

## Evaluation of Ammonia Slip Catalysts

*Master's Thesis in the Master's programme Innovative and Sustainable Chemical Engineering*

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Department of Chemical and Biological Engineering  
*Division of Chemical Engineering*  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Göteborg, Sweden 2013  
Master's thesis 2013



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Cover:  
Diesel exhaust aftertreatment system (Source: Johnson Matthey).

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### ABSTRACT

On-road transportation produces more than 20% of the air pollution. European emission standards are gradually establishing more restrictive limits on exhaust pipe gases. Euro VI standard will be fully applied in January 2014, setting new upper bounds for heavy duty vehicles. NO<sub>x</sub> maximum emissions are specially restricted, which leads to work under over-stoichiometric ammonia conditions. It increases the chances for ammonia to slip, requiring an efficient Ammonia Slip Catalyst to mitigate the release. It is made up of a lower Pt layer, in which NH<sub>3</sub> is oxidised into NO<sub>x</sub>, and an upper SCR layer, which reduces NO<sub>x</sub> with the stored NH<sub>3</sub>.

Design of experiments has combined different length, Pt load and SCR coating thickness, giving rise to 10 ammonia slip catalyst designs. They have been tested in heavy duty diesel engine bench in Johnson Matthey AB test cells. A pre-study of 4 of the catalysts has allowed getting an idea of catalysts functioning and checking the testing procedure. It consists of a conditioning and a urea swing, in which different temperatures (from 200°C up to 450°C) and ammonia to NO<sub>x</sub> ratio (ANR=1.0, 1.2, 1.4) are evaluated. The full study program has run all the catalysts twice, before and after the hydrothermal oven ageing. Temperature values at different radial, N<sub>2</sub>O formation, NH<sub>3</sub> slip and NO<sub>x</sub> conversion of the Ammonia Slip Catalysts have been the responses of interest.

The experimental data has been analysed by means of three methods. The overall performance has examined sums of averages of different periods of the experiment according to the operating conditions. Factorial analysis has revealed the significant factors on the responses when different situations apply. Finally, linear regression tools have brought representative models for the responses for temperature and ANR values tested.

Overall performance and regression analyses indicate that a catalyst with higher length, medium Pt load and thick SCR coating heads up the ranking from an overall point of view, so breaking down the analyses other catalysts become also suitable depending on the conditions.

Further research on these catalysts could confirm the findings of this project.

Key words:

Ammonia Slip Catalysts, Euro VI, Diesel, Heavy-Duty Vehicles, Dual layer, Platinum, SCR.



# Contents

ABSTRACT	I
CONTENTS	III
PREFACE	V
NOTATIONS	VI
1 INTRODUCTION	1
1.1 Background	1
1.2 Objective	1
2 LITERATURE REVIEW	2
2.1 Engine emissions	2
2.2 Legislation	2
2.3 Diesel aftertreatment system	5
2.3.1 Ammonia-SCR	6
2.3.2 Ammonia Slip Catalyst	8
3 GENERAL PROCEDURE	10
4 EXPERIMENTAL METHODOLOGY AND EQUIPMENT	11
4.1 Design of Experiments	11
4.2 Catalyst design factors	13
4.3 Engineering experimental design factors	15
4.3.1 Experimental set-up	15
4.3.2 Experimental methodology	17
4.3.3 Hydrothermal oven ageing	20
5 RESULTS AND ANALYSIS OF EXPERIMENTS	21
5.1 Pre-study	21
5.1.1 Temperature profile	21
5.1.2 Testing procedure	21
5.2 Full study	22
5.2.1 Temperature profile	22
5.2.2 Overall performance analysis	24
5.2.3 Factorials	26
5.2.4 Regression	30
6 DISCUSSION	37
7 FINAL REMARKS	39
7.1 Conclusions	39

7.2	Recommendations	41
8	REFERENCES	42
	APPENDICES	44
	Appendix 1. Vehicle Categories	45
	Appendix 2. Measurement procedures	46
	HC	46
	NO <sub>x</sub>	47
	CO	47
	CO <sub>2</sub> /O <sub>2</sub>	48
	N <sub>2</sub> O	48
	NH <sub>3</sub>	49
	Appendix 3. Pre-study results and analysis	50
	Appendix 4. Full study results and analysis	51
	Temperature profile	51
	Factorials	53
	Regression	54

## Preface

This MSc Thesis has been conducted in the company **Johnson Matthey**, at its technical centre in Gothenburg. The work in the company has last from the 21<sup>st</sup> of January 2013 until the 31<sup>th</sup> of May 2013.

*Johnson Matthey is a global company with a focus on catalytic and other specialized materials and systems. With a strong global network of technical centres and manufacturing plants, Johnson Matthey is a successful supplier of emission control solutions to major engine and vehicle manufacturers on five continents. Founded in 1817 and headquartered in Royston (UK), Johnson Matthey belongs to the 100 largest companies on the London stock market.*

I would like to offer my gratitude to the company Johnson Matthey AB for giving me the opportunity of working in such an interesting project. Especially I would like to thank the supervisor at the company, Per Marsh ([per.marsh@matthey.com](mailto:per.marsh@matthey.com)), whose support, help and expertise has been very valuable throughout the work.

I also would like to give gratitude to the examiner at Chalmers, Jonas Sjöblom, ([jonas.sjoblom@chalmers.se](mailto:jonas.sjoblom@chalmers.se)) for his guidance and assistance in the complex “DoE world”.

Furthermore, I want to thank my family for encouraging me during the project and supporting economically my time in Sweden. Without them this would have never been possible.

Finally, I would like to thank my friends who made these two years in such a cold country amusing but especially unforgettable.

*Gothenburg, May 2013*

Elena Sala Gil

# Notations

## Roman upper case letters

Tarea	Weighted area temperature
R <sup>2</sup>	Coefficient of determination of a linear regression

## Roman lower case letters

n <sub>lo</sub>	Engine speed at 50% of the declared maximum net power
n <sub>hi</sub>	Engine speed at 70% of the declared maximum net power

## Abbreviations

JM AB	Johnson Matthey AB
PM	Particulate Matter
LDV	Light Duty Vehicles
HDV	Heavy Duty Vehicles
WHSC	World Heavy Steady state Cycle
WHTC	World Heavy Transient Cycle
NMHC	Non-Methane Hydrocarbons
THC	Total Hydrocarbons
DOC	Diesel Oxidation Catalyst
CSF	Catalysed Soot Filter
SCR	Selective Catalytic Reduction
NAC	NO <sub>x</sub> Adsorber Catalyst
DEF	Diesel Exhaust Fluid
ASC	Ammonia Slip Catalyst
ANR	Ammonia to NO <sub>x</sub> Ratio
PGM	Platinum Group Metals
Av.	Average
CatX	Catalyst design number X
L	Length
PQ	Pure Quadratic error
LOF	Lack Of Fit error
FID	Flame Ionization Detector
IR	Infrared
GFCR	Gas-Filter Correlation Radiometry
NDIR	Non-Dispersive Infrared Sensor

❖ This symbol represents an observation comment

# 1 Introduction

## 1.1 Background

Air pollution has a great impact on human health and the environment. Air quality has improved over the last years, but there are still significant air quality problems, especially in urban areas and highly dense populated regions. Authorities and citizens are more and more concerned about this problem.

Exhaust gases emissions are one of the main contributors to the air pollution, so having full control of them is nowadays a critical matter.

In a short time period, a new European Emission Standard for heavy-duty vehicles (Euro VI) will be applied, setting new upper limits for the gases escaping from the tail pipe. Significant  $\text{NO}_x$  reduction is required, which demands (for diesel engines) higher amounts of Ammonia, increasing its probability to slip to the environment.

More complex aftertreatment system is needed to prevent the  $\text{NH}_3$ -slip. A highly selective Ammonia Slip Catalyst becomes an essential part of the aftertreatment system, composed of Diesel Oxidation Catalyst, Catalysed Soot Filter, Selective Catalytic Reduction and the Ammonia Slip Catalyst.

Different designs of the Ammonia Slip Catalyst have been studied in this project.

## 1.2 Objective

The purpose of this work has been the application at industrial scale of chemical reaction kinetics and catalysis, conducted on the basis of Design and Analysis of Experiments.

The main aims of this project dealing with the technical part have been:

- Developing an efficient procedure for the design of an optimal Ammonia Slip Catalyst for a heavy-duty diesel engine.
- Finding the optimal test method for evaluating the catalysts performance in order to achieve the following targets:
  - minimum  $\text{N}_2\text{O}$  production
  - minimum  $\text{NH}_3$ -slip concentration
  - maximum  $\text{NO}_x$  conversion
- Choosing an ASC design fulfilling the above-mentioned targets within the factors ranges tested.

From an academic point of view, it has been desired:

- Getting to know the exhaust composition and its aftertreatment solutions.
- Learning about the state-of-the-art in the heavy duty aftertreatment  $\text{NO}_x$  reduction options.
- Increasing the knowledge in Design of Experiments as a development tool.
- Being able to analyse the results from the experimental running.
- Learning about developing a method to evaluate Ammonia Slip Catalysts.
- Getting an initial approach of how to develop a project.

## 2 Literature Review

This chapter includes the basic theoretical knowledge for a good understanding of the project.

### 2.1 Engine emissions

Engine exhausts are composed of a gaseous part, mainly hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ); a liquid portion containing unburned fuel and lubricant oils; and a solid part of dry carbon. Liquids and solids constitute what is known as particulate matter (PM).

All these pollutants have severe effects in both the natural environment as well as the living beings health. CO is poisonous; HCs are carcinogen and photochemical active substances, promoting the tropospheric ozone and the photochemical smog; and  $\text{NO}_x$  produces acid rain as well as photochemical smog and eutrophication. PM forms aerosols of ultrafine which are highly responsible of respiratory problems. (1)

Gasoline engines produce lower amounts of PM, but higher levels of exhaust gases in comparison with diesel engines. Diesel engines are being increasingly more demanded for their convenient combination of fuel efficiency (l/km) and power density ( $\text{W}/\text{m}^3$ ) as well as their high lifetime in comparison with gasoline engines. They work under lean conditions, that is, they use excess air in the combustion, which lowers the fuel consumption and leads to mostly complete combustions. This fact decreases  $\text{CO}_2$  emissions, one of the main contributors to global warming through the green-house effect.

Significant progress has been done on the engine itself in order to reduce its harmful exhaust gases but an aftertreatment system is still needed to mitigate the undesired products from releasing for legislative (see 2.2) and environmental reasons.

### 2.2 Legislation

European emission standards establish the allowed limits for exhaust pipe emissions of new vehicles in the European Union market. They apply to most vehicle types including cars, trucks, trains, tractors, etc., excluding seagoing ships and aeroplanes. For each vehicles family different emission stringency applies.

Compliance is warranted by standardized test cycles, compulsory to be sold in the EU. New standards do not apply to vehicles already on roads.

No specific technology is mandated to be used in order to meet the legislation limits, but the available one is considered when setting the standards.

The emissions restrictions are gradually introduced by means of stages. The stages are typically known as Euro 1, Euro 2, Euro 3, etc. for Light Duty Vehicles (LDV) and Euro I, Euro II, Euro III, etc. for Heavy Duty Vehicles (HDV), that is buses and trucks. (2)

Focusing on HDV (object of this project), the present standard is the Euro VI. It was approved in January 2012 by the Working Party Pollution and Energy and finally adopted by the World Forum on June 2012. It entered in force gradually from the beginning of 2013 and will be fully applied in January 2014. It will affect most of the countries of the European Union. (3)

Euro VI introduces global harmonized test procedures covering typical driving conditions in the European Union, USA, Japan and Australia. The World Heavy-Duty Transient Cycle (WHTC) consists of a second based sequence of normalized speed and torque values. The World Heavy-Duty Steady state Cycle (WHSC) tests 13 modes of operation, in which different speeds and loads are combined within the conditions range for heavy-duty vehicles. Diesel engines (compression ignition) use both of the tests, the transient and the stationary; while gasoline engines (spark ignition) only require transient testing. (4)

HDV emissions regulations for carbon monoxide (CO), hydrocarbons (HC), non-methane hydrocarbons (NMHC), methane (CH<sub>4</sub>), nitrogen oxides (NO<sub>x</sub>) and particulate matter (PM) from the 1980's can be seen in Table 1 and Figure 1. (3)

❖ HC (many times defined as total hydrocarbons, THC) can be split into NMHC and CH<sub>4</sub>. Methane has very long life in the atmosphere and large and relatively constant mixing ratios in the troposphere. NMHC live from 30 to 30000 times shorter than methane, showing greater variability and coming from more localized sources. Since such sources usually are of anthropogenic origin, total concentrations of NMHCs are often used as a measure of air pollution (5). HC is only applied to diesel engines and NHMC and CH<sub>4</sub> to gasoline engines.

Table 1: Maximum emission levels allowed for heavy-duty vehicles engines since the 1980's.

Emission level	Year of enforcement	Operating conditions	Max.emissions (g/kWh)					
			CO	HC	NMHC	CH <sub>4</sub>	NO <sub>x</sub>	PM
Euro VI	2014	Steady state	1.5	0.13	-	-	0.4	0.01
		Transient	4	-	0.16	0.5	0.46	0.01
Euro V	2008	Steady state	1.5	0.46	-	-	2	0.02
		Transient	4	-	0.55	1.1	2	0.03
Euro IV	2005	Steady state	1.5	0.46	-	-	3.5	0.02
		Transient	4	-	0.55	1.1	3.5	0.03
Euro III	2000	Steady state	2.1	0.66	-	-	5	0.1
		Transient	5.45	-	0.78	1.6	5	0.16
Euro II	1996	Steady state	4	1.1	-	-	7	0.15
Euro I	1991	Steady state	4.5	1.1	-	-	8	0.36
Euro 0	1988	Steady state	11.2	2.4	-	-	14.4	-

Euro VI levels introduce a reduction of the allowed maximum limits of 50% or even more with respect to Euro V, except for CO that remains the same.

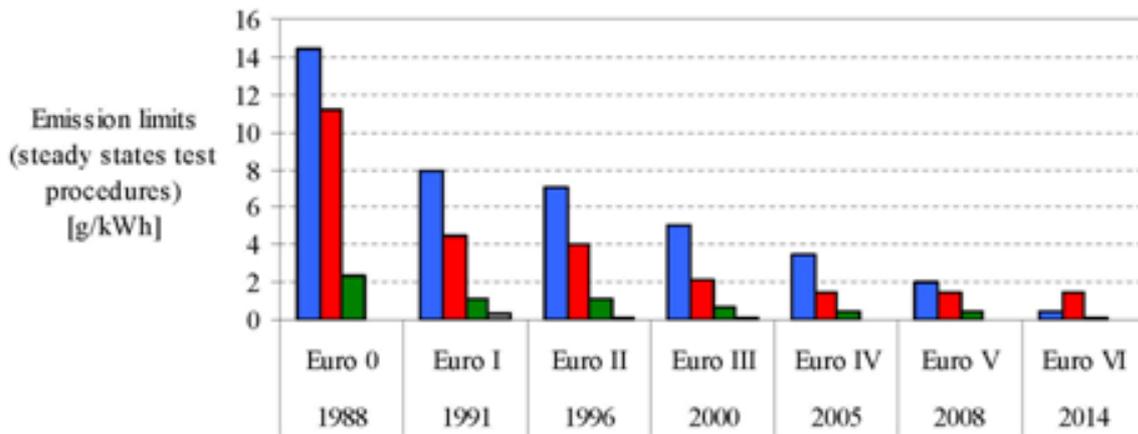


Figure 1: Emission limits for NO<sub>x</sub> (blue bar), CO (red bar), HC (green bar) and PM (grey bar) for heavy duty vehicles engines since the 1980's.

Furthermore, an ammonia concentration limit is applied. Ammonia is poisonous if inhaled in great quantities and it is an irritant to eyes, nose and throat in lesser amounts. Ammonia-air mixtures can become explosive in certain proportions (1 volume NH<sub>3</sub> to 2 volumes air) and it is even more dangerous if mixed with oxygen. (7) It is allowed a maximum of 10 ppm for diesel (WHSC + WHTC) and gasoline (WHTC) engines. (6)

For N<sub>2</sub>O gas there is not an established limit yet, but probably it will be set in future updates of the standard. Nitrous Oxide is a green-house effect gas with an impact of about 300 times higher than CO<sub>2</sub>. (8)

Maximum emissions compliance has to be demonstrated over the normal useful life period of the engine. The different categories of heavy duty vehicles (see Appendix 1, Table 17) require diverse emission durability periods according with Euro VI:

Table 2: Emission durability periods of Euro VI.

Vehicle Category <sup>1</sup>	Euro VI
<b>N1, M1 and M2</b>	160 000 km / 5 years
<b>N2</b> <b>N3 ≤ 16 ton</b> <b>M3: Class I, Class II, Class A, Class B ≤ 7.5 ton</b>	300 000 km / 6 years
<b>N3 &gt; 16 ton</b> <b>M3: Class III, Class B &gt; 7.5 ton</b>	700 000 km / 7 years

Table 2 shows the mileage or period of time (whichever sooner) along which the engine must fulfil the maximum limits exposed in Table 1. (6)

<sup>1</sup> Mass designations (in metric tons) are "maximum technically permissible mass".

## 2.3 Diesel aftertreatment system

Figure 2 shows the pathway of the exhaust gas since it is produced in the diesel engine until it is released to the air.

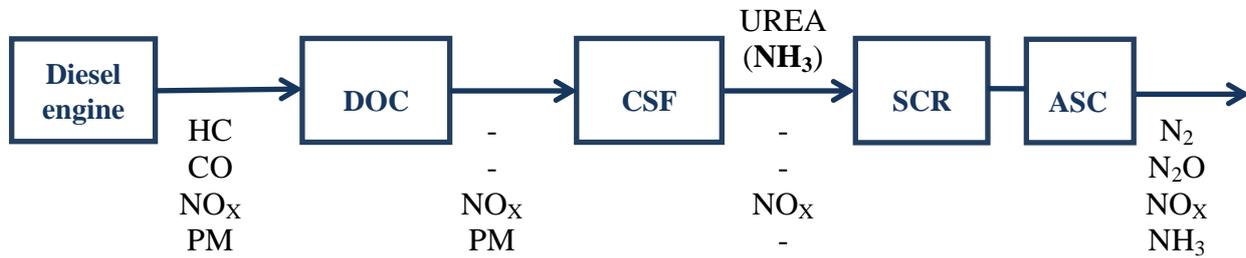
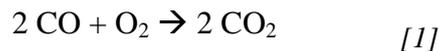


Figure 2: Block diagram of the aftertreatment system.

