

POLITECNICO DI TORINO

MASTER'S DEGREE

In Automotive Engineering

MASTER'S DEGREE THESIS

Validation analysis of an SCR for an Heavy Duty application



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Anno Accademico 2018/2019

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Abstract

Due to the stringent emission standards widespread in all automotive markets the development of technologies and procedures of validation and calibration of aftertreatment components takes a predominant importance every day.

The object of the thesis is to describe, comment and follow the procedure of validation of a brand new Selective Catalytic Reduction SCR as fresh and aged component, starting from the base theoretical knowledge about the chemical reactions, structure and designing.

The procedure adopted implies the installation of the tested catalysts with the use of an engine, 4 cylinder 3.0L same class of the one for which the SCR was designed, as emissions and flow generator with the addition of the Diesel Oxidation Catalyst DOC-Diesel Particulate Filter DPF designed for the application. Two types of automated tests have been developed to acquire the most important informations related to efficiency, maximum NH₃ storage inside the component, time and load needed to achieve the slippage of NH₃ after saturation and behavior of the component during the NH₃ unloading phase; requirements for the validation activity and the future calibrations.

One automated cycle was also prepared for the ageing procedure.

The presented results will show trends in line with the EURO VI legislation similar to the CHINA VI rules for which the component was designed. For a deeper analysis few comparisons have been taken into account related to the components tested; a lower Cells Per Square Inch cpsi, cpsi_1, in comparison to an high cpsi, cpsi_2, components with the same and with different mixers; the final mixer permits an increase of the conversion performances in line with an arrangement of first release mixer and Clean Up catalyst, tests related to the change of DOC-DPF monolith related to the brand new exhaust system and the already homologated one used as reference for which negligible differences have been noted.

At two third of the ageing procedure, the component deterioration has been evaluated in an average loss of about 30% of the loading capacity and a maximum loss of 50%.

Sommario

Il lavoro di tesi si inserisce in un progetto più ampio di sviluppo di un nuovo motore ed un nuovo sistema di aftertreatment per un'applicazione Heavy Duty per il mercato asiatico svoltosi nelle sale prova FEV. Nel dettaglio, il progetto di tesi riguarda l'analisi, la caratterizzazione e la validazione di un SCR (Selective Catalytic Reduction) sviluppato all'interno del progetto stesso; riferimento per i test svolti e' un componente omologo già in produzione con omologazione EURO VI.

SCR e' uno dei sistemi che si possono trovare in ambito automobilistico ma anche in applicazioni stazionarie, utilizzati per la riduzione degli Ossidi di Azoto (NO_x) all'interno dei gas di scarico attraverso l'iniezione di urea ($(NH_2)_2CO$).

La base teorica del lavoro di tesi e' stata nella comprensione delle reazioni chimiche che regolano il lavoro dei catalizzatori, in particolare la comprensione dei meccanismi di catalizzazione interni e dei materiali catalitici capaci di abbassare l'energia di attivazione di particolari reazioni a discapito di altre; il componente ha una struttura in cordierite con un washcoat di Cu-Zeolite capace di avere una forte selettività verso la molecola di N₂. Sono state indagate le interazioni che hanno i vari componenti della linea di scarico tra di loro; in particolare al variare dei punti di lavoro dei singoli componenti e le efficienze relative i restanti sistemi rispondono in maniera diversa dai riferimenti presi; l'efficienza di conversione di un SCR dipende dal rapporto NO₂/NO_x che il DOC-DPF in grado di fornire, specialmente al di sotto della temperatura di utilizzo ottimale del catalizzatore urea, 300°C-450°C e un portata minima di 200kg/h. Inoltre anche le distanze tra i componenti sono motivo di cambiamenti nel comportamento dell'intero sistema perché alla base di perdite temperatura e pressione. Fondamentale per l'omologazione è anche il processo di invecchiamento che comporta una de-attivazione termica della Zeolite con una conseguente diminuzione della capacità di questa di intrappolare le molecole presenti all'interno dei gas incombusti.

Nello svolgimento della tesi sono state riportate nel dettaglio tutte le variabili e le loro influenze:

- Temperatura ingresso SCR che ha il peso maggiore nel raggiungimento delle efficienze richieste. Fondamentale come emerso nelle prove, tenere questa

variabile nella finestra di utilizzo ottimale; al di sopra dei 250°C per attivare i processi chimici necessari ma al di sotto dei 500°C per evitare l'ossidazione delle molecole di NH₃.

- Portata dei gas combusti capace di innalzare la conversione del NO_x a temperature minori poiché migliora l'effetto aerodinamico del mixer. Inoltre a portate maggiori i tempi richiesti per il massimo accumulo di NH₃ ed il completo rilascio diminuiscono.
- Rapporto NO₂/NO_x che influenza l'efficienza di conversione a basse temperature ma inficia anche a temperature ottimali di esercizio i tipi di reazione chimica che si vanno a svolgere. Questa variabile è legata alle efficienze di conversione dei sistemi DOC '*Diesel Oxidation Catalyst*' e DPF '*Diesel Particulate Filter*' .
- Slip '*scivolamento*' dell'ammonia NH₃¹. Avere all'interno del componente a disposizione NH₃ è fondamentale per tenere percentuali di conversione sufficientemente alte. Questa deve essere regolata tenendo in considerazione la capacità del componente di immagazzinare questa sostanza al variare dei punti di funzionamento, specialmente al variare della temperatura.

La preparazione delle prove al banco specifiche per lo svolgimento del lavoro di tesi ha riguardato l'installazione di un motore omologato EURO VI per una equivalente applicazione europea del progetto con la calibrazione della combustione come da rilascio di produzione. L'intero sistema di scarico progettato per l'applicazione specifica è stato strumentato in modo da avere informazioni di temperatura su tutta la linea ed inserendo le linee calde per la misura delle emissioni da parte dei banchi analisi a monte e valle del SCR così come i sensori veicoli sono analizzate le emissioni di Ossidi di Azoto NO_x ed ammonia NH₃.

L'attività ha previsto l'implementazione di due test automatici:.

¹ NH₃ non subisce reazioni in atmosfera che portano alla formazione di acidi di azoto, e dunque non contribuisce all'acidificazione delle piogge come invece gli ossidi di azoto; tuttavia può portare (per ricaduta sui suoli e trasformazioni ad opera di particolari batteri) all'acidificazione dei suoli e, di conseguenza, delle acque di falda, in forti concentrazioni provoca gravi danni alla vegetazione. E' un importante precursore di acidi secondari. (16)

- *Alpha sweep*: Iniezioni calibrate di urea per raggiungere specifici rapporti di NH_3/NO_x , per la verifica dell'efficienze di conversione per specifici punti di funzionamento che sono stati considerati di valore indicativo per il tipo di utilizzo del componente.
- *Load-unload*: Cicli di immagazzinamento e rilascio di NH_3 per testarne i tempi di riempimento e rilascio ma soprattutto le quantità massime accumulabili all'interno del componente grazie alla proprietà della Zeolite di intrappolare meccanicamente le molecole.
- Sviluppo di piani quotati riguardanti emissioni di NO_x , temperature del sistema di scarico e portate di gas di scarico al fine di stabilizzare i componenti nei punti di utilizzo richiesto fissando i punti motore adatti, attività necessaria non solo per la scelta dei punti di lavoro ma soprattutto per l'elaborazione dei dati sperimentali e dei modelli chimici creati.

L'elaborazione dei dati ha portato alla validazione del componente perché conforme con le emissioni registrate dal componente di riferimento. Gli alpha sweep hanno portato alla conoscenza delle efficienze del componente finale. Esso presenta un numero di celle cpsi, cpsi_2, maggiore rispetto agli altri due testati con cpsi_1, sono stati montati il mixer finale, mixer_2, ed uno di prova fornito in prima battuta mixer_1; le efficienze si sono dimostrate in linea con il rapporto quantità di urea iniettata- quantità di NO_x da convertire in N_2 , al di sopra delle aspettative si è dimostrato il componente finale con l'utilizzo del mixer destinato alla produzione. Di grande importanza per questi test sono state le temperature di utilizzo, tenendo in considerazione che la finestra ottimale di utilizzo del componente è compresa tra i 300°C e i 450°C e portate al di sopra dei 200kg/h di gas combusti per evitare incrostazioni di ammoniaca su iniettore e pareti. Per i Load-unload test l'attenzione si è spostata sulla capacità di trattenere le quantità di NH_3 in eccesso e di analizzarne il rilascio, i tempi in cui ciò avviene sono dipendenti dalle portate di gas di scarico; maggiori le portate più rapide saranno le due fasi. Le attività per questi test sono state svolte solamente con il componente a cpsi_2 e mixer_2, hanno portato alla creazione di modelli chimici riguardanti l'ossidazione e le reazioni di riduzione delle emissioni NO_x . Partendo dalle tre reazioni base che legano la presenza di NO , NO_2 , NH_3 , O_2 , tenendo in considerazione le energie di attivazione di ciascuna reazione chimica e delle informazioni

dei rapporti NO_2/NO_x provenienti dal piano quotato è stato sviluppato un modello di conversione delle emissioni di ossidi di azoto misurati monte e valle SCR, in abbinamento a modelli ossidazione di NH_3 all'interno del mixer e del componente stesso. Le quantità accumulate di NH_3 nel componente e in seguito scaricate vengono dall'equilibrio delle quantità di Ad-Blue iniettato, le quantità convertite ed ossidate e le emissioni di ammoniaca a valle del componente. Le quantità massime di accumulo sono state maggiori per punti di utilizzo a basse portate 100kg/h-200kg/h e temperature di utilizzo rientranti nella finestra ottimale.

La procedura di invecchiamento ha riguardato, in accordo con il cliente di FEV, l'individuazione di un ciclo di invecchiamento ottimale da dover ripetere in due intervalli per un totale di circa 150 ore totali; il ciclo ha previsto tre fasi di rigenerazione intervallate da fasi in modo di combustione normale. Nel mezzo alcuni dei test svolti in precedenza sono stati ripetuti. I risultati dopo due terzi dei cicli totali hanno portato ad un fattore di riduzione della capacità di carico della Zeolite di circa il 30%, riduzione riguardante in maniera particolare punti di lavoro a basso e medio carico poiché a temperature alte il fenomeno di ossidazione è predominante e quindi non sono state riscontrate importanti diminuzioni della massa accumulabile.

1 Introduction

Due to the stringent emission standards released during last years, a system able to reduce nitrogen oxides at the tailpipe has got mandatory.

SCR *Selective² Catalytic Reduction* is quite common system in the industrial stationary application since the 1980's. It was used at first in Japanese power plants in 1970's and later introduced in Europe and in 1990's in the USA for gas turbine applications. Since mid 2000's, SCR technology was introduced in automotive field for diesel applications. Urea SCR has been chosen by several manufactures as leading technology to be compliant with Euro V homologation (2008) and with JP 2015 NOx limits both equal to 2g/kWh for heavy duty and bus applications. In light-duty vehicles, SCR was introduced in some US EPA Tier 2 vehicles, while others used NOx absorbers. By about 2012-2015, most of the Tier 2 vehicles with NOx absorbers have been converted to urea-SCR. In Europe, SCR was introduced on certain Euro 5 models, with a much wider application of the technology in Euro 6 vehicles. (1). Diesel Exhaust Fluid (DEF in North America , Ad-Blue in Europe) is a non-toxic fluid composed of purified water and automotive grade aqueous urea, usually 32.5% urea in water.

The thesis activity is part of wider project of development of a new engine and aftertreatment system for an heavy duty application 4cylinder 3.0L diesel engine for a Chinese application with the aim of homologation in September 2019. The tests were performed inside FEV's static test bench.

The thesis project had a duration of 5 months in which the SCR components was analyzed following the procedure of using an equivalent engine, respect the one designed for the project already on the market and homologated EURO VI, used like a burner and the installation of the complete exhaust system will be present on vehicles to have upstream of the SCR component similar exhaust flows to the one had on vehicle. The main concepts related to the procedure is to find measure of the efficiencies, loading capacity and unloading phase trend and time needed for both fresh and aged component. The test

² The activity is the amount of reactant that is converted by the catalyst per unit time per unit gram catalyst. Selectivity is desired as the amount of desired product (or products) as a fraction of total products and byproducts formed, usually expressed by a percentage.

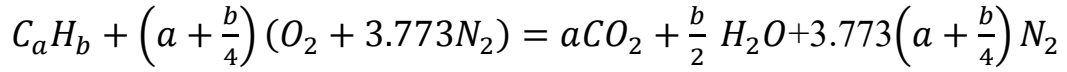
developed brought the use of test Automator systems like VTA because of the long time needed and the amount of corrections to be made in parallel with the measures on-going.

The chemical and structural aspects related to the SCR have been taken into account. Procedures was designed to put in evidence the effects of the main parameters studied in deep in the theoretical part: temperature range, NO_2/NO_x ratio, NH_3 loading, space velocities, residues and oxidations.

The ageing cycle, the whole procedure and the effects on the component have been taken into account from theoretical and experimental point of view. The thermal degradation of the component was evident on whole engine map, especially at low and medium loads.

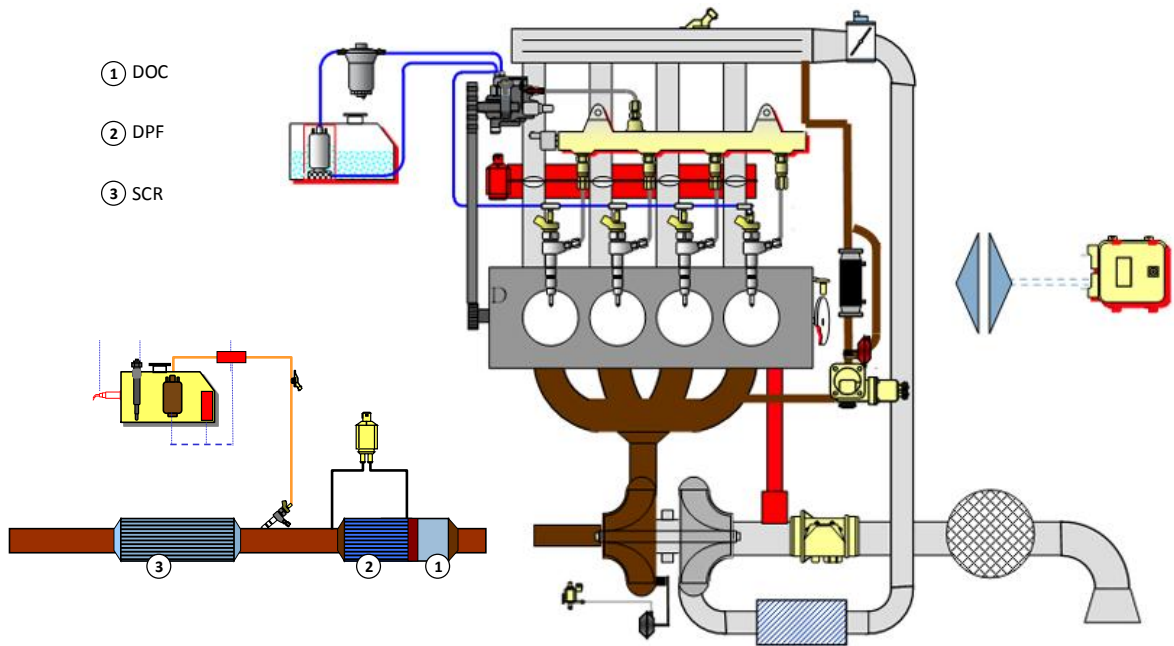
The results of the activity are in line with the homologation ranges and in line with reference component tested. All parameters taken into account will be at the base of the future activity of calibration in which the base models are: Efficiency model, NO_2/NO_x model, stoichiometry calibration and NO_x model for both fresh and aged component.

2 Aftertreatment system overview



Equation 1. Ideal chemical equilibrium for hydrocarbon combustion

The base idea related to the aftertreatment system is to transform not complete products of combustion in CO_2 , H_2O and N_2 . To have this result a series of reaction must be triggered using specific catalysts able to convert up to efficiencies of over 90% pollutant emissions in the products of Equation 1. For this purpose a catalysts able to oxide CO, HC and Soluble Organic Fraction of the soot and to burn solid particles is needed and at the same time a catalyst able to reduce NOx emissions must be added. For Diesel, typical application includes a DOC close coupled to DPF, a NOx reduction system SCR (with possibility to add a CUC *Clean Up Catalyst* for the oxidation of NH_3 slip), NOx absorber, LNT; for specific applications requiring high performance addition of more than one of this components in series could be required.



DOC Diesel Oxidation Catalyst is a monolith made by a steel casing in which an internal honeycomb structure with a Cordierite structure (specific surface area $0.3 \text{ m}^2/\text{g}$ and large pores) or sinusoidal structure made by Fe-Cr Alloy (with no porosity) is enforced. On the

substrate a washcoat or carrier is coated made by γ Alumina ($\gamma\text{Al}_2\text{O}_3$), Zeolite and other ceramic compounds able to get to a specific surface area of $100 \text{ m}^2/\text{g}$. Inside the washcoat catalytic materials are present. It is a flow-through filter, Pt loading is fundamental for the oxidation of high molecular weight hydrocarbons present in diesel fuel; the efficiency of this component and its temperature of light-off (temperature at which the component reaches the efficiency of 50%) are one of the key points for the DPF regeneration efficiency and at low temperature NO_2/NO_x ratio is of huge influence on SCR behavior.

DPF *Diesel Particulate Filter* is needed to oxidize the soot cake made on the walls triggering the regeneration phase in an optimal way. It is a mechanical filter, wall through filter with an honeycomb structure with only one opening per each channel made usually by Cordierite or SiC.

SCR is the most widespread solution , at least for Heavy Duty application, for an effective reduction of NO_x emissions. The use of the system implies the addition to the vehicle of a large additional tank for the AD-Blue, 15 liters with an experimental consumption of 1L urea per 20L of diesel, an additional low pressure pump working at 5 bar, and additional injector and vehicle sensors.

2.1 SCR general overview

Before going in deep of the component characteristics a general overview of the washcoat production is explained.

Different methods can be used for the preparation of Cu-based Zeolite, in literature mainly four of them can be found (2):

- Conventional wet ions exchanged: It is used in all types of field to exchange metal ions with Zeolite. A zeolite in its proton or ammonia form is added to a solution containing desired metal ions, while stirring. Temperature can be varied to get optimal distribution; to increase ions diffusion in the Zeolite, especially for small pores zeolite, higher temperature are used. After exchange process the sample must be filtered and washed properly. The risk of this procedure is the over exchange of metal precursors³, yielding metal or metal oxide clusters. Correct timing choices can get to a very active catalyst.
- Chemical Vapor Deposition (CVD) is a technique mostly used to cover flat surfaces with a few layers of metals. Generally, when correct salts, conditions and flows are being used, it is also possible to use this method to deposit ions inside the zeolite pore structure.
- Solid state ion exchange is possible for Cu-zeolite systems and was recently applied in the preparation for SCR-catalysts. In this method a Cu-containing precursor and the zeolite are mixed and consequently heated to high temperatures in a flow, in order to get the metals mobile and inside the zeolite framework.
- Direct sintering with Cu precursors.

³ In chemistry, a precursor is a compound that participates in a chemical reaction that produces another compound. The metal precursor used for the Cu exchanged Zeolite SCR in automotive application is the Copper Nitrate $Cu(NO_3)_2$. It is the precursor of CuO.

Method	Advantages	Disadvantages
Wet ion exchange	▪ Easiest method experimentally	▪ Yields high amounts of waste
	▪ Copper in the desired cationic locations	
Chemical vapor deposition	▪ Limits waste	▪ Develops CuAlO_2 phase which causes bad selectivity
	▪ Techniques already available industrially	
Solid-state ion exchange	▪ Limits waste	▪ High temperature needed
	▪ Easy experimental method	▪ Sample needs to be dry to avoid damage to zeolite.
Direct synthesis	▪ Limits waste	▪ More expensive structure directing agents
	▪ Good distribution over zeolite	

Table 1. advantages and disadvantages of different synthesis methodologies to prepare Cu based SCR

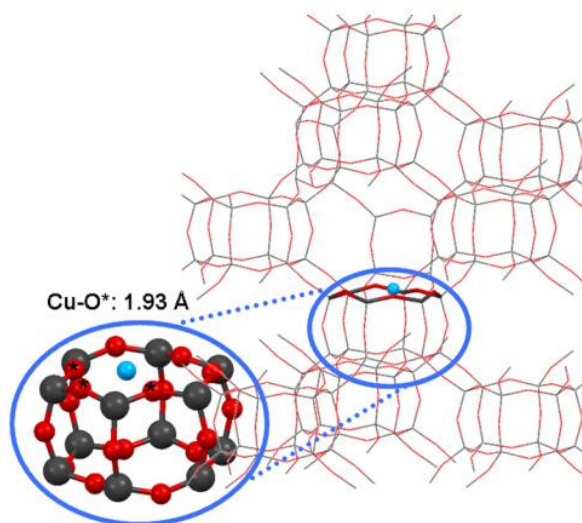


Figure 1. Representation of location of Cu in the Cu-exchanged Zeolite structure

2.1.1 SCR structure

SCR is a monolith with a structure similar to the one of the DOC. It is an honeycomb with a substrate made of cordierite. Ahead of the monolith, it is present the mixer with the injection seat. The design of its location and its length and the choice of the cone angle is of primary importance for the mixing of the urea solution and the exhaust gasses so like the design of the mixer; together they have the object of spreading the urea solution all over the component avoiding problem of crystallization as possible and taking always more importance as the flow rate increases for the level of the SCR efficiency and load spreading over all the washcoat. The mixer component, it can be present upstream or downstream the injector, is made of few blades with calibrated angles studied to widespread the mixture. Reducing pressure losses, and at the same time enhancing mixing, is achieved avoiding elbows in the pipe. Density of cells *cpsi*, as our tests showed, affects the behavior of the catalyst especially at high temperature and in term of loading capacity. Higher wall thickness means having larger heat capacity and thermal inertia of the component affecting the NH_3 oxidation because of the component capacity to store heat and higher light off temperature when cold reducing the general efficiency of the system, at the same time reducing the thickness could bring to structural problems of the monolith. Higher number of cells means having possibilities for the flow to enter inside the washcoat enhancing all the reactions.

Mixer designing and positioning of the injector seat are fundamental to reach the NO_x reduction percentage required. Solids materials include urea, products of not complete urea decomposition as well as reaction products between various compounds in the system. Formation of solid deposits may occur at the injector nozzle outlet, and close to the wall at low flow rate and temperature because of urea crystallization due to evaporation of water, a correct design of the component is able to reduce deposits and fouling at low temperature as well as avoiding urea deposits close to the injector tips and on the mixer blade walls. Limiting curves for the calculation of the urea injection rate for steady state conditions are the following (3):

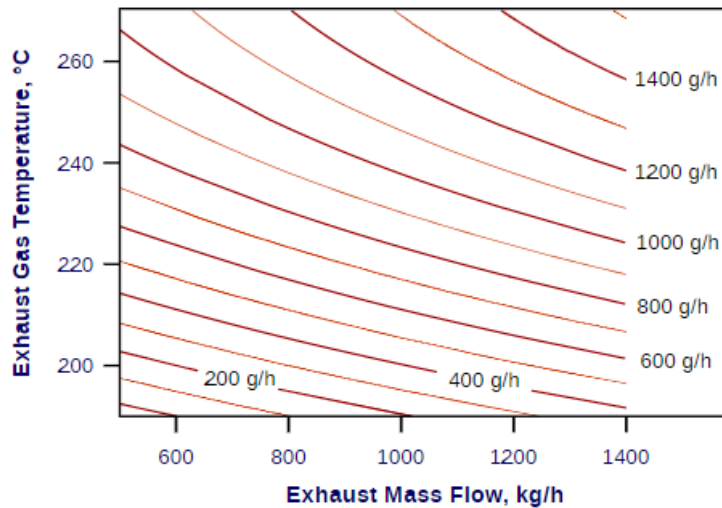


Figure 2. Limiting curves of urea injection flow rate for residue formation

Common applications presents the injector seat location in an elbow of the pipe with the injector tips inclined of an angle of 30° and a low pressure zone made close to injector, downstream of it to make a swirl motion able to move away the droplets of urea from the injector nozzles. Mixer blades fixed to the pipe at a certain distance from the injector are designed to have a correct mixing of urea solution with the exhaust gas and a correct NH_3 uniformity across the inlet surface of the SCR. Different solutions can be adopted in term of blades inclination and turbulences formation using particular pipe shaping of the mixer or using a grid of blades; pressure drop across this part of the component, pressure drop across the deposits made through the blades are parameters able to affect all the exhaust system. A check of the difference of backpressure to the turbine outlet was made when a second mixer was tested on the bench and an increase of backpressure of 20mbar was noted between the two solutions.

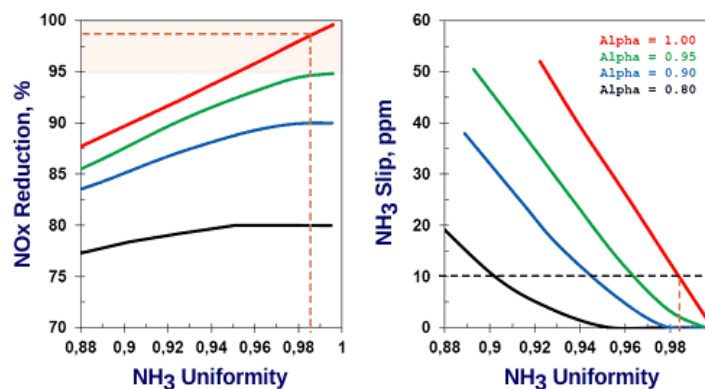


Figure 3. NOx reduction % and NH3 Slip Vs NH3 uniformity spreading

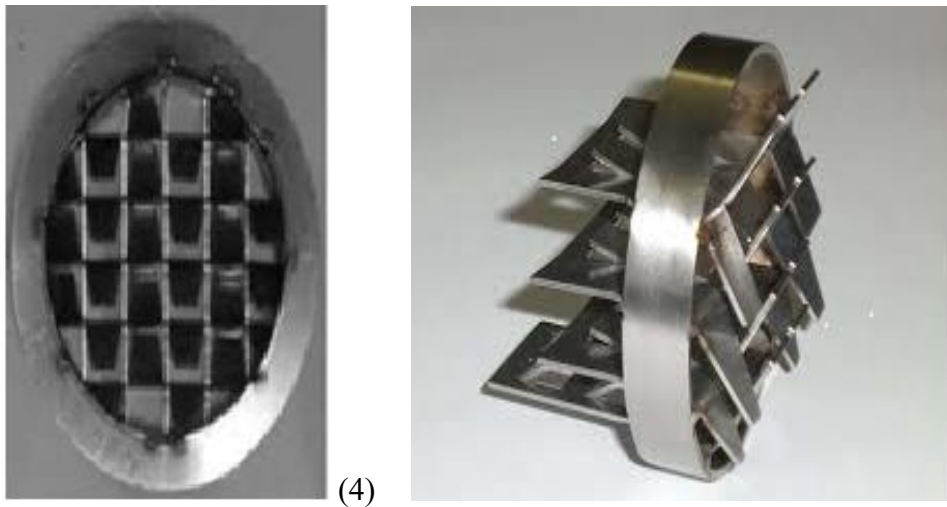


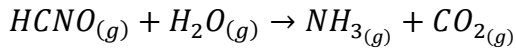
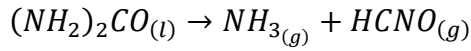
Figure 4.comparison of blades grid. Same aerodynamic concepts of mixer1 and mixer2

2.1.2 SCR chemical

The first chemical reactions performed after the injection are the hydrolysis⁴ and thermolysis⁵ of the urea. Urea (*AdBlue*, in Europe, is a solution of 32,5% of urea in water or DEF in North America) is used in cars because of difficulties to store pure NH_3 inside the vehicle for its toxicity and hazardous characteristics; in vehicle it is transformed in aqueous ammonia $\text{NH}_3 \cdot \text{H}_2\text{O}$ less hazardous and easier to handle respect anhydrous ammonia. Regardless of injection method, dosing and mixing design are of primary importance to achieve high efficiencies for a wide range of temperature. The low temperature level for injection cut-off, in order to avoid fouling of system by crystallization is generally in the range of 200°C - 250°C , not enough for some off-cycle tests; best designed systems can achieve 180°C , this enhances the possibilities to have solid deposits of ammonium nitrate and/or ammonium sulphates. Complete transformation is reached in range of 360°C - 400°C . The commercial injector are able to reach $100\mu\text{m}$ to $30\mu\text{m}$ referring to SMD. When *AdBlue* is sprayed following reactions take place:

⁴ Hydrolysis is the act of separating chemicals when water is added

⁵ Thermolysis, or thermal decomposition, is the process of chemical decomposition caused by heat. The reaction is usually endothermic as heat is required to break chemical bonds in the compound undergoing decomposition.



