (K\(_{\text{NH3}} = k_{a1}/k_{d1}\)). The equilibrium constant for the nitrosamidic intermediate, K\(_{\text{NO}}\), is reported\(^2\) to be in the range of 4-40 m\(^3\)/mol. A value of 20 is chosen which corresponds to an order in NO of 0.8 in the concentration range of 100-1000 ppm NO. The SIMUSOLV package has been used to integrate the ODE’s, see Figure A3.6 and Table A3.3. The difference between the experimental response with and without NO adsorption is very small. This is due to the low value of the equilibrium constant (K\(_{\text{NO}}=20\) means a value of K\(_{\text{NO}}C_{\text{NO, inlet}}\) of 0.14, as with ammonia adsorption this does not lead to a sharp profile in the reactor, Figure 6.6). A better fit, Figure A3.7, can be obtained by varying the reaction rate constant (k) and the K\(_{\text{NO}}\) simultaneously. However, these parameters are strongly correlated, see equation A2.67, and it was therefore not clear which parameter was responsible for the shape of the curve.

It was not possible to explain the experiment with this model. However, the generally observed reaction orders in NO (smaller than one) can be explained.

*Appendix 3*
Final remark

Obviously, the models to describe a transient SCR reactor are not sufficiently accurate yet. This is mainly due to a lack of knowledge in reaction mechanism and ammonia adsorption phenomena.

<table>
<thead>
<tr>
<th>Table A3.3: The estimated parameters of the nitroso complex model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\text{NH}_3}$ (m$^3$/mol)</td>
</tr>
<tr>
<td>$K_{\text{NO}}$ (m$^3$/mol)</td>
</tr>
</tbody>
</table>

Literature

Samenvatting

Het doel van dit proefschrift is een bijdrage te leveren aan de ontwikkeling van een systeem om NOₓ te verwijderen uit de afgassen van dieselmotoren door middel van selectieve katalytische reductie (engels; Selective Catalytic Reduction, SCR) met ureum. Hiertoe zijn katalysatoren op laboratorium schaal getest. Ook is een ureum injectiesysteem ontwikkeld en zijn tests op een 0.4 liter direct geïnjecteerde dieselmotor verricht.

Het te ontwikkelen systeem zou ongeveer 70 procent NOₓ reductie moeten kunnen halen. Dit percentage is gebaseerd op toekomstige wetgeving voor ‘heavy duty’ diesel motoren (zie §1.2). De emissie van nevenproducten (zoals N₂O, NH₃, sulfaatdeeltjes, ureum condensatieprodukten, zie §2.2) zal beperkt moeten blijven. Vooral de SO₂ oxydatie, welke resulteert in emissie van sulfaatdeeltjes, zal laag moeten zijn in verband met de emissie eisen betreffende uitstoot van deeltjes (zie §2.2.3).

ALS SCR in transiente (niet steady state, zoals een vrachtwagen) toepassingen gebruikt wordt, komen er een aantal eisen bij. De hoeveelheid NOₓ die door de motor geproduceerd wordt is afhankelijk van o.a. het vermogen en het toerental, die beide snel variëren. De ureum injectie moet dus geregeld worden; als er teveel ureum geïnjecteerd wordt leidt dit tot emissie van ureum ontdelingsprodukten (voornamelijk NH₃). Te weinig ureum leidt tot onvoldoende NOₓ reductie. Een andere beperking die aan het systeem opgelegd wordt is de grootte; de activiteit van de katalysator zal hoog moeten zijn in uitaatgassen van dieselmotoren.

Standaard vanadium katalysatoren, die gebruikt worden in deNOₓ units bij elektriciteitscentrales, voldoen niet aan deze eisen. Het temperatuurbereik, 300-450°C, waarin deze katalysatoren gebruikt kunnen worden komt niet overeen met de temperaturen in uitaatgassen van dieselmotoren, 100-600°C. Dit bereik kan wat beperkt worden aangezien temperaturen boven de 550°C zelden voorkomen en temperaturen beneden de 300°C niet veel aan de totale NOₓ uitstoot bijdragen (zie §2.2.1). Het resulterende temperatuurbereik heeft dan nog steeds een vrij groot gebied (450-550°C) wat niet gedekt wordt door de standaard vanadium katalysatoren. Daarom zijn katalysatoren, zowel zelf ontwikkelde zeoliet katalysatoren als ook commerciële vanadium katalysatoren, getest (hoofdstuk 3).