Hydrocarbons and carbon monoxide are oxidized by the Diesel Oxidation Catalyst (DOC) whose active species correspond to the Platinum Group Metals (Pt and Pd). It preferentially promotes reactions [1] and [2], since diesel engine works under lean conditions, i.e. the air/fuel ratio is higher than 1.



NO<sub>x</sub> and PM exhaust contents are coupled inversely. Working at low temperatures (poorer fuel efficiency) produces low NO<sub>x</sub> but high PM, whereas high temperature operations give rise to high NO<sub>x</sub> and low PM.

PM is a mixture of soot, carbon-based particles formed during fuel combustion, and ash, metal-based particles from engine oil burning.

Particulate matter is retained by a wall-flow filter catalysed by platinum. Half of the channels are sealed at the inner face in a chessboard pattern and the remaining alternate channels are sealed at the outer face. The exhaust is forced to pass through the walls on which 90% of the particles are deposited, as it can be observed in Figure 3.

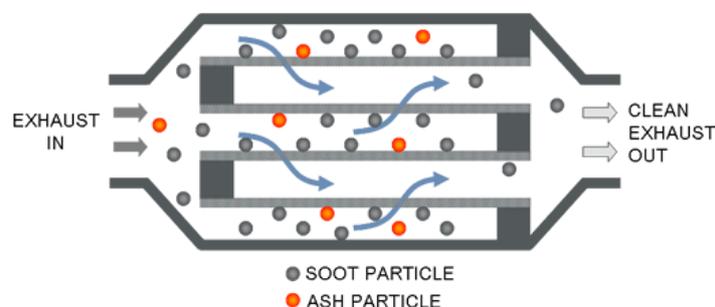
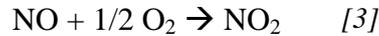


Figure 3: Diesel Particulate Filter mode of operation. (9)

The Catalysed Soot Filter (CSF) has to be regenerated, burning the retained PM what avoids it to block the filter.

Regarding nitrogen oxides, actual exhausts contain more than 90% of the NO<sub>x</sub> as NO, which is partly oxidized to NO<sub>2</sub> at the DOC and the CSF:



After those two catalysts, the NO<sub>x</sub> is ideally 50% in the form of NO and 50% as NO<sub>2</sub>, but still the nitrogen oxides need to be reduced. Different alternatives are available: Selective Catalytic Reduction (SCR), NO<sub>x</sub> Absorbers Catalysts (NACs), or plasma. The non-thermal plasma has been promising at lab-scale but it is not considered at a commercial level. NO<sub>x</sub> Adsorbers Catalysts are special traps which chemically adsorb nitrogen oxides onto the alkaline metal oxides. The saturation of the trap leads to a short regeneration step. Lean conditions turn into rich (air to fuel ratio lower than 1) which promotes NO<sub>x</sub> to be desorbed and reduced to N<sub>2</sub> by the precious-metal-containing washcoat.

Selective Catalytic Reduction consists of using a reductant substance, such as hydrocarbons or ammonia, to reduce NO<sub>x</sub>. Hydrocarbon-SCR uses fuel (already present in the exhaust or injected) as a reductant source producing the following desired reaction [4]:



The poor selectivity of reaction [4] makes N<sub>2</sub>O formation selectivity very high and also favours reaction [5] to occur.



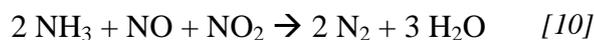
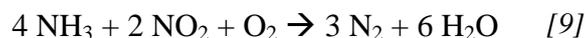
Ammonia-SCR has shown to be the highest selectivity option to NO<sub>x</sub> reduction.

### 2.3.1 Ammonia-SCR

The safest way of supplying ammonia to the SCR is by means of urea in aqueous solution form, called AdBlue® for Europe and Diesel Exhaust Fluid (DEF) for North America. It contains 32.5% in weight of urea in deionised water. Urea decomposition takes place in both the gas phase (reaction [6]) and the catalyst (reaction [7]):



Ammonia and NO<sub>x</sub> present different selective reaction pathways according to the relative amounts of the reactants:



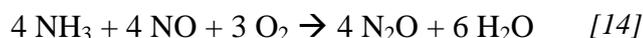
Reaction [8] is referred to as the “standard SCR reaction”. Reaction [10] is much faster than [8], while reaction [9] is much slower than [8]. Anyway these three last mentioned reactions occur simultaneously when reactants contain both Nitrogen Oxides. (10)

Non-selective ammonia oxidation reactions also could take place:



Reactions [11] to [13] oxidize ammonia by  $\text{O}_2$  and it is no longer available for  $\text{NO}_x$  reduction. The partial oxidation (reaction [11]) produces no unwanted products but the total oxidation (reaction [12] to [13]) does. (1)

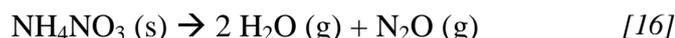
Other possible occurring non-selective reaction produces the undesired nitrous oxide:



Hence,  $\text{N}_2\text{O}$  comes from 2 sources:  $\text{NH}_3$  oxidation by  $\text{O}_2$  (reaction [13]) and  $\text{NH}_3$  reaction with  $\text{NO}$  (reaction [14]).

Previous experiments show that at low temperatures Nitrous Oxide contains one nitrogen from each reactant, so that reaction [14] prevails; while at high temperatures both nitrogens come from the same reactant, pointing towards reaction [13]. (10)

Temperatures lower than  $200^\circ\text{C}$  could produce  $\text{NH}_4\text{NO}_3$ , an explosive compound, by means of reaction [15]. Later on, it could decompose releasing  $\text{N}_2\text{O}$  (reaction [16]).



An example of a highly active and selective catalyst for the ammonia-SCR catalyst is vanadium ( $\text{V}_2\text{O}_5$ ), which is the one used for this project. (1)

The Ammonia-SCR provides maximum efficient  $\text{NO}_x$  removal as long as a significant amount of  $\text{NH}_3$  is stored on its surface. This could produce ammonia desorption during high temperature lapses since it affects the catalyst storage capacity. Furthermore, at some conditions, over-stoichiometric ammonia availability is also needed what increases even more the  $\text{NH}_3$  slips.

### 2.3.2 Ammonia Slip Catalyst

Table 1 shows that  $\text{NO}_x$  allowed levels should be reduced 80% between Euro V and Euro VI normative. It requires higher ammonia storage capacity of the catalyst and even more over-stoichiometric ammonia (more aggressive urea dosing), what leads to greater amounts of ammonia slip.

Both environmental and legislative reasons show that preventing the unreacted- $\text{NH}_3$  from slipping out of the exhaust pipe is a necessity.

A proposed option is its oxidation to  $\text{N}_2$ . Figure 4 shows different  $\text{NH}_3$  oxidation pathways corresponding to reactions [11], [12] and [13].

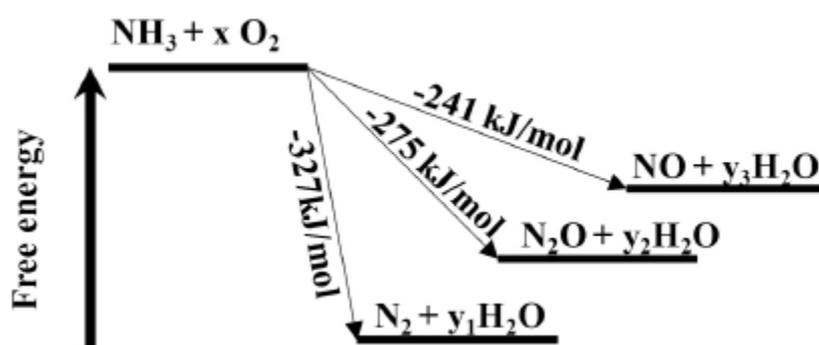


Figure 4: Free energy for ammonia oxidation to different products.

$\text{N}_2$  is the most thermodynamically favourable product although  $\text{N}_2\text{O}$  or  $\text{NO}$  are also feasible. The selectivity towards them depends on catalyst properties and reaction conditions, albeit the three species can be normally found.

For this reason, not only ammonia oxidation in air can be done since almost certainly the undesired  $\text{N}_2\text{O}$  and  $\text{NO}$  would also be present. A more complex system is required: the Ammonia Slip Catalyst (ASC).

The ASC must show high activity and selectivity towards  $\text{N}_2$ , be able to work in a broad range of conditions dealing with temperature, flow rate and exhaust gas composition and also present a good performance against hydrothermal ageing. (11)

First generation of ASCs used Pt supported on an appropriate oxide, showing a very low selectivity towards  $\text{N}_2$ , but high for  $\text{N}_2\text{O}$  and  $\text{NO}_x$ . Then, a dual layer Ammonia Slip Catalyst was proposed. Dual layer architectures are quite common in automotive exhaust catalysts.

The dual layer ASC internal structure is schematically represented in Figure 5.

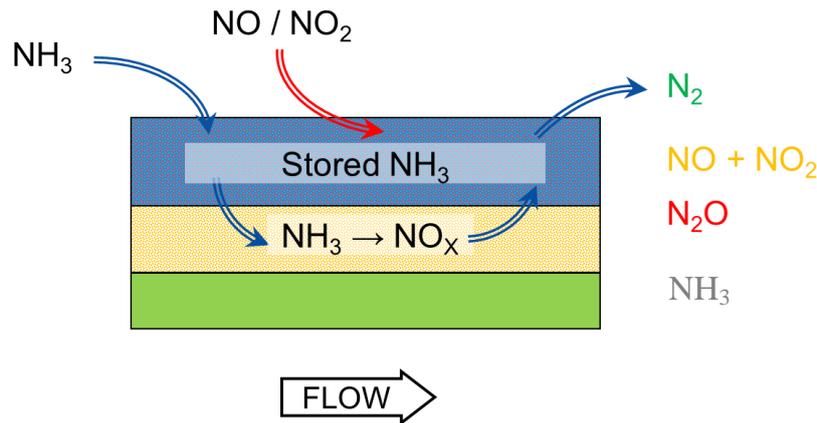


Figure 5: Internal structure of the Ammonia Slip Catalyst.

The substrate is a ceramic monolith made of cordierite. Cordierite is composed of several inorganic oxides with high thermal and mechanical resistance, so that large variations of temperature or mechanical stresses cannot spoil the catalyst. The honeycomb shape with very fine squared channels provides a high surface area due to its large structure of pores. (1)

The lower layer is the base metal oxide washcoat containing the platinum active species, where the high rate  $\text{NH}_3$ -oxidation reactions [11] to [13] take place, apart from the NO oxidation to  $\text{NO}_2$ , represented by reaction [3]. Note the very low selectivity to  $\text{N}_2$  (reaction [11]).

The SCR coating corresponds with the top layer where the Ammonia is stored to reduce (reactions [8] to [10]) the produced  $\text{NO}_x$  in the oxidation reactions of the previous layer as well as the non-reduced  $\text{NO}_x$  coming in the flow from the SCR catalyst. In this way, a portion of the  $\text{NH}_3$  is oxidized and other portion is stored. Unfortunately, reaction [14] could also take place, producing the undesired  $\text{N}_2\text{O}$ .

Kamasamudram et al. (2011) states that  $\text{NH}_3$  storage is instantaneous (generally assumed to have zero activation energy) so that preventing all the Ammonia from getting oxidized on the platinum component. It shows different performance of the Ammonia Slip Catalyst depending on temperature. At low temperatures,  $\text{NH}_3$ -storage profile approaches that of the SCR, while it declines rapidly with temperature when light-off of the Pt-based component is achieved. Oxidation of ammonia competes with storage. (11)

However, Scheuer et al. (2011) reports that the SCR layer acts as a diffusion barrier for the ammonia to achieve the platinum layer. So that the thicker SCR, the lower  $\text{NH}_3$  conversion, but the higher  $\text{N}_2$  selectivity, since the Pt layer loses participation in the process. Then, a trade-off is needed as long as the type SCR material is known. If not, a higher effective diffusivity material could be chosen, so that higher  $\text{NH}_3$  conversion could be achieved without losing  $\text{N}_2$  selectivity. (12)

Therefore, the ASC represents a complex superposition of a platinum-based oxidation component bringing high activity and a SCR component giving high  $\text{N}_2$ -selectivity.

Ammonia Slip Catalysts are in research level to prevent unreacted- $\text{NH}_3$  from slipping out to the environment. (11)

- ❖ Chemical reactions introduced in section 2.3 correspond to Ammonia to  $\text{NO}_x$  ratio equal or higher than 1, which matches with the ANR range that is going to be tested.

### 3 General Procedure

The general procedure of the process has dealt with the design and analysis of experiments whose main parts are conducted along the project.

First of all, a **design** of the catalysts and the engineering experimental factors have been done in which the values of the different variables are decided. They can be seen in Table 3. A **pre-study** of these designs has taken place, just running selected designs to get an idea of how the full test program would work. It has provided information about the magnitude range of the output measured variables, the adequacy of the test procedures, the accuracy of the measurement technology, etc. This insight has permitted predicting the behaviour of other catalysts designs within the range of the pre-tested permitting a more efficient planning of the full test program. The **test procedures** have been revised according to the few conducted experiments.

Once there is a little clue of how the catalysts designs might behave, the **planning** of the full test program has taken place, considering experimental order, running time for each sample, nature of the design factors, possible interaction between them, maximum decrease of the experimental error, and many other factors dealing with the design of the experiments. The **full** program of **experiments** has been run in the test cells the company owns ensuring that it is hold in the proper safety and health conditions. This step has comprised three phases: a first experimental run of all the catalyst, a hydrothermal oven ageing, and a second and last run of the ASCs to evaluate the effect of the ageing.

The **evaluation** of the **data** has been one of the most important parts of the process, in which differences amongst the output compositions of the diverse catalyst designs have been detected and probably explained.

All the information needed to give a conclusion regarding the optimum catalyst design and the efficiency of the ASC evaluation method has been already collected. **Internal and external reports** have been written. The internal one is a detailed report where all the information regarding the experiment is contained. The external report avoids or masks the secret details of the experimental settings and results. The general conclusions and findings have been reported in both documents.

A draft of the internal report has been handed-in (just in JM AB) for checking its adequacy and expected outcomes. A draft of the external version has been evaluated by the technical directors of the company who approved its publication.

The final internal report has been handed-in and presented in the company, while the final external one in Chalmers University of Technology.

## 4 Experimental Methodology and Equipment

### 4.1 Design of Experiments

Experimentation plays an important role in product development. Observation of the system when working allows elucidating how it operates, dealing to an empirical model of the system performance. The consistence of the model with reality depends to a large extent on the way data are collected, so it is important to approach a suitable strategy of experimentation. A well-design experiment maximizes the amount of information from the minimum number of experiments, gains control over reliability of the performance and enhances an easy and correct evaluation of the results.

To approach the design and analysis of experiments by a statistical method, Montgomery (2005) proposes the following sequence of steps:

- a) Recognition and statement of the object of experimentation. Everyone involved in the experiment must have an idea and agree of why and with which purpose Ammonia Slip Catalysts are going to be studied. That is why team working and regular updating is very important during the project, not to lose the overall objective of characterizing or factor screening of these new catalysts.
- b) Selection of response variables.  $\text{NO}_x$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$  contents at the pipe output are considered to provide useful information about the catalyst performance, since minimizing them is one of the main objectives of the project.
- c) Choice of factors, levels and ranges. The factors influencing the performance of the exhaust aftertreatment can be classified as:
  - Potential design factors → They are desired to be varied in the experiment. A further classification is:
    - *Design factors* are those actually selected for the design, i.e. length, Pt loading and SCR coating thickness; and for the operation such as ammonia to  $\text{NO}_x$  ratio.
    - *Held-constant factors* are not of interest for the aim of the project, so they are fixed. It is the case of the speed, which is set to C value (see 4.3.2).
    - *Allowed-to-vary factors* represent the variability of the catalysts to which the design factors are applied. It means the little possible existing differences between the theoretical levels values and the real catalyst ones.

Held-constant factors and allowed-to-vary factors are assumed to have little effect on the responses.

- Nuisance factors → They may have large effect to consider and are often classified as follows:
  - *Controllable factors* like the heavy duty engine bench used or its torque which defines the operating temperature. Other examples could be the DOC, CSF or SCR catalysts considered in the experiments.
  - *Uncontrollable factors* such as the temperature profile of the ASC along its radius. It cannot be controlled in any way, but measured and therefore considered.
  - *Noise factors* are those natural and uncontrollable factors that cannot be controlled in the experiment.

This whole step c) requires of process knowledge, provided by a combination of practical experience and theoretical understanding.

- d) Experimental design. The experimental design is a simple step as long as the pre-experimental planning phases (a, b and c) are conducted properly. It comprises the choice of the design having in mind the three basic principles of experimental design: randomization, replication and blocking. Randomization is important when running order may affect the response. It is not the case of this project, in which a conditioning phase takes place before each catalyst test. Replication corresponds to independent repetitions of each factor combination, allowing estimating the experimental error as well as providing more precise parameters calculation. Catalyst samples are quite expensive, so replication is not possible to be carried out. Repeated measurements have been the solution, which provide variability estimation. Blocking improves the precision of the results as it mitigates or freezes the error transmitted from nuisance factors.

When choosing the most adequate experimental design it is important not to forget about the overall objective. There are different strategies of experimentation, such as the “best-guess approach”, used by professionals very experienced in the process that it is being studied, since the combination of factors tried does not follow any pattern, just the experimenter intuition. Other approach could be the “one-factor-at-a-time” strategy, which starts by running a factors combination baseline and changing only one factor level in successive runs. It does not provide information about interaction effects, just main effects. The best approach when coping with several factors is factorials, since they try all factors combinations providing high amount of information regarding their joint effect on a response with low number of experiments.

### 2<sup>k</sup> design

In this project it is aimed to characterize the process, hence number of factor levels is convenient to be low. 2<sup>k</sup> is a suitable design for factor screening. It consists of k factors, each at 2 levels and the can be of quantitative or qualitative nature.