Equation 2.chemical reaction regulating the transformation of urea solution in ammonia and CO₂⁶

As water evaporates from the droplets and urea concentration increases, the vapor pressure of water decreases. This results in a lower water evaporation rate and increasing the likelihood of liquid droplets interacting with the wall. The conversion of injected urea into ammonia increases with temperature and droplets residence time. In figure6 and figure7 typical trends are shown; the effect of increased gas velocities is explained by increased heat transfer. (3)

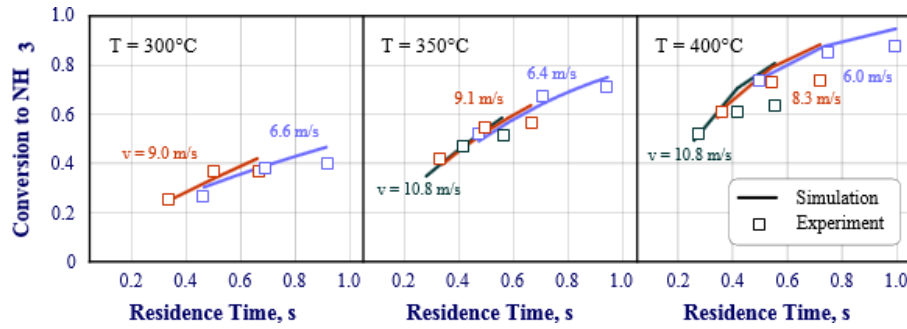


Figure 5. Conversion to NH₃ vs residence time, at different temperature and flow velocities

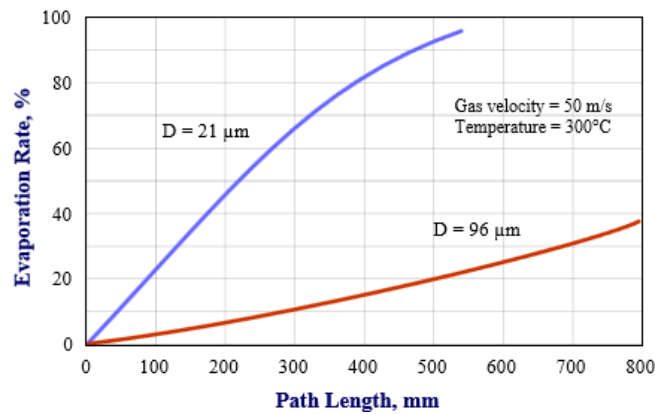
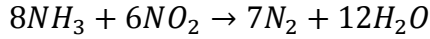
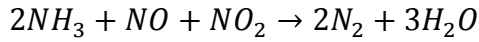
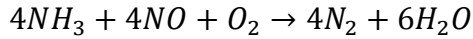


Figure 6. Evaporation rate across the path length

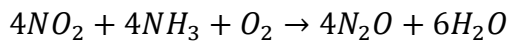
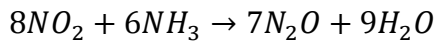
⁶ First equation is related to the evaporation of water, followed by thermolysis of urea in NH₃ and isocyanic acid and finally the hydrolysis of acid in NH₃ and CO₂

For what concerns the reduction of NO_x, main reactions are:



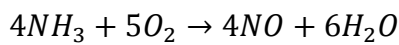
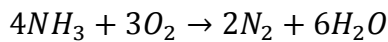
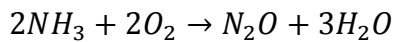
Equation 3. Main reactions related to NO_x reduction

First reaction represent the dominant reaction system, while the second one is really fast, third one is referred to the reaction with only NO₂. As it will be shown later, calculation on urea dosing is made referring to calculation of NO_x in NO₂ equivalence. It has been found that the reaction of equation 3 are inhibited by water; moisture is always present in diesel exhaust and other flue gases. In case of increased NO₂ to exceed NO level, the N₂O formation pathways are triggered:



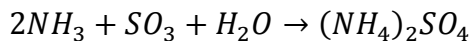
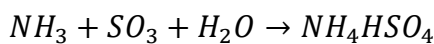
Equation 4. Chemical formation of N₂O

Fundamental for the evaluation of the urea injection are the processes related to the NH₃ oxidation, at minimum temperature level of 450°C, third equation is the one representing the complete oxidation producing NO:



Equation 5. NH₃ oxidation

Due to the presence of sulfur in the exhaust as for diesel engine, after oxidation of SO₂ to SO₃, the reaction with NH₃ brings to deposits inside the monolith and pipes of NH₄HSO₄ and (NH₄)₂SO₄. This are main examples of catalyst deactivation.



Equation 6. chemical reactions for catalyst deactivation

What concerns the catalysts used during the years for SCR applications, the leading point for the technology evolution has been the temperature ranges of utilization; stationary industrial applications implies lower temperature respect mobile applications. Possible solutions are:

- *Pt* based catalyst on a $\gamma\text{Al}_2\text{O}_3$ or ZSM-5 carrier. The major reactions triggered are $6\text{NO} + 4\text{NH}_3 \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$, with a triggering temperature of about 200°C , and $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2$, last one triggered at temperature over 225°C .
(1)
- V_2O_5 Vanadia based catalyst supported by $\gamma\text{Al}_2\text{O}_3$. TiO_2 increases the range of temperature utilization up to 425°C , when selectivity is lost and the ammonia oxidation is prevalent. . It presents a large sensitivity to NO_2 presence . For common utilization in European and US markets zeolites-SCR presents better performances respect Vanadia based catalysts, whose application is still deep rooted in countries where Sulphur presence in fuel is not limited yet; same peculiarities is valid for *NOx Absorbers* (5). TiO_2 is unable to store sulfur nitrate and this enhance its resistance to pollution (6). Thermal stability of $\text{V}_2\text{O}_5/\text{TiO}_2$ is lost over 550°C due to conversion of TiO_2 from *anatase* to *rutile* with a surface area much lower, to stabilize the washcoat up to 700°C $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$ is used.
- *Zeolite* catalyst, Cu-Zeolite and Fe-Zeolite are the most common active components for SCR mobile technology; the active component is placed as washcoat on the ceramic monolith. Main advantage of this type of catalyst is in the large range of utilization respect the other applications, able to fulfill to the high thermal stresses of regeneration phase. High efficiency range is 200°C up to over 650°C . Copper-zeolite shows less sensitivity to NO_2 concentrations respect Iron based zeolite for which an higher *PGM* loading is asked to DOC.

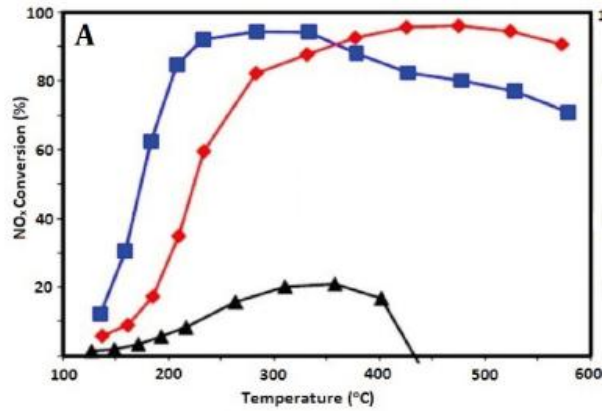


Figure 7. NO_x conversion in Cu exchanged Zeolite (blue), Fe exchanged Zeolite (red), Vanadium based (black). Space Velocity is 30000h⁻¹ (2)

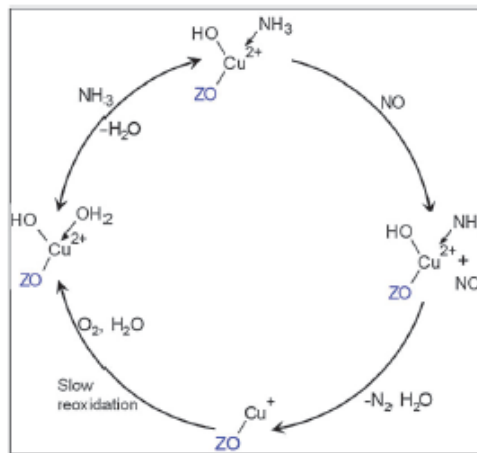


Figure 8.. Role of copper in Cu-SZZ 13 (*chabazite* Zeolite). Possible ammonia-water ligands are left out of clarity. ZO stands for Zeolite-cation exchange sites (2)

2.1.3 SCR influencing parameters

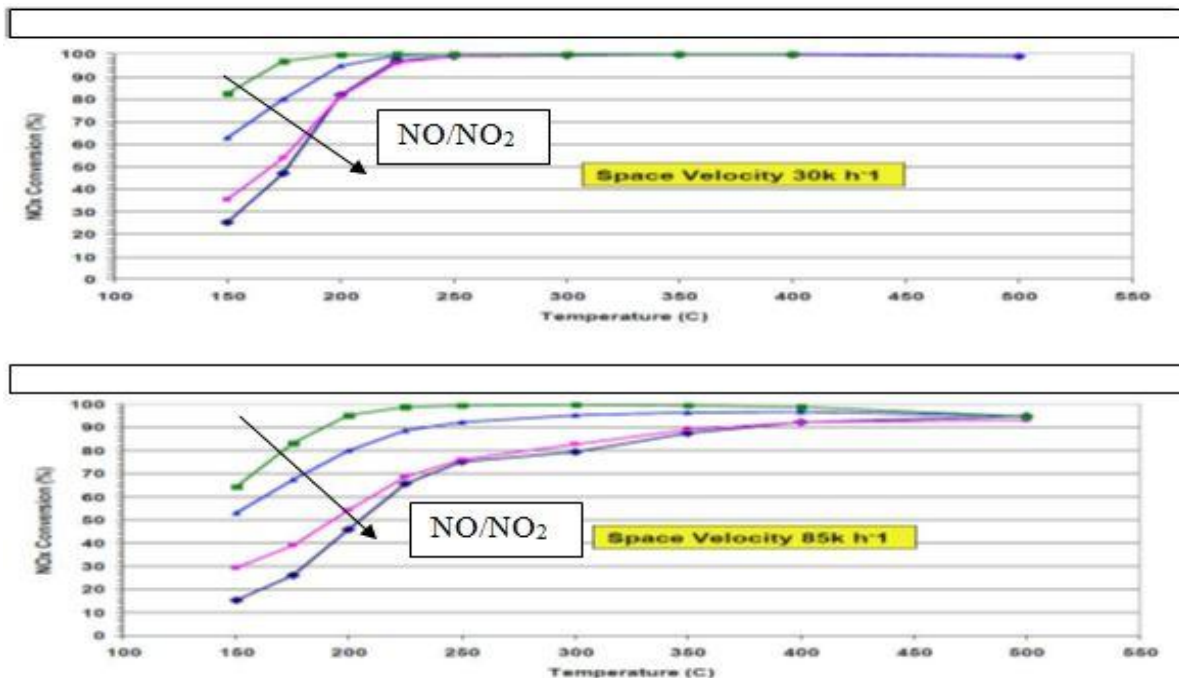
- NO_x level and NO₂/NO_x as showed in the table.1 affects the dosed quantity of urea but at the same time their ratio affects the conversion efficiency at low temperature ranges. Equations.3 present main reactions, the second one is the fastest one because it presents the lower energy of activation. Over a temperature of 350°C first equation is dominant because of temperature high enough to overcome activation energy. Taking in consideration a relation of type of Arrhenius equation⁷ here following is shown an indication of the parameters for the reactions of equations3 (7). Optimal Ratio is considered NO₂/NO equal to 1.

⁷ $K = A \exp(-E_a/RT)$. K is the rate constant, A is the pre exponential factor, typical for each reaction; E_a is the activation energy; R is the universal gas constant; T is the absolute temperature

REACTION	ACTIVATIO ENERGY[J/MOL]	PRE-EXPONENTIAL FACTOR
$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$	146941.9	6.47E15
$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$	107878.8	4.99E15
$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$	197178.9	1.09E17
$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$	146941,9	1,68E11

Table 2.Activaton energy and pre-exponential factors for main SCR chemical reactions

- Increasing the space velocity SV^8 NOx conversion efficiency decreases at lower temperature ranges where the effect of the ratio NO_2/NOx prevails, even if at same ratio huge SV differences corresponds to huge differences in conversion efficiency, at higher temperature ranges differences are reduced because of higher heat transfer. Higher SV means lower possibilities of wall wetting because of a lower injection penetration.



⁸ Space Velocity is an index referred to the inverse of residence time [s⁻¹]. $SV = \text{gas flowrate/volume} = uA/LA = u/L$ (u = Superficial velocity of gas, m/s; L = monolith tube length, m; A = total frontal area), where $u = Q/A$, with Q at STP

- NH₃ loading is a key point in term of conversion efficiencies, calibration of this parameters as trade-off between temperature, operating conditions and slip is the major issue of the phase. Achieving high conversion efficiencies with lower loading is fundamental so like achieving enough loading in case of slip. Trends of NH₃ slip is shown as function of temperature. A sudden increase in temperature usually achieved with tip-in manouvres or passing from an urban to an extraurban environment is one of the most common situation in which a slippage is triggered.

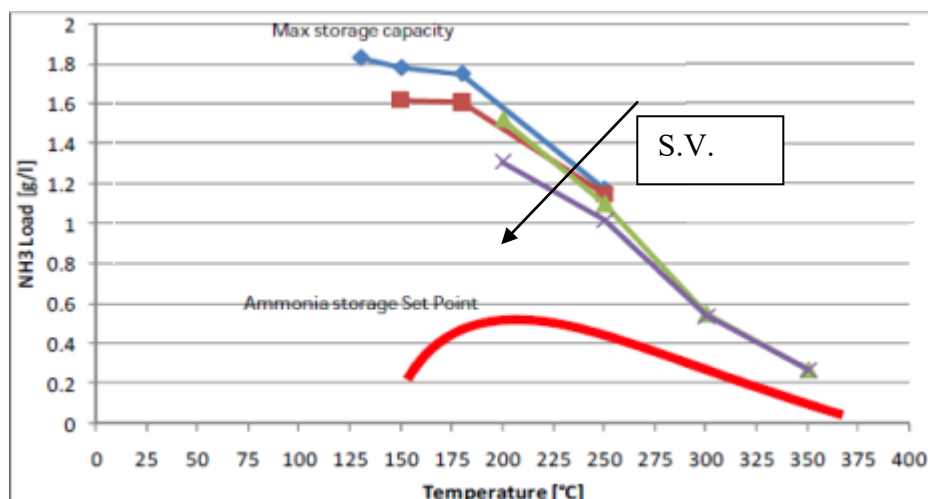


Figure 9. NH₃ loading Vs temperature for different SVs

- SCR temperature is the major factor influencing chemical reaction in term of reaction rates and activation energy, NH₃ oxidation and slippage, composition of NO_x emissions and time of loading and unloading.

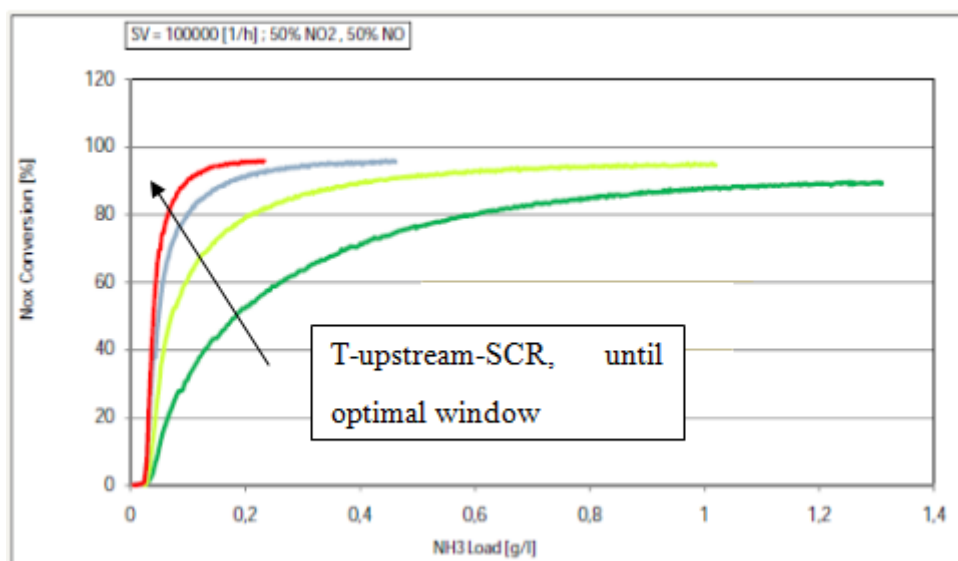
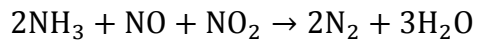


Figure 10. NO conversion Vs NH₃ loading for different temperature trends

2.2 NH_3 to NO_x stoichiometry

For the calculation of Ad-blue injection, the reference chemical equilibrium is considered



Due to the fact that in diesel engine exhaust flow about 10% of the NO_x emission is represented by NO_2 engine out with over 40% of the ratio upstream SCR, molar mass of NO_x is calculated in equivalence of NO_2 . For these reasons the molar masses involved in the chemical equilibrium are:

$$\text{NH}_3 = 17,03 \text{ g/mol} \quad \text{NO}_x = 46,01 \text{ g/mol.}$$

So it's possible to write, considering 1 NO_x : 1 NH_3 , considering each gram of NO_x (1/46 mol) the reagent will be 1/46 mol of NH_3 , meaning 0,37 g of NH_3 .

The factor 0,37 is used by the ECU for the pre-control calculation of injected Ad-blue (filtered by the factor 5,425 referred to the conversion of Ad-Blue in Urea); this factor can be considered valid in most cases but the case in which temperatures inside SCR reaches 450°C causing oxidation of NH_3 and cases in which quantities of NO_2 increases out of normal engine usage (due to physical reactions of diesel engine a NO_2/NO_x ratio over 0.5 is never expected) . These two cases make increase the factor, $fac_stoich_NO_x\text{to}NH_3$, up to 0,9 for high quantities of NO_2 (over $\text{NO}_2/\text{NO}_x = 0,5$) and temperatures of SCR over 500°C .

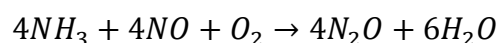
		NO2/NOx		
Temp. upstream SCR	y\x	0.5	0.75	1
	450	0.37	0.40	0.492
	500	0.42*	0.46*	0.55*
	550	0.58*	0.62*	0.72*

Figure 11. NO_x to NH_3 conversion factors depending on NO_2/NO_x on x-axis and SCR temperature on y-axis

For its structural molecular configuration Zeolite is able to store atoms inside its structure. It represents a sort of '*mechanical filter*' whose ability was already deployed inside also other catalysts for example to trap hydrocarbons in DOC and in some NO_x absorbers used

as washcoat in way to store hydrocarbons, when rich mixture is triggered during regeneration, and NO_x inside its 'cages' triggering with utilization of *Pt* as catalyst the production of N₂ and CO₂. During formation process of the Zeolite the pores size opening of the structure is chosen in way to trap only the molecules desired in the structure and the rate of storing and decreasing of molecules concentration; the smallest pore structure with 8MR (Membered Ring) with an opening of 3.8 Å X 3.8 Å has shown the highest conversion efficiencies for the SCR applications (2). Increasing the kinetic energy of the molecules, higher temperature, enhances the possibilities of the molecules to go out from the cages. Several studies have been performed during last years to find a valid model of absorption/desorption of the NH₃ in zeolite, the ones studied are developed through the Arrhenius law, due to the fact that most impact on the phenomenon come from temperature. For what concerns the desorption phenomena, the reference 7 of bibliography, factors concerning surface site coverage θ , concentration of species and inhibition factors are taken into account. The activation energy considered is $118,876(1 - 0,36\theta)$ and a pre exponential factor of 2,97E8. The activation energy for absorption process is considered null.

Due to the occurrence of NH₃ slip, an additional catalyst must be added to reduce NH₃ emissions to the tailpipe. Ammonia slip catalyst (ASC or Clean Up Catalyst CUC) is the device able to oxidize it producing N₂, NO, N₂O and H₂O. Generally it is positioned downstream SCR in the same monolith. It presences a cordierite substrate with washcoat of γ Al₂O₃ and *Pt* as catalyst to enhance the oxidations. Its volume is similar to NO₂ pre-catalyst with lower *PGM* loading, in ranges between 5g/ft³ to 90g/ft³. Reactions are the one described in the equation.5, the N₂ formation is the most thermodynamically favorable product, even if NO and N₂O products are also feasible. With an high ratio of NO/NH₃ at SCR out (up to two times NO respect NH₃), due to a bad mixing upstream SCR or lower than stoichiometric urea injection or NH₃ oxidation in NO, up to 80% of NH₃ can be converted in N₂O with the reaction



Equation 7. Chemical reaction in ASC NH₃ to N₂O

Production of NO in the *ASC* brings to a reduction of total NO_x conversion efficiency of the system, in-fact it is used for high reductions NO_x applications (8).

2.3 Ageing consequences on SCR

Most of emissions standards specify 'emission durability' requirements over a certain vehicle life, defined as a certain mileages, hours of work or years over which system is still expected to stay in applicable emission limits considered as the homologation limits accounting for a certain *deterioration factor*. Example of vehicle life for *HDVs* for the EPA standards established in 2004 is 435000 miles, 22000 hours or 10 years whichever occurs first, for homologation of EURO VI 300000km are taken into account. During ageing procedures some deterioration sources act on the component to lower the conversion performances:

- *Thermal Degradation* comes from high temperatures required to the catalyst, especially for diesel aftertreatment system that has to work in a large range of utilization from low temperature of ECE+EUDC cycles (about 150°C) to over 600°C. Sintering of precious metal inside washcoat can take place.
- *Poisoning deactivation* due to major factors; lube oil additives phosphorous *P*, zinc *Zn*, calcium *Ca* and Sulphur *S* and *S* content in diesel fuel. These are not organic particles in the oil additives able to make masking phenomena on the catalyst, usually the worst one is *P* that together with other additives (other than *S*) make irreversible poisoning of the catalyst. For the design of the catalyst is fundamental to understand where the poisons are placed inside the washcoat. As shown in the figure placing catalysts depth in the carrier is a valid way to avoid phosphorous poisoning, in addition to this using a carrier not sensitive to poisons and with high enough pores to avoid phenomena of fouling preventing passages in the pore is also major issue. *Zn* and *Ca* remains quite close to the surface of the carrier with a maximum depth of 10-15 µm (9).

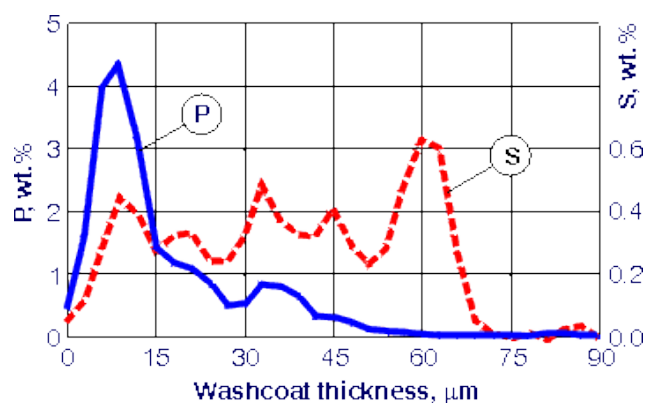


Figure 12. P and S concentration over the whole washcoat thickness

For what concerns only the Zeolite-based SCR, over the years many SCR based on different type of Zeolite have been designed. Beta-Zeolite showed good thermal stability but also tendency to store HCs, oxidation of these one would bring to high deterioration due to the exothermal energy. Smaller pores chabazite Zeolite shows lower tendency to this phenomenon. Presence of SO_2 and SO_3 in the exhaust flow triggers the formation of $(\text{NH}_4)_2\text{SO}_4$ at low temperature, instead at high temperature CuSO_4 formation is detected. Starting from 375°C up to 500°C desulfation is triggered, this is able to restore the component.

Additional reduction of conversion efficiency for Zeolite-based SCR or also deactivation is due to main reasons :

- Hydrothermal deactivation by steam in the exhaust system.
- Chemical deactivation by agents found in an exhaust stream of a typical fossil fuel engine.

The main drawback of using zeolite is the decreased activity at high temperatures due to hydrothermal deactivation. Especially for medium and large pore zeolites, at temperature exceeding 700°C and in the presence of steam, the catalysts deactivate quickly and show lower SCR activity. The main cause of this deactivation is de-alumination of the zeolite framework, the aluminum inside the framework becomes unstable and is removed from the tetrahedral framework locations. Additional consequence is that the Cu also starts to migrate and forms CuO or copper aluminate clusters. Small pores zeolite are much less susceptible to this hydrothermal deactivation, although H_2O can still enter the pores easily;

the kinetic diameter of H₂O is 2,65Å while the pore diameter of the largest pore being the 8MR with dimensions of 3,8Å X 3,8Å.

Another type of deactivation found under automotive conditions is the storage of hydrocarbons, and sequentially cooking of these hydrocarbon molecules inside the zeolite pore system. Hydrocarbons are always present in the exhaust stream, but even more during cold start of engine. The built-up hydrocarbons inside the zeolite can burn during the regeneration cycle of the DPF filter, creating more heat locally inside the pore zeolite, which can in turn thermally destroy the zeolite. One of the reasons Cu-SSz-13⁹ is more stable for this deactivation has to do with the fact that for molecules with a larger diameter of 3,8Å (methane) is very difficult to enter the pores.

Chemical deactivation of NH₃-SCR catalysts is due to contaminants from oil and fuel and chemicals from different catalysts in the exhaust system, like Pt, originating from the DOC. The volatilized Pt from the DOC produces severe deactivation of the SCR catalyst, where it is known to oxidize NH₃ towards NO_x and N₂O. Other impurities like P, Ca, Mg and Z come from oil additives.

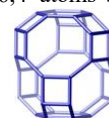
⁹ With SSz-13 is defined the structure of the molecule of exchanged zeolite. **SSZ-13** (framework type code CHA) is an aluminosilicate zeolite mineral possessing 0.38 × 0.38 nm micropores. This structure is defined with 8, 6, 4 atoms with an

accessible volume of 17,27%. Structure are the followings:
cha)



l6r(t-hpr)

and



cha(t-cha)

Deactivation factor	Influence on catalytic performance	Main deactivation mechanism	Secondary deactivation mechanism
Ca	<ul style="list-style-type: none"> ▪ Decrease in NO conversion ▪ Increased NH₃ slip 	<ul style="list-style-type: none"> ▪ Pore blocking or filling by CaO and CuO aggregates 	<ul style="list-style-type: none"> ▪ Decrease of isolated Cu²⁺ ions and CuO formation
Zn	<ul style="list-style-type: none"> ▪ Decrease in NO conversion ▪ Increased NH₃ slip 	<ul style="list-style-type: none"> ▪ Pore blocking or filling by ZnO and CuO aggregates ▪ Decrease of isolated Cu²⁺ ions and CuO formation 	
Pt	<ul style="list-style-type: none"> ▪ Decrease in NO conversion ▪ Strong influence on N₂ selectivity ▪ Increase in NO oxidation activity 	<ul style="list-style-type: none"> ▪ Pt promotes NO and NH₃ oxidation 	<ul style="list-style-type: none"> ▪ Pore blocking or filling by Pt species
P	<ul style="list-style-type: none"> ▪ c o m p l e t e suppression of catalytic activity 	<ul style="list-style-type: none"> ▪ Decrease of isolated Cu²⁺ ions and CuO formation ▪ Pore blocking/ filling by polyphosphates and CuO aggregates ▪ Disruption of zeolite framework 	
HC	<ul style="list-style-type: none"> ▪ Decrease in NO conversion (coking) ▪ Generation of local heat while burning them off 	<ul style="list-style-type: none"> ▪ Thermal destruction of zeolite framework ▪ Pore blocking or filling by HC species (coking) 	
Steam	<ul style="list-style-type: none"> ▪ Decrease in NO conversion 	<ul style="list-style-type: none"> ▪ Dealumination of zeolite framework ▪ Loss of Brønsted acidity ▪ Decrease of isolated Cu²⁺ ions and CuO formation 	

Table 3. Summarizing table for chemical deactivation of SCR (2)

3 Test Rig

Test cell instrumentation was driven by the necessity to mount a complete exhaust system similar to the one will be used inside vehicle trying to maintain same distances between components, because of avoiding issues related to temperature and backpressures, and at the same time the arrangement had to permit the installation of on-vehicle temperature, pressure and NOx and NH₃ sensors so like test bench probes, an NH₃ laser measurement system, thermocouples and pressure sensors.

The engine, source of exhaust flow, is of the same category of the one designed for the project application, it is used for the tests to compare reference component and tested component. It is a diesel 3L 4cyl engine whose characteristics are the followings:

Air Handling		<i>TCA</i>
Peak Power	kW(HP)@rpm	129(175)@3500
Peak Torque	Nm(kgm)@rpm	430(44)@1600
Turbocharger		Variable Turbine Geometry
After treatment System (reference components)		Hi-eSCR After Treatment System includes: DOC, DPF, SCR,CUC

Table 4.Engine parameters

Engine instrumentation was prepared to have the maximum control on all the parameters regarding the conditioning of the oil circuit, coolant circuit and air charge. This was done to be able to stabilize the system in order to have repeatability of the measurements and to not affect the exhaust flow emissions; especially in term of NOx susceptible to this parameters if out of a range of few grades, usually 4°C . On this inlet circuit a series of thermocouples PT100¹⁰ were mounted. On the exhaust system a series of TCK¹¹ are

¹⁰ PT100s are platinum thermo-resistances with 100Ω at 0°C working up to a temperature of 500°C.

¹¹ The type K thermocouple consists of a positive conductor in Nickel-Chrome alloy and a negative conductor in Nickel-Aluminum. The alumina stem version is ideal for use in ovens/systems with high temperatures of up to 1250°C.

installed. Key point for the tests needed for the validation is the engine cooling and engine auxiliaries cooling; tests requires long times of stabilization and long times of measure, issues related to low rpm due to the vibrations from engine to test cell mountings requested to damp this energy, and high loads where lot of thermal energy must be absorbed from the engine and the different actuators. Due to the vibrations, lot of efforts was asked to the mountings, and few types have been interchanged to have the best possible damping changing the stiffness of the plastic inside the components. This means to be able to stabilize for long times, needed for loading and unloading of the SCR quite slow at this loads, without problems of failure due to thermal-mechanical fatigue. For the high loads external fans were installed inside the cell to cool the engine auxiliaries.

In the test cell an eddy current brake is used. It uses the principle of the Foucault current to brake the engine, a disk moving in a magnetic field is subjected to the creation of induced currents which create a magnetic field opposite to the motion. Eddy current, called so due to vortex motion made by electrons under Lorentz 's law, transforms kinetic energy into heat energy.