De ontwikkeling van het ureum injectiesysteem werd gelijktijdig verricht (hoofdstuk 4). Dit systeem is getest op een kleine dieselmotor (hoofdstuk 5). Verder is gewerkt aan modellering en procesregeling (hoofdstuk 6). Dit proefschrift wordt afgesloten met enige aanbevelingen voor verder onderzoek om aan alle eisen te kunnen voldoen.

Het testen van katalysator

Voor het testen van katalysator zijn twee opstellingen gebouwd. De eerste is een ‘screening setup’ om de activiteit van katalysatoren voor de SCR reactie en de SO₂ oxydatie snel te kunnen evalueren. De tweede is een ‘test bench’ welke dient om veel belovende katalysatoren met uitaatgassen van dieselmotoren te testen. Katalysatoren die een hoge activiteit in uitaatgassen van dieselmotoren vertoonden (V₂O₅/TiO₂/WO₃ en Cu mordeniet), gaven ongewenste SO₂ oxydatie boven 400°C. Tevens daalde de NOₓ conversie boven 450°C door NH₃ oxydatie.
De nieuw ontwikkelde cerium mordeniet katalysator heeft een hoge SCR activiteit boven 400°C zonder SO\textsubscript{2} naar SO\textsubscript{3} te oxyderen. Ook geeft de NH\textsubscript{3} oxydatie N\textsubscript{2} in plaats van NO. Dit laatste geeft de mogelijkheid om met een kleine overmaat NH\textsubscript{3} te werken waardoor het regelprobleem sterk verminderd wordt. Echter, de activiteit van deze katalysator tussen 300 en 400°C is aan de lage kant. Daarom kan deze cerium katalysator alleen gebruikt worden bij hogere temperaturen (boven 400°C) of in combinatie met een andere component (bijvoorbeeld koper).

**Ontwikkeling van het ureum injectiesysteem**

Ammoniak wordt op grote schaal toegepast als de selectieve component bij de SCR reactie. De voornaamste reden om ureum te gebruiken is veiligheid. Ammoniak is een giftig gas wat onder druk bewaard moet worden.

Er is een ureum injectiesysteem ontwikkeld en het is gebleken dat ureum hetzelfde reageert als NH\textsubscript{3}. Voorwaarde is dat de temperatuur waarbij de ureumoplossing geïnjecteerd wordt hoog genoeg is (>300°C). Er zijn geen significante hoeveelheden bijproducten gevonden (N\textsubscript{2}O, ureum condensatieproducten). Echter, als ureuminjectie op grote schaal toegepast gaat worden, zijn enige additionele tests wenselijk; de analytische procedures hiervoor zijn beschreven in hoofdstuk 4.

Het ureum injectiesysteem bestaat uit een 'air blast’ verstuiver uitgerust met een 'isolatiekapje’ om vorming van bijproducten op de koude verstuiver te voorkomen. Deze verstuiver is gemonteerd op de bovenkant van een reactor welke een statische menger en twee katalytische monolieten bevat (V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}/WO\textsubscript{3} type). Deze opstelling is getest achter een 0.4 liter diesel motor. Tussen 270 en 450°C kon geen verschil in SCR activiteit worden aangetoond, tussen een laag zwavelige diesel (<10 ppm) en een gecertificeerde diesel (0.14 gewicht procent zwavel). Een NO\textsubscript{x} reductie van 70 procent bij 300°C zonder NH\textsubscript{3} uitstoot kan gerealiseerd worden bij een space velocity van 5000h\textsuperscript{-1}. Hogere space velocities, 15000h\textsuperscript{-1} bij 270°C, gaven onvoldoende NO\textsubscript{x} reducties en substantiële NH\textsubscript{3} uitstoot. De NO\textsubscript{x} conversie bereikt de 70% wel weer bij hogere temperaturen, maar de ammoniak uitstoot blijft aanwezig. Daarom is de space velocity die gebruikt kan worden bij toepassing op een heavy duty dieselmotor naar verwachting ongeveer 5000-15000h\textsuperscript{-1}.

**Modellering**

De dynamische SCR reactie, over de gebruikte V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2}/WO\textsubscript{3} katalysator, is gomodelleerd, rekening houdende met de niet stationaire diffusie van NO en NH\textsubscript{3} in de poreuze katalysator (de 'washcoat', §6.1.4). Het dynamisch gedrag hangt voornamelijk af van de hoeveelheid geadsorbeerde NH\textsubscript{3} op het katalysatoroppervlak: de NH\textsubscript{3} buffer. Deze buffer is een complexe functie van temperatuur, ureum/NO verhouding, activiteit van de katalysator, uitleergas debiet en andere adsorberende componenten. Daarom zijn NH\textsubscript{3} (§6.2.1) adsorptiecurves gemeten. Er zijn waarschijnlijk tenminste twee type adsorptieplaatsen, een reversibele en een irreversibele. Literatuuronderzoek en verdere metingen geven aan dat in de aanwezigheid van NO er (dus) ook meerdere complexe processen plaats (kunnen) vinden. Meer onderzoek is nodig om de exacte rol van de NH\textsubscript{3} adsorptieplaatsen te kunnen achterhalen.