Setting two levels for each factor drives to assume that the response is approximately linear over the chosen range. It can be a reasonable assumption as long as a complete replicate design, i.e. 2 or more samples for each factor combination, is available as all interaction effects can be calculated. In this way, a first-order model with main and interaction effects terms is able to represent some curvature in the response function. However, sometimes the linearity assumption is violated and a second-order model (pure quadratic effects) is more appropriate. To check it in order to avoid this complex model, it is possible to add replicated runs at the design centre (if factors are quantitative), the so-called centre points. They do not affect the effect estimates of the 2<sup>k</sup> factorial and allow independent error estimation.

- e) Performing. It is convenient before running the full experiment to do a pre-study to check the measurement system, to have an idea of the response range, to test the experimental error, etc. It permits revising previous steps, introducing convenient changes if considered.

Later the catalyst full program can be conducted and it is important to monitor the process to check that it is going as expected.

- f) Statistical Analysis Data. Results and conclusions are objective if statistical methods are used to analyse the data, which should not be complex if the experiment has been carried out as designed. Often simple graphical methods are a key tool in the analysis; this is the case of this project in which graphical representation of the different ASCs performance provides a lot of the needed information. Also, hypothesis testing and confidence interval play an important role as well as the obtainment of an empirical model that correlates

measured emissions with the design factors. Residual analysis and model adequacy checking are precious steps for further analysis.

Regarding the empirical model, linearity assumption in the factor effects is a concern; that is why centre points analysis becomes essential on the process.

- g) Conclusions and Recommendations. Once the NO<sub>x</sub>, N<sub>2</sub>O and NH<sub>3</sub> emissions data are analysed, it is time to draw conclusions about the optimal catalyst design.

The explained process is sequential since after conclusions are presented probably new questions rise up, so new hypothesis are formulated and so on. In this project, for time restriction, the analysis of the results has dealt to the optimum catalyst choice. (15)

- ❖ The analysed responses are assumed to follow normal distributions, so that, the hypothesis testing can be done by the t-test or the F-distribution (depending on the case) under a 95% or a 99% level of confidence.

## 4.2 Catalyst design factors

Multifunctional catalyst architectures, such as the ASC, require a higher number of design parameters in comparison with conventional single layer catalysts (12). For this reason, 2<sup>k</sup> design represents a good choice.

The catalyst design factors are length, platinum load, and SCR coating thickness. Therefore it makes up a 2<sup>3</sup> factorial, represented by 8 different factors combinations.

Furthermore, two replications at the centre point are considered to give rise to a total of 10 catalyst designs. Their factors levels, provided by JM AB according to its experience in the field, can be observed in Table 3.

Table 3: Original factors levels.

Catalyst design	Length	Pt. load	SCR coating thickness
1	Medium	High	Nominal
2			Low
3	High	Medium	Nominal
4			Low
5	Medium	Low	Nominal
6			Low
7	Medium	Medium	Average
8			Average
9	Low	Medium	Nominal
10			Low

Regarding the SCR coating thickness, *Nominal* values represent the current dimension for the on-use catalysts. *Low* values correspond with a smaller thickness. And *Average* is the medium value between *Nominal* and *Low*.

Catalyst 1 can be considered as a reference catalyst since it is the actual company product in the market.

Catalysts 7 and 8 correspond to the centre points.

Factors combinations of Table 3 are scaled and depicted on Figure 6.

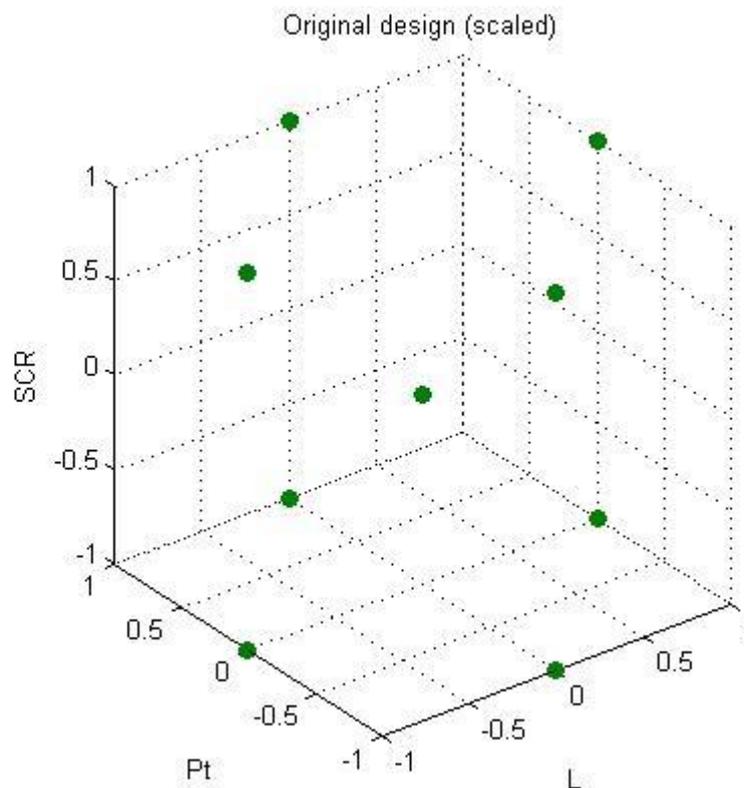


Figure 6: Original design of experiments.

This design representation could result inconsistent with what is expected from a  $2^3$  factorial: a cubic design with side edges parallel to factors axis, since it has been turned, showing more than 2 levels per factor.

In 5.2.3, it can be seen how it has been proceed with this drawback for the analysis of the results.

- ❖ Catalyst number 9 has been damaged during the testing preparation, so that the study has been carried out without it (see 5.2.3)

## 4.3 Engineering experimental design factors

### 4.3.1 Experimental set-up

The experimental runs are conducted in test cells provided by Johnson Matthey AB. They are properly equipped with fire alarms, gas detectors, etc. and other complex systems to ensure the safety of the workers and the equipment.

Conditions inside the test cells are usually atmospheric pressure, temperature around 20°C and a humidity value of approximately 10g/kg (water vapour/dry air). When the engine is being run, the ideal humidity thresholds comprise from 9.5 to 10.5g/kg.

The Ammonia Slip Catalysts are studied in a heavy duty engine bench with EuVI fuel. For availability reasons, the pre-study is conducted in a 5 litres Euro V engine, while the full study in a 7 litres Euro V engine. The differences between them are considered to be proportional, so that the evaluation of the results will end up at the same final conclusions.

Figure 2 depicted the actual pathway of the exhaust gas along the aftertreatment system, which is repeated in the experimental set-up as reality is desired to be reproduced. Figure 7 shows it, representing also the following measurements:

- PEATUR → Pressure After Turbo
- TEATUR → Temperature After Turbo
- TEBCT → Temperature Before Catalyst
- TEACT → Temperature After Catalyst
- R → Full set of sample measurements. R1 is the engine out sample line and R2 is the ASC outlet sample line.
- DP → Pressure Drop

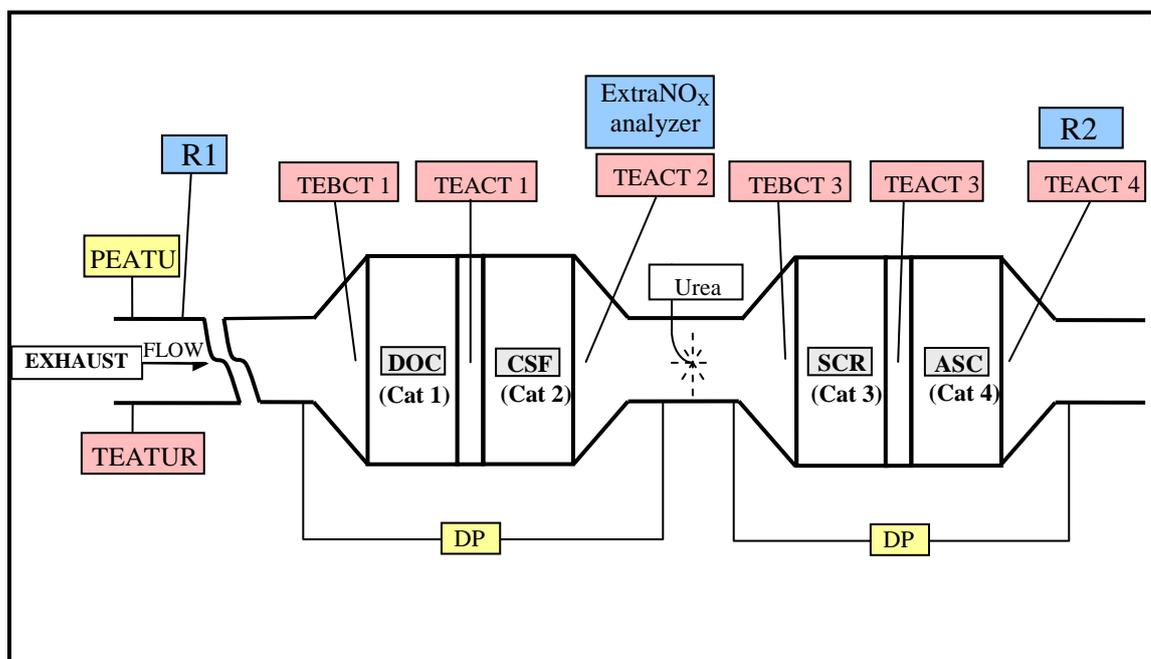


Figure 7: Outline of the testing set-up.

In the engine out (R1), HC, NO<sub>x</sub>, CO<sub>2</sub>/O<sub>2</sub> and CO contents are measured. In the aftertreatment out (R2), the same gases are registered, as well as N<sub>2</sub>O and NH<sub>3</sub>. NO<sub>x</sub> is also measured before the SCR and ASC as it can be seen in Figure 7. Appendix 2 explains the measurement principles of the in-situ analysers used to register the different gases contents.

Urea injection is made spraying, but the pipe between the CSF and the SCR is relatively longer than it appears in Figure 7 to allow urea and exhaust to mix uniformly.

Table 4 shows the characteristics of the aftertreatment catalysts used in the experimental set-up in combination with the ASC sample.

*Table 4: Aftertreatment catalysts characteristics.*

<b>Catalyst</b>	<b>Diameter x Length (inches)</b>	<b>Active substance load (g/ft<sup>3</sup>)</b>
<b>DOC</b>	10.5 x 4.6	40 g/ft <sup>3</sup>
<b>CSF</b>	10.5 x 10	15 g/ft <sup>3</sup>
<b>SCR</b>	10.5 x 4	-

DOC is a Pt/Pd catalyst, CSF includes only Pt and SCR is an extruded catalyst made of V.

The diameter of all four catalysts is 10.5 inches, a quite common value for heavy duty aftertreatment catalysts.

The substrates for the Ammonia Slip Catalysts are ceramic monoliths made up of cordierite with a cell density of 300cell/in<sup>2</sup> and a wall thickness of 5/1000inches, i.e. 300/5 cpsi substrates.

As the exhaust aftertreatment pipe is not thermally isolated and the operating temperatures are high, it is possible to have a thermal gradient in the radial dimension of the ASC. It could affect the exhaust flow to some extent, bringing different space velocities hence different residence times. It ends up in uneven conversions depending on the radius. Sukumar et al. (2012) have proved different selectivity to each of the products varying the space velocity.(16)

In order to study the temperature gradient in the ASC, thermocouples are integrated 15 millimetres deep (in the flow direction) at the rear face, where highest temperature variations could exist. These devices measure with an accuracy of ±1°C together with the deviation of ±1°C when registering the value electronically, ending up into a ±2°C overall possible error.

For the pre-study, they are uniformly distributed (north, south, east and west) in the whole diameter at the rear face as:

- 1 thermocouple in the centre (0%)
- 4 thermocouples at 66.68mm from the centre (50%)
- 4 thermocouples at 113.35mm from the centre (85%)
- 4 thermocouples at 126.68mm from the centre (95%)
- 4 thermocouples at 133.35mm from the centre (outer diameter, 100%)

In the full study, only one thermocouple at each considered radius is placed (see 5.1). The 5 devices are situated in the south pointing direction, which has shown greater variation. Figure 8 shows a representation of the thermocouples placement in millimetres.

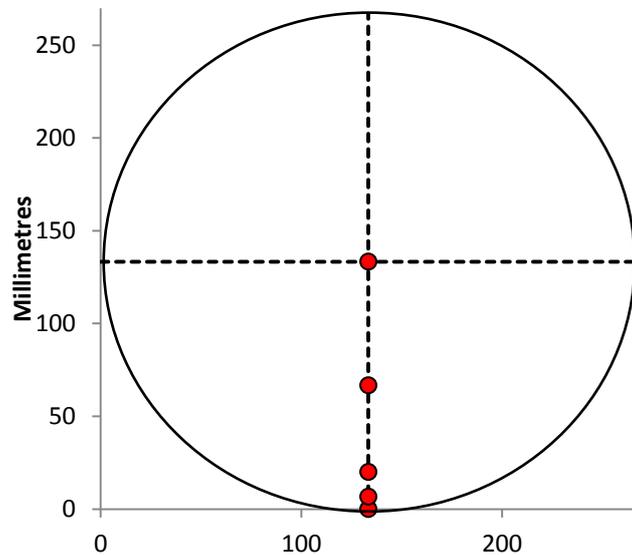


Figure 8: Thermocouples distribution on the rear face of the ASCs.

- ❖ The noted differences between the pre-study and the full study set-up are justified in section 5.1.

### 4.3.2 Experimental methodology

First step of the experimental part is the **assembly** of the set-up. Right after, the later on explained methodology is tried without urea, what is known as the **1<sup>st</sup> base line**. The purpose of it is elucidating the NO<sub>x</sub> release depending on the operating conditions and being able to calculate how much urea to inject in order to achieve the desired ammonia to NO<sub>x</sub> ratio (ANR) at the different experimental points. The **2<sup>nd</sup> base line** consists of running the experimental methodology (now with urea) without the ASC in order to know the exhaust composition after the SCR and analysing exclusively the ASC performance of the full program of experiments.

Some items later on mentioned require previous explanation:

- The engine is run at C speed which is a standardized value expressed as:

$$\text{C speed} = n_{10} + 75\% (n_{hi} - n_{10})$$

where  $n_{10}$  is the engine speed at 50% of the declared maximum net power, and  $n_{hi}$  is the engine speed at 70% of the declared maximum net power.

C speed represents the high flow conditions, i.e. the engine run at that speed emits higher amount of exhaust gas. In this way, it is ensured that not the all the  $\text{NO}_x$  is mitigated in the SCR and the ASC performance can be analysed.

For both the pre-study and the full study engines, C speed corresponds to around 2200rpm approximately.

- Many catalysts show certain loss of activity in the initial operation lapse. After it, the activity remains stable over the time for a long period. For this reason, new catalysts must be “degreened” before emission tests, under certain conditions and for a specific period of time depending on the manufacturer and the catalyst properties. The catalyst degreening is referred as the conditioning phase. (17)

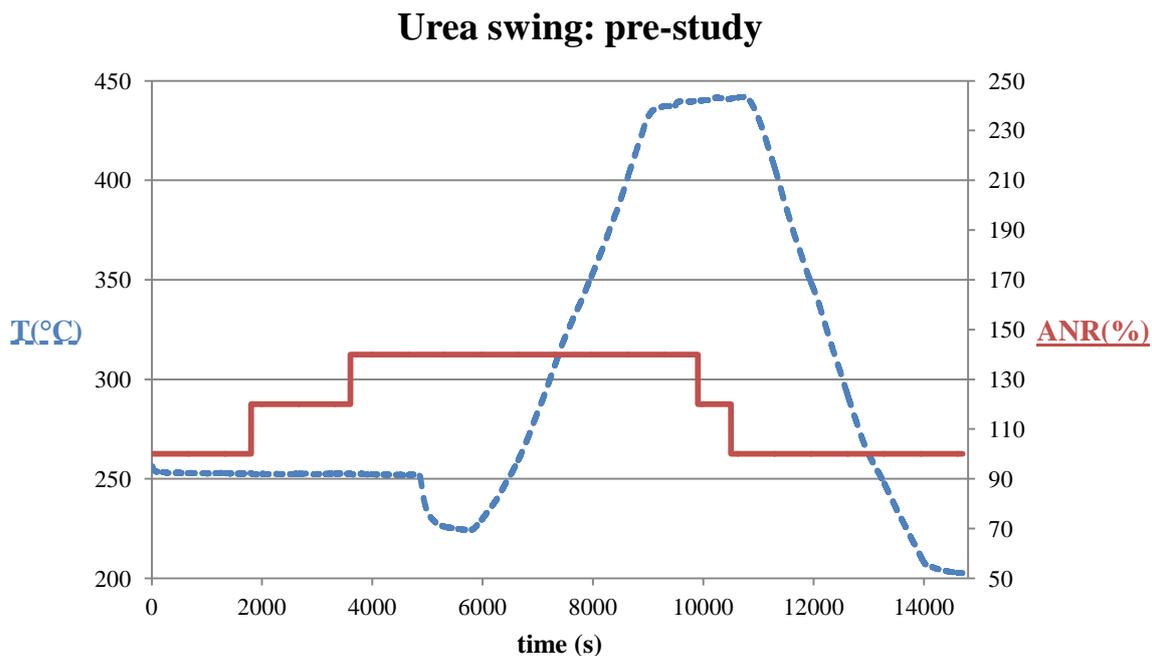
Johnson Matthey usually applies a “standard methodology” to run the experiments. An “alternative methodology”, which is faster, has been used in the pre-study of the catalysts. It has shown to provide high amount of information in a very low time-consuming test, so that it has been decided to use the same methodology for the full study program (see section 5.1).

It starts by the Evaluation Protocol, a conditioning phase in which the engine is run at maximum capacity (A100) for 1 hour. The central 20 minutes include urea injection at global  $\text{NH}_3/\text{NO}_x$  molar ratio (ANR) of 1.2.

The urea swing consists of running the engine at C speed at  $250^\circ\text{C}$  with ANR=1.0 (pre-study: 30 minutes, full study: 1 hour), ANR=1.2 (pre-study: 30 minutes, full study: 40 minutes) and ANR=1.4 (pre-study: 20 minutes, full study: 40 minutes). Maintaining ANR=1.4, the temperature is decreased to  $225^\circ\text{C}$  until stabilization (around 15min). Then, the temperature is ramped slowly (1 hour) to a maximum value (ideally  $450^\circ\text{C}$ ) at which ANR is held at 1.4, 1.2, and 1.0 for 30 minutes (10 minutes each step). Finally the temperature is decreased gradually (for 1 hour) to  $200^\circ\text{C}$  at ANR=1.0.