Brake model	borghi & saveri FE 260-S
Shaft diameter	50 mm
Rotor diameter	380 mm
Maximum torque	702 Nm
Maximum rpm	1200
Maximum power	260 HP
Moment of Inertia	0,176 Kg/m ²

Table 5. Eddy current brake data

3.1 Test cell ambient conditioning, combustion air conditioning, coolant conditioning, fuel flow measurement

Here after main devices of the test cell are described so to have a complete view of condition parameters affecting the emissions.

Fuel flow measurement is made using the AVL FUEL BALANCE. It is used just to perform a measurement of the fuel flow without conditioning, made in the test cell by an external circuit. It uses the principle of gravimetric measurement, the amount of fuel to the engine is measured by the decrease of weight of a specific vessel over the unit of time. The fuel consumption is determined using an appropriate weighing vessel, which has the role also of accumulator up to 1800g of fuel, linked by a bending beam to a capacitive displacement sensor. Due to the fact that the weighting vessel has to be refilled for each measurement this is a discontinuous measurement principle. The measuring frequency of the device is 10 Hz with an accuracy of 0,12% and a measuring range up to 150 kg/h.

The conditioning of the fuel is made through an external circuit divided into two part. Main part related to the heat exchanger of the diesel out of the fuel balance; it is heated in heat exchanger, with a relative pressure up to 0,8 bar, connected to the low pressure pump, fuel filter and to the engine inlet. The secondary part is used for the conditioning of the water mixed to coolant prepared to heat the fuel. Coolant conditioning comes from a first heating and a second cooling through an heat exchanger with cold water. The circuit is designed to have fuel temperature at 40°C.

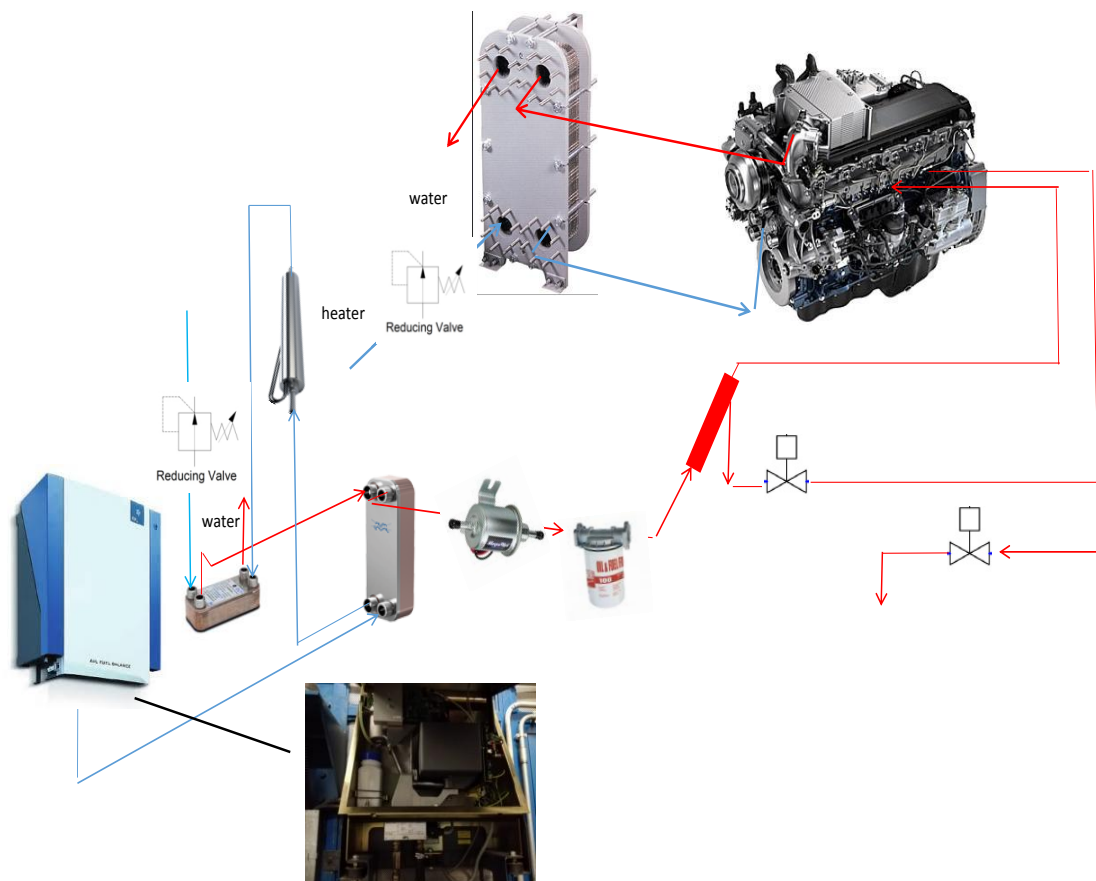
The engine coolant heat dissipation is performed through an heat exchanger with cold water, designed to dissipate heat release at full load to fix a temperature of 90°C in the circuit at the engine out pipe. The oil heat exchanger is positioned inside the engine block and it uses the coolant to subtract heat.

For the Charge Air Cooler CAC a BOWMAN heat exchanger is installed inside the cell. As for procedure asked from FEV client, the flow of the cold water exchanging heat with the charge is regulated for 50°C of engine charge inlet for the point in maximum power. Water flow is fixed in this condition for all working points.

Charge Air Flow (kg/min)	Pressure Drop (kPa)	Water flow (l/min)	Pressure Drop (kPa)	Heat Rejection (kW)	Engine Power (kW)
9,8	5,4	80	12	25,4	190

Table 6. Charge Air Cooling parameters

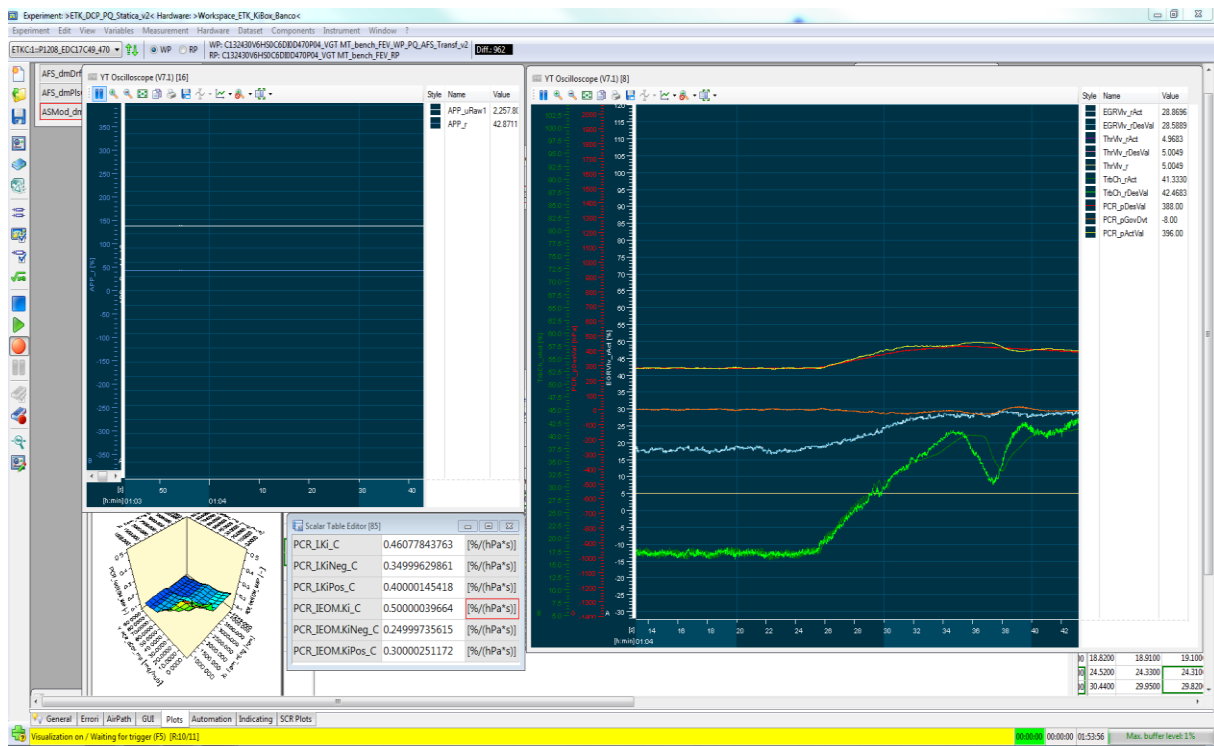
For the **Inlet charge** from engine filter the condition is set for 20°C and 50% humidity. For the **cell temperature conditioning** is present an heating battery for a target of 20°C-25°C and air venting of 22000 m³/h both for inlet and outlet venting.

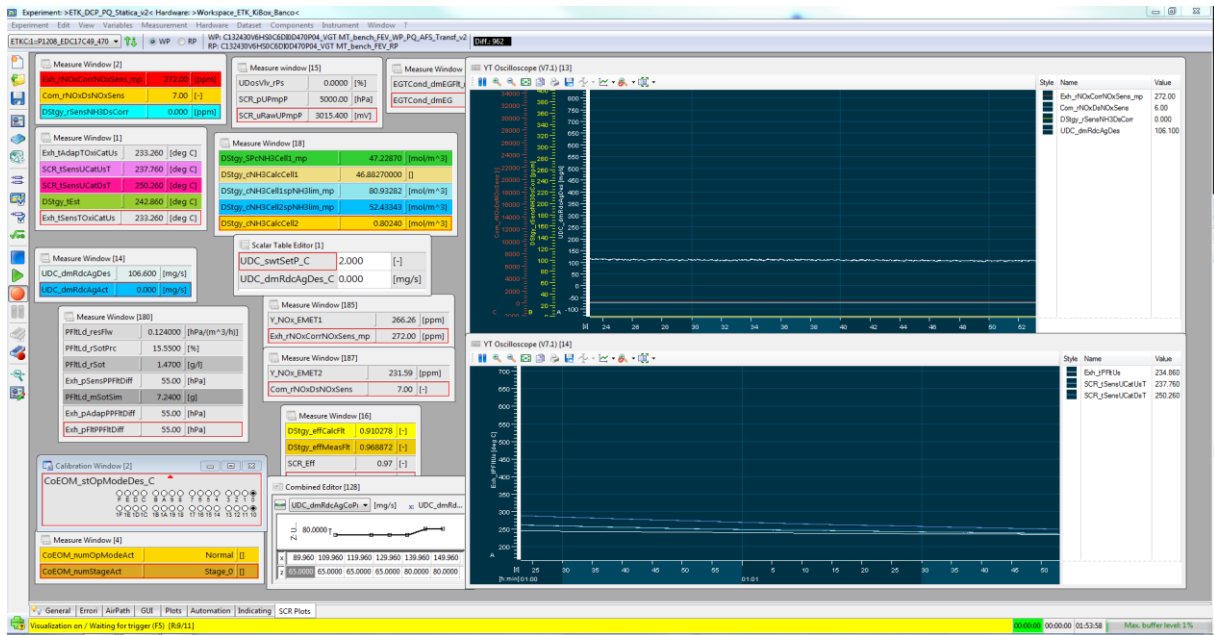


3.2 VTA, INCA and FEVitAss softwares

Test cell automation software **FEVITASS** is an in-house software developed by FEV Italia. It's equivalent to a commercial automation software, it presents real time acquisition and control, speed, pedal and PME control mode, automatic cycles, PID control, measurement logger in csv format, limits monitoring CAN communication and communication with external devices (AVL i60, 415, 439, Kistler KiBox, INCA, VTA).

The ECU interface was the **INCA** software (version 7.1). It's a software published by **ETAS** for the calibration, measurement, logging and diagnostic of a system. In our specific case was used for the programming of the ECU. It allowed us to change several parameters fast enough to realize rapid corrections of maps during the automatic tests, managing all parameters with the software for automatic tests VTA control commands. Due to the fact that characterization of the tested component is performed without a calibration of urea injection quantities, through INCA was possible to set to zero all the corrections and load governors used in the ECU; VTA calculates the desired injection quantities of Urea.





Vehicle Test Automator - Next Generation (VTA-NG) is a software application, which is used to support an automated test flow for calibration in test cars, in this case adapted to the use inside a test cell. In this way you can ease the daily calibration work by automation of nearly any type of calibration task.

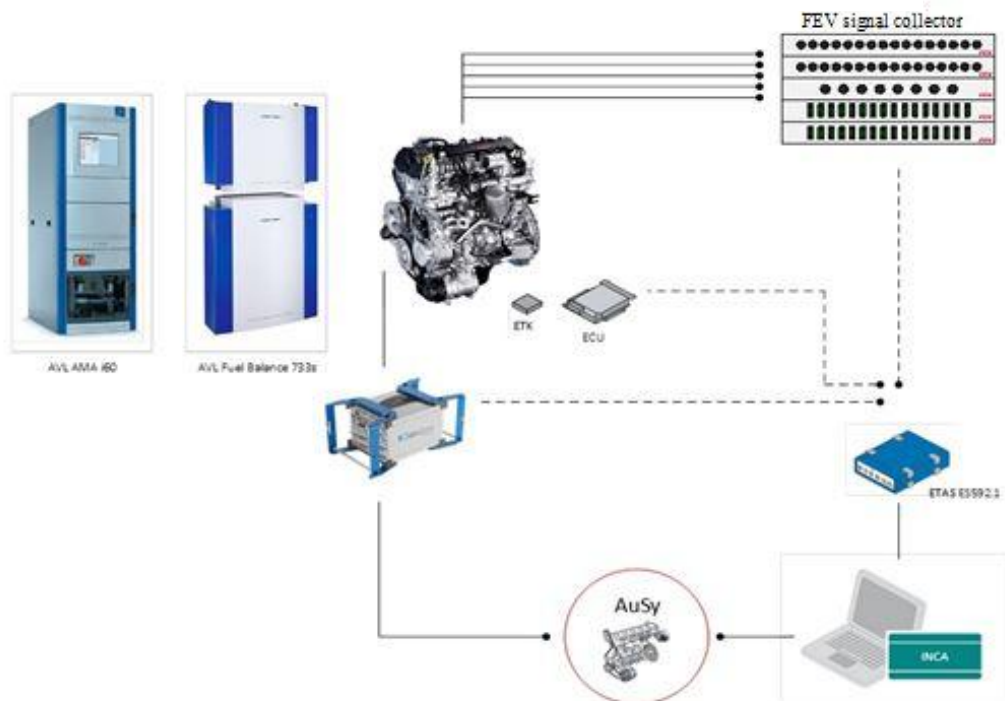


Figure 13. Test cell schematisation

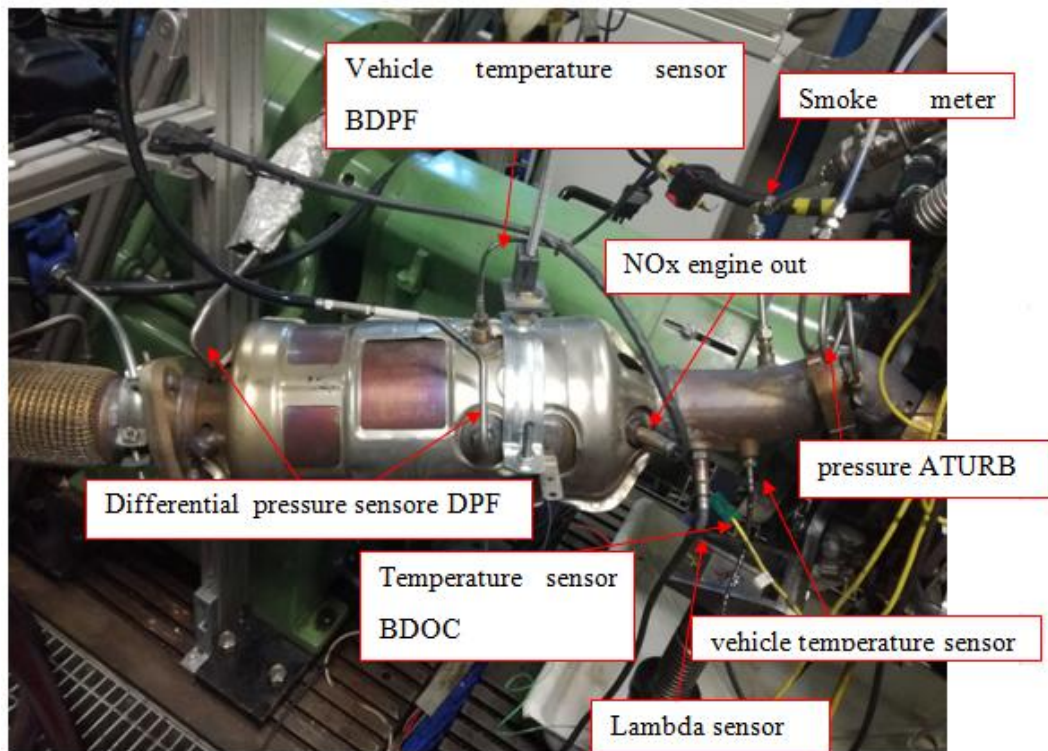


Figure 15.DOC-DPF instrumentation

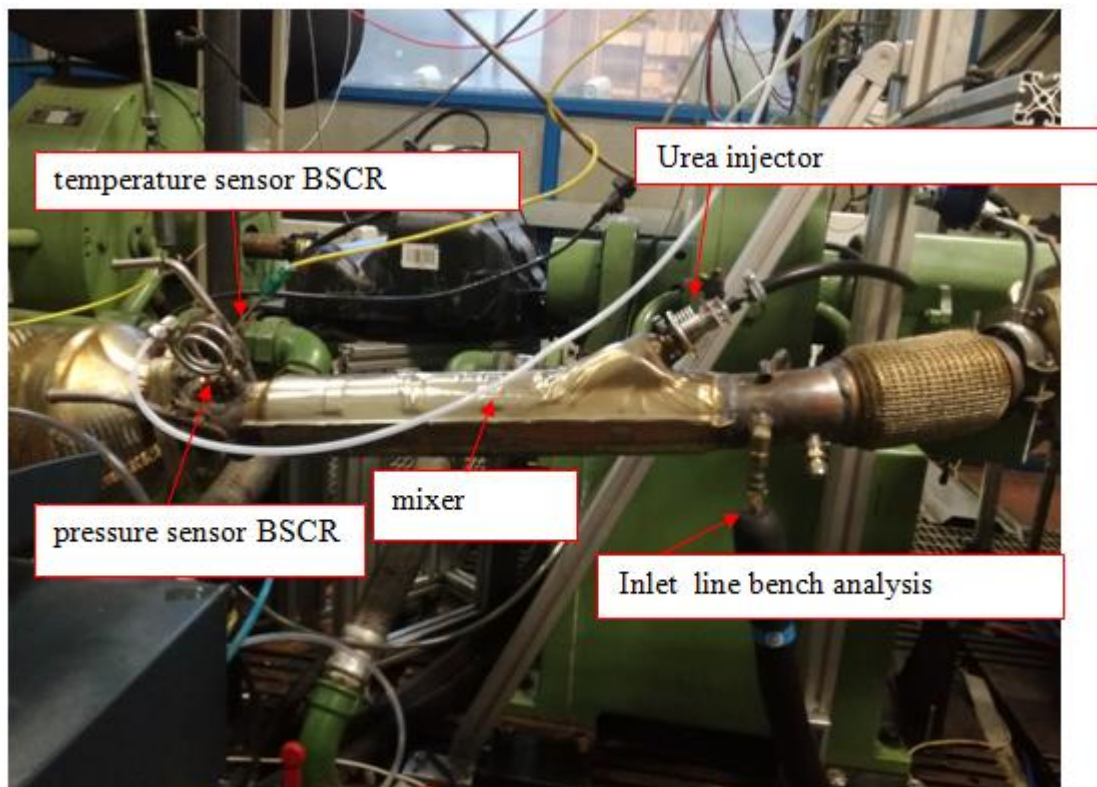


Figure 16.Mixer instrumentation

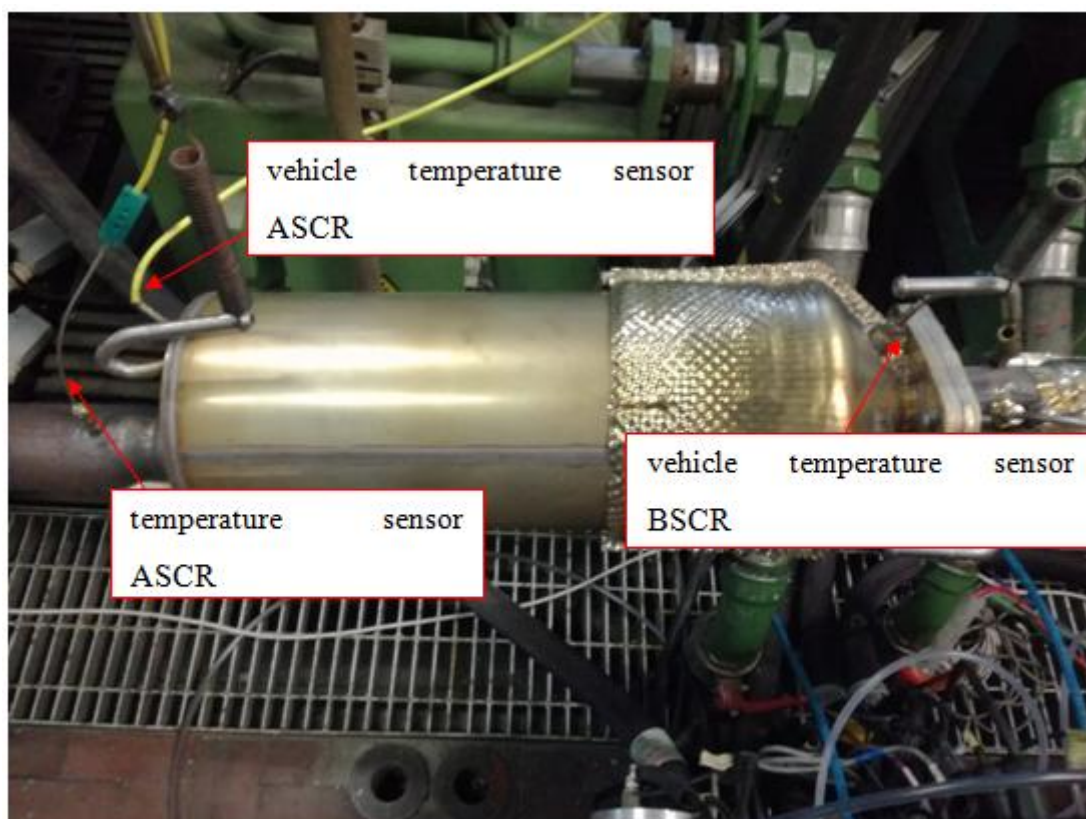


Figure 17.SCR instrumentation

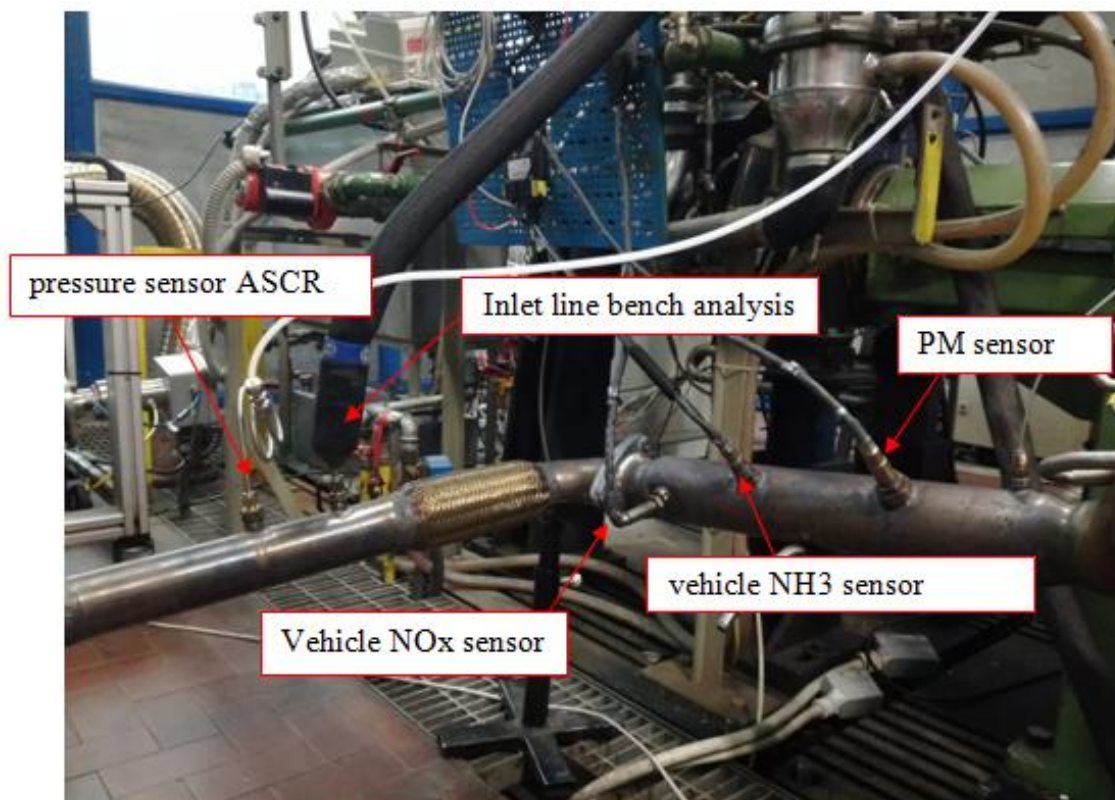


Figure 18.Tail pipe instrumentation

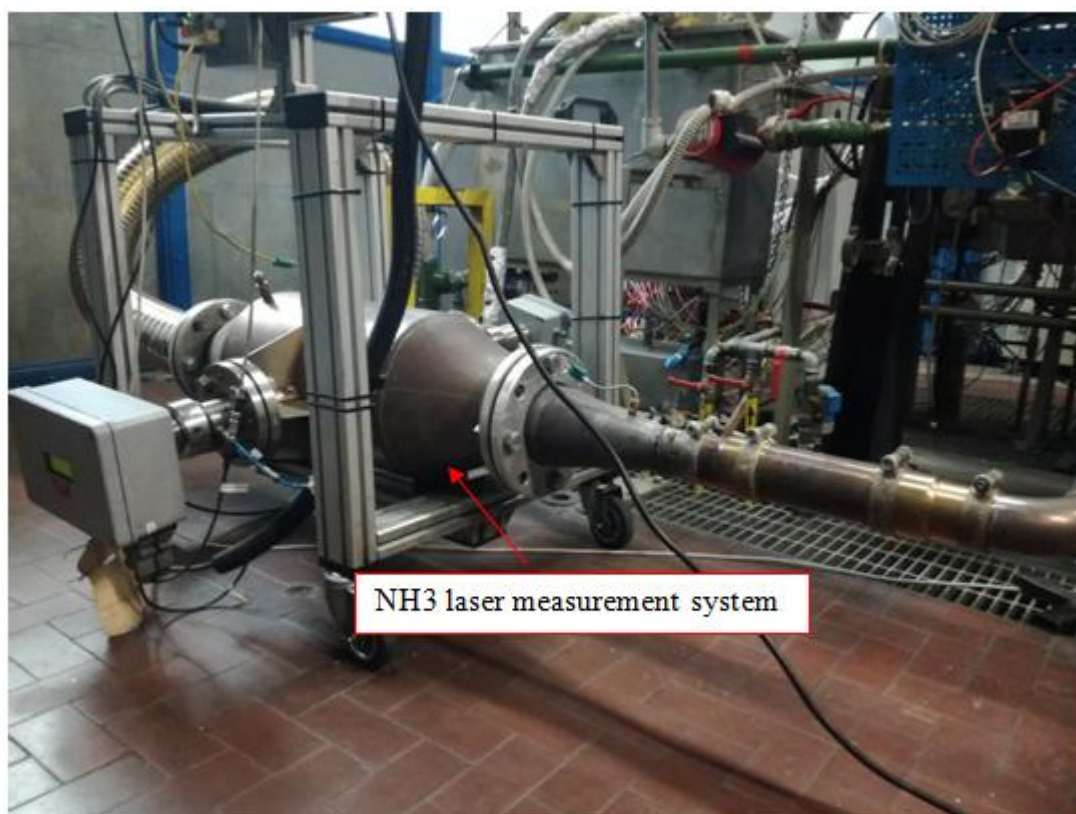


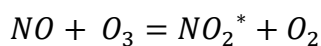
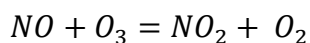
Figure 19: NH₃ Laser measurement system

3.4 Emissions test bench and vehicle NOx, temperature and pressure sensors

For the correct use of the ECU controls of the ATS and for a double check performed during the automatic tests by VTA and the operator itself, the exhaust line instrumentation presents vehicle NOx and NH3 sensors and the two heated lines of the emissions bench. The emissions bench used is the AVL AMA i60.

3.4.1 CLD device

It performs the NOx measurement with the *ChemiLuminescent Detector CLD*. It is only able to measure NO, so NO₂ must be first transformed in NO through the use of a catalyst, at the end the measure is on NOx=NO+NO₂ emissions. Measurement is based on the light coming from the chemiluminescent reaction of NO and O₃. When a gaseous sample to be measured is blended with dilute O₃ in a reaction chamber, a chemical reaction converts NO and O₃ into NO₂. Approximately 10% of these reactions produce NO₂ in an energetically excited state (NO₂*). The molecules return from their energetically excited state to their base state after a brief time; the excess of energy is released as photons. The light generated is measured with photodiodes or photomultipliers. The light's intensity is directly proportional to the concentration of NO in the measuring cell.