Om de dynamische metingen met diesel uitleergassen te kunnen interpreteren is ook een eenvoudig model afgeleid (§6.1.2). Het bestaat uit slechts één differentiaalvergelijking. De belangrijkste aannames zijn ideale hydrodynamica ('plug flow') en de kinetiek is vereenvoudigd tot eerste orde in NO en nulde orde in NH\textsubscript{3}. Als parameters moet de reactiesnelheid en de ammoniakbuffer opgegeven worden. Dit model beschrijft het dynamisch
gedrag kwalitatief goed en kan daarom wellicht in complexere regelconfiguraties gebruikt worden. Uiteraard is dit model alleen geldig in de buurt van het werkpunt waarvoor de input parameters bepaald zijn.

Procesregeling

De meest eenvoudige methode om dit proces te regelen is de NO\(_x\) output te meten en de ureuminjectie hieraan te koppelen. Echter, sensoren die snel, nauwkeurig en goedkoop de NO\(_x\) en/of NH\(_3\) concentratie kunnen meten zijn niet beschikbaar. In dit onderzoek is hiervoor een chemoluminiscentie NO\(_x\) analyser gebruikt (respons tijd 10 seconden). Zelfs met een dergelijke analyser kunnen timing problemen optreden bij hogere NO\(_x\) conversies (gebruik makende van een PID algoritme) resulterende in NH\(_3\) emissie.

In de praktijk kan de NO\(_x\) output van de motor geschat worden op basis van andere beter te meten variabelen (snelheid en vermogen). Als het lukt de NO\(_x\) output nauwkeurig te schatten is een zogenoemde 'open loop' regeling het meest voor de hand liggende systeem. De ureuminjectie wordt dan aan de NO\(_x\) voorspellings gekoppeld. Dit was voor de diesel motor die gebruikt werd in dit onderzoek niet mogelijk omdat de afwijkingen die optraden vrij groot waren. Aangezien deze oplepen tot zo'n 30 procent is de maximale conversie die te behalen is 70 procent (aangezien overall 70 procent reductie gehaald moet worden is de speelruimte hiervoor dus te klein). Opgemerkt dient te worden dat deze voorspelling wellicht verbeterd kan worden als meerdere variabelen dan alleen het vermogen en het uitlaatgas debiet gebruikt worden.

Aangezien het in dit onderzoek niet mogelijk bleek de NO\(_x\) produktie van de motor nauwkeurig te schatten is de NO\(_x\) analyser ingezet. Door nu de NO\(_x\) concentratie na de katalysator te meten kan voor al te grote fouten in de initiële schatting gecorrigeerd worden. Opgemerkt wordt dat de eisen die aan een eventuele sensor gesteld worden nu minder zijn aangezien alleen voor fouten gecorrigeerd wordt.

Echter, als NH\(_3\) uitstoot onvermijdelijk is (bijvoorbeeld door desorptieverschijnselen als gevolg van temperatuurschommelingen) kan een oxydatie katalysator gebruikt worden om deze emissie te elimineren. Aangezien er in zo'n geval geen gevaar voor ammoniakemissie is kan een 'open loop' regeling voor de ureuminjectie toegepast worden. Een dergelijk systeem, een vanadium katalysator boven op een Pd katalysator, is ook getest. Tachtig procent reductie kon gehaald worden (378°C, 7000h\(^{-1}\)) bij een overdosis van 10-20 procent NH\(_3\) equivalenten zonder ammoniakuitstoot. Stappen in de NO\(_x\) output van de dieselmotor tot 100 ppm (25% relatief) resulteerden in slechts 10 ppm verandering van de NO\(_x\) concentratie na de katalysatoren.

Een nadeel van dit systeem is de grote sulfaatproduktie bij hogere temperaturen. In de experimenten die met de Pd oxydatie katalysator gedaan zijn was dit niet van belang aangezien met een laag zwavelige (< 10 ppm) diesel gewerkt werd. Deze sulfaatemissie zou ook voorkomen kunnen worden bij 0.05 gewicht procent zwavel houdende diesel als de nieuwe cerium katalysator gebruikt wordt.
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Curriculum Vitae

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