- ❖ The temperature levels are set before the SCR catalyst (TEBCT 3 in Figure 7) since the thermal drop between that point and the ASC inlet (TEACT 3 in Figure 7) is very low.

Figure 9 and Figure 10 show graphical representations of the urea swing conditions of temperature and ANR. Apparently they are almost the same; the only difference lays on the time period that catalysts are tested at  $250^\circ\text{C}$  (initial part of the experiment).



*Figure 9: Pre-study urea swing conditions.*



*Figure 10: Full study urea swing conditions.*

**The full experimental test is conducted twice, the first one before the hydrothermal ageing (see section 4.3.3) and the second one after it. From now addressed to as “degreened” and “aged” catalysts, respectively.**

- ❖ The noted differences between the pre-study and the full study methodologies are justified in section 5.1.

### 4.3.3 Hydrothermal oven ageing

The durability of the catalyst fulfilling the emission upper limits for which it has been designed is an important issue to face. As it has been explained in section 2.2, Euro VI establishes different durability periods (see Table 2) in which maximum emission limits (see Table 1) have to be complied, i.e. catalyst must be still active.

Catalyst deactivation is usually a gradual process that comes with operating time and conditions, and it is mainly caused by high temperatures and/or poisoning.

The evaluation of catalyst deactivation is referred to as catalyst ageing which can be applied by three methods:

- field ageing
- engine bench ageing
- hydrothermal oven ageing

Field ageing is a very expensive and time consuming method since the catalyst is installed on the vehicle and operated over the specific desired time. Engine bench ageing are accelerated ageing tests which require equivalence between the real life mileage and the duration of the test. The most challenging task in designing accelerated aging tests is the determination of the equivalency between the real life mileage and the duration of the test. Even if it is a challenging task, they are very common in the development of automotive catalysts.

However, for catalyst development and evaluation of its thermal stability, hydrothermal oven ageing is the chosen methodology because it is fast and simple. (17)

It consists of subjecting the ASCs for 100 hours to 550°C in the oven in a controlled atmosphere composed of 10% steam and 90% both air and N<sub>2</sub>. The air and the N<sub>2</sub> are mixed at room temperature and are added to the steam chamber, consisting of a water bath at 40°C. This takes place after the first full experimental run.

The point of this is ageing catalysts the same overall time that they could be subjected to so severe conditions in their whole useful lifetime. Therefore, it represents long time or mileage. However, it is very difficult to determine to how many years or thousands of kilometres it is equivalent, it is a tricky matter with which JM AB always faces. If the time or mileage was determinable, it would correspond to last row and vehicles N3=16tons (from the second row) of Table 2, which are the vehicles to which the studied ASCs will be applied. A classification of the EU vehicles can be looked up in Appendix 1 (Table 17).

Section 5 (Results and Analysis of Experiments) shows the differences between the catalysts before and after the ageing. On the literature several statements have been found. Kamasamudram et al. (2011) report little change in the PGM-component of the ASC when subjected to hydrothermal ageing since its ability to oxidize ammonia remained virtually unchanged. Differently, SCR-component is considerably affected as the NO<sub>x</sub> could not be properly converted to N<sub>2</sub>, increasing catalyst's overall selectivity to nitrogen oxides. (11)

## 5 Results and Analysis of Experiments

This section comprises the presentation of data provided by the experiments with its corresponding analysis.

### 5.1 Pre-study

The pre-study has tested just catalysts number 1, 3, 6 and 10, since they are the corner configurations of the design, so that the whole factors scope is covered. This previous sight permits having a general idea of how the tested catalysts work at the operating conditions.

#### 5.1.1 Temperature profile

Temperature variations between the centre and different radiuses at the rear face of the ASC have been measured as explained in section 4.3.1. Further radiuses from the centre provide higher temperatures deviations which are more noticeable in the stable temperature periods than in the changing ones. Analysing the worst situation, i.e. the steady lapse of highest operating temperature (450°C), it has been noticed that the south pointing direction thermocouples shows the greatest deviations on temperature, maybe because of exhaust flow reasons. For the full study program only temperature in this direction at the same radius values has been registered (see Figure 8).

It has been considered important not to remove all the thermocouples for the full study of the ASCs to verify that, in the whole operating conditions range and with all the catalysts designs, the radial thermal variation remains acceptable.

#### 5.1.2 Testing procedure

The methodology used in the pre-study has been considered a suitable approach to deal with the full test program. It provides high amount of information in relatively low running time. This approach is called “alternative methodology” since it consists of a faster test than the “standard methodology” usually used by Johnson Matthey AB.

The full test program uses this “alternative methodology” with little modifications. At the initial  $T=250^{\circ}\text{C}$ , the time at each ANR value is increased with respect to the pre-study since it has been seen that for ammonia slip takes longer time to reach stability at low temperatures (see Appendix 3, Figure 16). For this reason, the first part of the urea swing is extended on time (see 4.3.2., Figure 10).

## 5.2 Full study

The analysis of the full study results (both the degreened and the aged catalysts) has taken place in different ways, considering both the thermal variation along the catalyst diameter and the three emission responses of interest.

NH<sub>3</sub> slip is directly analysed as ppm emitted after the ASC, while NO<sub>x</sub> conversion (%) and N<sub>2</sub>O formation (ppm) are examined considering only the ASC contribution to each response; so that 2<sup>nd</sup> base line is used to know which is the inlet of each component to the ASC (see 4.3.2).

The degreened and aged catalysts correspond to the ASC designs before and after the hydrothermal oven ageing respectively.

### 5.2.1 Temperature profile

The temperature at the centre and at different radiuses has been measured at the rear face of the ASC as explained in 4.3.1.

Figure 17 and Figure 18 (degreened and aged catalysts, respectively) from Appendix 4 show the thermal variations between the centre and the different radiuses where the temperature has been measured. These variations correspond to a specific experimental point, in which the operating temperature is maximum, 450°C, representing a possible worst case in terms of thermal deviation.

The further from the centre, the greater difference; so that only the difference centre-outer diameter is going to be further analysed at all experimental measured points. For each of the different operating temperatures or range of temperatures, the average is calculated. Table 5 shows the averages at the degreening and Table 6 the averages at the aging (see 4.3.2 Experimental Methodology and Equipment for further understanding of the calculations).

Table 5: Average temperature variations of the degreened catalysts.

	250°C	ramp up	450°C	ramp down	av.
<b>Cat1</b>	22.89	32.18	34.71	22.82	<b>28.15</b>
<b>Cat2</b>	16.07	20.31	22.38	16.17	<b>18.73</b>
<b>Cat3</b>	23.71	36.38	42.87	25.36	<b>32.08</b>
<b>Cat4</b>	22.50	29.59	34.28	22.07	<b>27.11</b>
<b>Cat5</b>	23.86	31.56	34.44	23.59	<b>28.36</b>
<b>Cat6</b>	20.40	25.57	27.84	20.27	<b>23.52</b>
<b>Cat7</b>	21.79	29.12	31.44	21.22	<b>25.89</b>
<b>Cat8</b>	21.43	30.73	33.80	22.09	<b>27.01</b>
<b>Cat10</b>	16.76	20.76	20.23	15.63	<b>18.34</b>
av.	<b>21.05</b>	<b>28.47</b>	<b>31.33</b>	<b>21.02</b>	<b>25.47</b>

Table 6: Average temperature variations of the aged catalysts.

	250°C	ramp up	450°C	ramp down	av.
<b>Cat1</b>	19.65	24.70	27.55	20.09	<b>23.00</b>
<b>Cat2</b>	19.54	23.22	24.30	18.48	<b>21.39</b>
<b>Cat3</b>	19.86	25.95	27.35	18.87	<b>23.01</b>
<b>Cat4</b>	27.04	36.78	42.90	28.41	<b>33.78</b>
<b>Cat5</b>	16.64	21.58	24.70	17.08	<b>20.00</b>
<b>Cat6</b>	9.20	10.55	11.31	9.09	<b>10.04</b>
<b>Cat7</b>	22.69	32.68	36.41	23.24	<b>28.75</b>
<b>Cat8</b>	25.83	34.09	38.77	25.41	<b>31.03</b>
<b>Cat10</b>	22.54	27.03	34.23	24.72	<b>27.13</b>
av.	<b>20.33</b>	<b>26.29</b>	<b>29.72</b>	<b>20.60</b>	<b>24.24</b>

Red numbers show the highest average variations in columns or rows and green numbers the lowest ones. The central columns, which correspond with the highest operating temperatures, give the greatest variations, while the extreme columns, linked with the lowest experimental temperatures, provide smaller variations.

Regarding the rows, Cat3 (degreened) and Cat4 (aged), which are the longest samples, show the largest differences of temperature. The shorter catalyst (Cat10) gives the lower thermal deviation for the degreened case, but not for the aged one, which is represented by Cat6 (medium length). Nevertheless, it can be seen in Figure 18 (Appendix 4) how Cat6 aged reflects very large variation at a radius 95% from the centre and very low at the outer diameter. It can be considered an anomaly caused by some type of experimental error.

The degreened catalysts show higher thermal variation averages than the aged for all operating conditions (comparing columns from Table 5 with Table 6).

The variations of temperature shown in Table 5 and Table 6 are quite high; approximately 25°C for both catalyst states degreened and aged. However, this is not influencing the weighted area temperature. It has been calculated as follows:

$$T_{area} = 0.25 \cdot av_{0\%-50\%} + 0.4725 \cdot av_{50\%-85\%} + 0.18 \cdot av_{85\%-95\%} + 0.0975 \cdot av_{95\%-100\%}$$

The coefficients represent the contribution of each ring to the whole catalyst area. The variables are the averages of the temperatures at the extremes of the considered ring at each measured time point.

Plotting Tarea versus the inlet temperature at the ASC for each catalyst and each state (degreened and aged), the thermal variation considering the area can be observed. In Appendix 4, Figure 19 shows the highest temperature variation catalyst at 250°C, represented by Cat10 at the degreened state. The deviation is of around 3°C. Figure 20 shows the case of 450°C at which Cat4 at the aged state seems to have the highest variation, which corresponds with 5°C.

These results seem to be contradictory with Table 5 and Table 6 which concluded that averaged thermal variations are higher for the degreened samples. However, Figure 19 and Figure 20 just represent extreme values and not averaged ones.

Therefore, maximum variations of 3°C and 5°C for operating conditions of 250°C and 450°C respectively can be considered almost negligible taking into account that thermocouples accuracy rounds  $\pm 2^\circ\text{C}$  (see 4.3.1). This means that no different residence times are registered along the ASC, ending up in even conversions regardless the catalyst radial point.

## 5.2.2 Overall performance analysis

This method of analysis considers each catalyst as a completely different sample, without taking into account the catalyst design factors.

Averages of each response for each of the different operating conditions periods ([250°C, 1.0], [250°C, 1.2], [250°C, 1.4], [ramp up, 1.4], [450°C, 1.4], [450°C, 1.2], [450°C, 1.0] and [ramp down, 1.0], see 4.3.2 for a better understanding of the experimental methodology) are calculated. For each ANR value, the averages are summed together.

ANR=1.4 at the ramp up accounts for two values, apart from the average, the peak value. A summed only considering the peak value is also calculated, in order to avoid the masking effect produced by such a high number.

Table 7 outlines these calculations.

Table 7: Methodology of the overall performance analysis.

	ANR		
	1.0	1.2	1.4
250°C	av.	av.	av.
225°C			av.
Ramp up			av. or max.
450°C	av.	av.	av.
Ramp down	av.		
200°C	av.		
	SUM	SUM	SUM, SUM PEAK

NH<sub>3</sub> slip and N<sub>2</sub>O formation averages are added to each other. In this way, two sums of averages for each catalyst and ANR are available. They have no physical sense, but consider equal contributions of each catalyst, allowing analysing the overall performance.

Catalysts with maximum NO<sub>x</sub> conversion sum of averages and minimum NH<sub>3</sub>+N<sub>2</sub>O sums of averages for each ANR are desired.

Table 8 and Table 9 show that the overall best performance is represented by catalyst number 3 for almost all the cases (except ANR=1.0) regardless the catalyst ageing state. Cat3 consists of a long ASC, with medium Pt load and nominal SCR coating thickness (which corresponds with the highest tested thickness) (see Table 3).

Table 8: Overall performance analysis of the degreened catalysts.

DEGREENED									
N <sub>2</sub> O+NH <sub>3</sub>	Min				NOx	Max			
	ANR			Peak		ANR			Peak
	1.0	1.2	1.4	1.4		1.0	1.2	1.4	1.4
Cat1	42.67	79.31	379.67	493.07	Cat1	127.33	148.64	312.91	321.39
Cat2	45.52	91.41	393.74	524.14	Cat2	145.53	153.86	318.34	325.44
Cat3	<b>21.26</b>	<b>57.15</b>	<b>283.91</b>	<b>415.83</b>	Cat3	157.93	<b>171.89</b>	<b>364.25</b>	<b>367.75</b>
Cat4	25.17	81.73	352.39	509.29	Cat4	131.40	163.35	353.00	356.94
Cat5	46.85	109.47	397.07	518.20	Cat5	155.72	158.57	328.91	335.14
Cat6	38.91	113.71	428.21	567.00	Cat6	179.59	158.21	321.73	342.08
Cat7	57.71	128.18	454.28	583.12	Cat7	<b>190.84</b>	164.49	327.29	334.40
Cat8	56.47	125.21	435.60	562.72	Cat8	180.18	164.08	329.60	338.67
Cat10	117.66	188.39	600.69	731.54	Cat10	132.94	112.18	213.52	227.14

Table 9: Overall performance analysis of the aged catalysts.

AGED									
N <sub>2</sub> O+NH <sub>3</sub>	Min				NOx	Max			
	ANR			Peak		ANR			Peak
	1.0	1.2	1.4	1.4		1.0	1.2	1.4	1.4
Cat1	57.48	108.10	381.07	490.15	Cat1	163.56	145.09	289.20	322.43
Cat2	53.29	105.54	408.99	535.34	Cat2	159.72	144.19	291.04	327.85
Cat3	<b>27.04</b>	<b>72.64</b>	<b>319.28</b>	<b>446.04</b>	Cat3	<b>187.58</b>	<b>165.08</b>	<b>332.43</b>	<b>369.71</b>
Cat4	40.86	94.56	388.17	518.47	Cat4	166.97	159.66	318.78	356.85
Cat5	72.83	143.44	491.34	541.92	Cat5	185.77	154.35	301.50	336.90
Cat6	76.01	149.34	527.00	580.40	Cat6	170.61	148.39	287.39	331.61
Cat7	72.42	129.74	485.21	596.04	Cat7	177.22	148.30	289.58	335.15
Cat8	66.02	131.34	471.42	572.45	Cat8	174.98	148.24	290.27	342.71
Cat10	129.61	192.70	608.77	692.14	Cat10	120.68	100.52	205.39	234.90

When analysing the N<sub>2</sub>O and NH<sub>3</sub> sums separately, it appears Cat3 as the best result only for the ammonia slip. Lowest N<sub>2</sub>O sums for the degreened case are given by Cat4, whose difference with Cat3 falls in its lower SCR coating thickness, i.e. reaction [14] is less promoted, as less NH<sub>3</sub> amount can be stored. For the aged case, Cat6 is preferred in terms of N<sub>2</sub>O since it includes less Pt load and lower SCR coating thickness, preventing as much as possible reactions [13] and [14] to occur.

However, when considering N<sub>2</sub>O and NH<sub>3</sub> emissions together, ammonia effect weights greater in the overall performance, pointing towards Cat3 as the best analysed catalyst from a general point of view.

### 5.2.3 Factorials

#### Missing catalyst

The 9 available Ammonia Slip Catalyst designs, of which 7 are factors combinations and 2 are centre points, are tested in the full experimental program.

The  $2^3$  factorial requires a minimum of 8 observations, so it has been decided to predict the responses for the missing catalyst, Cat9.

Table 3 shows that design differences between Cat1 and Cat2, Cat3 and Cat4, and Cat5 and Cat6 lie on the SCR coating thickness. The same happens between Cat9 and Cat10. Then, for each response, the average of the variations between the previous mentioned pairs of catalysts is applied as the deviation between Cat9 and Cat10, taking into account that Cat10 measurements are available.

This prediction seems to be risky as it assumes SCR coating to have a linear response and not to interact with the rest of the factors. However, extreme values (low and high) have been randomly tried as predictions of Cat9 responses and no significant changes on the results have been noticed. For this reason, the above explained prediction has been considered as suitable.

- ❖ The Cat9 predicted results are only used in the factorial analysis (section 5.2.3), in which having the full data is a must. The rest of the analysis has not included this prediction in order to be as much realistic as possible.

#### Rotation of the design

As already introduced in section 4.2, the original design of experiments (Figure 6) does not fit with a standard  $2^3$  factorial which consists of a cubic design with two levels per factor without considering the centre points (medium levels). Table 10 (1<sup>st</sup> block) shows that the only factor with 2 levels is the SCR coating thickness.

In order to deal with this drawback, the factors levels have been scaled in terms of -1, 0, +1, according to the lower, medium and higher levels of the factors respectively (Table 10, 2<sup>nd</sup> block). Then, a cosine rotation has been applied in the L-Pt plane, giving rise to the redefinition of L and Pt factors (Table 10, 3<sup>rd</sup> block). The original factor of the length has become  $Pt \cdot L$ , and Pt has become  $Pt/L$ , two redefinitions which complicate the factorial analysis since they have an ambiguous physical meaning.

Table 10: Factors levels transformations.

Cat	3 levels Original			3 levels Scaled			2 levels Rotated			2 levels Rescaled		
	L	Pt	SCR	L	Pt	SCR	Pt*L	Pt/L	SCR	Pt*L	Pt/L	SCR
1	Medium	High	High	0	1	1	0.71	0.71	1	1	1	1
2			Low	0	1	-1	0.71	0.71	-1	1	1	-1
3	High	Medium	High	1	0	1	0.71	-0.71	1	1	-1	1
4			Low	1	0	-1	0.71	-0.71	-1	1	-1	-1
5	Medium	Low	High	0	-1	1	-0.71	-0.71	1	-1	-1	1
6			Low	0	-1	-1	-0.71	-0.71	-1	-1	-1	-1
7	Medium	Medium	Medium	1	0	0	0	0	0	0	0	0
8			Medium	1	0	0	0	0	0	0	0	0
9	Low	Medium	High	-1	0	1	-0.71	0.71	1	-1	1	1
10			Low	-1	0	-1	-0.71	0.71	-1	-1	1	-1

Figure 11 shows the rotated design which fits with a  $2^3$  design cubic design with the side edges parallel to the factors axis.