Equation 8. Reactions inside CLD

The AMA i60 inside the test cell has only one analyzer common for NO and NOx, this means that during the tests performed the emissions bench were set on NOx measurement but to have complete overview of the utilization points an engine map of the emissions had to be performed before the beginning of the activity; this was done connecting the two heated lines of the AMA in the same point before SCR, on one line the NO measurement is performed and on the other the NOx one.

3.4.2 Vehicle NOx sensor

The most common in-situ NOx measurement technology relies on yttrium-stabilized ZrO₂ (YSZ) electrochemical sensors, similar in construction and operating principle to broadband oxygen sensors. The sensor uses two or three electrochemical cells in adjacent chambers. The first cell electrochemically pumps O₂ out of the sample so it does not interfere with the NOx measurement in the second cell. The need to remove O₂ allows this type of NOx sensor to serve a dual purpose; it can also detect exhaust O₂ level.

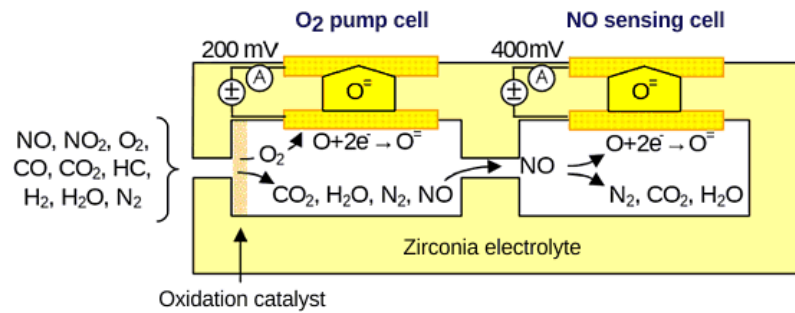


Figure 20. Schematic principle of the NOx sensor

The O₂ in the first cell is reduced and the resulting O²⁻ ions are pumped through the zirconia electrolyte by applying a bias of approximately -200 mV to -400 mV. The pumping current is proportional to the O₂ concentration. The remaining gases diffuse into the second cell where a reducing catalyst causes NOx to decompose into N₂ and O₂. As with the first cell, a bias of -400 mV applied to the electrode dissociates the resulting O₂ which is then pumped out of the cell; the pumping current of the second cell is proportional to the amount of oxygen from the NOx decomposition. All HC and CO in the exhaust gas should be oxidized before the NOx sensing cell to avoid interference. Also, any NO₂ in the sample should be converted to NO prior to NOx sensing to ensure the sensor output is proportional to the amount of NOx.

NOx sensors based on YSZ ceramics are cross-sensitive to ammonia and other nitrogen compounds. The sensitivity of commercially available NOx sensors decreases in the following order: NO > NH₃ > NO₂. The cross-sensitivity to ammonia is caused by the oxidation of NH₃ to NO/NO₂ in the first chamber (oxygen pump cell) of the sensor. The cross-sensitivity is particularly strong at low concentrations. Within the concentration range of 0-200 ppm, the signal outputs from NO and NH₃ are practically indistinguishable.

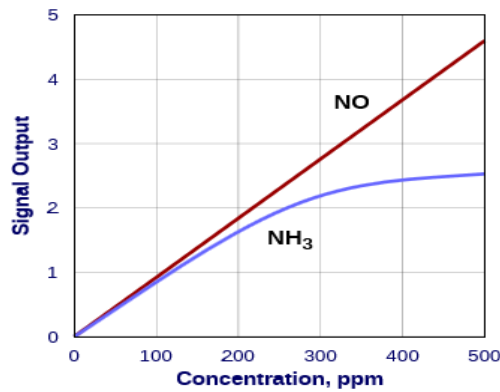


Figure 21. Sensor cross-sensitivity to ammonia

While the cross-sensitivity to NH_3 makes it challenging to distinguish between NO_x and ammonia slip downstream of the SCR catalyst, signal processing methods have been developed to make it possible to determine if NH_3 interference with the NO_x measurement is significant (10).

Measuring range	0-3,000 ppm
NO_x accuracy at 90 ppm	± 10 ppm
Max. permissible temperature (sensor control unit)	125°C
Response time NO_x	$\sim 1,800$ s

Table 7. NO_x vehicle sensor specifications

3.4.3 Vehicle NH_3 sensor

As with O_2 and NO_x sensors, the NH_3 sensor relies on O ion conductivity. An NH_3 sensing electrode is selective to NH_3 so that only the amount of O ions required to oxidize NH_3 will be conducted from the reference electrode through the yttria doped zirconia solid electrolyte. The current is then proportional to the amount of NH_3 in the exhaust gas; related to the current amount needed to transform oxygen ions. Both electrodes are exposed to the same exhaust gas—no air reference channel or oxygen pumping is required. An integral heater is fabricated into the device to maintain the sensor temperature. The characteristic that is measured is the EMF that is made between two platinum plates on the side of the NH_3 sensing cell, first put on the reference side and the second one on the side

of the catalyst triggering the oxidation of NH_3 with the oxygen ions. Commonly sensors shows negligible sensitivity to common concentration of NO , CO , HC upstream SCR and an self-compensation effect for the presence of O_2 and H_2O for common air-fuel ratio used for diesel engines.

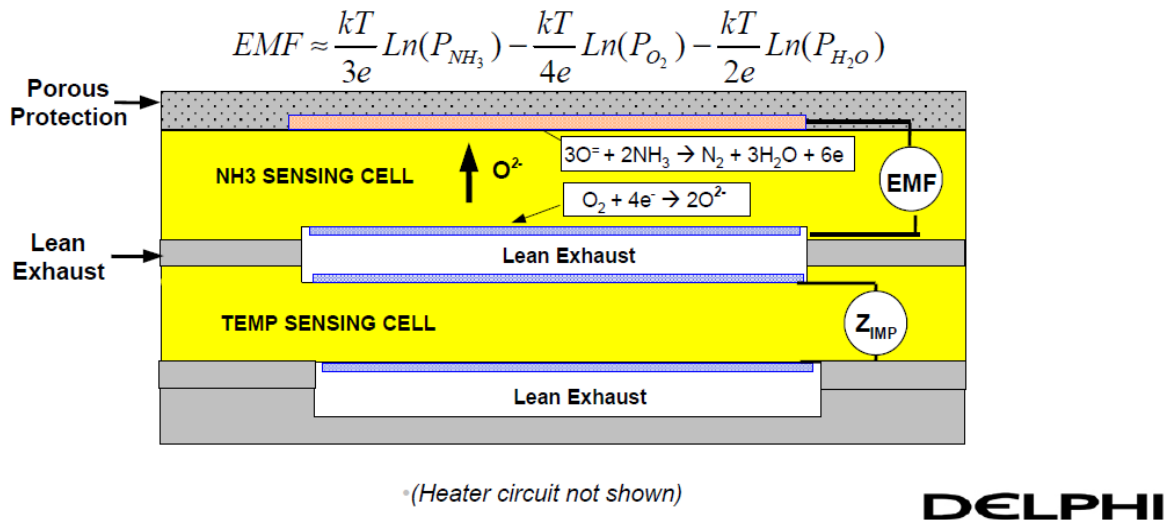
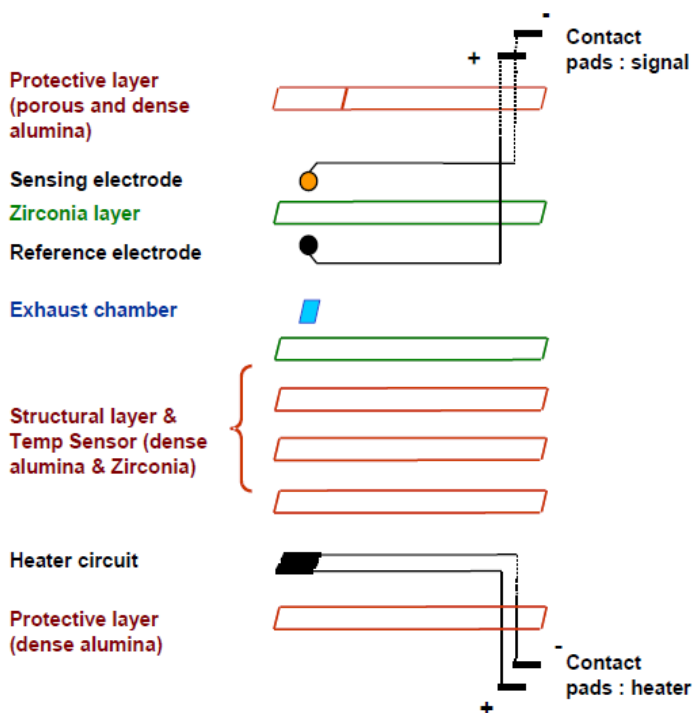


Figure 22. NH_3 sensor schematic (11)



As shown in the NH_3 sensor layout of figure.21, an integrated heater provides fast time activity; a temperature sensor is included. Alumina layer provides electrical isolation between heater and sensor circuits.

Figure 23. Functional schematic of DELPHI NH_3 sensor (11)

Measurement range	0-100 ppm
Tollerances	±5 ppm NH3 at 10ppm of NH3
Temperature range	200°C-450°C
NOx exhaust gas content	0-500ppm
H₂O exhaust gas content	1% to 8% by mass
Response time	T ₆₀ =3s T ₉₀ =5s
Durability Target	5000 h-250,000 km

Table 8. NH3 vehicle sensor specifications

3.4.4 O₂ sensor working principle

Here described is the O₂ sensor working principle, key point for a complete understanding of the NOx and NH3 sensor working principle because at the base of the evaluation of the oxygen content for both sensors.

O₂ sensor is based on the particular behavior of the Zirconium dioxide (ZrO₂) . A high temperatures (>650°C) it exhibits two mechanism:

1. ZrO₂ partially dissociates producing mobile oxygen ions and therefore becomes a solid electrolyte for oxygen. A ZrO₂ disc coated with porous electrodes connected to a constant DC current source allows ambient oxygen ions to be transported through the material. This liberates an amount of oxygen at the anode proportional to the charge transported (electrochemical pumping). (12)
2. ZrO₂ behaves like an electrolyte. If two different oxygen pressures exist on the either side of a piece of the material, a voltage (Nernst Voltage) is generated across it. (12)

$$\Delta V = \frac{k_B T}{e} * \ln \left(\frac{c_1}{c_2} \right)$$

equation 9.Nernst Voltage equation

- k_B =Boltzman constant ($k_B=1.38 \times 10^{-23}$ J/K)
- T temperature
- e elementary charge ($e=1.602 \times 10^{-19}$)
- c_i Ion concentration in mol/kg

3.5 *NH₃ laser measurement system*

NEOM_LaserGasII_NH₃ is the measurement device installed to detect the NH₃ slip during the a high temperature SCR working points, Urea slip tests and Load-Unload tests. Data acquisition is used to check the vehicle NH₃ sensor results and their alignment during post-process.

The device operates with the principle of 'Infrared Absorption line Spectrometry', which operates on the principle that gas molecules absorb light at specific wavelength. The monitor conducts measurements using the correlation between the amount of laser light absorbed by the molecules of the object gas and the concentration of the gas. Absorption spectroscopy refers to the spectroscopic techniques that measure absorption of radiations, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum.

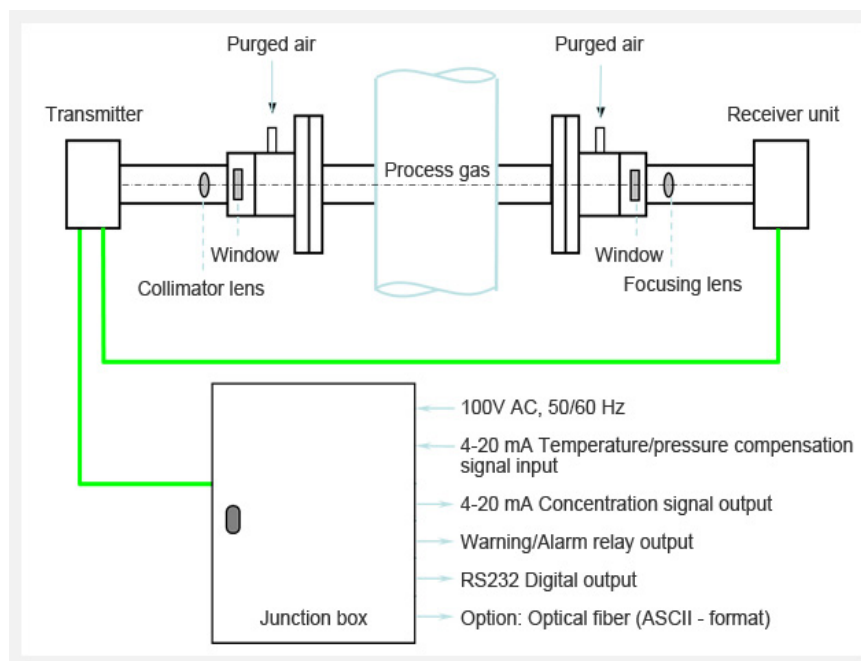


Figure 24. General structure of NH₃ laser analyzer

Lower detection unit [ppm]	0,15
Maximum temperature gas [°C]	600
Measurable range (Optical path length)[m]	6
Response time[s]	2
Span drift	Less than 4% of the measurement range during maintenance interval
Zero drift	Less than 2% of the measurement range during maintenance interval
Ambient temperature	-20°C ~ +55°C

Table 9.NH₃ laser main parameter

4 Test Matrix

The objective of the project is to have a validation of the component using as guideline the reference component already homologated for EURO VI. This was possible with the use of two tests procedures designed to give the opportunity to the SCR catalyst to be examined varying the influencing parameters described in the section 1.2.3.

After the test cell instrumentations and settings of all parameters to be aligned with the reference condition specified by the FEV client and with the data of reference component, in term of cooling circuit temperature and pressure losses, temperature of the fuel and water cooling flow of the intercooler heat exchanger, a first characterization of the engine must be developed for all the engine map. Key point is the measurement of NO, NO₂ (AVL AMAi60 has a single channel for the analyses of NO_x so two heated lines are set upstream SCR in a single point measuring on one CLD the NO emissions and with the second one NO_x emissions), exhaust flow, temperatures upstream DOC, DPF, SCR and temperature and pressure correlated to normal engine processes. This first measurement analysis is developed using automated tests. Engine calibration is the one used on on-road vehicle with a refined combustion process and after treatment and regeneration calibration but also with specific controls refined for vehicle usage that must be adapted and fixed for engine test bench usage; one example could be the control calibration of the VGT, in some working points vibrations are able to make unstable the controls with lose of normal power supply of the engine.

Tests developed on the two components, the alpha sweep, take in consideration the efficiencies in steady state condition according to different values of temperature, exhaust flow and NO₂/NO_x ratio, varied with different engine speeds, and different quantities of Urea related to the ranges 0~1,65 of stoichiometric value. This fixes the maximum efficiencies the component can reach and the efficiencies related to the single working utilization point; this is the base to understand in absolute way if the component manages to copy the behavior of the tested component. Second test, load-unload, is more related to the calibration activities and the internal design of the SCR structure and mixing layout. The influence of the space velocity is much more important because also time needed to Loading-Unloading of the component is analyzed. Loading part of the tests gives the

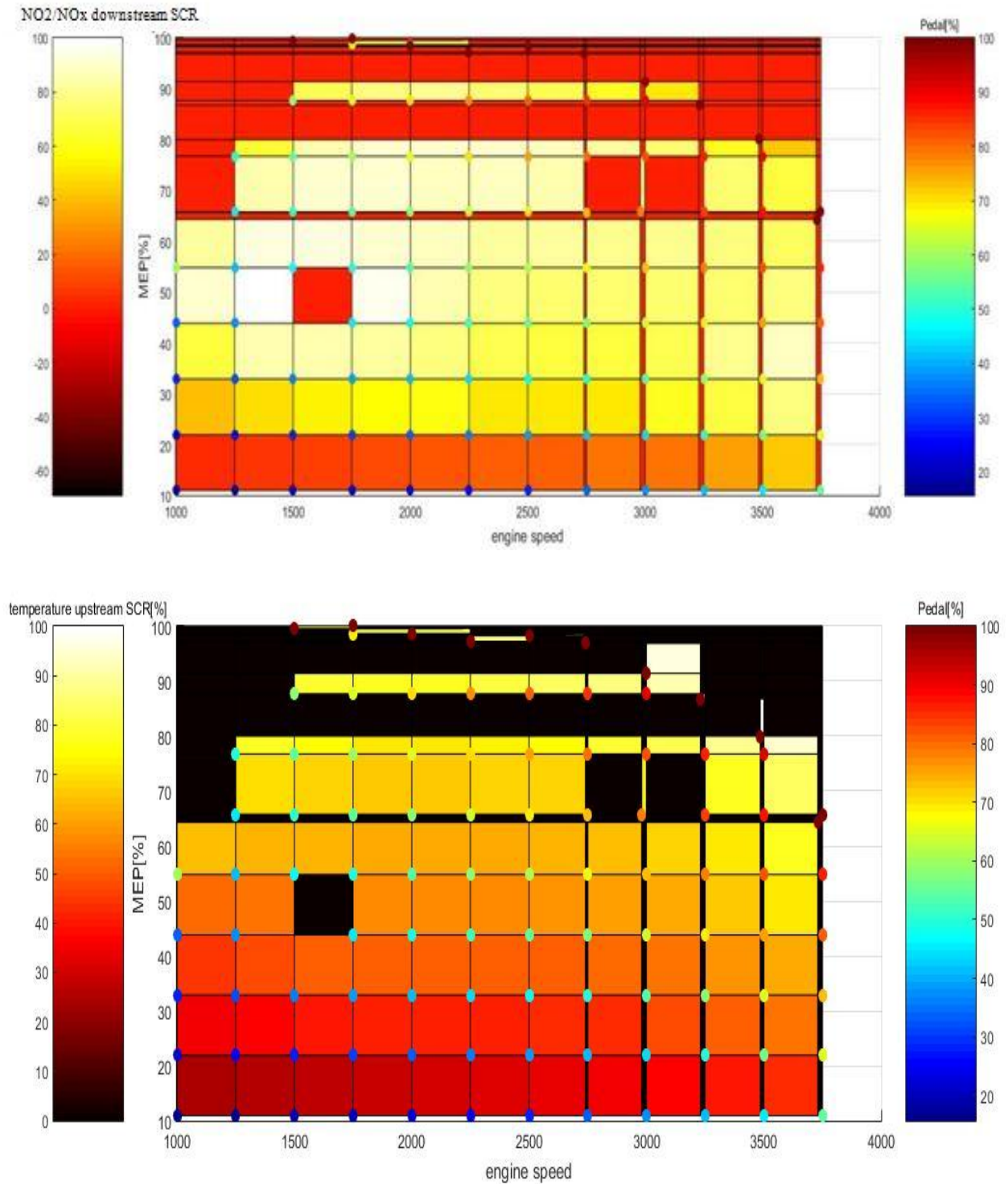
opportunities to validate the time needed and the trend of SCR efficiencies for particular points of the engine map. After a certain stabilization time referred to the maximum time or point accepted as a complete stabilized condition or a threshold level of SCR efficiency reached, the unloading curve takes in consideration the time needed to empty of NH₃ the internal component under the same working conditions (same exhaust flow temperature, NO_x ratio and space velocity). This is one of the key point in term of calibration trade-off between higher efficiencies related to a massive injection of Ad-Blue in each working points and the possibilities of NH₃ slip related to a too high injection or SCR loading for the specific working condition. An example could be a sudden passage from city usage conditions to highway conditions; due to lower temperatures, lower space velocities, higher possibilities of NH₃ loading for city conditions to higher temperatures reached due to the higher loads during highway run that could bring to high possibilities of NH₃ slip. For the development of the designed tests vehicle sensors, bench analysis and NH₃ laser measurements are sampled and checked; if the two measured quantities for vehicle and bench are within a boundary layer of 2% of normalized error, the calculations are performed to continue with the automated test, otherwise after a further stabilization time, bench emissions and laser measurement are assumed as correct.

For data processing and comparison of the components under tests, some excel files and matlab codes have been developed. With the use of these codes it was possible to prepare first maps for the SCR calibration and run all data acquisition in way to plot efficiencies reached for both the tests. It was developed, to reduce time for preparation to each point of start of Urea slip tests and Loading/Unloading tests a couple of matlab codes able to look for required working points where it was possible to have the temperatures and exhaust flow conditions required inside the engine map. To reduce time, in prevision of SCR calibration, a third code was developed to put inside the calibration maps required by the ECU software additional points that could have an high enough degree of confidence related to the distance from the closest experimental points.

4.1.1 Engine maps

Here shown are engine maps used for the evaluation of the operative working points for the test plans.

For all the charts Pedal position is set as scatter plot in the matlab code, the other quantities as the main maps.



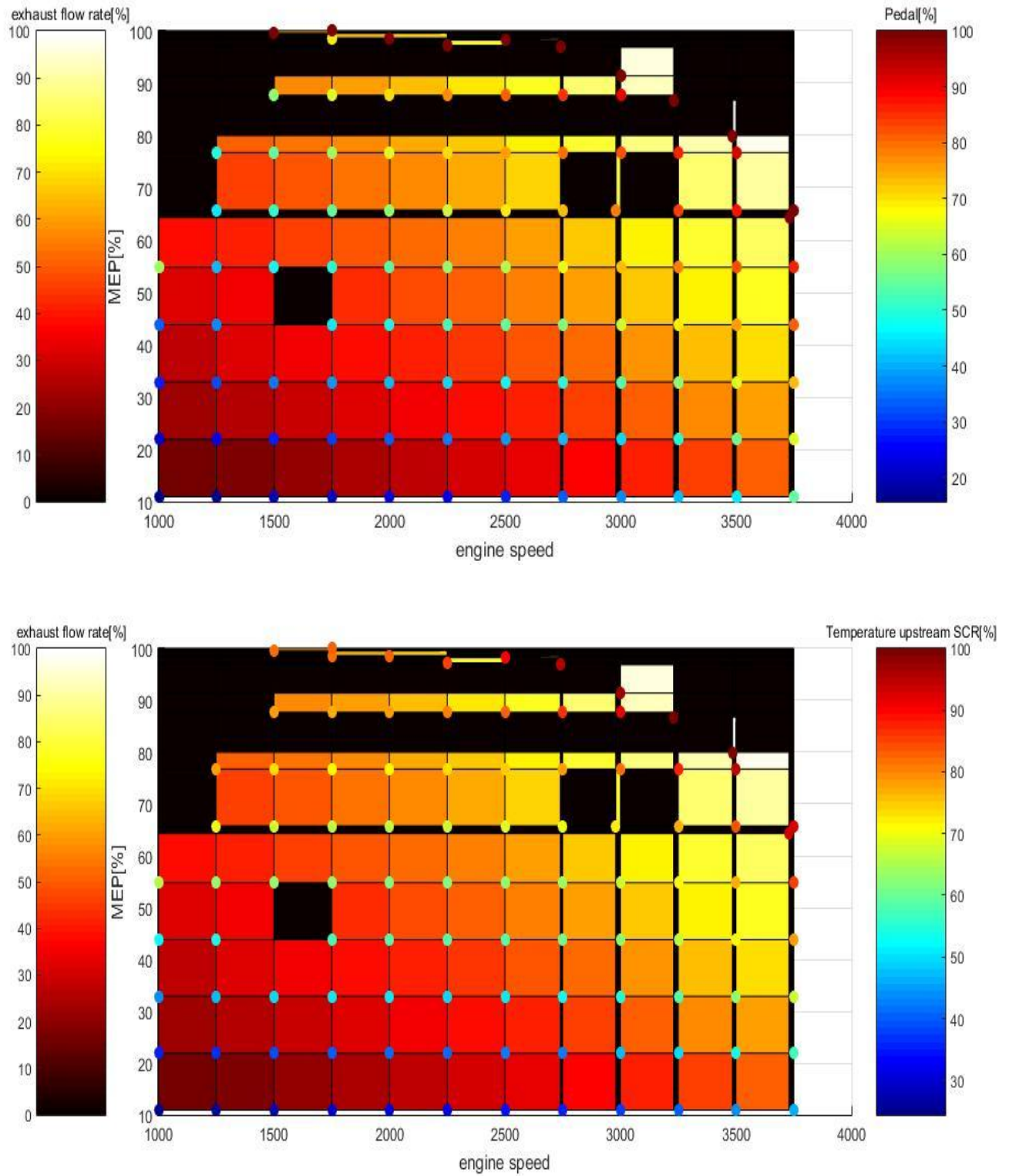


Figure 25. Main engine maps used for the working points evaluation

For the figure25 the temperature upstream SCR is set as scatter plot.

4.1.2 Bucket test

For a correct evaluation of the Urea injection and for a correct indication during the post process of the data, the bucket test was performed so that injector behavior and ECU injection logic could be checked. While the engine was run in normal mode, the urea injector was dismantled and sealed to a bucket and the injector seat was closed. Two injection quantities were forced through the ECU calibration variable. Through the MDA tool implemented in INCA the integral of the injected quantities was performed until a certain target in term of quantity was reached and compared to the weighted mass of liquid injected in the bucket; both tests were performed with the same engine and test cell conditions. The precision balance used is a *KERN EG 420-3NM* with a division¹² of 0.001g and an homologated division of 0.01g.

Constant Urea injection quantity	Urea injected quantity (integral)	Net bucket Weigth	Difference
[mg/s]	[g]	[g]	[%]
50	48	50	-5.4%
500	67	69	-4.0%

Table 10. Bucket test results

4.2 Mathematical relations

Main relation for the calculation of the injection quantity of Ad-blue is the equation:

$$\alpha_{actuated} = \frac{Urea\ injection / 5.425}{fac_stoich_NOx\ to\ NH3 * NOx}$$

$$NOx = \frac{\mu_{NO2}}{\mu_{exh}} * [NOx_{wet}] * exhaust\ flow$$

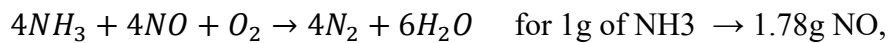
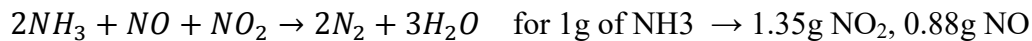
equation 10.alpha factor

¹² The lowest weight value readable on the digital display

$$Efficiency = 1 - \frac{NOx_{upstreamSCR}}{NOx_{downstreamSCR}}$$

equation 11. Efficiency definition

where Urea injection is converted in NH₃ with a factor 5.425 as from literature, NH₃ injected. The factor *fac_stoich_NOxtoNH3(0,37 without considering oxidation)* is related to the chemical relation of equation.3. This is the most common factor that can be found on specific literature, it is related to the conversion of NO_x in equivalent of NO₂ used in the equations related to conversion of 1mol of NO_x to 1mole of NH₃, section2.2 . This assumption has been checked also writing a matlab code in which the reaction of equation.3 are used to calculate in more rigorous way the consumption of NH₃ and as consequence the load for each time sampling. The code works in way to distribute the NH₃ conversion on the three equations, with the assumption that all the relations are triggered together using first the fast conversion until a not complete conversion in term of gram per mole is present and then the NO and NO₂ emissions are consumed with the related relations; a more theoretical way is to use the fast reaction until one of the emissions of NO or NO₂ finishes, these emissions are divided from the total NO_x using the engine map previously run, and then using the related reaction to complete the NH₃ conversion with emission type still present. Due to the fact that NO₂/NO_x ratio is always lower than 0.5, the three models of conversion are quite similar.



Quantity of NH₃ converted using the conversion factor is calculated for each sapling event, sampling frequency is 2Hz :

$$NH3_{converted} = (NOx_{upstreamSCR} - NOx_{downstreamSCR}) * \frac{46}{29} * exhaust_{gas}$$

$$NH3_{slip} = NH3_{downstream SCR} * \frac{17}{29} * exhaust_{gas}$$

From these equations it can be written as mass conservation equilibrium of NH3 in SCR

$$NH3_{load} = NH3_{injected} - NH3_{converted} - NH3_{slip} - NH3_{oxidated}$$

equation 12. NH3 equilibrium inside SCR

$$benchNH3_{unload} \backslash NOx_{converted} = \frac{[NH3_{load}(i-1) - NH3_{load}(i)]}{mean(NOx[g]) * facNOxttoNH3}$$

or

$$benchNH3_{unload} \backslash NOx_{converted} = \frac{[NH3_{load}(i-1) - NH3_{load}(i)]}{mean(NH3_{consumed from chemical model})}$$

equation 13. Bench NH3 unload/NOx converted factor definition

NH3 oxidation is quantified using an ECU model developed by FEV's customer, it was not transparent for our activities but it gave us an important indication of the phenomenon; other factors to study this reaction were developed during the post process of the data and also an internal model was developed. It takes in consideration of the ideal reactions in the catalyst. The key points are measuring the O₂ difference upstream and downstream the tested component, considering the difference as the result of a reduction of concentration due to NO conversion and a reduction of concentration due to oxidation. The model works sufficiently well as the oxidation increases with a large time of stabilization needed to bench analysis for the measures. From literature also the factor *fac_stoich_NOxttoNH3* coefficient can be calibrated to take in consideration of oxidation, its range is from 0.37 up to 0.55 for higher temperatures. Same procedures and calculations are used for the unload phase.

- some of the results that were analyzed during the post process of the data, these will not be shown later in the results for brevity but for all tests the same procedure has been followed.

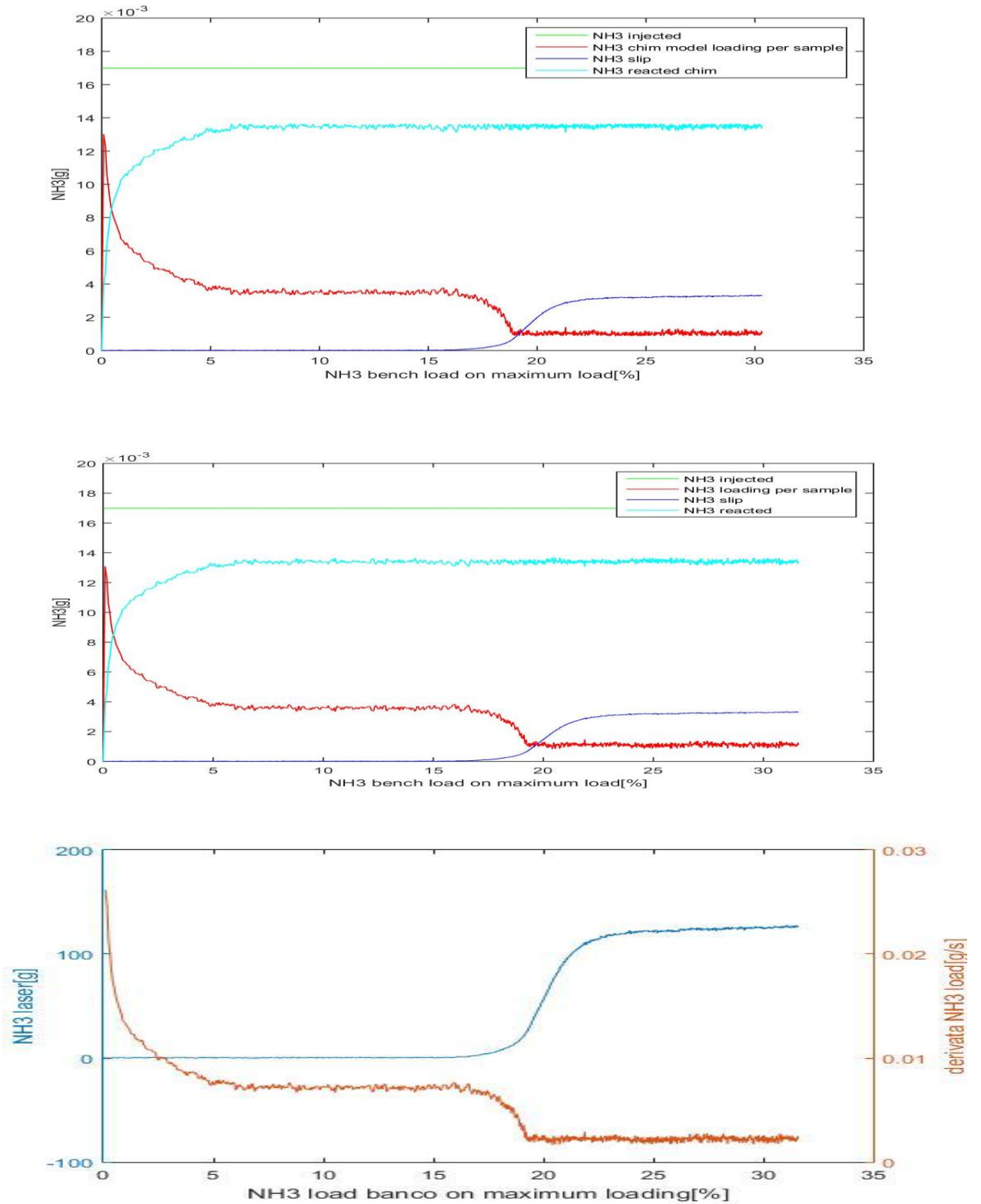


Figure 26. NH3 equilibrium for conventional and chemical model, 300kg/h-300°C, load

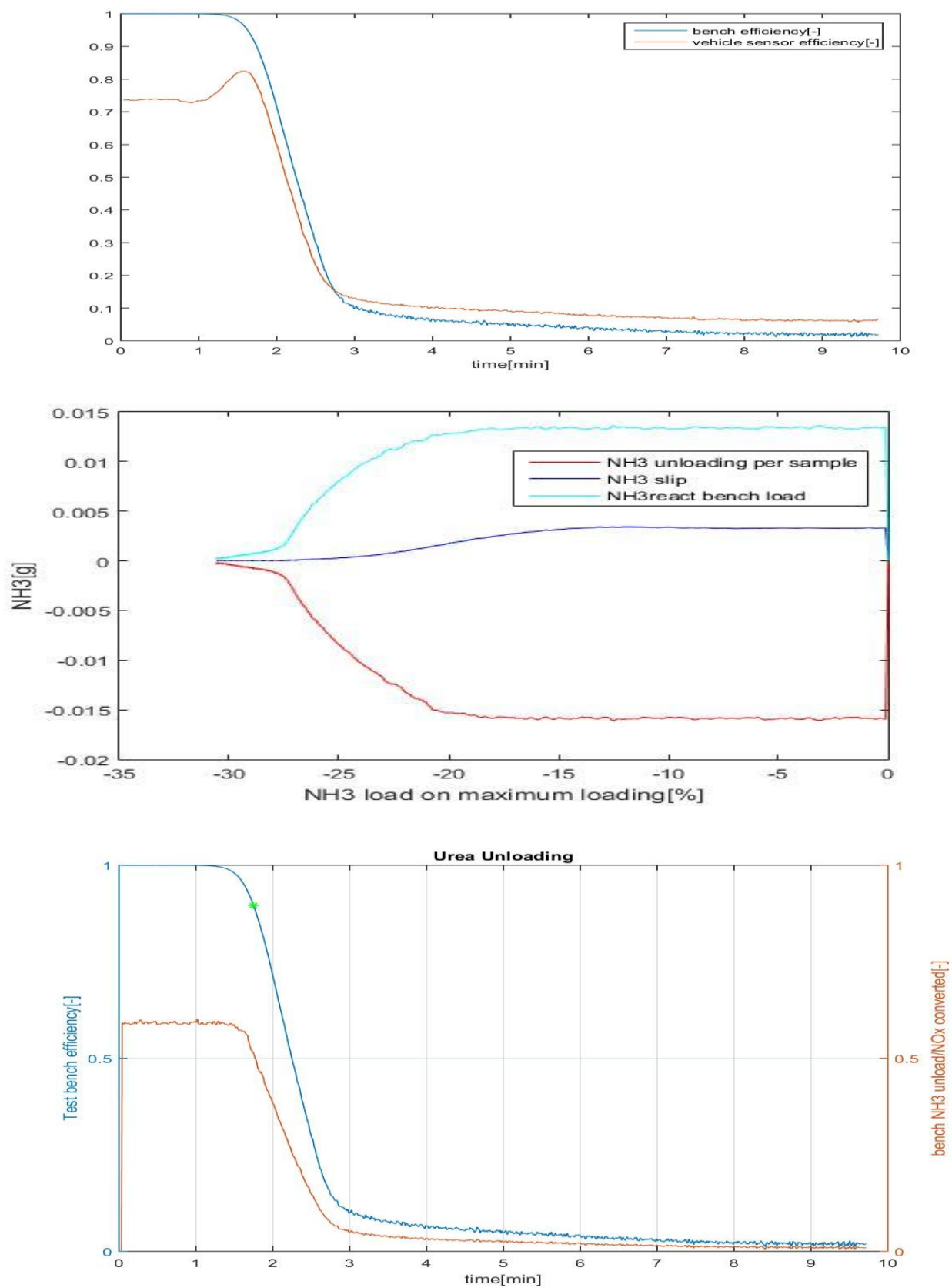


Figure 27. NH₃ measurement and exhaust gas flow vs time, 300kg/h-300°C, unload

4.3 VTA test flow chart

Vehicle Test Automator VTA is a software developed for in-vehicle automated test but it can be adapted also for the use during test bench activities. With the use of automated system it was possible to develop long time based test with the possibilities to correct some calibration parameters to stay in the assigned target, to set time counters, to activate and stop bench analysis, to compare informations from vehicle sensors with the informations of the emissions bench, to trigger the injection time and to calculate the injection quantities.

In the section 4.3.1 and 4.3.2 will be shown the main key parts of the work flow implemented for the tests so to have a complete view of all the procedures repeated for each working point for both Alpha sweep and Load-unload. Both flow charts can be divided into following parts:

- Acquisition of the variables and maps needed for the tests and saving of these one in specific variables. During this procedure the engine is already set at the particular point for the test.
- Preparation of the test bench and stabilization of the temperatures of the exhaust system and triggering of the logger.
- Start of the work flow for the activity scheduled.
- Stop of the logging and save of the data, bring back to the initial calibration all the variables and maps with the value saved at the initial point.
- Continuously during the previous point, checks of the temperatures are performed changing automatically the calibration to stay in target.

4.3.1 Alpha sweep

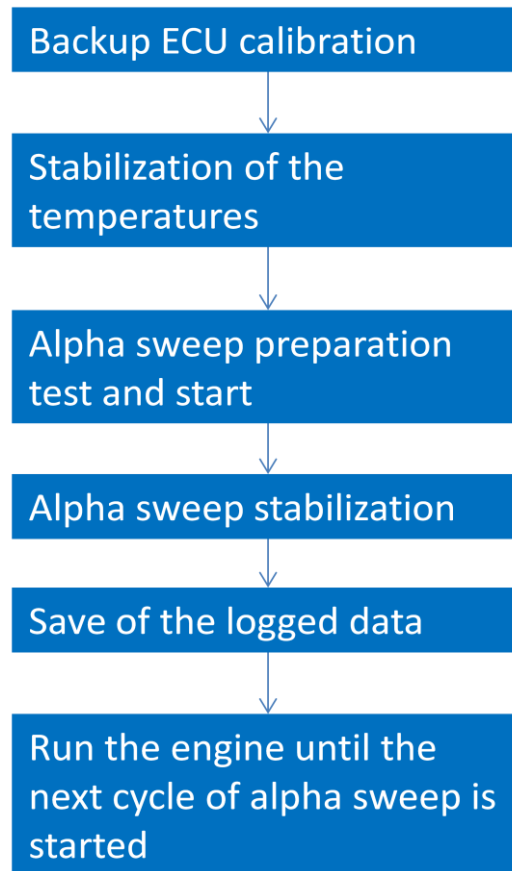


Figure 28.Alpha sweep flow chart

A regeneration phase is performed to not have residues from previous tests, the engine is run to the particular rpm and MEP quantity, taking in consideration the engine maps of section 4.1.1, set to have the temperature asked for the tests. After some minutes of stabilization, the first cycle of the work flow is started.

- Backup ECU calibration: get and save the injection map and the related variable, minimum and maximum values desired and actuated for the boost.
- Stabilization of the temperatures : acquisition of temperature measurements upstream and downstream SCR with TCK and vehicle sensors and addition or reduction of fuel injected quantities to reach the temperature target. Stabilization time is in the range of few minutes and checks of the difference between thermocouples and vehicle sensors are performed.
- Alpha sweep preparation and start: acquisition of the variables, described in section 4.2, for the urea injection quantity for the specified alpha. Checks of the

measurements of NH₃ vehicle sensor and NH₃ laser for the alignment of the two values. The quantities of NH₃ slip taken in consideration for the calculation is the one measured by the laser. Starting of the test is triggered, emissions bench are set in measure, urea injection is triggered.

- Alpha sweep stabilization: As shown in Table 11 for each test rpm, temperature and stabilization time are prescribed for each point. In this section for each point the time counter is set and temperature checks using the same strategy of the second section is performed all the test long.
- Save the logged data: at the end of the measure acquisition from bench emissions and vehicle sensors, logged data are saved.
- Run the engine until the next cycle of alphas sweep is performed: the engine is run in automatic way until the beginning of the next cycle. The next alpha value is acquired and saved and will be used for the calculation of the urea to inject for the next cycle.

Speed	T before SCR	Alpha	Stabilization time per alpha
[rpm]	[°C]	[-]	[sec]
3500	450	0;0.5;0.8;0.9;1;1.1;1.2;1.3	300
	300		900
	235		2400
1500	450	0;0.5;0.8;0.9;1;1.1;1.2;1.3	300
	300		900
	235		2400

Table 11. Alpha-sweep test plan

4.3.2 Load-unload

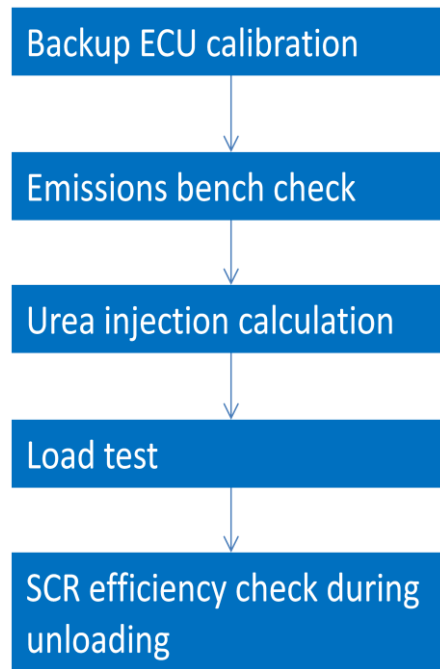


Figure 29. Load-unload flow chart

A regeneration phase is performed to clean the component from the urea residues of the previous tests, the engine is run to the working point in which the desired exhaust flow and temperature is had.

- Emission bench check: status of the emission bench is checked and set to measure.
- Urea injection calculation: calculation of the urea injection is performed. Same logic of the alpha sweep test is used with the elaboration of the quantities from the laser measurements system and bench emissions.
- Load test: in parallel way the following operations are performed: check efficiency reaching the 90%, check of the NH₃ emissions from laser and vehicle and compare between them, time counter set for a maximum of 3 hours for the slowest test (lowest exhaust flow and lowest temperatures) and check of the time in which the NO_x emissions and ammonia emissions are constant, stabilization of the temperatures with the same logic of the alpha sweep tests and control of the state of emissions bench (always in measure but for long tests, it was set few minutes of purge phase). Until maximum time is reached or the time set in which emissions

are considered stable is reached or for a manual stop of the load test to check only 20ppm of NH₃ slip as reference for maximum load, the load test phase is run.

- SCR efficiency check during unloading: After the load test phase, the urea injection quantity is stopped while controls on the engine, temperatures and exhaust flow are still on. Emissions bench is in measure for all the unloading phase, it finishes at the reaching of the efficiency of 0.05%.

4.4 Ageing procedure

Many catalysts exhibit in the short, initial period a certain deterioration/stabilization of performances followed a long time in which these remains stable, until a definitive decrease of performances is enhanced due to the utilization. To fix performances during first period a degreening procedures of 2-3 hours at high loads must be run before starting of emissions measurements. Different ageing procedures can be applied, hydrothermal oven ageing¹³, burner ageing¹⁴ and as for the thesis specific application a test bench ageing procedure has been developed. This ageing procedure implies a certain number of cycles designed to replicate in about 100h of work what could be the deterioration of a component over a whole vehicle life. Each company replicate its own cycle but here are the guidelines. Cycles are designed to have temperature at the entrance of the SCR (in general at engine out) as high as possible, taking in consideration of thermal loads resistance on catalyst materials and factors corresponding to an over temperature peak ageing; this is to simulate what happens during regeneration, DeNO_x and DeSO_x phases, keeping this condition for long part of the cycles with small parts in normal mode and rapid heat up phases. Peak temperature reached and medium temperatures during ageing cycles are fundamental, but at the same time also rapid changes in temperature and the their frequencies are key points for a procedure of rapid ageing. At the end of the

¹³ Hydrothermal oven procedures is developed to reach over 900°C, in a controlled atmosphere composed by a flow controlled gas mixture of 10% of water and 90% of gas (to replicate conditions of exhaust diesel flow), component inside oven can fulfill static (component is immersed in the gas mixture) and dynamic cycles (flow mixture passes through the catalyst); the second choice has proved to be less effective than the first one. (17)

¹⁴ It implies same concepts of test bench ageing; to create the typical exhaust gas flow conditions an air blower of about 300 kg/h, NO_x supply, soot burner and quality diagnostic of catalyst and flow must be added.

procedure over 50% of the phase was in *RGN* mode and degradation of the SCR is checked all over the procedure.

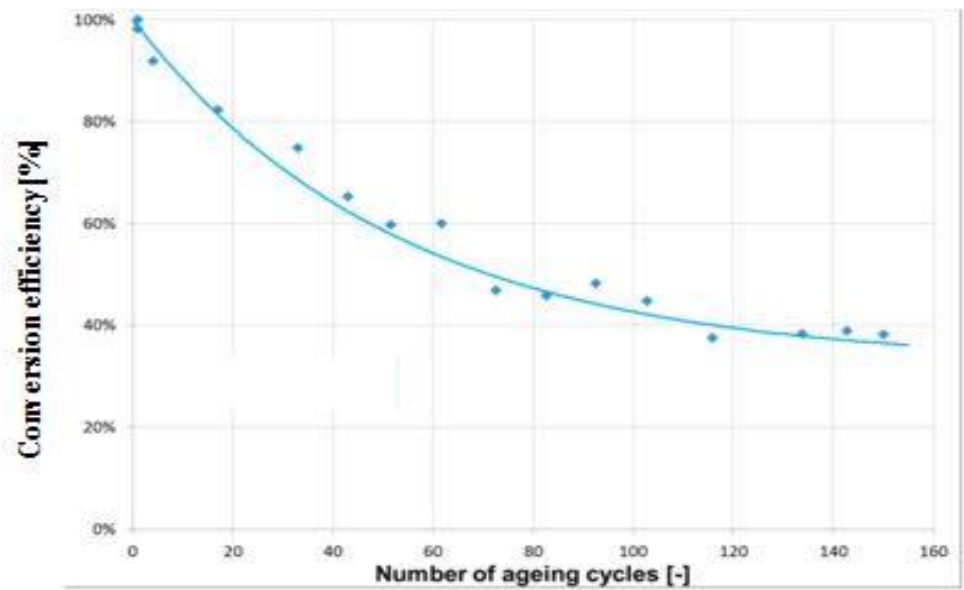


Figure 30.SCR degradation over ageing procedure

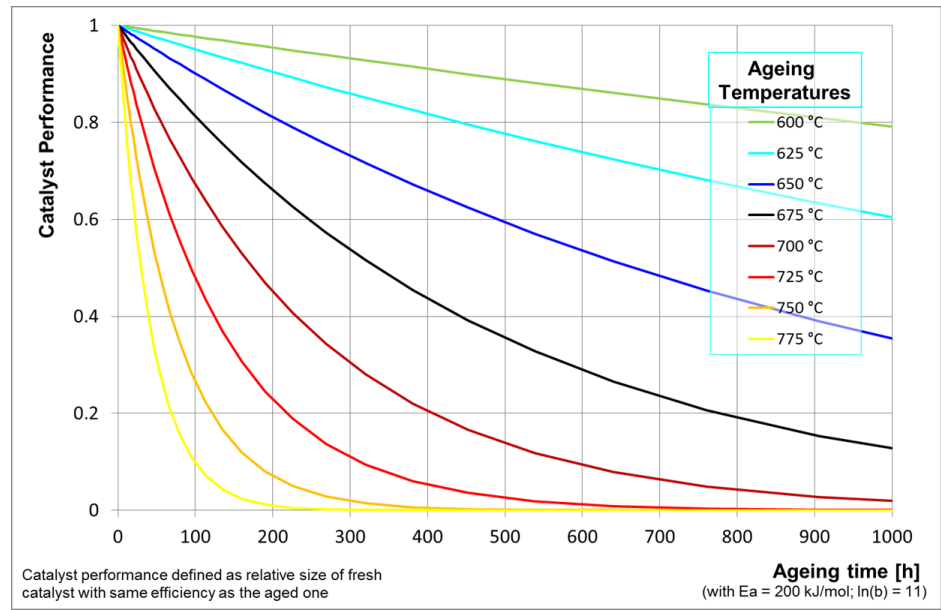


Figure 31.catalyst performance example over ageing time

Here shown is the trend of performance of catalyst over ageing time for different temperature, too high temperature can bring to component degradation that are not correspondent to vehicle normal performance losses, even if reduction of time procedures

can be quite important. OEMs developed internal models and trends to calculate the time reduction factor to take into account for each range of temperature that exceed normal usage conditions referring to the activation energy related to self-diffusion¹⁵ processes inside the catalyst. As summary it can be affirmed that at accelerated test bench procedures temperature, changes in temperatures, usage of different fuels (more or less rich in sulfur content can be used) can be simulated over the entire vehicle life, impact of soot loading and regeneration for local heat spots, impact of poisoning and ashes, water presents in cold start conditions cannot be taken into account.

4.4.1 FEV customer test procedure

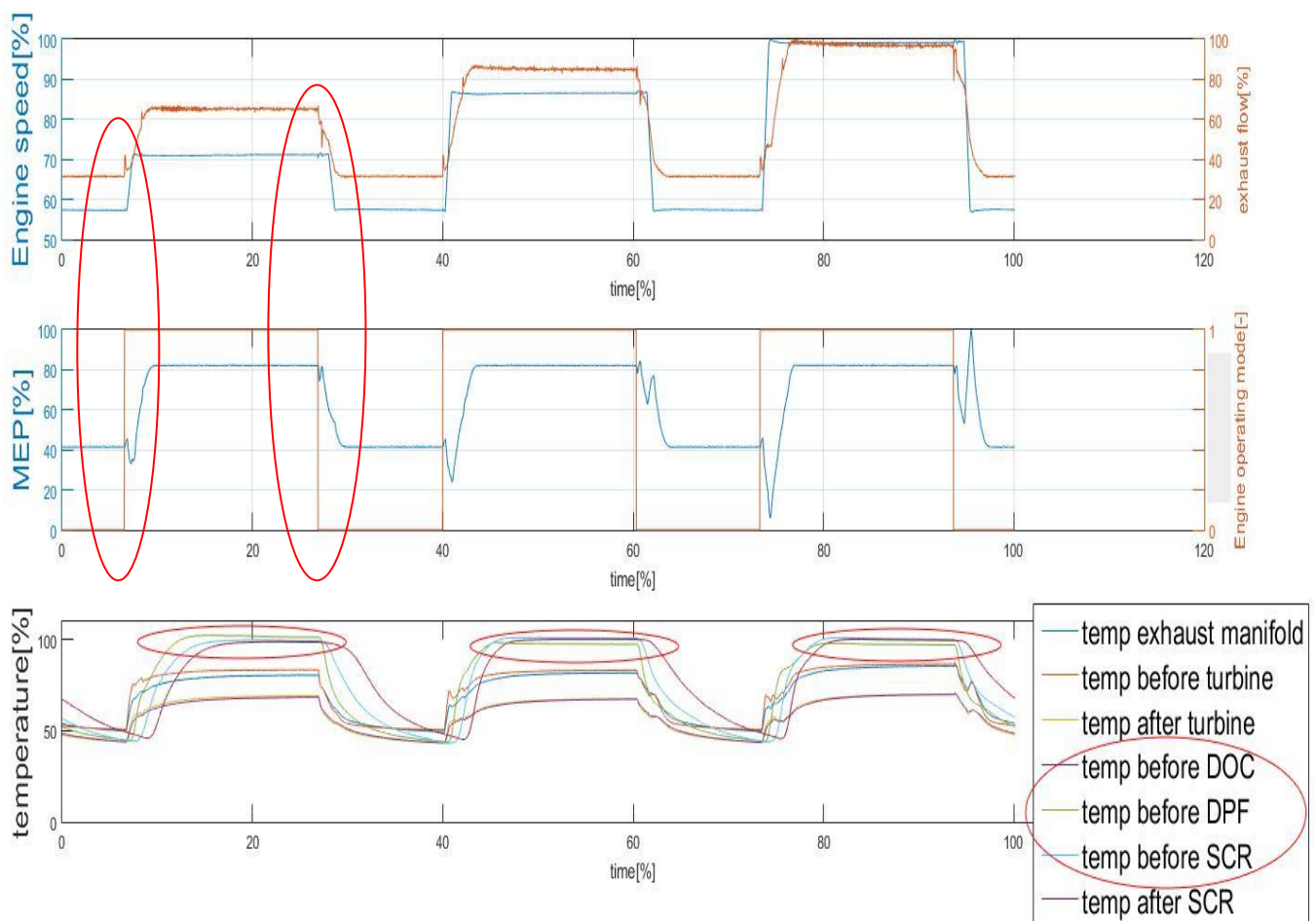


Figure 32.FEV customer test cycle

¹⁵ These processes are related to the motion of molecules inside a porous surface, as for catalyst washcoat. ``The large effect of roughness on self-diffusion occurs because the self-diffusivity, is a direct function of the individual molecular trajectories, the total trajectory length or residence time, and therefore decreases significantly as the roughness factor, ξ , increases.`` (18)

In figure32 a FEV customer cycle is presented. The cycle must be representative of the FUL(Full useful life) of the vehicle, in term of number of regeneration phases and combustion modes for the most relevant engine speed and loads. The complete procedures is divided into two parts; after the first two third of the total cycles, about 90 hours, some alpha sweep and load-unload tests are executed to check the ageing level of the component and of all the exhaust system. After these tests the second phase of the procedure will be performed. Due to the fact that tested SCR component is far from the engine and DOC-DPF is present before, no DeSOx phase is present during the procedure but the ageing is due only to the thermal deactivation. The cycle is made of 4 normal modes and 3 regeneration phases; as seen in figure32 normal modes have same working points while the regeneration phases are different chosen taking in consideration of the most common engine utilization points on the road and taking in consideration of the temperature reached by the DOC-DPF and SCR. The selection of the points is made in such a way that the temperature before DPF must be some hundreds of degrees higher than the temperature used for the tests, a calibration variable in the ECU is used for this. The cycle is composed of a normal modes for 40% of the time and regeneration modes for 60% of the time. The engine operating mode, as ECU variable bit number, is 0 for the normal mode and 1 for regeneration mode. During the cycle the injection of urea are controlled by the already implemented customer's logic, in the logic are present calculation of injection due to SCR components protection and reduction of NOx emissions. In the morning, before beginning of the first test of the day, during DCP points, measure of the emissions are recorded and in this way it is possible to check the ageing enhancement of the component. Tests are made with an automated cycle implemented in VTA. A counter is set until 100 cycles, for each cycle the counter is added of one unit and the speed, MEP, operating mode of the engine is controlled by the flow chart. For each step and operating mode, it is controlled the time range, speed and MEP. Before a change of working point and operating mode from normal to regeneration phase and vice-versa through the change of the ECU bit correspondent, the operating mode is changed at first and then with a ramp of about 15 seconds the working point. At the end of the procedure it is checked if the ageing of the component is complete looking if the deactivation of the tested component and loss of conversion efficiency is the expected one, if not some ageing cycles are added until the ageing procedure is completed.

5 Results presentation, part I-Fresh component

5.1 Alpha sweep test

For the alpha-slip tests the analysis in steady state conditions of the efficiencies reached by the component in fixed and pre defined working points is performed. The results prepared for each working point analyzed will show the efficiency reached for different ratio of urea injected. Other two charts are proposed to show the NO_x and NH₃ emissions measured by the bench analyzers and vehicle sensors; it can be shown in this way the differences in time response of the two technologies, estimated in 4 seconds, and in the precision of the two measuring systems; it will be clear in this way the sensitivity to NH₃ of NO_x sensors. At the end it will be shown some photos of the urea residuals for the working points at the lowest space velocities.

For the presentation of the test at first will be declared the engine speed and the temperature, the four charts will follow and if relevant for the validation the pictures of the residuals close to the mixer will be shown.

The sampling frequency used for the signal elaboration is 2Hz.

In the graph legends act is meant actuated, up is meant upstream SCR, ds is meant downstream SCR.

Emissions are calculated as percentage on the maximum recorded for each emissions species.