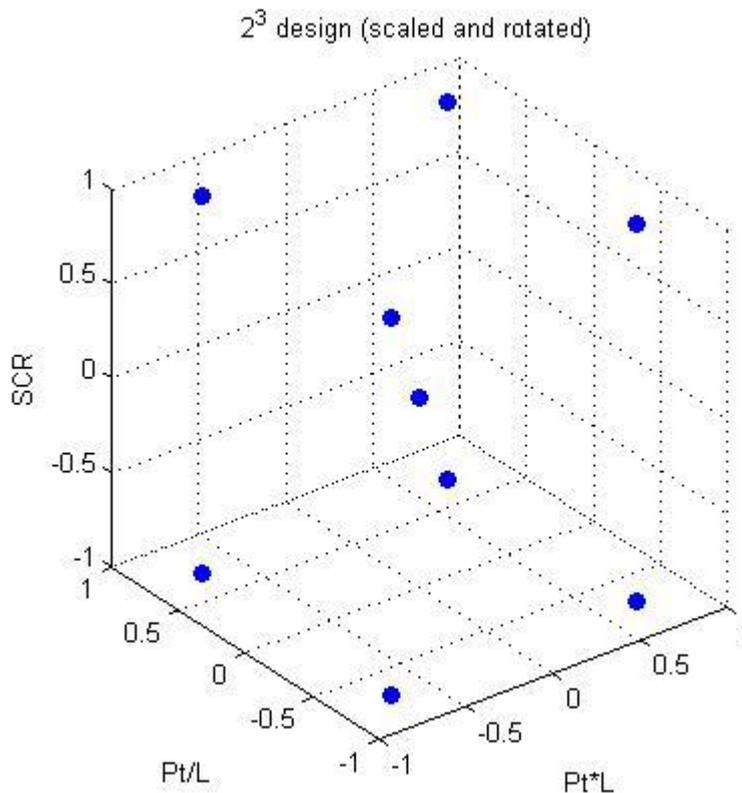


Figure 11: Rotated design of experiments.

Finally, the rotated design has been rescaled (Table 10, 4<sup>th</sup> block) to ease the analysis of the experimental data.

Two-level factorial analyses have been carried out: with 3 and 4 factors.

### 2<sup>3</sup> factorial

The three considered factors are the ones resulted after the rotation of the design. From now on, they will be called:

**A:** SCR coating thickness

**B:** Pt/Length

**C:** Pt\*Length

Figure 10 shows how different temperatures are tested at different ANR values. The steady state periods of the experimental methodology, outlined in Table 11, are considered in order to analyse for each of them the N<sub>2</sub>O formation, NH<sub>3</sub> slip and NO<sub>x</sub> conversion responses.

Table 11: Operating conditions at which responses are analysed by factorials.

Conditions		
	T	ANR
<i>Low temperatures</i>	200°C	1.0
	225°C	1.4
		1.0
	250°C	1.2
		1.4
<i>High temperatures</i>		1.0
	450°C	1.2
		1.4

Each pair of conditions provides lots of data for each response since the sampling frequency is 1 second if the measurements are continuous or 5 minutes if they are step-wise; it depends on the operating conditions (see Appendix 2). Therefore, averages for each response, calculated as in Table 7, are analysed.

The Analysis of the Variance (ANOVA) has been conducted and the significant factors for each response and experimental conditions are shown in Appendix 4, regarding both the degreened catalysts (Table 18) and the aged catalysts (Table 19). The significance of the factors and interactions and the Pure Quadratic error are checked by means of the F-distribution.

## ➤ DEGREENED CATALYSTS

N<sub>2</sub>O formation is mainly affected by A and B at low temperatures, whereas C takes prominence when the temperature is high. There are almost no interactions between the factors.

NH<sub>3</sub> slip is influenced by B and C at low ANRs and by the three factors when the ANR is high; that is, SCR coating increases its importance under NH<sub>3</sub> inlet excess since the NH<sub>3</sub> slip strongly depends on the ammonia stored and therefore on the SCR layer thickness.

At high temperatures, BC interaction, representing Pt<sup>2</sup> (Pt/Length \* Pt\*Length = Pt<sup>2</sup>), shows significant effect. It means that a second order model representation could be adequate.

For the degreened case, SCR coating thickness (A factor) has completely no effect on the NO<sub>x</sub> conversion whose significant factors are B and C and their interaction at the whole range of temperatures and ANRs. Lower Pt activity, lower NH<sub>3</sub> oxidized into NO<sub>x</sub> and therefore lower NO<sub>x</sub> amount is registered in the outlet.

BC interaction, as explained lines above, represents the second order term for the Pt, whose noticed importance makes sense as a pure quadratic error has been detected. This means that a first-order model including main effects and interaction terms is not enough to represent the performance of the catalyst. The curvature of the response is not adequately outlined by a twisted plane but by a maximum or a minimum within the considered factors levels.

The triple interaction shows also a little effect which presumably have arisen just due to the high BC interaction considering that no A effect has been observed.

At high ANRs and temperatures all interaction effects seem to be significant even if the A factor is not substantially influencing the NO<sub>x</sub> conversion.

## ➤ AGED CATALYSTS

The main noticed variation of the aged catalyst is the arisen importance of the A factor with respect to the degreened catalysts. SCR coating is the most affected item when the catalysts are subjected to hydrothermal oven ageing since it loses NH<sub>3</sub> storage capacity and then N<sub>2</sub> selectivity goes down, increasing N<sub>2</sub>O and NO<sub>x</sub> release.

N<sub>2</sub>O formation for the aged catalysts is mainly affected by factor B and some of its interactions; it is reasonable since higher Pt amount ends in higher N<sub>2</sub>O amount formed, as reaction [13] is promoted.

NH<sub>3</sub> slip comes affected by almost all single factors. C factor shows important influence for all of the investigated conditions; that is, Pt\*L interaction is relevant since as higher Pt amount and higher length, greater amount of ammonia is oxidized into NO<sub>x</sub> in the lower layer of the ASC, preventing NH<sub>3</sub> from slipping out of the pipe.

Factors influencing the NO<sub>x</sub> conversion are equivalent to those perceived for the degreened catalysts, with the addition of the SCR coating thickness significance at high temperature values. It means that there is a noticeable trend of increasing NO<sub>x</sub> conversion when the SCR coating thickness is higher. Probably this factor was not influencing importantly for the degreened case as thickness of the SCR layer was large enough not to detect important variations between the different catalysts.

The usefulness of the factorial analysis conducted lays mainly on the understanding of how the ASC works according to the variations on the operating conditions. Furthermore, pure quadratic error on the NO<sub>x</sub> conversion has been detected for most of the cases. The information given regarding the best catalyst choice is quite poor in the absence of regression models; i.e. knowing just the significant factors affecting the responses does not let take a decision.

- ❖ The 2<sup>3</sup> factorials included, on a first approach, also blocking effects. The temperature, the ANR or both were restricting the study. However, these blocking variables were perceived in most cases as the only significant effects as they were of such a magnitude that other factors influence to the responses were completely masked. For this reason, it was decided to conduct the analysis in the standard way.

### 2<sup>4</sup> factorial

This factorial design adds one more factor with respect to the previously explained analysis. The extra factor is the ANR, which takes 1.0 and 1.4 as low and high levels respectively. 1.2 corresponds to the medium level (centre point).

The Analysis of the Variance (ANOVA) of this 2<sup>4</sup> factorial has been carried out, finding most of the significance variance attributed to the ANR factor. It has such a high effect on the experiments that masks other possible factors affecting the responses.

For this reason, it is not worthy to include this analysis results which do not provide any useful information.

## 5.2.4 Regression

Regression methods are useful tools to study the variables affecting a specific response and the way they do it.

Original design factors, their linear interactions and a second order interaction of the Pt have been considered in order to find a suitable model. The main factors are Length, Pt load and SCR coating thickness, whose levels can be observed in Table 3: Original factors levels. Table 3. They have been scaled from -1 to +1 for a better understanding of the results. These main factors and their interactions have made it possible to come across with a model for each response at the different operating conditions. The responses are calculated as the averages of the period of time in which certain combination of conditions are held constant (as in Table 7).

Table 12: Operating conditions at which responses are modelled by regression.

Conditions		
T	ANR	Models
250°C	1.0	N <sub>2</sub> O, NH <sub>3</sub> , NO <sub>x</sub>
	1.2	N <sub>2</sub> O, NH <sub>3</sub> , NO <sub>x</sub>
	1.4	N <sub>2</sub> O, NH <sub>3</sub> , NO <sub>x</sub>
450°C	1.0	N <sub>2</sub> O, NH <sub>3</sub> , NO <sub>x</sub>
	1.2	N <sub>2</sub> O, NH <sub>3</sub> , NO <sub>x</sub>
	1.4	N <sub>2</sub> O, NH <sub>3</sub> , NO <sub>x</sub>

Only second order interaction for Platinum has been considered in the regression as the factorial analysis has proven its importance.

Table 12 shows the combination of steady state experimental conditions at which each response is represented by a model, giving rise to 18 models for the degreened catalyst and other 18 models for the aged samples.

The significant factors and interactions of the models and their coefficients have been checked in order to decide the suitable terms to be included. Furthermore, “R-squared” have been calculated, residuals plotted and Lack of Fit and Pure Quadratic errors checked. The considered level of confidence for the hypothesis testing (accepting or refusing hypothesis) has been of 95%.

Table 20 and Table 21 in Appendix 4 show the possible 36 models and the corresponding analysis to check the adequacy of the regression.

### **Coefficients and models significances**

The models include the main factors and interactions which have been proved to be significant by means of the t-test, while the model is checked by F-distribution. If an interaction effect is relevant but some of its main factors are not, the main factors have also to be included in the model. It implies the risk of finding that the complete model is not significant. This is the case of the N<sub>2</sub>O model at 250°C and ANR=1.0 for the degreened case, in which both main factors are negligible but the interaction is important. For the rest of the cases, at least one of the main factors of the interaction is significant and the model so.

### **Lack of Fit**

Lack of Fit error is examined by means of the F-distribution, revealing potentially lacking of more linear terms.

For both, the degreened and the aged catalysts, there is no lack of fit error observed for none of the models.

### **Pure Quadratic error**

Pure Quadratic error is examined by means of the F-distribution, uncovering the non-linear responses.

There many models for both states of ageing showing Pure Quadratic errors. Second order term for Pt has been already included in the regression, so within the extreme levels of the length or/and the SCR coating thickness, the responses present a maximum or a minimum peak that has not been considered in the experiment. It is not possible identifying the exact responsible factor/s for the PQ error in each of the cases.

## Residuals

Residuals values vs. predicted responses have been plot to check the adequacy of the models. No anomalies have been found for any of the models, all of them show unstructured residuals representation; that is, they do not show any obvious pattern which could underline model inadequacies.

Table 13 shows the significant factors and interactions considered in each model for the degreened catalyst. It can be observed that NO<sub>x</sub> conversion at 250°C and ANR=1.0 cannot be represented by any combination of factors. This is consistent with the fact that no significant factors have been found for these conditions in the factorial analysis neither.

Table 13: Summary of the regression for the degreened catalysts.

### DEGREENED

T	ANR	Model		R <sup>2</sup> adj(%)	"Best cat."
250°C	1.0	N <sub>2</sub> O	L, Pt, (L*Pt)	49.07	10/5,6/10
		NH <sub>3</sub>	L	65.36	3,4
		NO <sub>x</sub>			
	1.2	N <sub>2</sub> O	Pt	66.11	5,6
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (Pt <sup>2</sup> )	90.84	3,4/10/1,3,5/1,2,5,6,7,8/5,6
		NO <sub>x</sub>	L, Pt, SCR, (L*SCR), (Pt <sup>2</sup> )	99.82	10/5,6/2,4,6,10/3,10/1,2,7,8
	1.4	N <sub>2</sub> O	L, Pt, SCR, (L*Pt), (Pt <sup>2</sup> )	91.11	10/5,6/2,4,6,10/10/1,2,7,8
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (Pt <sup>2</sup> )	89.64	3,4/10/1,3,5/1,2,5,6,7,8/5,6
		NO <sub>x</sub>	L, Pt, (Pt <sup>2</sup> )	94.56	3,4/5,6/1,2,7,8
450°C	1.0	N <sub>2</sub> O	L, Pt, SCR, (Pt <sup>2</sup> )	82.08	10/10/1,3,5/5,6,10
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (L*SCR), (Pt*SCR), (Pt <sup>2</sup> )	99.99	3,4/10/2,4,6,10/1,2,5,6,7,8/3,10/6/5,6,10
		NO <sub>x</sub>	L, Pt, SCR, (L*SCR), (Pt*SCR), (Pt <sup>2</sup> )	99.96	10/5,6/2,4,6,10/3,10/6/1,2,7,8
	1.2	N <sub>2</sub> O	L, Pt	54.86	10/5,6
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (Pt <sup>2</sup> )	99.39	3,4/10/2,4,6,10/1,2,5,6,7,8/5,6,10
		NO <sub>x</sub>	L, Pt, (Pt <sup>2</sup> )	97.24	3,4/5,6/1,2,7,8
	1.4	N <sub>2</sub> O	L, Pt, (Pt <sup>2</sup> )	89.58	10/5,6/5,6,10
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (Pt*SCR), (Pt <sup>2</sup> )	99.87	3,4/10/2,4,6,10/1,2,5,6,7,8/5,10/5,6,10
		NO <sub>x</sub>	L, Pt, SCR, (L*Pt), (Pt*SCR), (Pt <sup>2</sup> )	99.92	3,4/5,6/2,4,6,10/1,2,5,6,7,8/5,10/1,2,7,8

Table 14 shows the terms that have been included in the models for the aged catalysts. It can be observed that the three responses for all operating conditions can be represented by a model.

Table 14: Summary of the regression for the aged catalysts.

**AGED**

T	ANR	Model		R <sup>2</sup> adj(%)	"Best cat."
250°C	1.0	N <sub>2</sub> O	L, Pt, (L*Pt)	74.94	10/5,6/10
		NH <sub>3</sub>	L	51.35	3,4
		NO <sub>x</sub>	Pt, (Pt <sup>2</sup> )	72.21	5,6/1,2,7,8
	1.2	N <sub>2</sub> O	Pt	76.53	5,6
		NH <sub>3</sub>	L, Pt, SCR	83.93	3,4/10/1,3,5
		NO <sub>x</sub>	L, Pt, SCR, (L*Pt), (Pt*SCR), (Pt <sup>2</sup> )	99.98	3,4/5,6/2,4,6,10/1,2,5,6,7,8/5,10/1,2,7,8
	1.4	N <sub>2</sub> O	Pt	78.08	5,6
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (L*SCR), (Pt <sup>2</sup> )	99.27	3,4/10/1,3,5/1,2,5,6,7,8/3,10/5,6,10
		NO <sub>x</sub>	L, Pt, SCR, (L*Pt), (L*SCR), (Pt*SCR), (Pt <sup>2</sup> )	100	3,4/10/2,4,6,10/1,2,5,6,7,8/3,10/5,10/5,6,10
450°C	1.0	N <sub>2</sub> O	L, Pt, SCR, (Pt*SCR), (Pt <sup>2</sup> )	94.41	10/5,6/1,3,5/5,10/5,6,10
		NH <sub>3</sub>	L, Pt, (L*Pt)	95.5	3,4/10/1,2,5,6,7,8
		NO <sub>x</sub>	L, Pt, SCR, (L*Pt)	97.76	3,4/5,6/1,3,5/1,2,5,6,7,8
	1.2	N <sub>2</sub> O	L, Pt, SCR, (L*SCR), (Pt*SCR), (Pt <sup>2</sup> )	97.65	10/5,6/1,3,5/4/5,10/5,6,10
		NH <sub>3</sub>	L, Pt, SCR, (L*Pt), (L*SCR), (Pt*SCR)	99.93	3,4/10/2,4,6,10/1,2,5,6,7,8/10/5,10
		NO <sub>x</sub>	L, Pt, SCR, (L*Pt), (Pt*SCR), (Pt <sup>2</sup> )	99.99	3,4/5,6/1,3,5/1,2,5,6,7,8/5,10/5,6,10
	1.4	N <sub>2</sub> O	Pt, SCR, (Pt*SCR), (Pt <sup>2</sup> )	89.83	5,6/1,3,5/6/5,6,10
		NH <sub>3</sub>	L, Pt, (L*Pt)	93.45	3,4/10/1,2,5,6,7,8
		NO <sub>x</sub>	L, Pt, SCR, (L*Pt), (Pt*SCR), (Pt <sup>2</sup> )	99.97	3,4/5,6/1,3,5/1,2,5,6,7,8/5,10/5,6,10

In rough outlines, it can be asserted that high temperature models include higher number of terms than low temperature models for both the degreened and the aged catalysts. L and Pt are present in almost all the models, and also its interaction.

The aged catalysts present models with higher number of terms and therefore slightly larger R<sup>2</sup> than the degreened catalysts. It is explained by the addition of SCR to many of the models and not only as a main factor, but also interacting with other variables. SCR coating ability to

store  $\text{NH}_3$  is partly lost during the ageing, so that is why it becomes a very sensitive factor on the responses and then significant for the models.

Both the degreened and the aged catalysts include higher number of terms at  $450^\circ\text{C}$  than at  $250^\circ\text{C}$ , giving rise to greater “R-squared”, reaching in some cases 100%.

Higher number of model terms deals to higher  $R^2$ , so adjusted  $R^2$  statistic has been calculated.  $R^2_{\text{adj}}$  not always increases as variables are added to the model, only if the new terms improve the regression. That is why, in Table 13 and Table 14, models with higher number of terms not always give the greater adjusted  $R^2$ , as it happens in Table 20 and Table 21.