5.1.1 Reference component *cpsi_1 mixer1*(reference mixer) with CUC

- 1500rpm- 235 °C

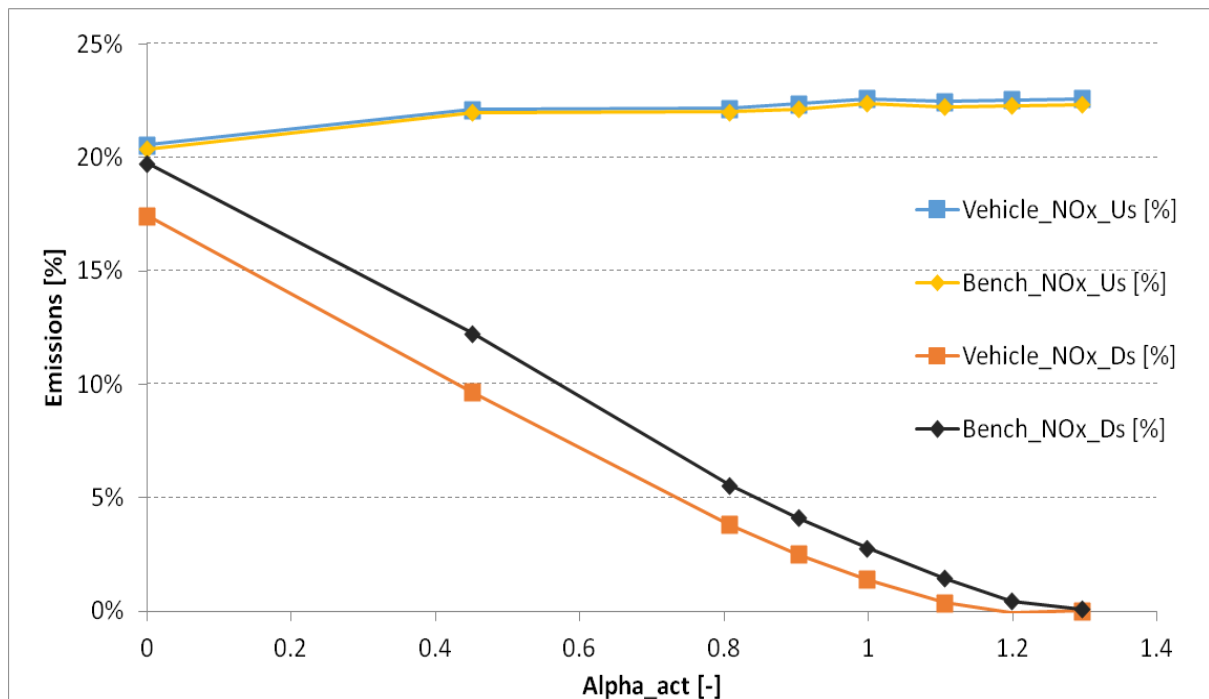
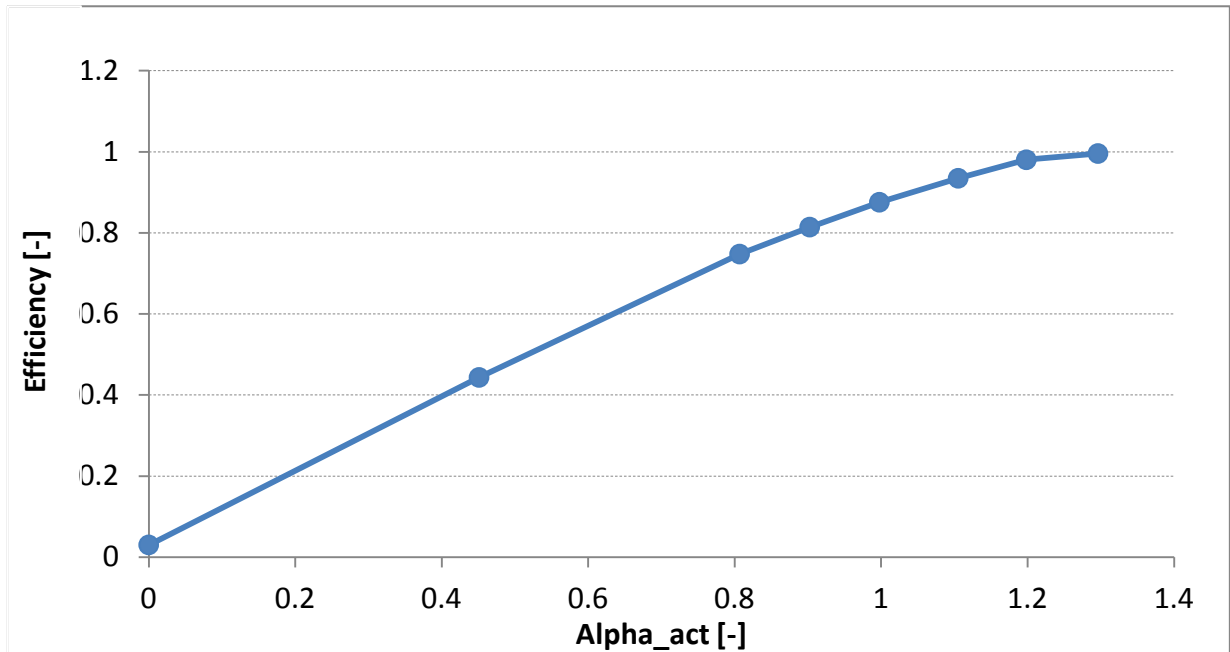


Figure 33. Alpha sweep 1500x235 reference component *cpsi_1* reference mixer w/ CUC

- 1500rpm- 300°C

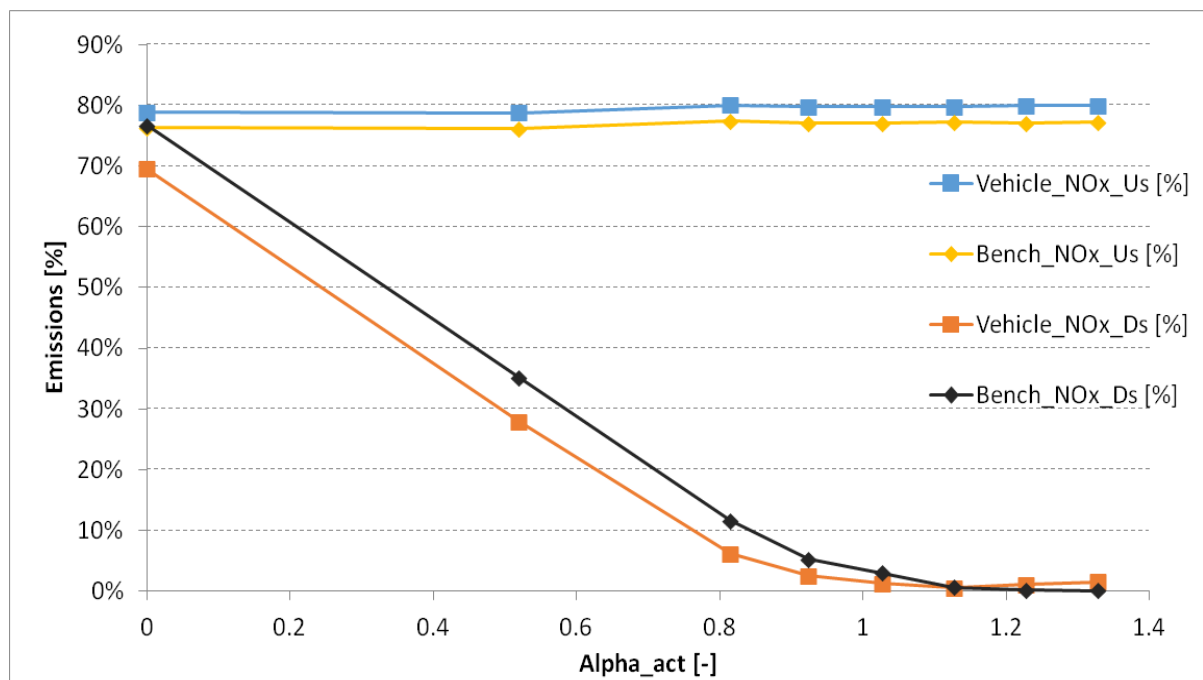
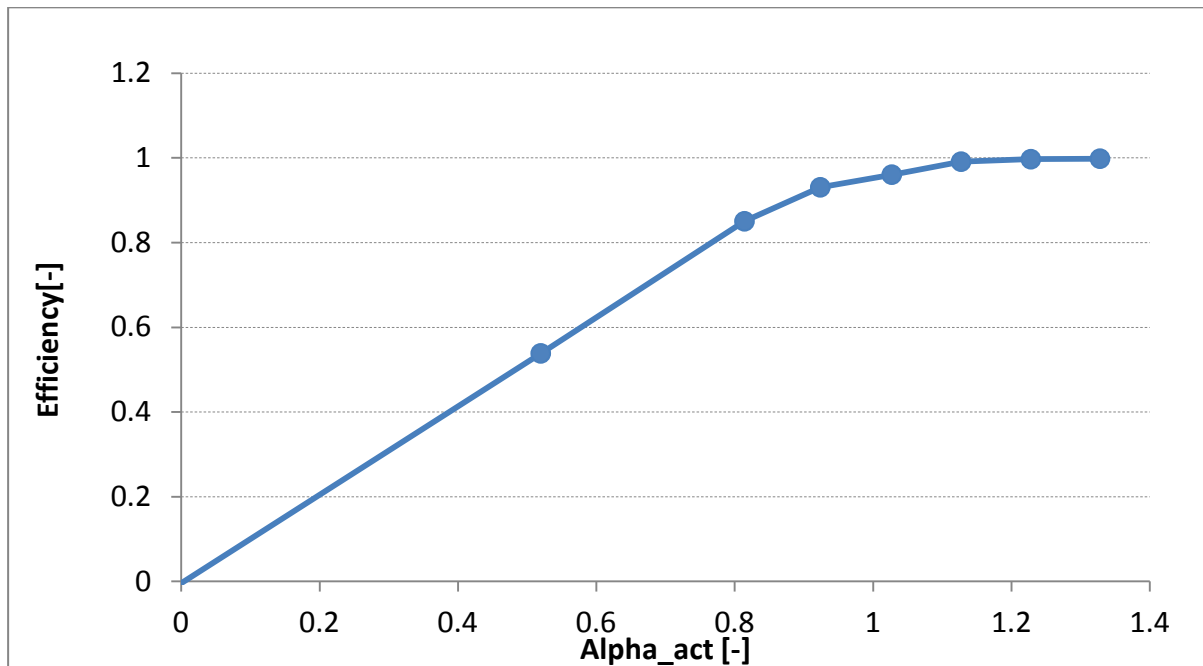


Figure 34. Alpha sweep 1500x300 reference component cpsi_1 reference mixer w/ CUC

• 1500rpm- 500°C

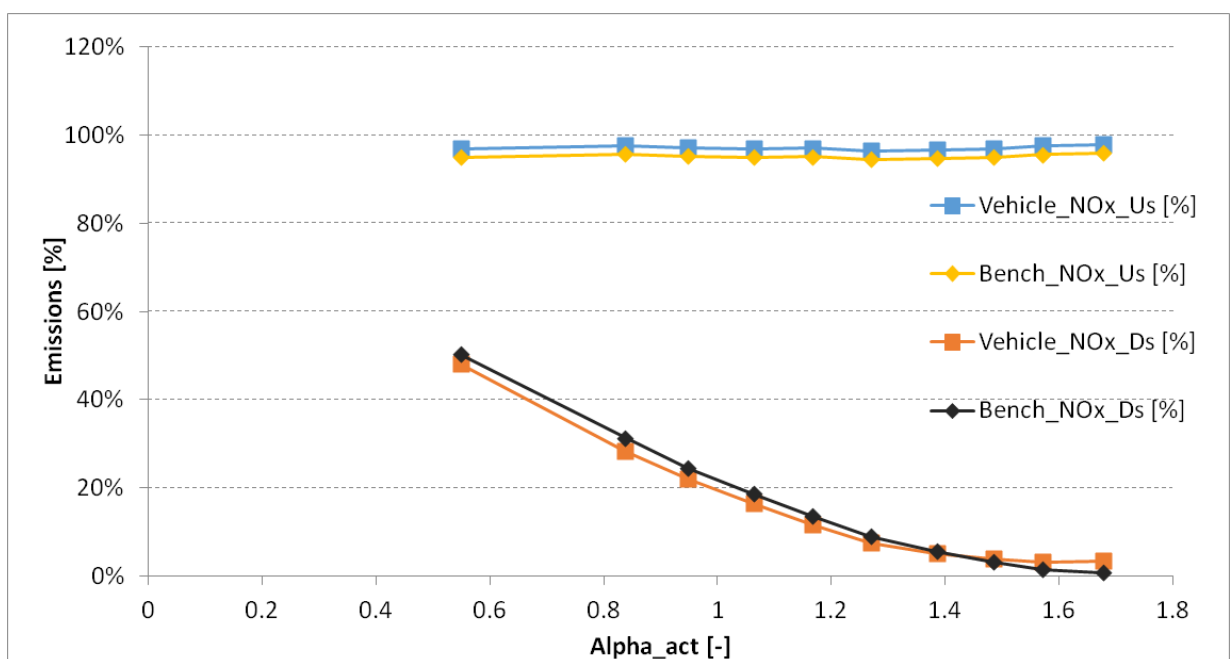
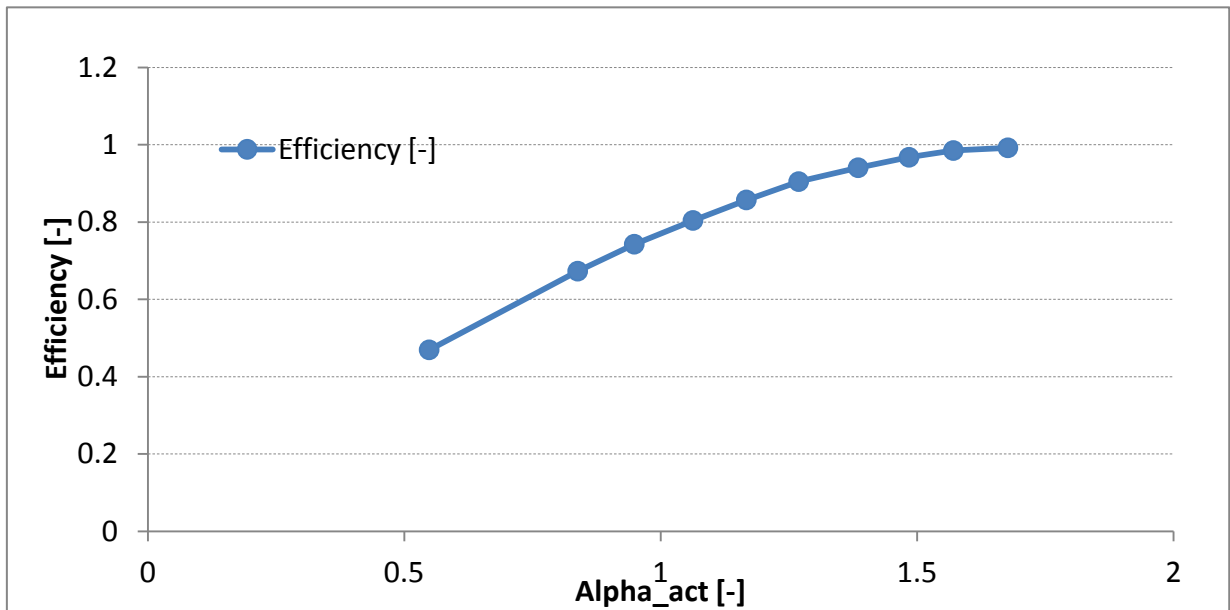


Figure 35. Alpha sweep 1500x500 reference component cps1_1 reference mixer w/ CUC

• 3500rpm-235°C

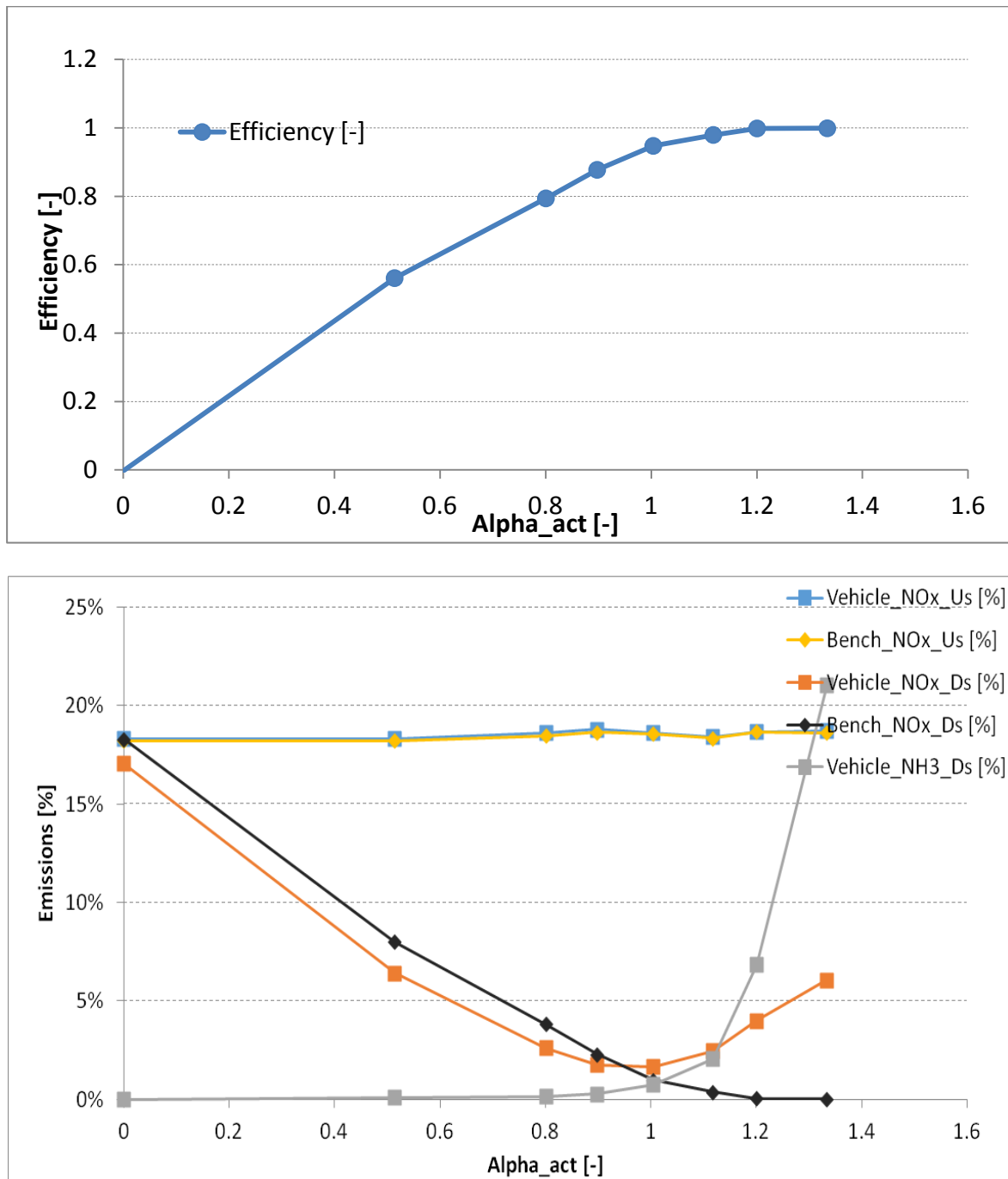


Figure 36. Alpha sweep 3500x235 reference component cpsi_1 reference mixer w/ CUC

• 3500 rpm-300 °C

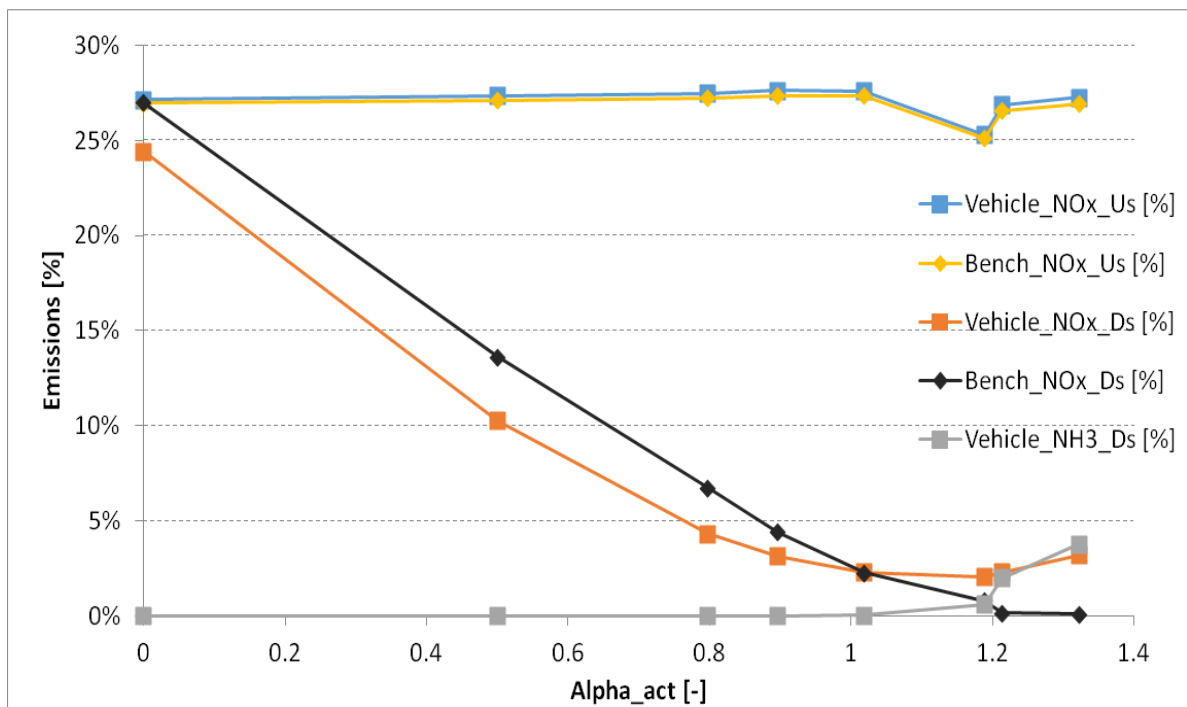
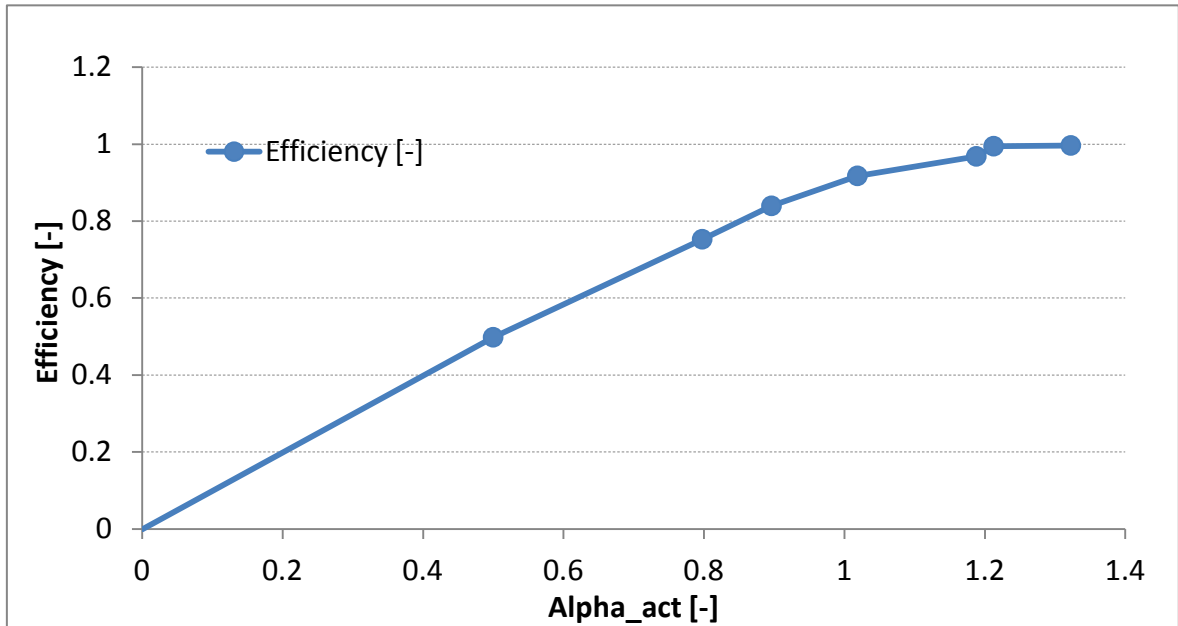


Figure 37. Alpha sweep 3500x300 reference component cpsi_1 reference mixer w/ CUC

• 3500rpm- 500°C

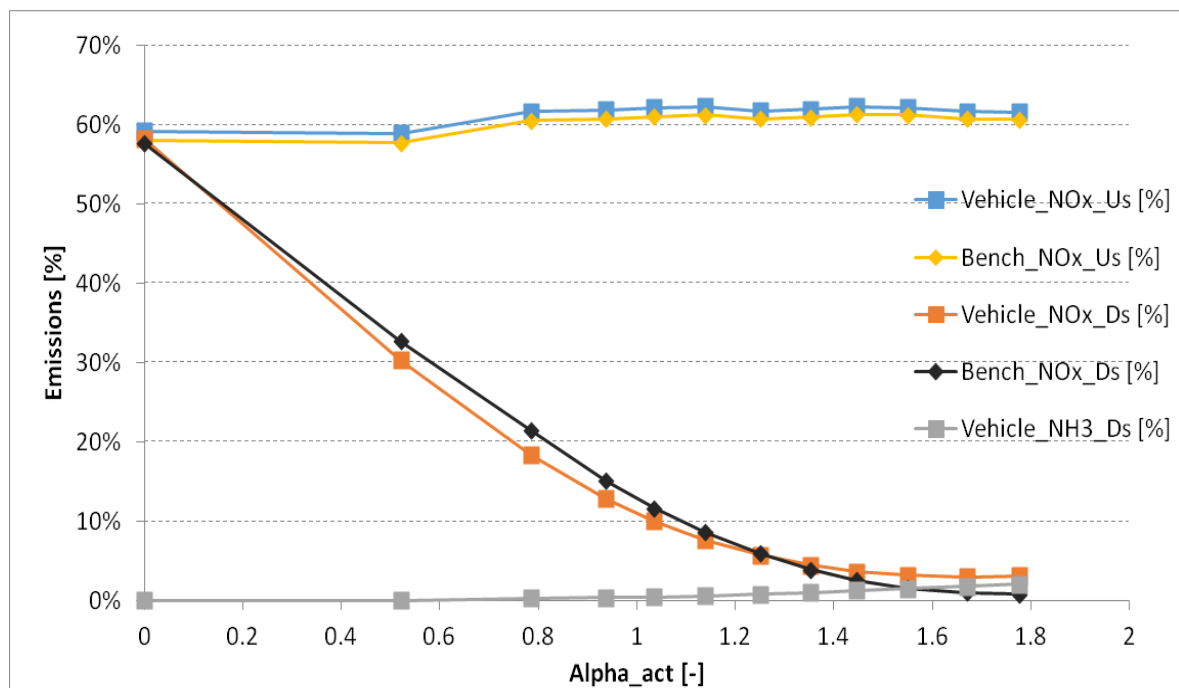
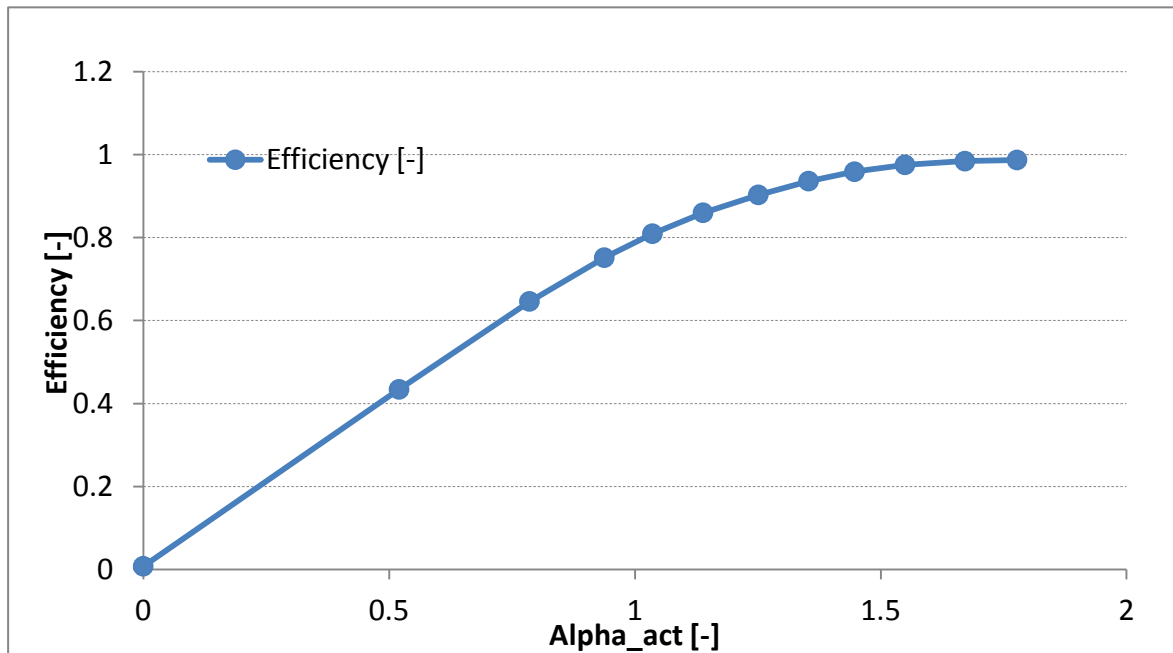


Figure 38. Alpha sweep 3500x500 reference component cpsi_1 reference mixer w/ CUC

5.1.2 Tested component *cp_{si}_1 mixer1* without CUC

- 1500rpm-235°C

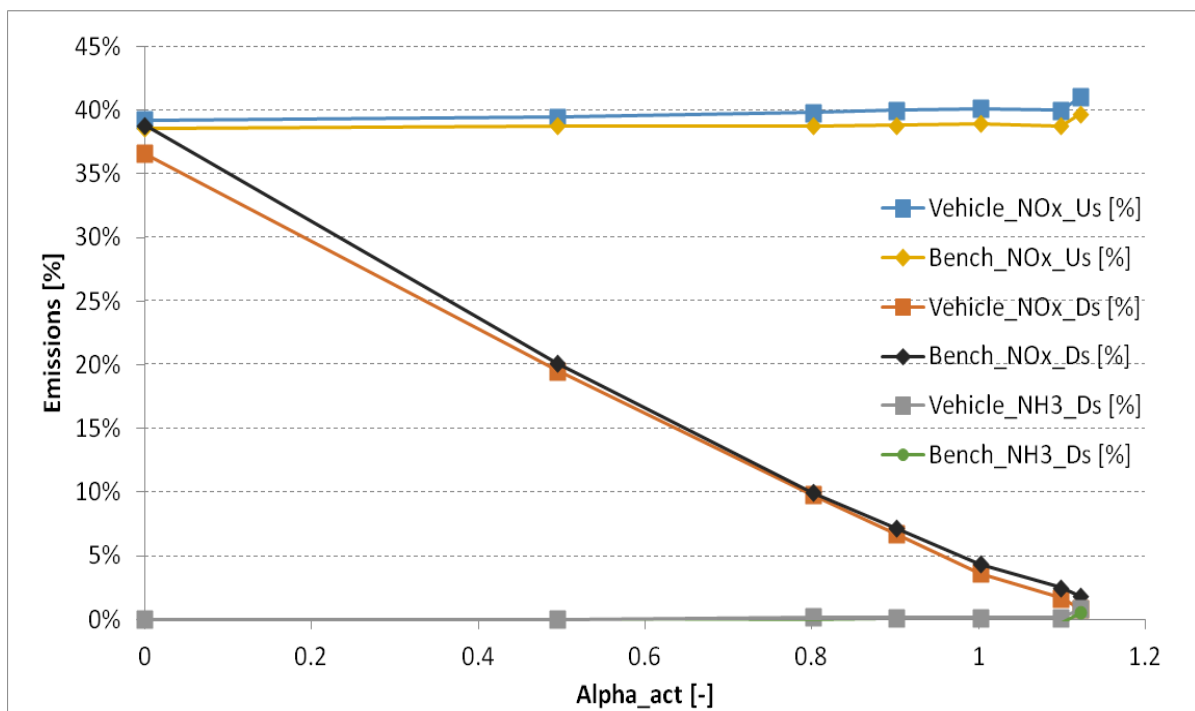
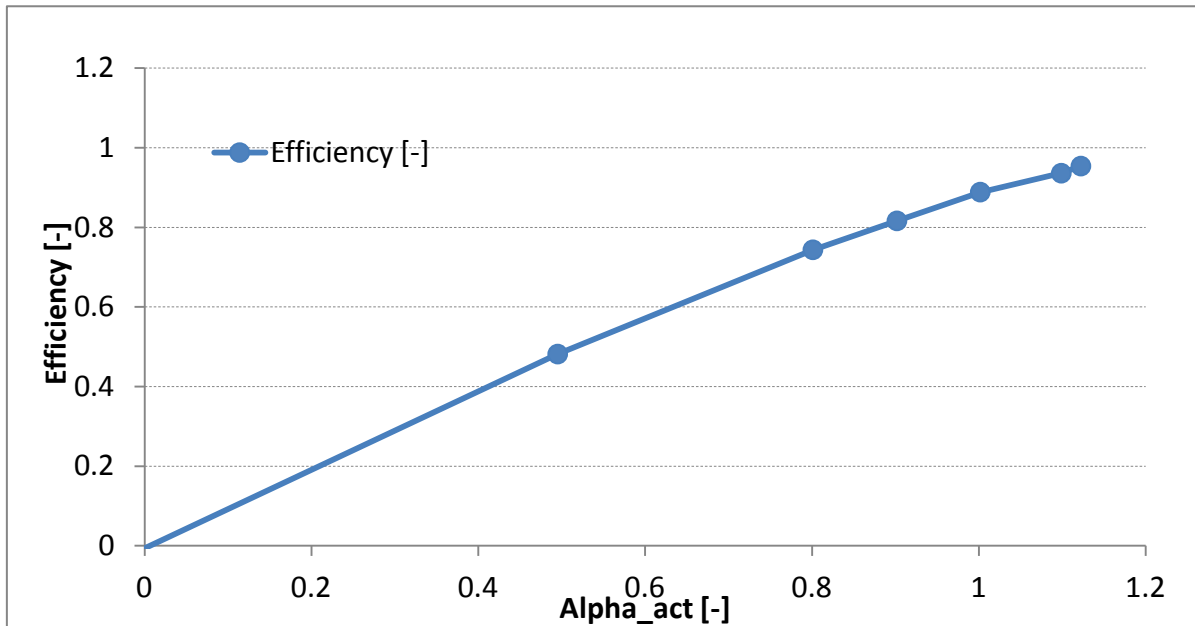


Figure 39. Alpha sweep 1500x235 tested component *cp_{si}_1 mixer1* w/o CUC

• 1500rpm-300°C

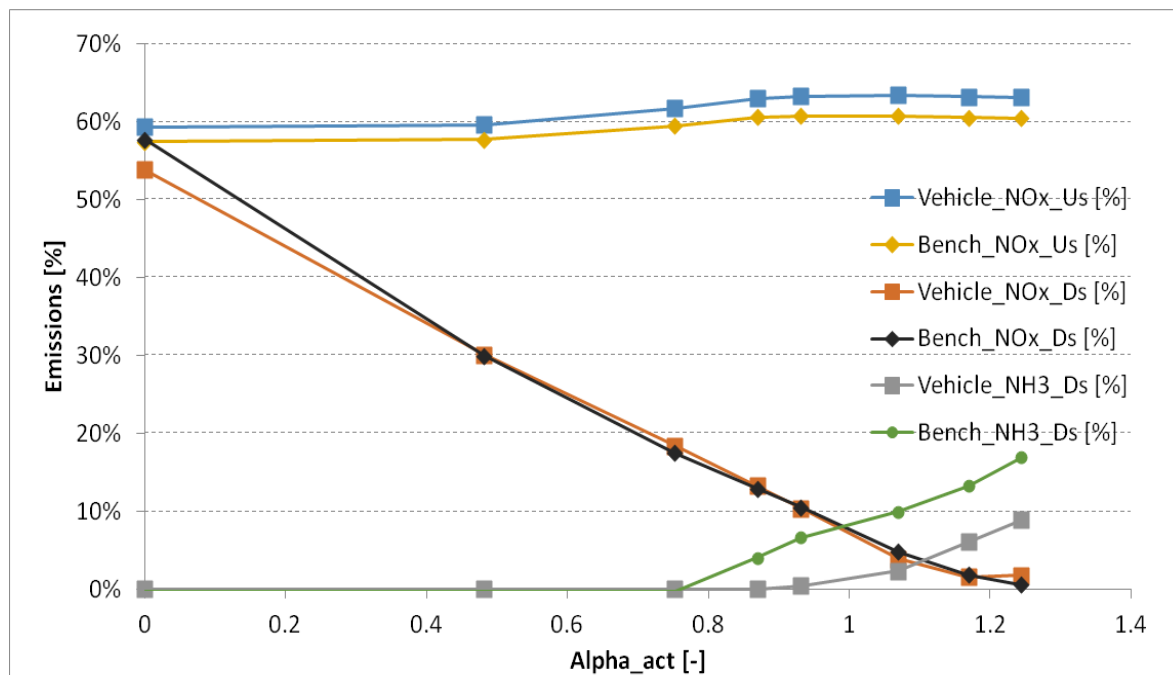
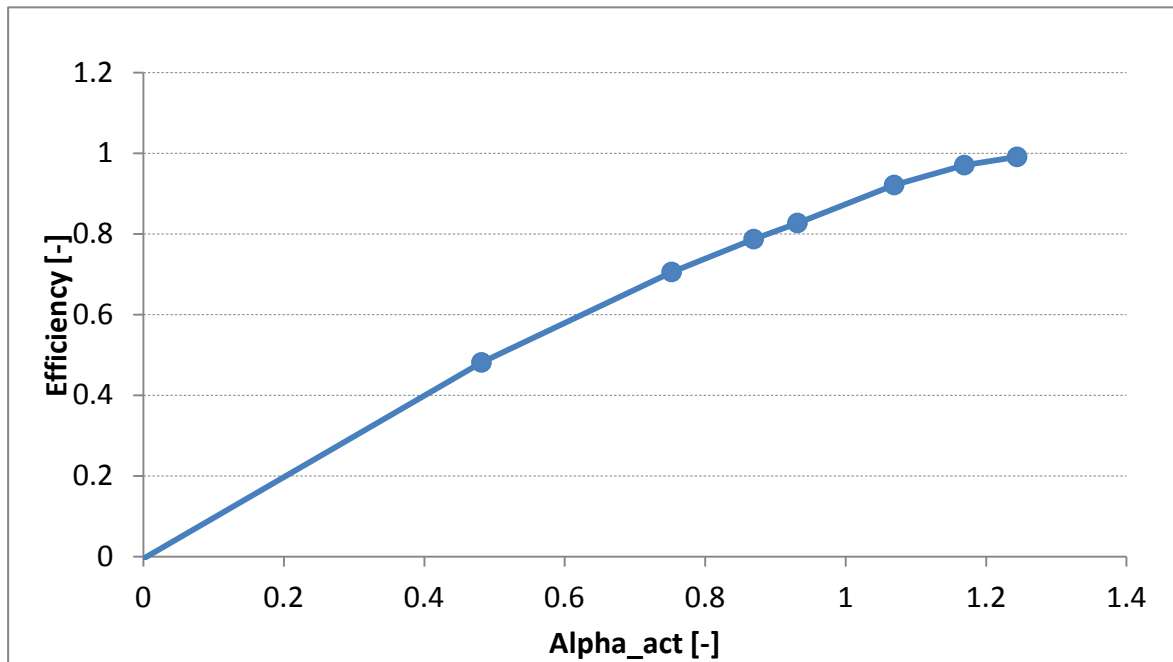


Figure 40. Alpha sweep 1500x300 tested component cpsi_1 mixer1 w/o CUC

• 1500rpm-500°C

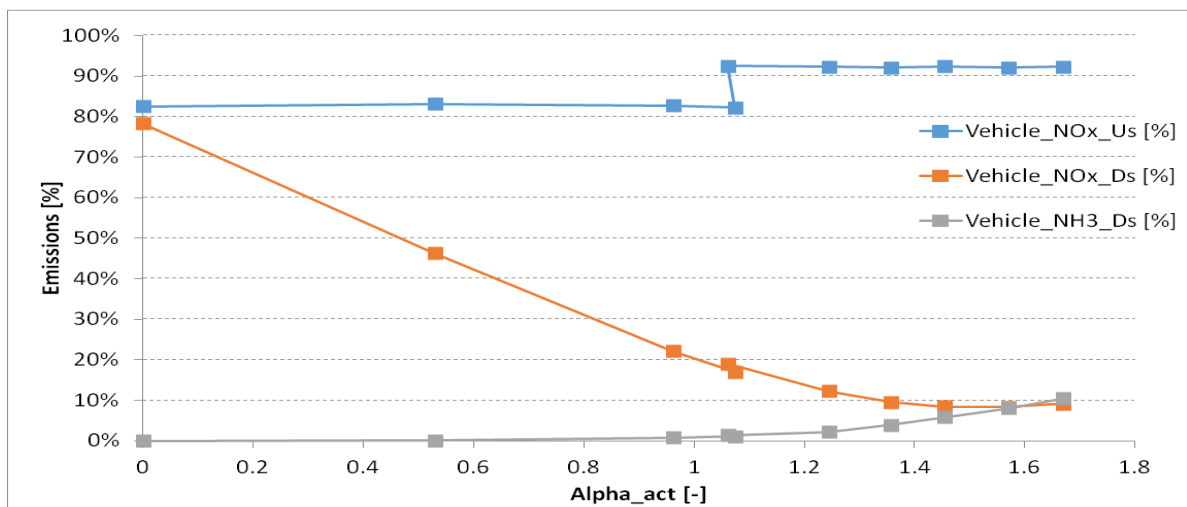
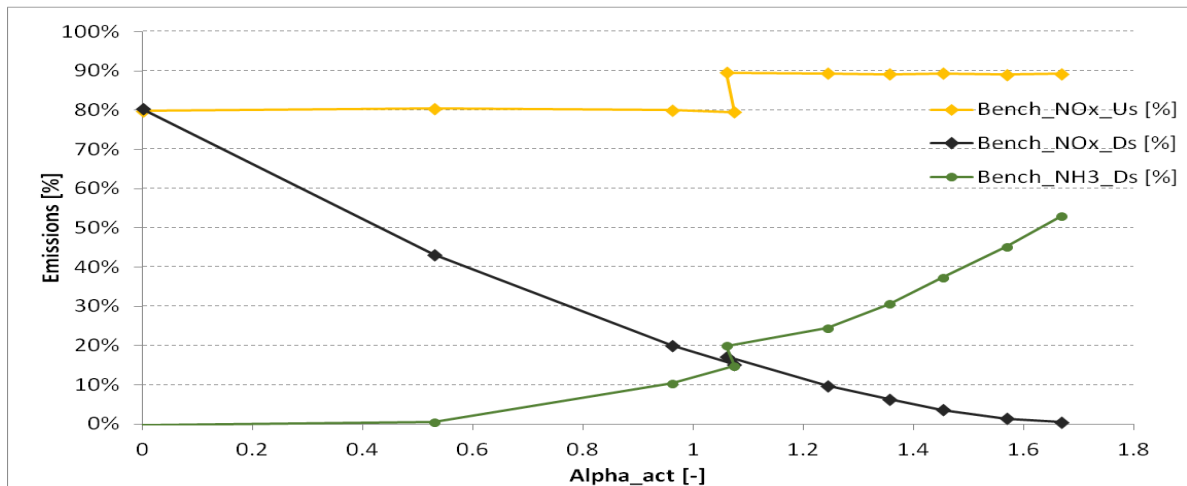
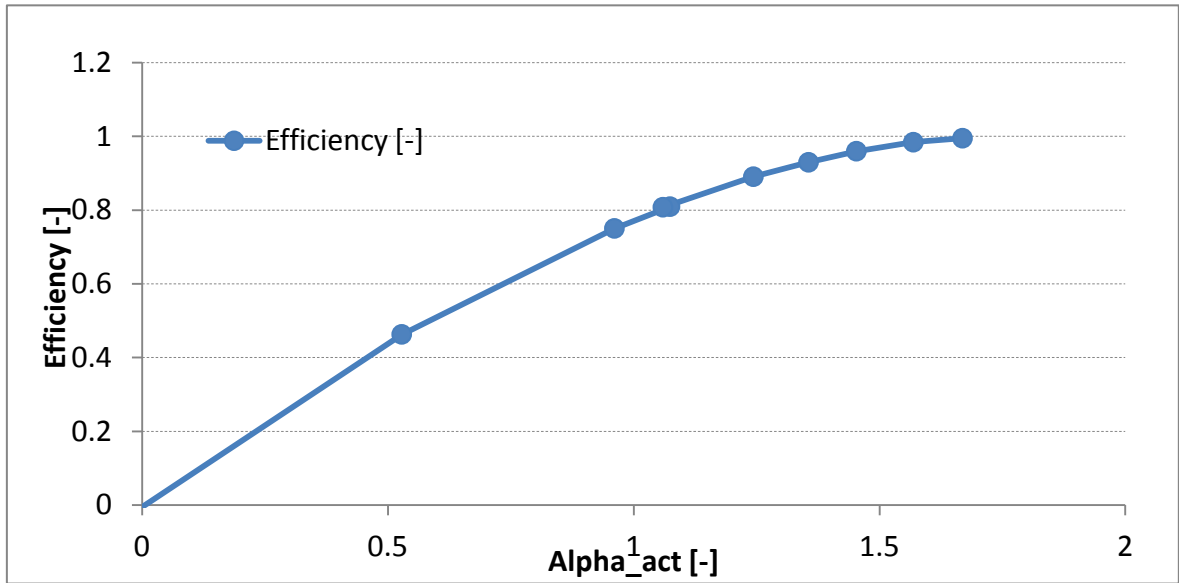


Figure 41. Alpha sweep 1500x500 tested component cpsi_1 mixer1 w/o CUC

• 3500rpm-235°C

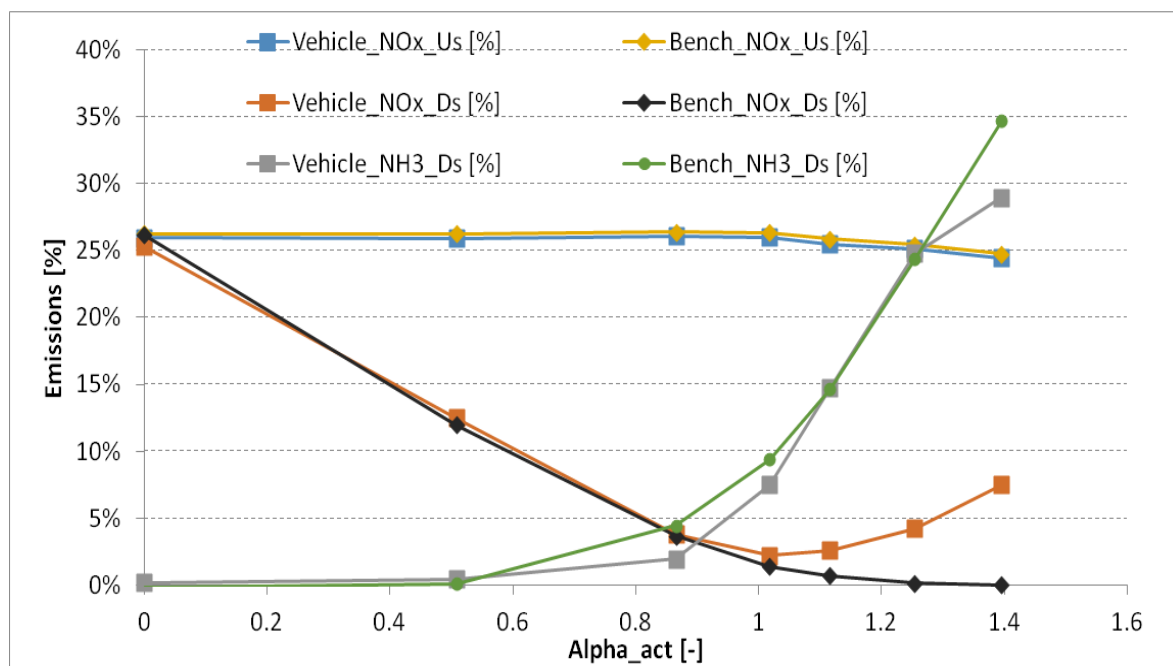
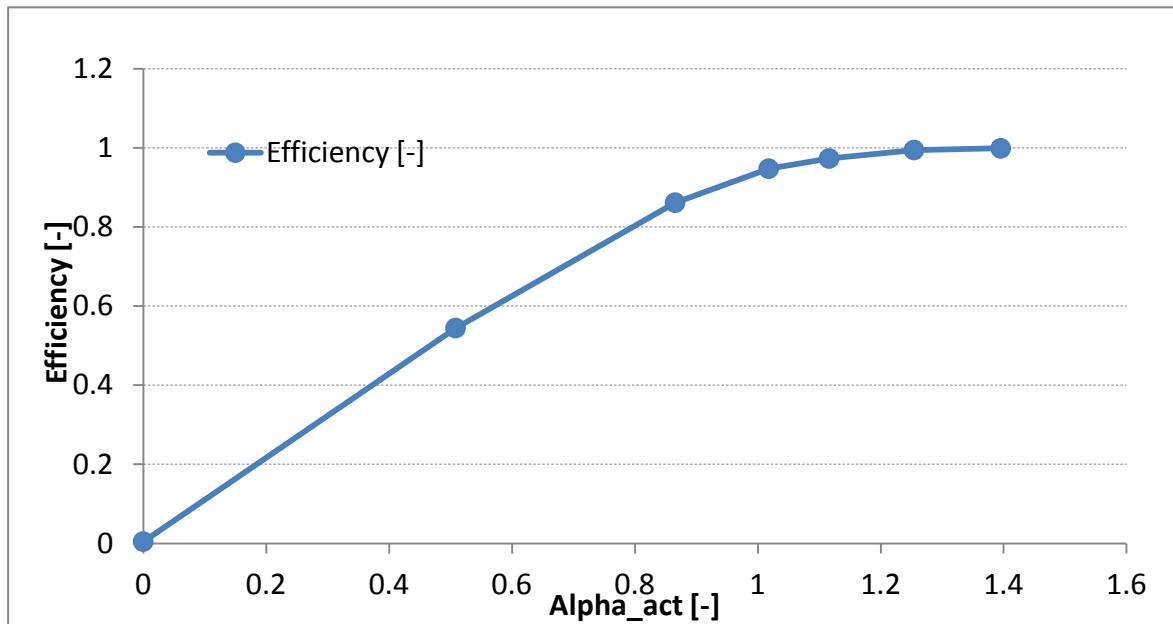


Figure 42. Alpha sweep 3500x235 tested component cpsi_1 mixer1 w/o CUC

• 3500rpm-300°C

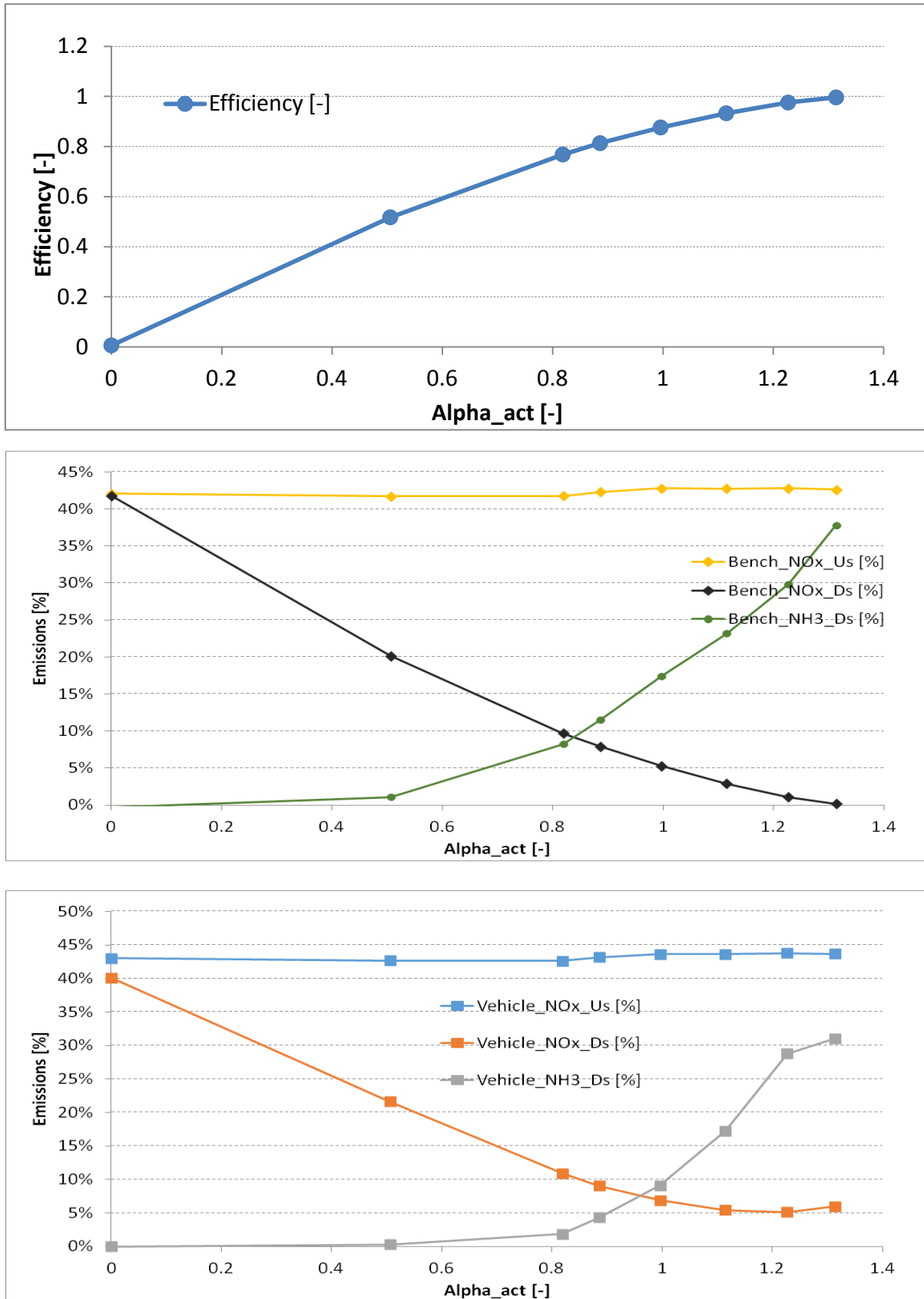


Figure 43. Alpha sweep 3500x300 tested component cpsi_1 mixer1 w/o CUC

• 350rpm-500°C

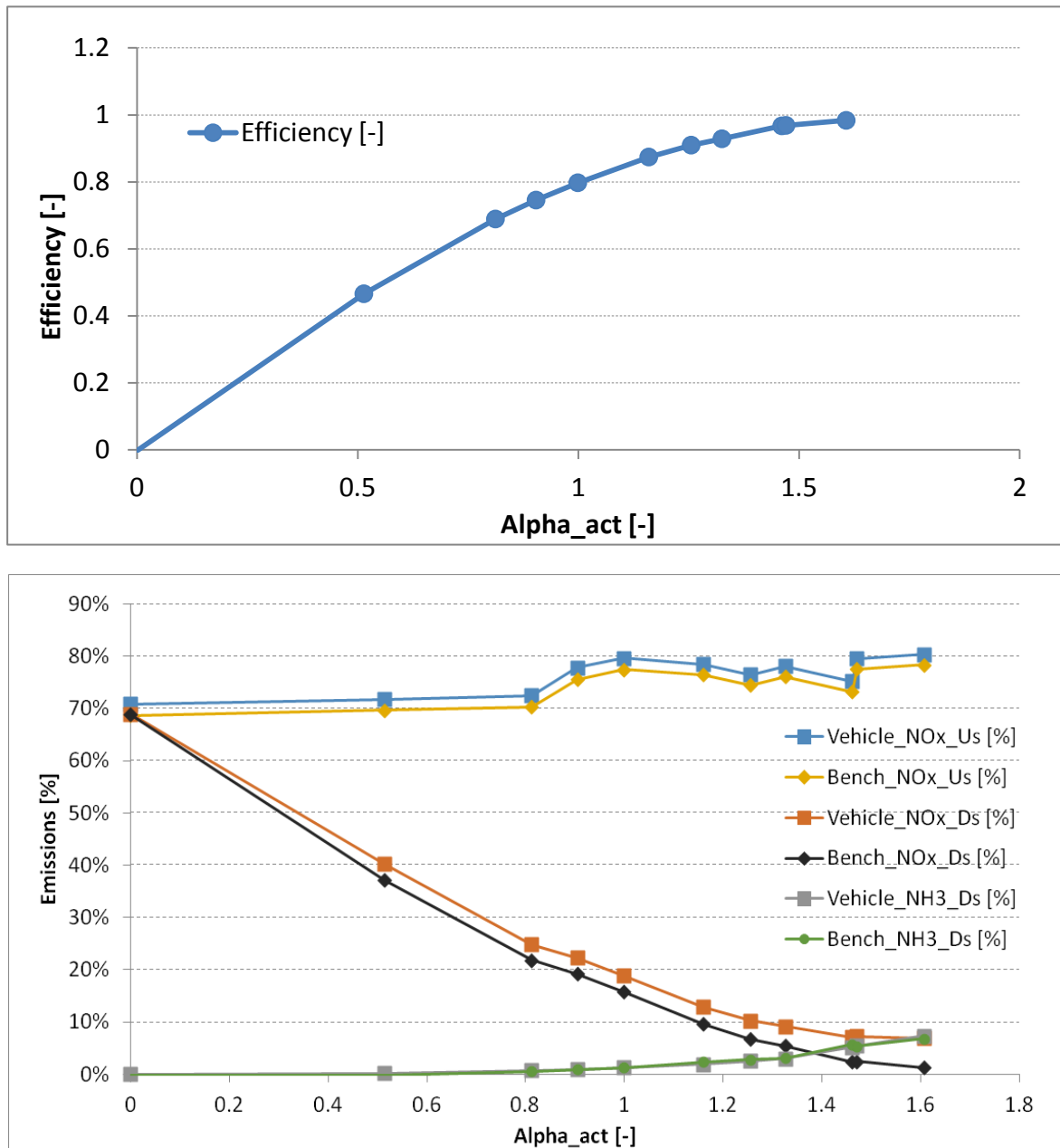


Figure 44. Alpha sweep 3500x500 tested component cpsi_1 mixer1 w/o CUC

5.1.3 Tested component *cpsi_2 mixer2* without CUC

- 1500 rpm-235°C

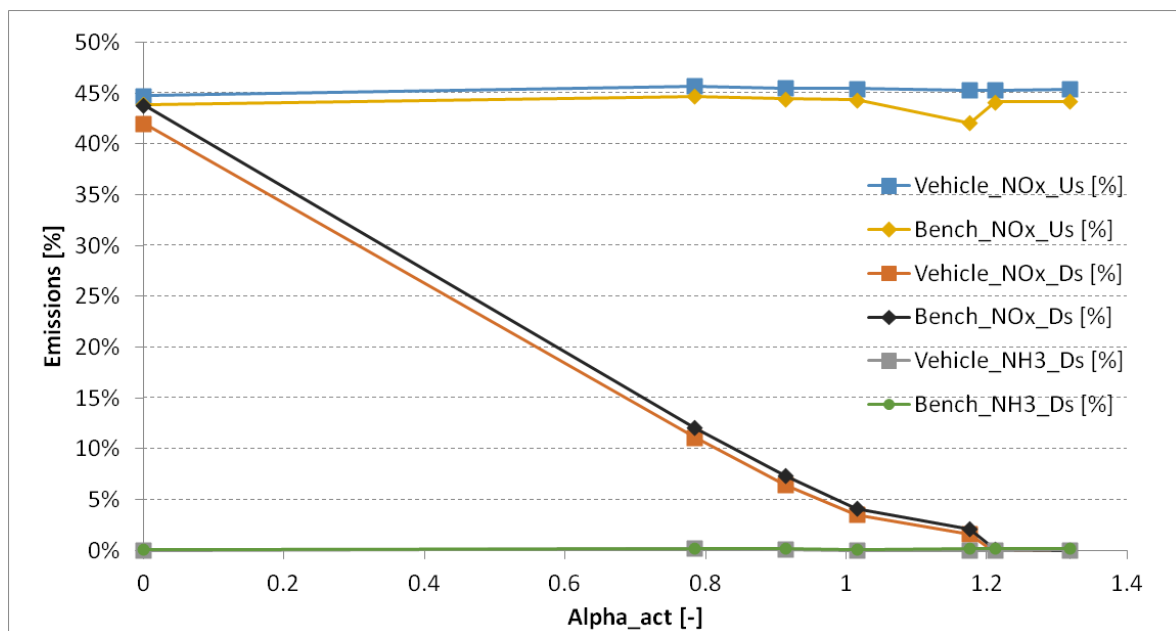
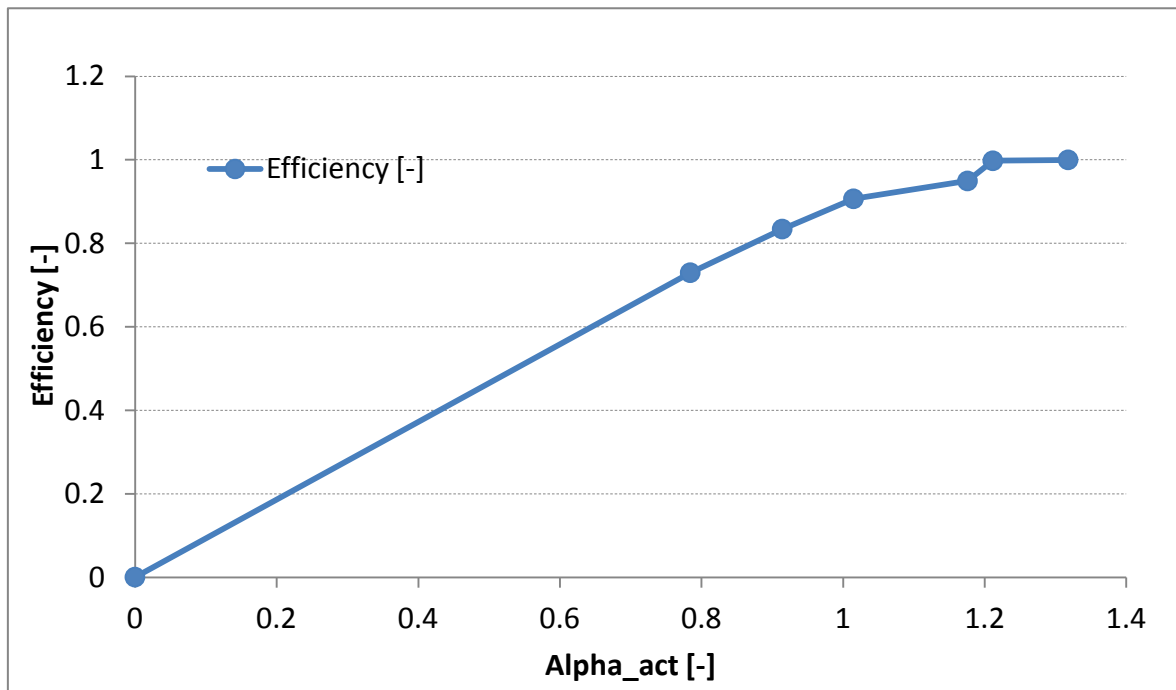