Last columns of Table 13 and Table 14 shows the suitable catalysts for each of the cases according to the models obtained (Appendix 4, Table 20 and Table 21); that is, for each term of the model (important attention to the sign) there is/are catalyst/s fulfilling the requirement. For instance, the  $\text{NH}_3$  model at  $250^\circ\text{C}$  and  $\text{ANR}=1.2$  for the degreened catalyst is:

$$\text{NH}_3 = 55.14 - 50.15 \cdot L - 39.54 \cdot \text{Pt} - 10.54 \cdot \text{SCR} - 34.87 \cdot (L \cdot \text{Pt}) - 35.57 \cdot (\text{Pt}^2)$$

As  $\text{NH}_3$  slip is desired to be as minimum as possible, all model terms should be maximised (negative signs). Maximum L is given by Cat3 and Cat4; Pt load is maximum for Cat10; greatest SCR comes from Cat1, Cat3 and Cat5;  $L \cdot \text{Pt}$  points towards Cat1, Cat2, Cat5, Cat6, Cat7 and Cat8; and  $\text{Pt}^2$  is maximum for Cat5 and Cat6. That is why in Table 14 this model shows as the best catalysts 3,4/10/1,3,5/1,2,5,6,7,8/5,6.

1<sup>st</sup> two columns of Table 15 show the number of times that each catalyst appears as a “best cat.” option for all the models depending of their ageing state. Cat6 (degreened) and Cat5 (aged) are the most numerous ones.

However, it is essential to consider how much the variable demanding a specific catalyst weights within the model. It can be measured by means of the magnitude of the regression coefficient since the variables of the models (main factors and interactions) have been previously scaled. Therefore, a larger regression coefficient implies higher influence of its variable, ending up in a “stronger” demand of the catalyst in question.

Last two columns of Table 15 show the sum of the regression coefficients (in absolute value) of the variables from all the models which demand each of the catalysts. Cat5 is the overall best performance catalyst for the degreened case; that is, the variables pointing to Cat5 as a best catalyst weight in overall much than those for the rest of the catalysts. For the aged case, it is Cat3 which is ranked in the first position. Putting the degreening and the ageing states together, again Cat3 is the best one, which is the same conclusion as extracted in the overall performance analysis (5.2.2).

As it can be seen, even if Cat6 (degreened) and Cat5 (aged) are the most numerically demanded catalysts, its pointing variables are weak within the models and the sum of the absolute regression coefficients does not rank them as the best catalysts.

Table 15: Overall analysis of the best catalysts by means of regression (red: highest)

	Number times as "best cat."		$\Sigma$ abs(reg. coeff.)		
	Degreened	Aged	Degreened	Aged	TOTAL
Cat1	15	19	311,8	183,36	495,16
Cat2	19	14	303,04	162,68	465,72
Cat3	15	21	384,85	<b>373,63</b>	<b>758,48</b>
Cat4	16	15	355,78	334,9	690,68
Cat5	28	<b>42</b>	<b>499,85</b>	256,97	756,82
Cat6	<b>32</b>	31	489,41	229,08	718,49
Cat7	12	11	281,18	155,18	436,36
Cat8	12	11	281,18	155,18	436,36
Cat10	32	30	304,42	218,88	523,3

Breaking down last two columns of Table 15 according to the two different temperatures used in the regression gives rise to Table 16. The previous noticed best catalysts (Cat5 and Cat3) prevail for the low temperature case, while their homologous with thinner SCR layer gain importance at high temperature values. During high temperature lapses, Ammonia desorption from the SCR layer could happen. As thicker is the layer, greater amount of  $\text{NH}_3$  can be desorbed (as higher amount was absorbed) increasing the undesired  $\text{NH}_3$  slip. For this reason, at 450°C thinner SCR coating layers are to some extent preferred.

Table 16: Temperature differentiation analysis of the best catalysts by means of regression (red: highest)

	$\Sigma$ abs(reg. coeff.)			
	Degreened		Aged	
	250°C	450°C	250°C	450°C
Cat1	162,19	149,61	93,06	90,3
Cat2	134,26	168,78	73,19	89,49
Cat3	181,31	203,54	<b>179,17</b>	<b>194,46</b>
Cat4	150,15	205,63	140,59	<b>194,31</b>
Cat5	<b>267,02</b>	232,83	142,78	114,19
Cat6	239,09	<b>250,32</b>	120,22	108,86
Cat7	131,63	149,55	72,24	82,94
Cat8	131,63	149,55	72,24	82,94
Cat10	139,16	165,26	161,91	56,97

It is important to notice that higher absolute regression coefficients, apart from representing a higher weight of the term in the model, means that the variable is very sensitive; that is, little changes on the variable produce great changes on the response. Sensitivity is good or bad depending on the situation or for what is desired a specific model. If a model should be

robust, then the final choice of the catalyst must consist of a trade-off between significances of the factors and their sensitivity.

The regression analysis considering  $N_2O$  formation,  $NH_3$  slip and  $NO_x$  conversion indicates Cat5 degreened and Cat3 aged performances as the best ones, at both tested steady state temperatures and the 3 experimented ANRs. Cat5 has medium length and low Pt, while Cat3 is long with medium Pt. This conclusion is mainly due to the ageing effect on the SCR layer, which loses ammonia storage capacity. For this reason, the aged catalyst prefer higher amount of Pt in order to oxidise in a higher extent  $NH_3$  into  $NO_x$ , and prevent it from slipping out of the pipe.

Breaking down even more the analysis, it could be possible to find the best catalysts for each ANR value or for each response.

## 6 Discussion

This chapter includes the evaluation of the results obtained in this study, putting together the findings from the different methods of data analysis. It is mainly a summary of the outcomes from the previous section, in which the results have been analysed in detail.

The variation of temperature along the rear face diameter of the catalyst designs has shown to be high when considering the worst case: absolute difference between the centre and the outer diameter for the highest temperature operating point. If instead the calculations are spread to the whole experiment, the absolute thermal variation seems to be less severe. Further analysis has come to calculate the difference of temperature as a function of the catalyst area. It has concluded to give maximum deviation of temperature of 3 and 5°C for the degreened and aged catalysts, respectively, which are considered small taking into account the accuracy of the measurement equipment.

The analyses of the N<sub>2</sub>O formation, NH<sub>3</sub> slip and NO<sub>x</sub> conversion experimental data have taken place by means of three different methods.

The overall performance analysis does not correspond to any scientific method, but it has been considered to be useful due to the testing procedure conducted. As all the catalysts have been tried out under the same experimental conditions, the contribution of the averages to the overall sum is equivalent. Cat3 has resulted to be the best overall performance catalyst as it produces the minimum amounts of N<sub>2</sub>O + NH<sub>3</sub> and the maximum NO<sub>x</sub> conversions for almost all the ANR values of the degreened catalysts and for all the aged samples. Cat3 also seems to be the most suitable one even if the ramp up peak value is considered.

Nevertheless, if taking into account N<sub>2</sub>O formation and NH<sub>3</sub> slip separately, Cat3 suitability is only supported by its low NH<sub>3</sub> slip, while N<sub>2</sub>O formation is minimised by Cat4 degreened and Cat6 aged. The NH<sub>3</sub> contribution to the whole performance of the catalyst seems to weight more than the N<sub>2</sub>O, and as the ASC has to face up to all three gases, Cat3 is the best choice from a general point of view.

Factorial analysis is a very useful tool to figure out which are the most significant factors affecting the variance of the responses N<sub>2</sub>O, NH<sub>3</sub> and NO<sub>x</sub>. 2<sup>k</sup> factorial method requires very specific conditions in order to be conducted properly, such as two levels for each factor or the availability of all the factors combination. Both failed in this project: Cat9 was missing and its responses have been predicted according to the rest catalysts functioning; and factor's levels were three instead of two for Pt and length variables. Coping with this situation by rotating the design until having two levels for each factor has originated the redefinition of the Pt and length into Pt/L and Pt\*L respectively, which are quite difficult to interpret.

Degreened and aged catalysts responses are each of them in general terms affected by the same factors apart from the SCR coating thickness in the NO<sub>x</sub> conversion, which only shows effect on the aging state. The hydrothermal oven ageing lessens the SCR layer ability to store NH<sub>3</sub>, which affects the working of the catalyst.

Pure quadratic error has been noticed for NO<sub>x</sub> conversion, revealing lack of linearity within the factors levels tested. It is not possible to figure out the factor/s responsible for this fact. This same finding is also supported by the regression analysis for some of the NO<sub>x</sub> conversion models.

This factorial analysis has not made possible the choice of the best catalyst performance. A regression analysis is needed.

The  $2^3$  factorial analysis with blocking effects and the  $2^4$  factorial have been omitted from the results considering the poor information extracted from them.

The regression analysis has been performed considering the original design factors, their interactions and second order Pt variable. All they have been scaled to ease the interpretation of the results. For the different temperatures, ANR values and responses, there are 36 possible models: 18 for the degreened catalysts and 18 for the aged. One of them have shown not to be significant so no model could be proposed, which is supported by no significant factors in the factorial analysis.

Apart from checking the significant variables and models and proposing regression coefficients for them, Lack of Fit and Pure Quadratic errors have also been analysed and “R-squared and residuals plot checked. The confidence level has corresponded to 95%. None of the models show Lack of Fit error, but many present Pure Quadratic errors even if  $Pt^2$  has been included in the regression. Residuals plots do not discover any inadequacy for none of the models.

A method has been applied to know the most demanded catalyst from a general view of all the models. Catalysts fulfilling each model term requirements have been reported. Summing up the absolute regression coefficient of each variable pointing to each catalyst, the “strength” with which each catalyst is required in an overall sense can be known.

Cat3, as it happened in the overall performance analysis, has resulted to be the best catalyst when both the degreening and the ageing are summed up together. Considering both states independently, Cat5 is the best degreened catalyst and Cat3 is the best aged one. Breaking down the analysis according to the temperatures, the homologous catalysts to the just mentioned with thinner SCR layer take importance at higher temperature; that is, Cat6 for degreening and Cat4 for aged seem to be also suitable at high T as their lower SCR coating thickness produces less amount of  $NH_3$  desorption. This finding show how important the ageing effect on SCR coating thickness is on the operation as it makes that higher amount of Pt and high length (Cat3) is preferred in order to prevent ammonia that SCR is not able to store anymore from slipping. However, greater absolute regression coefficients also represent higher sensitivity, so the choice of the catalyst must be done according to the desired level of robustness. If robustness is not important the previous discussion is very suitable, but if the model should be robust a trade-off choice between sensitivity of the variables and their weight in the models should take place.

Summing up, Cat3 represents the best overall performance for the  $N_2O$  formation,  $NH_3$  slip and  $NO_x$  conversion responses examined under the support of two different analysis methods. Overall performance analysis has concluded that at different ANR values Cat3 is the most preferred one, while regression analysis has checked this putting together the degreening and ageing states. Hence, it can be affirmed that catalyst with a high length, a medium Pt load and a thick SCR layer could be very appropriate from a general point of view.

## 7 Final Remarks

This chapter concludes the project summarising the main aspects and suggesting some recommendations for further research of the Ammonia Slip Catalyst.

### 7.1 Conclusions

The increasing world globalization and the present life style make transportation an essential foundation for the future development. Free trade and free circulation of people have increased in the last decades the transport of both goods and passengers, which already produces around a 23% of the present air pollution.

European Union has tried to solve this situation implementing gradually more and more restrictive standards, which set up exhaust gases upper limits for on-road vehicles. The new Euro VI standard will be fully applied in January 2014, fixing maximum levels for heavy duty vehicles.  $\text{NO}_x$  emission is especially further restricted, which needs more severe urea injection in order to let the ammonia-SCR storing significant amount of  $\text{NH}_3$  for  $\text{NO}_x$  reduction. It generates higher ammonia slips which are also limited. For this reason, a dual layer Ammonia Slip Catalyst is an essential part of the aftertreatment system and should be further analysed to find an optimal design.

Ammonia Slip Catalysts with different length, Pt load (lower layer) and SCR coating thickness (upper layer) have been proposed by means of Design of Experiments tools. A pre-study of some of the catalysts samples has been conducted at the Johnson Matthey AB test cells, using heavy duty engine bench. It permits getting a general idea of how the ASCs work and checking the adequacy of the testing set-up and procedure. The analysis of the pre-study results has led to remove part of the thermocouples and just maintaining the ones placed in the highest thermal deviation direction. The testing procedure has resulted to give high amount of information with a low-time consuming experiment, so that, the full study has kept on using this methodology, but introducing minor timing modifications.

The full study experiments have been carried out with the 9 available catalysts. It has been conducted twice: one with the catalysts on a degreened state, and another one with the catalysts subjected to hydrothermal oven ageing. This ageing treatment cannot be equated to a specific mileage or period of time of catalyst use.

Thermal variations along the rear face of the catalysts has shown no important deviations, which almost fall within the thermocouples accuracy. It confirms that no different residence times, caused by different temperatures, could be registered.

$\text{N}_2\text{O}$  formation,  $\text{NH}_3$  slip and  $\text{NO}_x$  conversion on the ASC have been the responses of interest. First method of analysis has been created specifically for this project according to the testing procedure. It weights together the overall performance of each of the catalysts, finding out that Cat3 shows the best working at the different ANR values tested.

Analysis of Experiments tools has been also applied to examine and interpret the full study results. The factorial analysis has been useful to understand how the catalysts work when different operating conditions are applied, getting to know the critical factors at the different temperatures and ANRs and for the different responses.

Regression analysis has let model the different responses at different conditions, reaching a total of 36 possible models. Some cases are not possible to be modelled, fitting with the cases

in which factorial analysis show no significant factors. That is, the response in question is not strongly dependent in none of the variables.

In addition, both the regression and the factorials have found a Pure Quadratic error in some of the  $\text{NO}_x$  conversion responses, noting the non-linearity of some of the factors within the tested levels. Furthermore, just few cases have shown significant Pt\*SCR interaction, which means that even if the two different layers of the catalyst influence each other, this interaction does not affect significantly the responses.

Regression models have been used to analyse the demanded catalysts from each of the models terms. Summing together the absolute regression coefficients of the terms desiring each catalyst, it is possible to find out the most demanded catalyst from an overall point of view. Cat3 shows the best performance as it has been already obtained with the previous analysis. For the degreened case Cat5 is preferred, followed by Cat6 at high temperature specially; and for the aged case, Cat3 is better, but Cat4 shows good working at high temperatures. Ageing effect on the SCR layer is mainly determining the results as thicker SCR layer is preferred at high temperatures (minimise ammonia desorption) and higher Pt load and length are required in the ageing state (oxidise higher amount of ammonia that cannot be stored). These conclusions can be done in the absence of robustness consideration, as higher absolute regression coefficients indicate higher sensitivity of the variables in question.

In the absence of further experimentation, Cat3 can be considered as the best catalyst performance of the tested samples. This statement can be done when considering  $\text{N}_2\text{O}$  formation,  $\text{NH}_3$  slip and  $\text{NO}_x$  conversion together, as the Ammonia Slip Catalyst will face up with all the three gases.

To conclude, it is important to mention that the Ammonia Slip Catalyst characterised by dual layer architecture becomes a very complex system to analyse. In the real life, the catalyst works on a wide range of conditions, which have been tried to simulate in the Johnson Matthey AB test cells. This broad range of working conditions complicates even more the understanding of the functioning and makes more difficult the choice of an optimum catalyst design. Anyway, different methods of analysis have agreed pointing towards Cat3 as the best of the examined catalysts.

## 7.2 Recommendations

This section intends to give some guidelines of how carrying out further research on the Ammonia Slip Catalysts:

- Pt load and SCR coating thickness should be consistent in terms of units. Both should be represented according to the same criteria; that is, or mass or mass/volume, but both in the same way.
- The design of the catalysts should be conducted following the factorials principles in order to be able to analyse the results on a more suitable way. It would permit to respect the original catalysts design factors, which have a clear meaning and can be directly interpreted.
- The testing procedure should be revised to in order to increase the steady state experimentation time and decrease the stationary periods. Stationary conditions are represented by the so-called “ramp up” and “ramp down”. They have shown not very relevant contribution to the analysis. For this reason, it would be convenient to set three different steady state temperatures, under which the three different ANRs are tested. For instance, 250°C, 325°C and 450°C at ANR 1.0, 1.2 and 1.4 can be experimented, giving rise to 9 different operating conditions with equidistant levels between them.
- NO<sub>x</sub> conversion response has shown an important Pure Quadratic error, which advertises of the presence of non-linearity within some of the catalysts levels. Even if Pt<sub>2</sub> is included in the models, this error does not disappear, so it could be linked to length or SCR coating thickness. The ideal solution to figure out the factor responsible for this error would be designing 3 extra catalysts for each catalyst design. The extra catalysts would differ from the original one on that only one of the factors at a time is set into its medium level. In this way, there would be, instead of 8 different designs (not considering centre points) 32 designs, which is completely unaffordable taking into account catalysts’ production cost.
- Cat3 has seemed to be the best of the tested designs. It should be further experimented by means of different tests, such us on-road testing. It is important to expose the sample to the real conditions and check if it works in the same way as in the engine bench. Furthermore, Cat3 should be subjected to the standardised WHSC and WHTC to study if it fulfils Euro VI normative limits.

## 8 References

1. **Heck, R. M. and Farrauto, R. J.** *"Catalytic Air Pollution Control"*. 2nd. s.l. : John Wiley & Sons, Inc., 2002. ISBN 0-471-43624-0.
2. "European emission standards". *WIKIPEDIA*. [Online] [Cited: 12 02 2013.] [http://en.wikipedia.org/wiki/European\\_emission\\_standards#Emission\\_standards\\_for\\_lorries\\_and\\_buses](http://en.wikipedia.org/wiki/European_emission_standards#Emission_standards_for_lorries_and_buses).
3. **United Nations Economic Commission for Europe (UNECE)**. *"UNECE to adopt new ceilings of emissions for trucks and buses"*. [Online] 20 01 2012. [Cited: 12 02 2013.] <http://www.unece.org/index.php?id=28534>.
4. **DELPHI**. [Online] 2012-2013. [Cited: 08 02 2013.] [www.delphi.com/pdf/emissions/Delphi-Heavy-Duty-Emissions-Brochure-2012-2013.pdf](http://www.delphi.com/pdf/emissions/Delphi-Heavy-Duty-Emissions-Brochure-2012-2013.pdf).
5. **Bowles, K.** Nonmethane Hydrocarbons. *TermWiki*. [Online] 12 01 2011. [Cited: 26 02 2013.] [www.ar.termwiki.com/EN:nonmethane\\_hydrocarbons\\_\(NMHCs\)](http://www.ar.termwiki.com/EN:nonmethane_hydrocarbons_(NMHCs)).
6. **DieselNet**. *Heavy-Duty Truck and Bus Engines*. [Online] [Cited: 18 02 2013.] [www.dieselnets.com/standards/eu/hd.php#stds](http://www.dieselnets.com/standards/eu/hd.php#stds).
7. **Jennifer Phillips. VÍGYAN Incorporated**. *Control and Pollution Prevention Options for Ammonia Emissions*. s.l. : Control Technology Center. U.S. Environmental Protection Agency, 04 1995. EPA-456/R-95-002.
8. **Lambert, C. K., Catavaio, G. and Girard, J. W.** "The Influence of Ammonia Slip Catalysts on Ammonia, N<sub>2</sub>O and NO<sub>x</sub> Emissions for Diesel Engines". *SAE Technical Paper 2007-01-1572*. 2007. ISBN 0-7680-1635-5.
9. UK and Ireland. *Castrol*. [Online] [Cited: 26 02 2013.] <http://www.castrol.com/castrol/extendedsectiongenericarticle.do?categoryId=9034603&contentId=7064146>.
10. **Vartia, Christian**. *Properties of Vanadia- and Zeolite-based catalysts for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>*. Department of Chemical and Biological Applied Surface Chemistry and Competence Center of Catalysis. Göteborg, Sweden : Chalmers University of Technology, 2006. p. 49, M Sc Thesis.
11. **Kamasamudram, K., et al.** "New Insights into Reaction Mechanism of Selective Catalytic Ammonia Oxidation Technology for Diesel Aftertreatment Applications". *SAE Int. J. Engines*. 04 12 2011. Vol. 4, 1, pp. 1810-1821. doi:10.4271/2011-01-1314.
12. **Scheuer, A., et al.** "Dual layer automotive Ammonia oxidation catalysts: Experiments and computer simulation". *Applied Catalysis B: Environmental*. s.l. : ELSEVIER, 28 10 2011. pp. 445-455. doi:10.1016/j.apcatb.2011.10.032.
13. **Komatsu, T., et al.** "Kinetic Studies of Reduction of Nitric Oxide with Ammonia on Cu<sup>2+</sup> Exchanged Zeolites". *Journal of Catalysis*. 1994. Vol. 148, 2, pp. 427-437. 0021-9517/94.
14. **Seiyama, T., et al.** "Catalytic Activity of Transient Metal Ion Exchanged Y Zeolites in the Reduction of Nitric Oxide with Ammonia". *Journal of Catalysis*. 1977. Vol. 48, 1-3, pp. 1-7. ISSN 0021-9517.
15. **Montgomery, D. C.** *"Design and Analysis of Experiments"*. 6th. s.l. : John Wiley & Sons, Inc., 2005. ISBN 0-471-48735-X.

16. **Sukumar, B., et al.** "Modeling of Dual Ammonia Slip Catalysts". *SAE Technical Paper 2012-01-1294*. 16 04 2012. doi:10.4271/2012-01-1294.
17. **DieselNet.** *Deactivation of Diesel Catalyst*. [Online] 2002. [Cited: 11 02 2013.] [www.dieselnets.com/tech/cat\\_d\\_deactiv.php](http://www.dieselnets.com/tech/cat_d_deactiv.php).
18. —. *Emission Standards: EU*. [Online] [Cited: 07 02 2013.] [www.dieselnets.com/standards/eu/#vcat](http://www.dieselnets.com/standards/eu/#vcat).
19. **J.U.M. Engineering.** [Online] [Cited: 31 01 2013.] [www.jum.com/products/analyzers/fid.html](http://www.jum.com/products/analyzers/fid.html).
20. "Chemiluminescence". *WIKIPEDIA*. [Online] [Cited: 31 01 2013.] [www.en.wikipedia.org/wiki/Chemiluminescence](http://www.en.wikipedia.org/wiki/Chemiluminescence).
21. **K2BW Environmental Equipment Services Co.** INFRARED GAS ANALYZERS AND GAS FILTER CORRELATION. [Online] [Cited: 01 02 2013.] [www.k2bw.com/5\\_c\\_18.htm](http://www.k2bw.com/5_c_18.htm).
22. **SICK MAIHAK GmbH.** [Online] 2.0. [Cited: 04 02 2013.] [www.sick.com/uk/en-uk/home/service/documentation/Documents/S700/S700%20OPERATING%20MANUAL%20V2010\\_1.pdf](http://www.sick.com/uk/en-uk/home/service/documentation/Documents/S700/S700%20OPERATING%20MANUAL%20V2010_1.pdf). 8009720.
23. **Siemens Laser Analytics AB.** [Online] 5.3, 10 2001. [Cited: 01 02 2013.] [http://infos.mpip.free.fr/siemens/Spectrometrie%20de%20Process/LDS%203000%20Operators\\_Man\\_En\\_1.0.pdf](http://infos.mpip.free.fr/siemens/Spectrometrie%20de%20Process/LDS%203000%20Operators_Man_En_1.0.pdf). CID 3002-1101.
24. **Sjöblom, J., et al.** "Use of experimental design in development of a catalyst system". *Catalyst Today*. 28 02 2005. Vol. 100, 3-4, pp. 243-248. doi:10.1016/j.cattod.2004.09.066.
25. **Wallin, M., et al.** "Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub> over zeolite H-ZSM-5: influence of transient Ammonia supply". *Journal of Catalysis*. 2003. Vol. 218, 2, pp. 354-364. doi:10.1016/S0021-9517(03)00148-9.

# Appendices

Appendix 1. Vehicle Categories

Appendix 2. Measurement Procedures

HC

NO<sub>x</sub>

CO

CO<sub>2</sub>/O<sub>2</sub>

N<sub>2</sub>O

NH<sub>3</sub>

Appendix 3. Pre-study results and analysis

Appendix 4. Full study results and analysis

Temperature profile

Factorials

Regression

## Appendix 1. Vehicle Categories

For the purpose of emission standards and other regulations, European Union classifies vehicles into different categories. Table 17 defines these categories.

Table 17: European Union Vehicle Categories. (18)

Category	Description
<b>M</b>	Motor vehicles with at least four wheels designed and constructed for the carriage of passengers.
<b>M1</b>	Vehicles designed and constructed for the carriage of passengers and comprising no more than eight seats in addition to the driver's seat.
<b>M2</b>	Vehicles designed and constructed for the carriage of passengers, comprising more than eight seats in addition to the driver's seat, and having a maximum mass ("technically permissible maximum laden mass") not exceeding 5 tons.
<b>M3</b>	Vehicles designed and constructed for the carriage of passengers, comprising more than eight seats in addition to the driver's seat, and having a maximum mass exceeding 5 tons.
<b>N</b>	Motor vehicles with at least four wheels designed and constructed for the carriage of goods.
<b>N1</b>	Vehicles designed and constructed for the carriage of goods and having a maximum mass not exceeding 3.5 tons.
<b>N2</b>	Vehicles designed and constructed for the carriage of goods and having a maximum mass exceeding 3.5 tons but not exceeding 12 tons.
<b>N3</b>	Vehicles designed and constructed for the carriage of goods and having a maximum mass exceeding 12 tons.
<b>O</b>	Trailers (including semi-trailers).
<b>G<sup>2</sup></b>	Off-Road Vehicles.

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<sup>2</sup> Symbol G shall be combined with either symbol M or N

## Appendix 2. Measurement procedures

The measurements are step-wise for the conditioning phase and the initial period of the urea swing (250°C), and continuous for the rest of the urea swing (see 4.3.2). In situ analysers of hot and moist gas samples are used, whose measuring principles are briefly explained:

### HC

Total hydrocarbon concentrations are determined using the Flame Ionization Detector (FID) principle. This technique provides a high selectivity to hydrocarbons and it is not affected by the presence of other exhaust components. It consists of burning the HC-containing sample into a flame, what produces a high number of ions. An electrostatic field is created by applying a high polarizing voltage between two electrodes at both sides of the flame. Anions move towards the collector electrode, while cations migrate to the high voltage electrode. The created ionization current, measured by an electrometer amplifier, is directly proportional to the hydrocarbon concentration of the sample. (19)

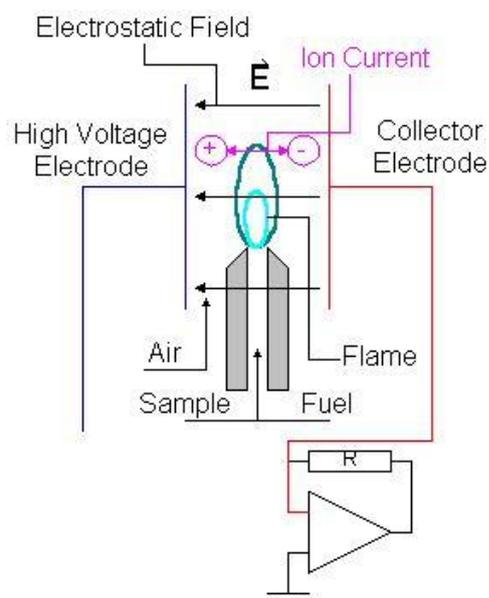
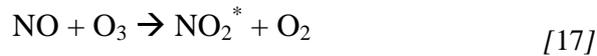


Figure 12: Flame Ionization Detector (FID) principle.

## NO<sub>x</sub>

NO<sub>x</sub> content is obtained by Chemiluminescence Analysis. It consists of a reaction producing an excited product, which decays to a lower energy level emitting light. In this case, NO reacts with ozone producing activated NO<sub>2</sub> and oxygen:



The exhaust is half-split into two identical streams. One of them is passed by a converter of NO<sub>2</sub> into NO. Both separated gas streams are fed into two parallel reactions chambers where the chemiluminescence reaction takes place. Each emitted photon is proportional to one molecule of NO reacted. By counting photons NO content can be determined.

The untreated stream reveals the NO content, while the converted one the NO+NO<sub>2</sub> content. By subtraction, NO<sub>2</sub> concentration can also be known. (20)

## CO

Carbon monoxide is measured by Gas-Filter Correlation Radiometry (GFCR). It uses a rotating gas-filled filter wheel containing two chambers. One is filled with the specie of interest while the other encloses an optically inert gas, such as nitrogen. This filter is placed between an IR source and a single chamber, where the gas sample is contained. When the wheel rotates, the light passes through only one side as well as through the sample chamber. IR energy is attenuated when it passes the chamber with the specie, but not when it does through the inert one as it can be seen in Figure 13. The difference in energy between both is inversely proportional to the specie content in the sample. The presence of interfering species affects to both filter chambers, so the attenuated energy cancels out and it does not affect the final result. (21)

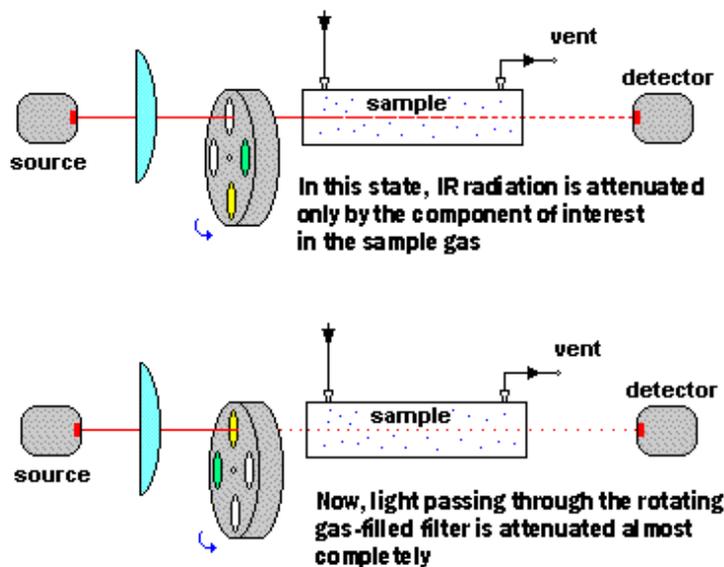


Figure 13: Gas Filter Correlation Infrared Photometer.

## CO<sub>2</sub>/O<sub>2</sub>

Carbon dioxide is measured by Gas-Filter Correlation Radiometry (GFCR), explained lines above.

The O<sub>2</sub> is measured by Paramagnetism. The measuring cell contains a suspended diamagnetic dumbbell in a way that could rotate out of the magnetic field. To keep it in a specific resting position, an opto-electrical compensation circuit is available. As the exhaust gas passes through the cell, the paramagnetic properties of O<sub>2</sub> change the magnetic field, forcing the dumbbell to shift its position. The opto-electronic compensation to recover the resting position is read by the software and evaluated as an O<sub>2</sub> concentration change.

If other gas components present also high magnetic susceptibility, measurements deviation could occur. However, it is not the case since the magnetic characteristics of other gases present in the exhaust are very small in relation to the oxygen one. (22)

## N<sub>2</sub>O

Nitrous oxide is measured by a Non-Dispersive Infrared Sensor (NDIR). As Figure 14 shows it consists of two parallel chambers through which infrared energy passes falling on a detector. One of the chambers is the measurement cell filled with the gas sample. The other one is the reference cell containing a non-absorbing gas (e.g. nitrogen). Before the detector an optical filter is placed so that only can pass the wavelength that the compound of interest can absorb. Comparing the output signals from both tubes, the amount of energy absorbed by the gas can be determined, what is proportional to the amount of interest gas. (21)

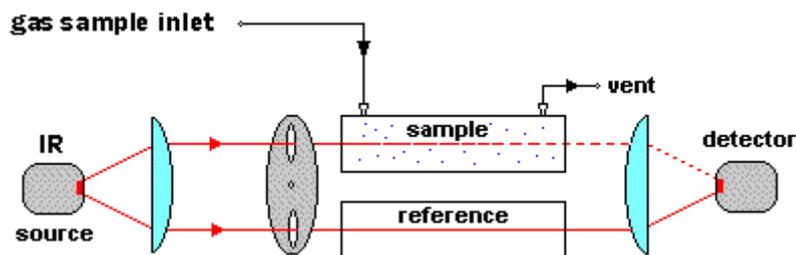


Figure 14: Infrared photometer.



### Appendix 3. Pre-study results and analysis

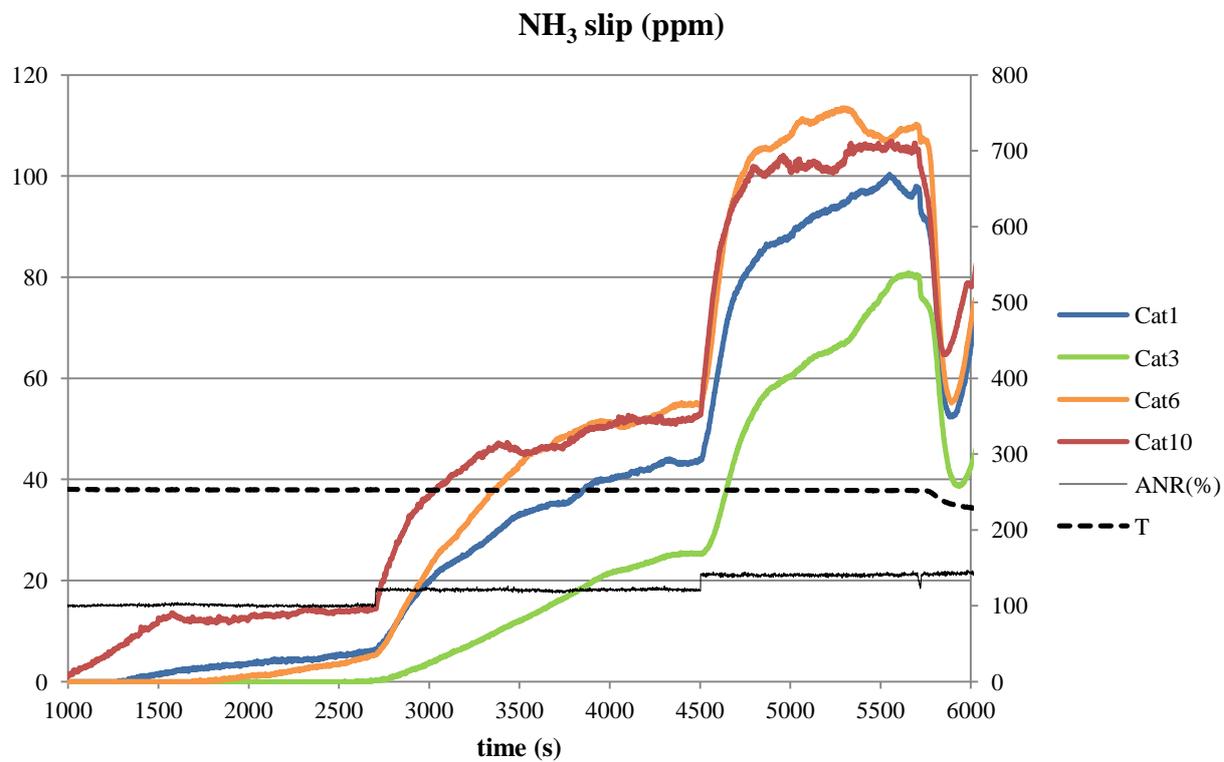


Figure 16: Pre-study NH<sub>3</sub> slip at 250°C.

It can be seen that no stability is reached at each of the ANR steps only for the Ammonia slip.

## Appendix 4. Full study results and analysis

### Temperature profile

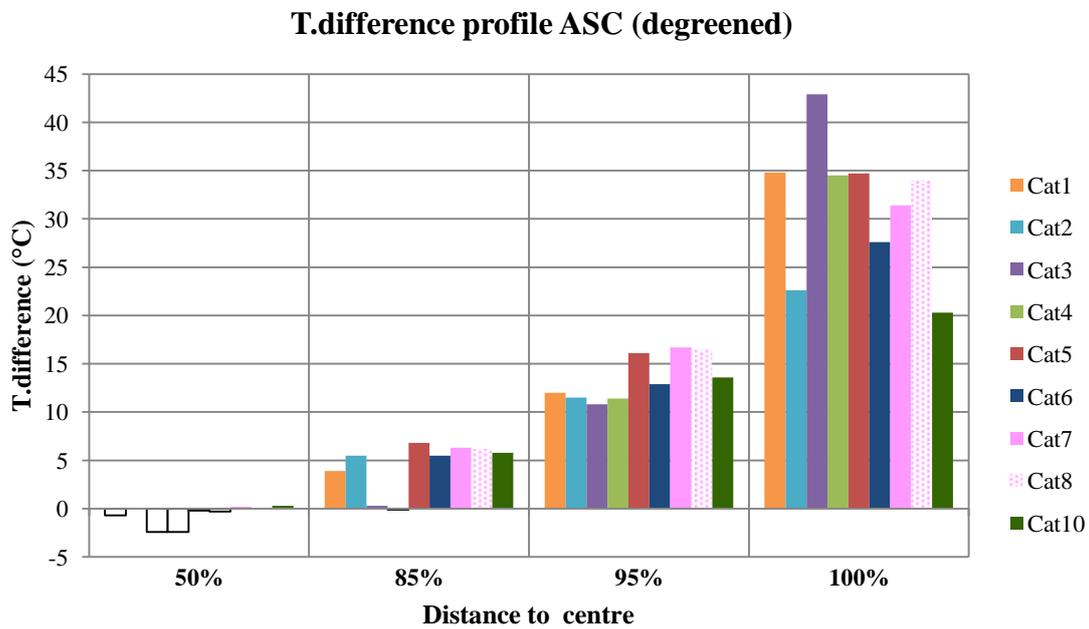


Figure 17: Temperature difference profile for the degreened ASCs.

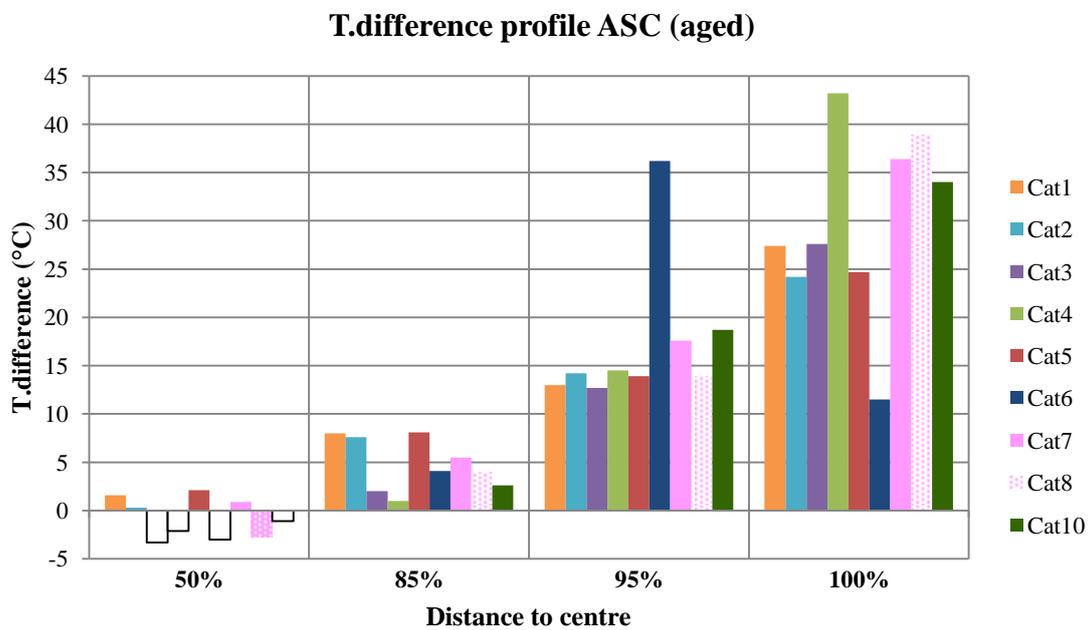
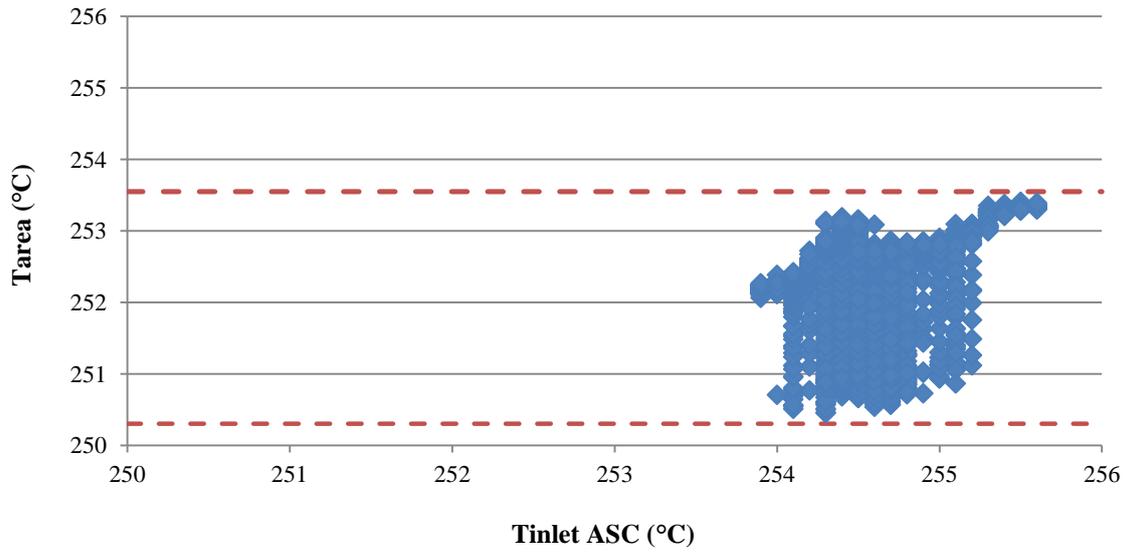


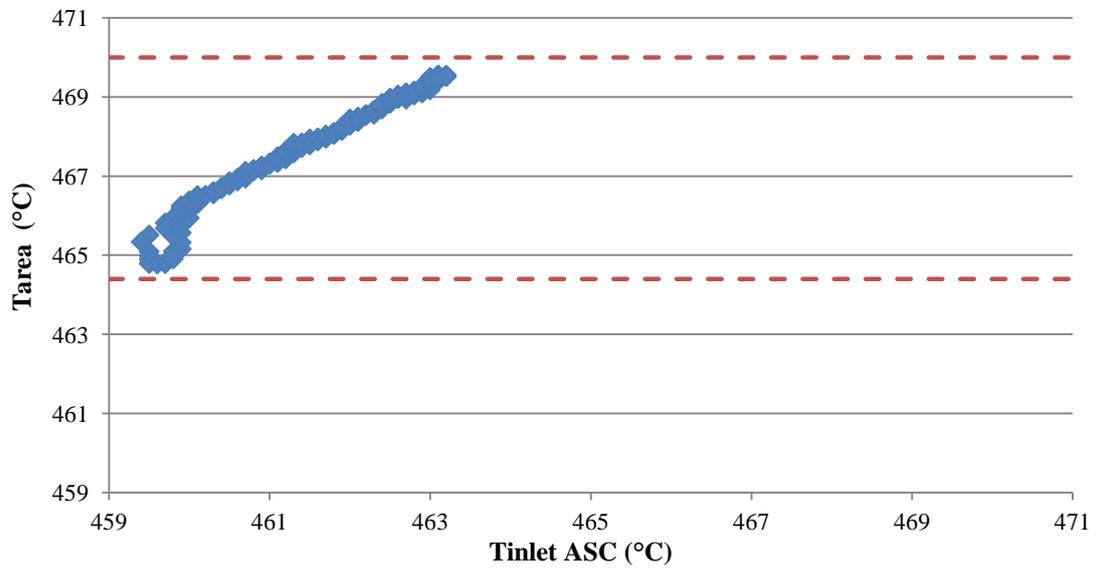
Figure 18: Temperature difference profile for the aged ASCs.

**250°C: Cat10, degreened**



*Figure 19: Maximum variation of temperature at 250°C.*

**450°C: Cat4, aged**



*Figure 20: Maximum variation of temperature at 450°C.*

## Factorials

In the following tables, intense red corresponds to a 99% of confidence level and light red to a 95%.

Table 18: Degreened catalysts significant factors of the 2<sup>3</sup> factorial.

DEGREENED	NH <sub>3</sub>												N <sub>2</sub> O												NO <sub>x</sub>											
	Conditions				N <sub>2</sub> O				NH <sub>3</sub>				NO <sub>x</sub>																							
	T	ANR	A	B	C	AB	AC	BC	ABC	pq	A	B	C	AB	AC	BC	ABC	pq	A	B	C	AB	AC	BC	ABC	pq										
200°C	1.0									X	X																									
225°C	1.4	X	X							X	X	X									X	X														
250°C	1.0									X	X																									
250°C	1.2	X	X							X											X	X														
250°C	1.4	X	X							X	X										X	X														
250°C	1.0	X	X	X						X	X										X	X														
450°C	1.2									X	X										X	X														
450°C	1.4	X	X							X	X	X									X	X	X													

Table 19: Aged catalysts significant factors of the 2<sup>3</sup> factorial.

AGED	NH <sub>3</sub>												N <sub>2</sub> O												NO <sub>x</sub>											
	Conditions				N <sub>2</sub> O				NH <sub>3</sub>				NO <sub>x</sub>																							
	T(°C)	ANR	A	B	C	AB	AC	BC	ABC	pq	A	B	C	AB	AC	BC	ABC	pq	A	B	C	AB	AC	BC	ABC	pq										
200°C	1.0									X	X																									
225°C	1.4	X	X							X	X										X	X														
250°C	1.0	X								X	X										X	X														
250°C	1.2	X	X							X	X	X									X	X	X													
250°C	1.4	X	X							X	X	X									X	X	X													
450°C	1.0									X	X										X	X														
450°C	1.2	X	X	X						X	X	X									X	X	X													
450°C	1.4	X	X							X	X	X									X	X	X													

## Regression

Table 20: Regression models for the degreened ASCs.

DEGREENED								
T	ANR		Model	R <sup>2</sup> (%)	LOF	PQ	Residuals	
250°C	1.0	N <sub>2</sub> O	$1.18 + 0.29 \cdot L + 0.4 \cdot Pt + 0.58 \cdot (L \cdot Pt)$	68.17	-	-	✓	
		NH <sub>3</sub>	$13.16 - 9.17 \cdot L$	69.7	-	-	✓	
		NO <sub>x</sub>						
	1.2	N <sub>2</sub> O	$6.15 + 2.26 \cdot Pt$	70.34	-	-	✓	
		NH <sub>3</sub>	$55.14 - 50.15 \cdot L - 39.54 \cdot Pt - 10.54 \cdot SCR - 34.87 \cdot (L \cdot Pt) - 35.57 \cdot (Pt^2)$	96.57	-	X	✓	
		NO <sub>x</sub>	$81.13 - 2.57 \cdot L - 11.36 \cdot Pt - 0.49 \cdot SCR + 3.23 \cdot (L \cdot SCR) - 14.66 \cdot (Pt^2)$	99.93	-	X	✓	
	1.4	N <sub>2</sub> O	$10.51 + 8.38 \cdot L + 13.24 \cdot Pt + 2.14 \cdot SCR + 8.58 \cdot (L \cdot Pt) + 9.98 \cdot (Pt^2)$	96.67	-	X	✓	
		NH <sub>3</sub>	$116.14 - 82.51 \cdot L - 73.36 \cdot Pt - 20.02 \cdot SCR - 63.18 \cdot (L \cdot Pt) - 68.52 \cdot (Pt^2)$	96.11	-	X	✓	
		NO <sub>x</sub>	$85.75 + 5.69 \cdot L - 7.06 \cdot Pt - 8.94 \cdot (Pt^2)$	96.6	-	-	✓	
450°C	1.0	N <sub>2</sub> O	$1.25 + 0.15 \cdot L - 0.01 \cdot Pt - 0.06 \cdot SCR - 0.29 \cdot (Pt^2)$	98.56	-	X	✓	
		NH <sub>3</sub>	$27.06 - 32.18 \cdot L - 9 \cdot Pt + 1.96 \cdot SCR - 26.17 \cdot (L \cdot Pt) - 3.92 \cdot (L \cdot SCR) - 4.23 \cdot (Pt \cdot SCR) - 18.08 \cdot (Pt^2)$	100	-	X	✓	
		NO <sub>x</sub>	$70.2 - 13.34 \cdot L - 29.76 \cdot Pt - 6.54 \cdot SCR + 13.16 \cdot (L \cdot SCR) + 1.55 \cdot (Pt \cdot SCR) - 20.53 \cdot (Pt^2)$	99.99	-	X	✓	
	1.2	N <sub>2</sub> O	$1.32 + 0.49 \cdot L + 0.39 \cdot Pt$	66.14	-	-	✓	
		NH <sub>3</sub>	$50.15 - 67.61 \cdot L - 27.44 \cdot Pt + 3.2 \cdot SCR - 47.13 \cdot (L \cdot Pt) - 29.99 \cdot (Pt^2)$	99.77	-	X	✓	
		NO <sub>x</sub>	$79.22 + 7.78 \cdot L - 10.54 \cdot Pt - 9.61 \cdot (Pt^2)$	98.28	-	-	✓	
	1.4	N <sub>2</sub> O	$1.97 + 0.59 \cdot L + 0.48 \cdot Pt - 0.41 \cdot (Pt^2)$	93.49	-	-	✓	
		NH <sub>3</sub>	$67.54 - 64.16 \cdot L - 8.16 \cdot Pt + 6.69 \cdot SCR - 34.29 \cdot (L \cdot Pt) + 5.5 \cdot (Pt \cdot SCR) - 13.54 \cdot (Pt^2)$	99.97	-	X	✓	
		NO <sub>x</sub>	$76.17 + 14.67 \cdot L - 8.44 \cdot Pt - 0.84 \cdot SCR + 5.8 \cdot (L \cdot Pt) - 1.96 \cdot (Pt \cdot SCR) - 6.02 \cdot (Pt^2)$	99.98	-	X	✓	

Table 21: Regression models for the aged ASCs.

AGED								
T	ANR		Model	R <sup>2</sup> (%)	LOF	PQ	Residuals	
250°C		N <sub>2</sub> O	$2.61 + 0.86 \cdot L + 1.34 \cdot Pt + 1.29 \cdot (L \cdot Pt)$	84.34	-	-	✓	
	1.0	NH <sub>3</sub>	$16.89 - 9.31 \cdot L$	57.43	-	-	✓	
		NO <sub>x</sub>	$54.64 - 3.86 \cdot Pt - 6.67 \cdot (Pt^2)$	79.16	-	X	✓	
		N <sub>2</sub> O	$10.3 + 6.56 \cdot Pt$	79.47	-	-	✓	
	1.2	NH <sub>3</sub>	$51.93 - 29.91 \cdot L - 27.1 \cdot Pt - 9.67 \cdot SCR$	89.96	-	-	✓	
		NO <sub>x</sub>	$80.54 + 7.74 \cdot L - 3.02 \cdot Pt - 0.55 \cdot SCR + 6.15 \cdot (L \cdot Pt) - 1.19 \cdot (Pt \cdot SCR) - 3.11 \cdot (Pt^2)$	99.99	-	X	✓	
	N <sub>2</sub> O	$14.99 + 9.28 \cdot Pt$	80.82	-	-	✓		
450°C	1.4	NH <sub>3</sub>	$102.86 - 79.48 \cdot L - 75.69 \cdot Pt - 11.15 \cdot SCR - 47.25 \cdot (L \cdot Pt) - 18.07 \cdot (L \cdot SCR) - 31.86 \cdot (Pt^2)$	99.82	-	X	✓	
		NO <sub>x</sub>	$78.8 + 13.2 \cdot L + 1.87 \cdot Pt - 0.4 \cdot SCR + 9.06 \cdot (L \cdot Pt) + 0.64 \cdot (L \cdot SCR) - 1.5 \cdot (Pt \cdot SCR) + 0.89 \cdot (Pt^2)$	100	-	X	✓	
		N <sub>2</sub> O	$1.71 + 0.12 \cdot L + 0.05 \cdot Pt - 0.13 \cdot SCR - 0.2 \cdot (Pt \cdot SCR) - 0.33 \cdot (Pt^2)$	97.91	-	-	✓	
	1.0	NH <sub>3</sub>	$28.29 - 25.68 \cdot L - 5.6 \cdot Pt - 11.42 \cdot (L \cdot Pt)$	97.19	-	-	✓	
		NO <sub>x</sub>	$63.87 + 7.91 \cdot L - 7.01 \cdot Pt + 3.27 \cdot SCR + 6.3 \cdot (L \cdot Pt)$	98.88	-	-	✓	
		N <sub>2</sub> O	$2.37 + 0.84 \cdot L + 0.22 \cdot Pt - 0.16 \cdot SCR + 0.66 \cdot (L \cdot SCR) - 0.29 \cdot (Pt \cdot SCR) - 0.62 \cdot (Pt^2)$	99.41	-	-	✓	
1.2	NH <sub>3</sub>	$55.08 - 50.2 \cdot L - 9.28 \cdot Pt + 6.55 \cdot SCR - 22.64 \cdot (L \cdot Pt) - 2.88 \cdot (L \cdot SCR) + 2.64 \cdot (Pt \cdot SCR)$	99.98	-	-	✓		
	NO <sub>x</sub>	$65.99 + 16.8 \cdot L - 2.48 \cdot Pt + 1.66 \cdot SCR + 9.98 \cdot (L \cdot Pt) - 0.75 \cdot (Pt \cdot SCR) + 2.44 \cdot (Pt^2)$	100	-	-	✓		
	N <sub>2</sub> O	$3.1 + 0.23 \cdot Pt - 0.31 \cdot SCR - 0.45 \cdot (Pt \cdot SCR) - 0.91 \cdot (Pt^2)$	94.92	-	-	✓		
1.4	NH <sub>3</sub>	$71.47 - 66.04 \cdot L - 18.73 \cdot Pt - 22.52 \cdot (L \cdot Pt)$	95.91	-	-	✓		
	NO <sub>x</sub>	$62.41 + 20.47 \cdot L - 0.93 \cdot Pt + 1.83 \cdot SCR + 10.08 \cdot (L \cdot Pt) - 1.09 \cdot (Pt \cdot SCR) + 3.7 \cdot (Pt^2)$	99.99	-	X	✓		