Figure 45. Alpha sweep 1500x235 tested component *cpsi_2 mixer2* w/o CUC

- 1500rpm-300°C

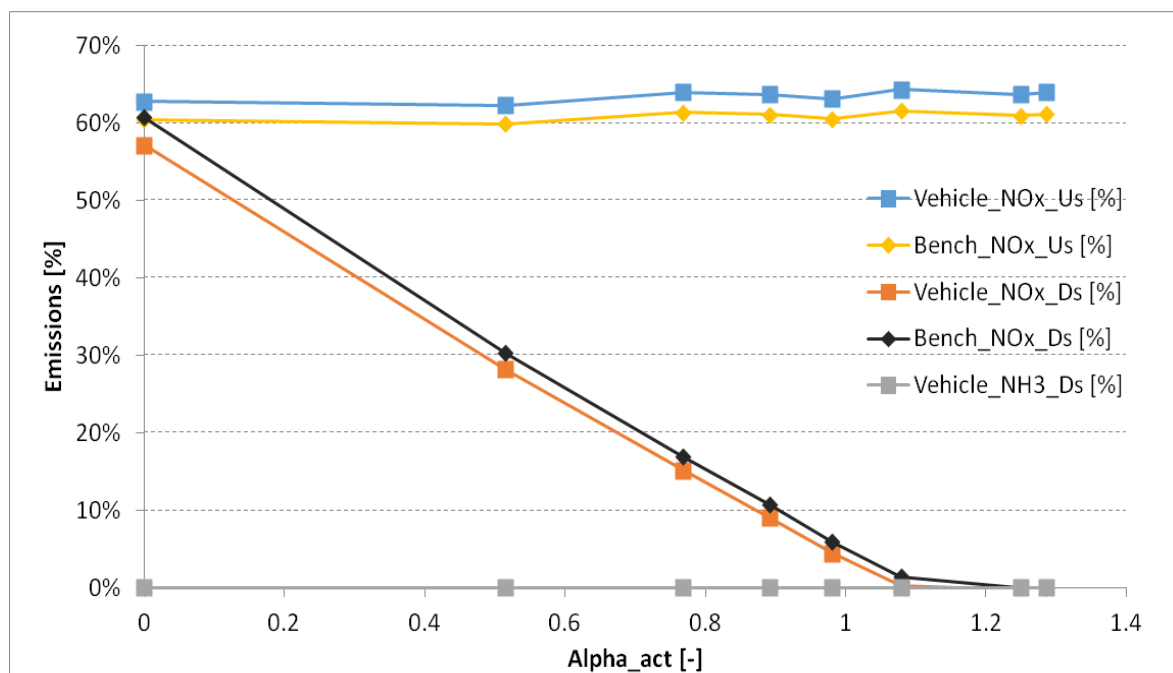
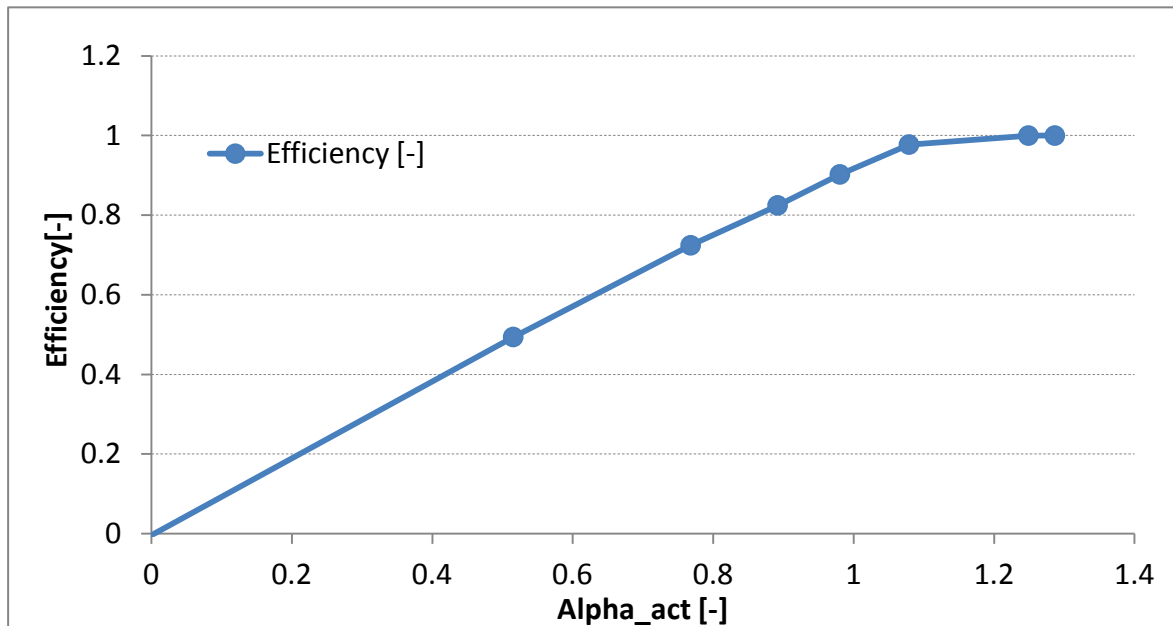


Figure 46. Alpha sweep 1500x300 tested component cpsi_2 mixer2 w/o CUC

- 1500rpm-500°C

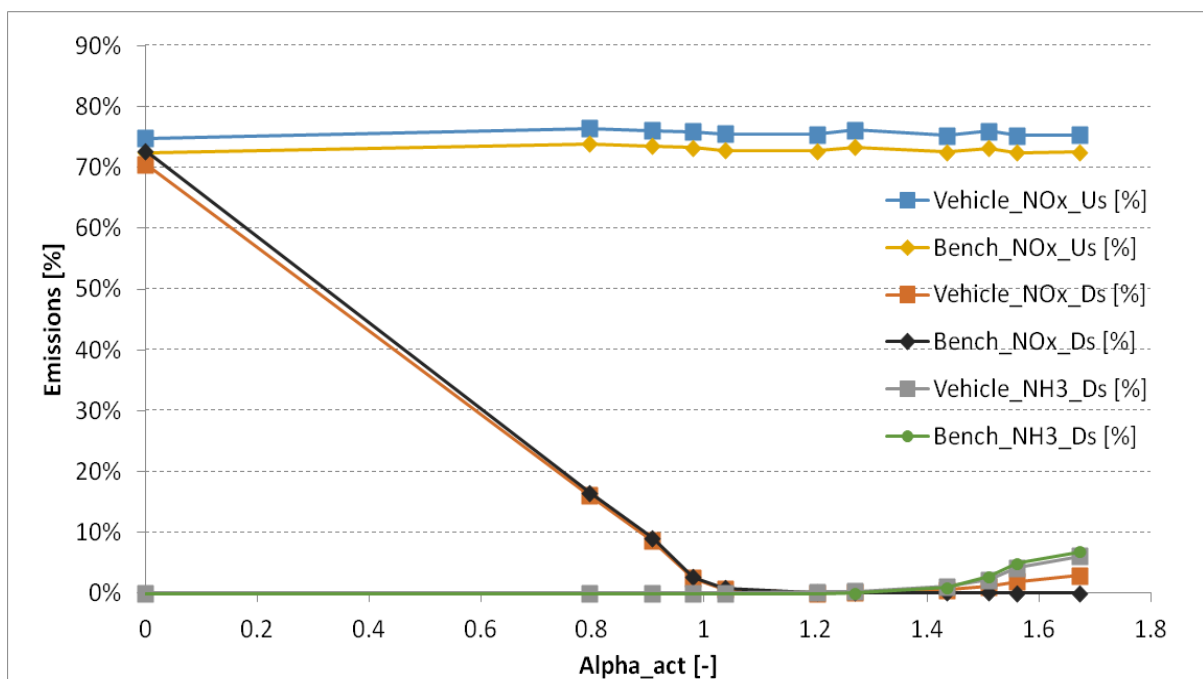
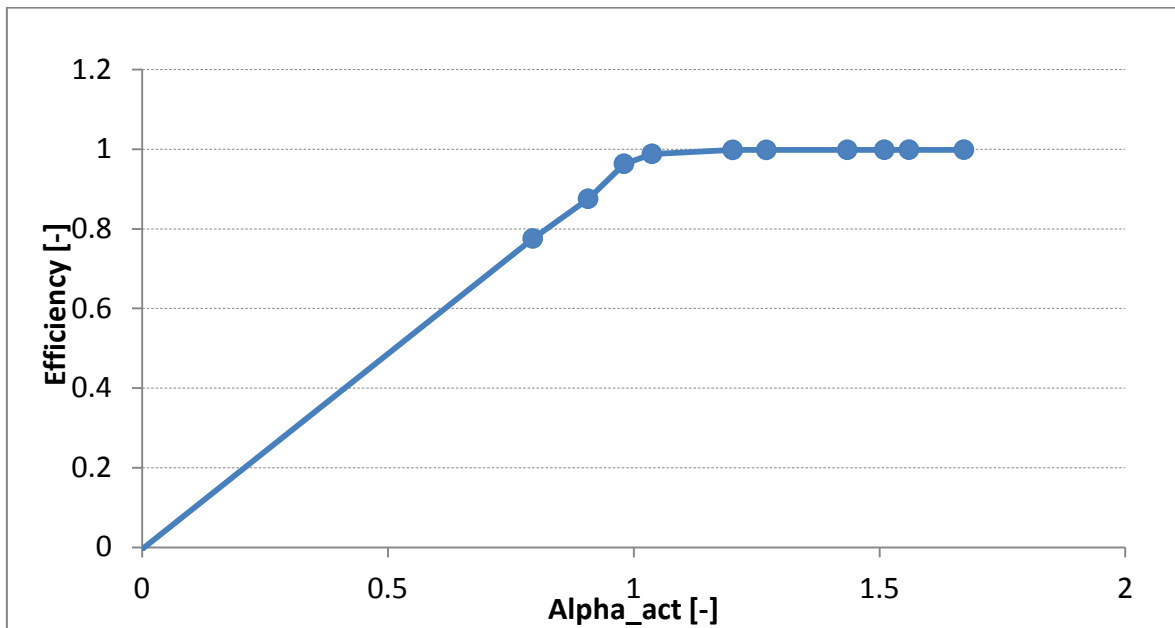


Figure 47. Alpha sweep 1500x500 tested component cpsi_2 mixer2 w/o CUC

• 3500rpm-300°C

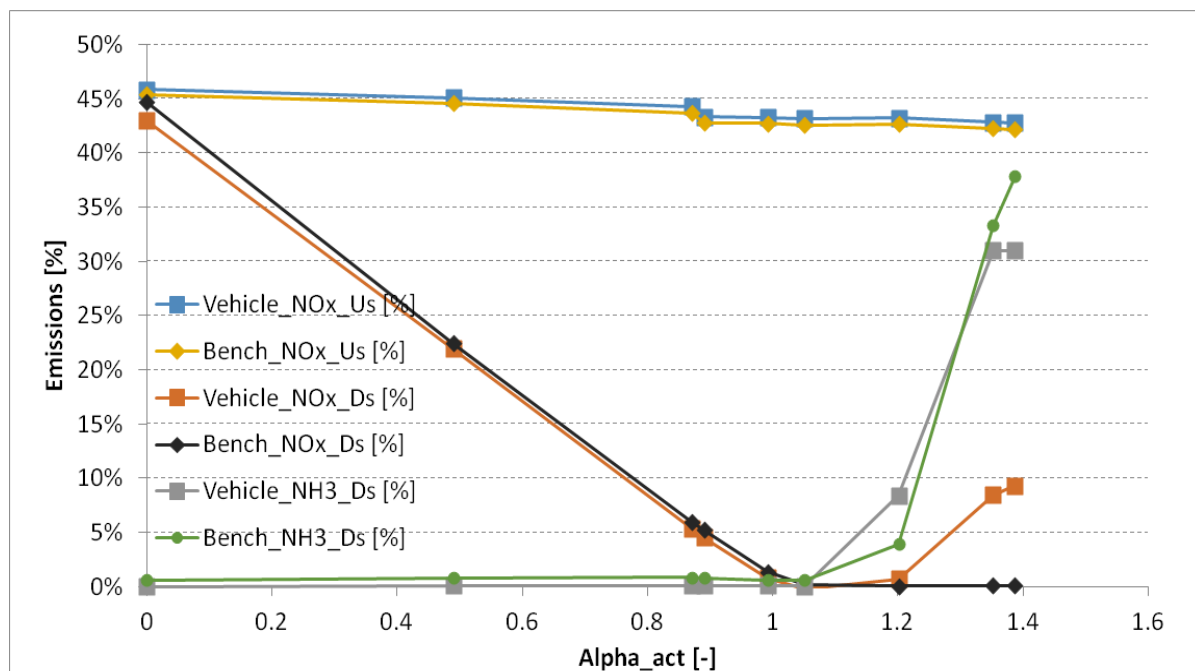
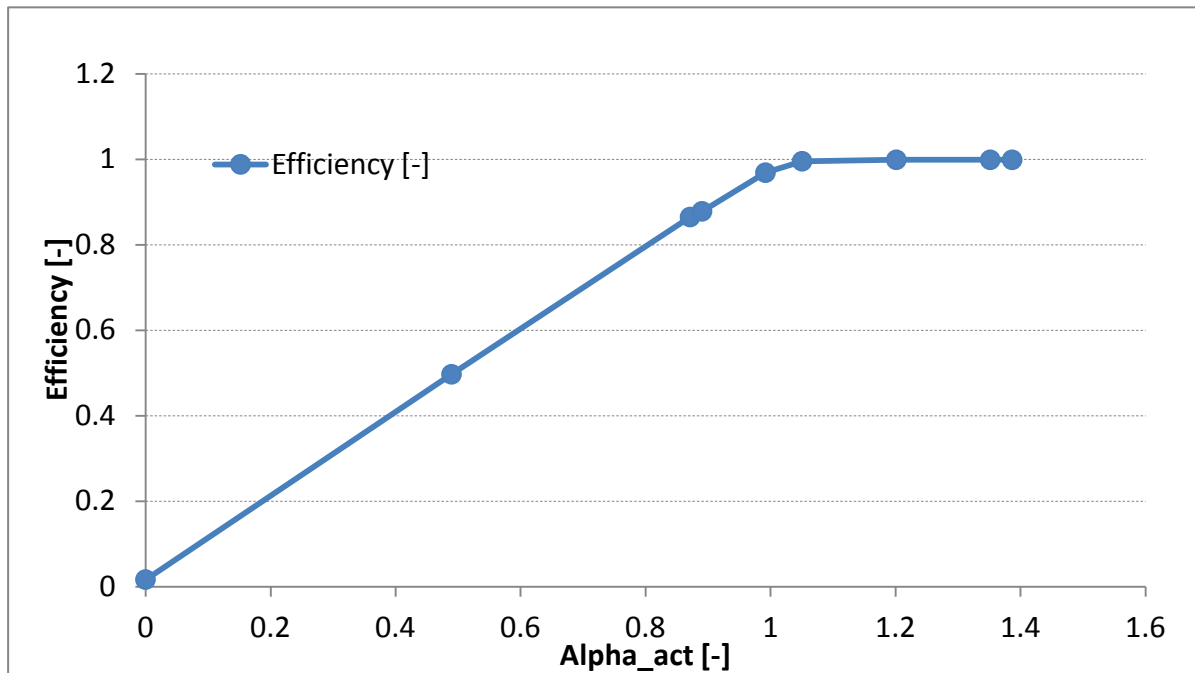


Figure 48. Alpha sweep 3500x300 tested component cpsi_2 mixer2 w/o CUC

• 3500rpm- 500°C

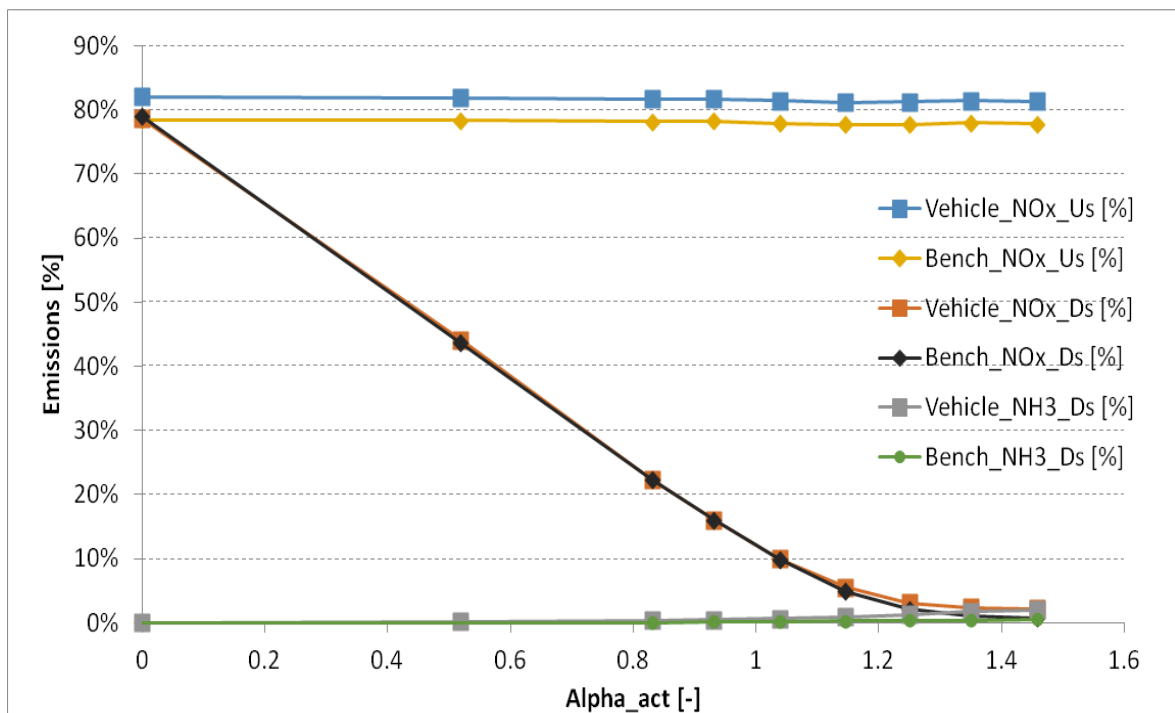
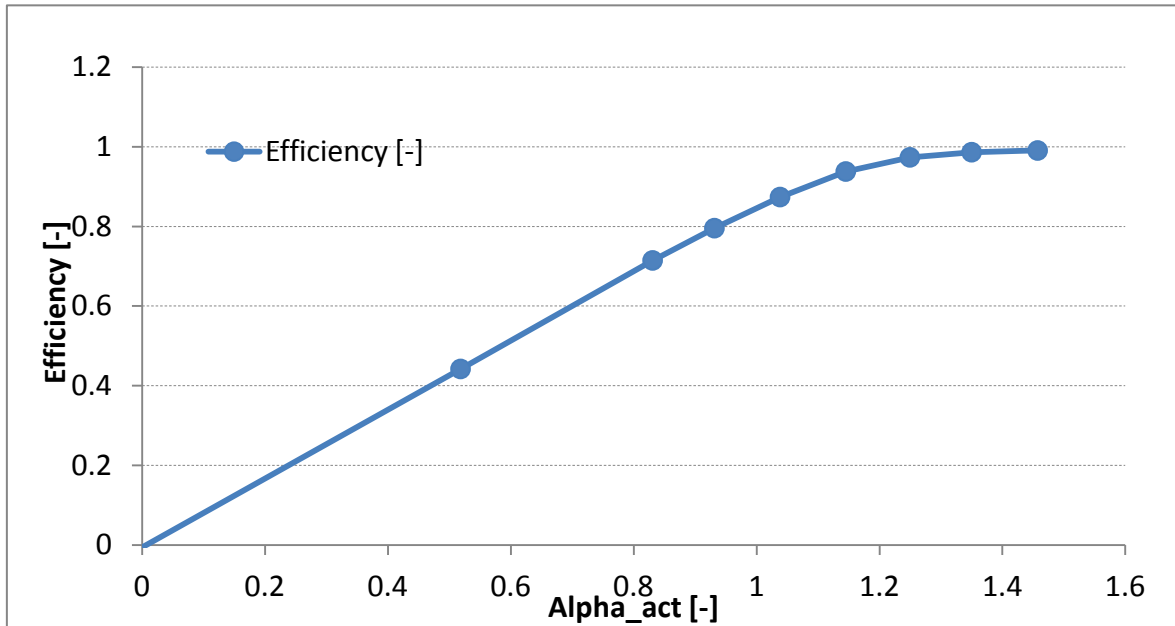


Figure 49. Alpha sweep 3500x500 tested component cpsi_2 mixer2 w/o CUC

Other tests have been performed to give evidence to some behaviors that affects the tested and reference components. The phenomena studied in deep are the efficiency curves in the working point 1500rpm 300°C. The differences between the two components was larger than the expected one. At the end of the analysis made to understand the causes, figure50 and figure51, it was seen that it was a just a particular deviation of the specific test.

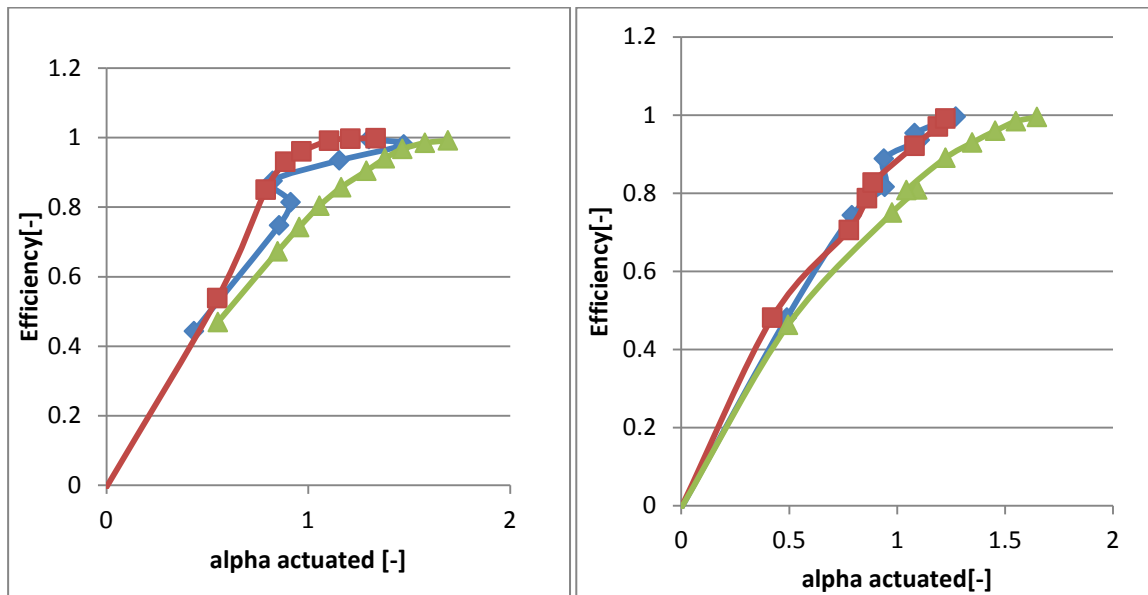


Figure 50. Reference (on the left) and tested (on the right) components efficiency vs. alpha actuated. Red 1500x300, blue 1500x235, green 1500x500

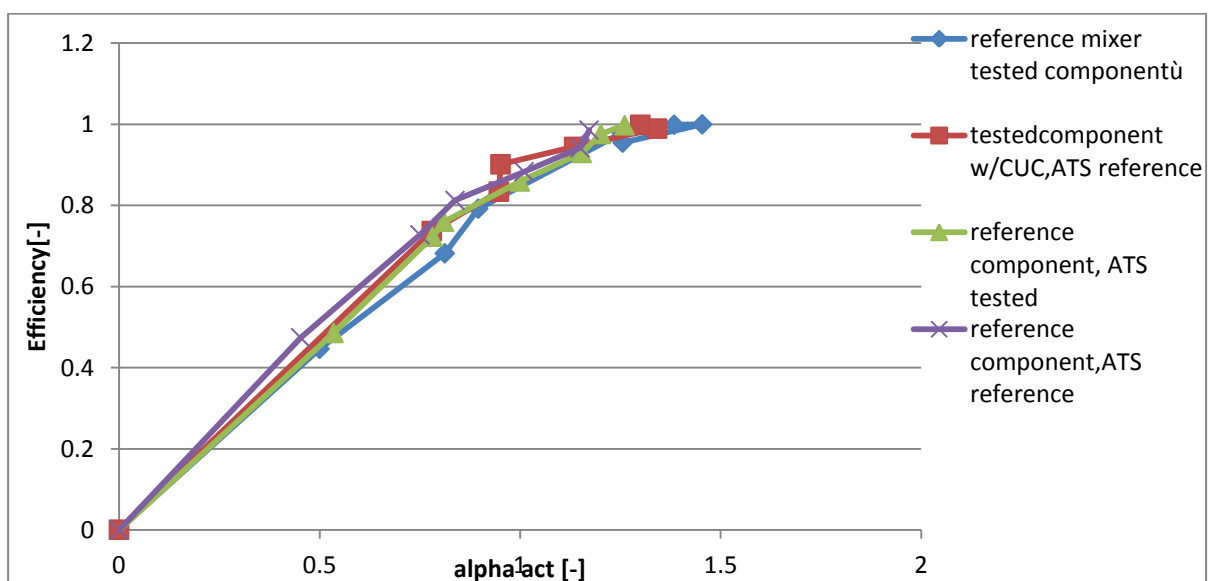


Figure 51. 1500x300 verification tests

Some important informations can be extrapolated from this data. First one is the efficiency of the three components for different working points, working points are specified in term of upstream temperature of the SCR and engine speed. Due to the fact that in this way the exhaust flow is not fixed the space velocity is changed for each tests so not always is possible to find the theoretical expected trend between the curves. Theoretical trends should include for a constant engine speed higher efficiency and a steeper curve for temperature close to 300°C, maximum efficiency of an Cu-Zeolite SCR is expected in the range 250°C - 450°C, while lower efficiencies are expected for temperature of 500°C, where oxidation phenomena influence the conversion efficiency and temperature of 235°C because of low temperature for the chemical reactions triggered, for that temperature and specially for low engine speed, urea deposits are expected; to avoid to begin a test with some of this deposits inside the component, engine was run for few minutes in regeneration mode. Higher values of conversion of NOx emissions are expected at lower space velocities. To take into account for the evaluation of the results is the actuated alpha from the automated test control, it can have some deviation from the one expected because of the change of fuel injected quantities for temperature control, meaning different emissions so a different urea-NOx ratio asked. This leads to some deviations from the expected efficiencies between the analyzed points and so also to measurement of NH3 slip unexpected. For graphs where an unexpected slip, for alpha lower than stoichiometric, is measured a concentration of NH3 downstream it could be due to the not perfect mixing or not optimal use of the complete washcoat for lacks of the mixer. To be taken into account in the next phase of calibration is the indication on the cross sensitivity of the vehicle NOx sensor to NH3. Urea crystallization was expected close to the mixer for lower temperature and lower space velocities, photos with an endoscopic have been made before and after the regeneration. No differences are expected between trends for cpsi_1 and cpsi_2 for alpha sweep tests; huge differences are expected for the NH3 loaded quantities and loading and unloading times.

The results reported in figure73 come from the data of the reference and tested components with cpsi_1 and mixer1.

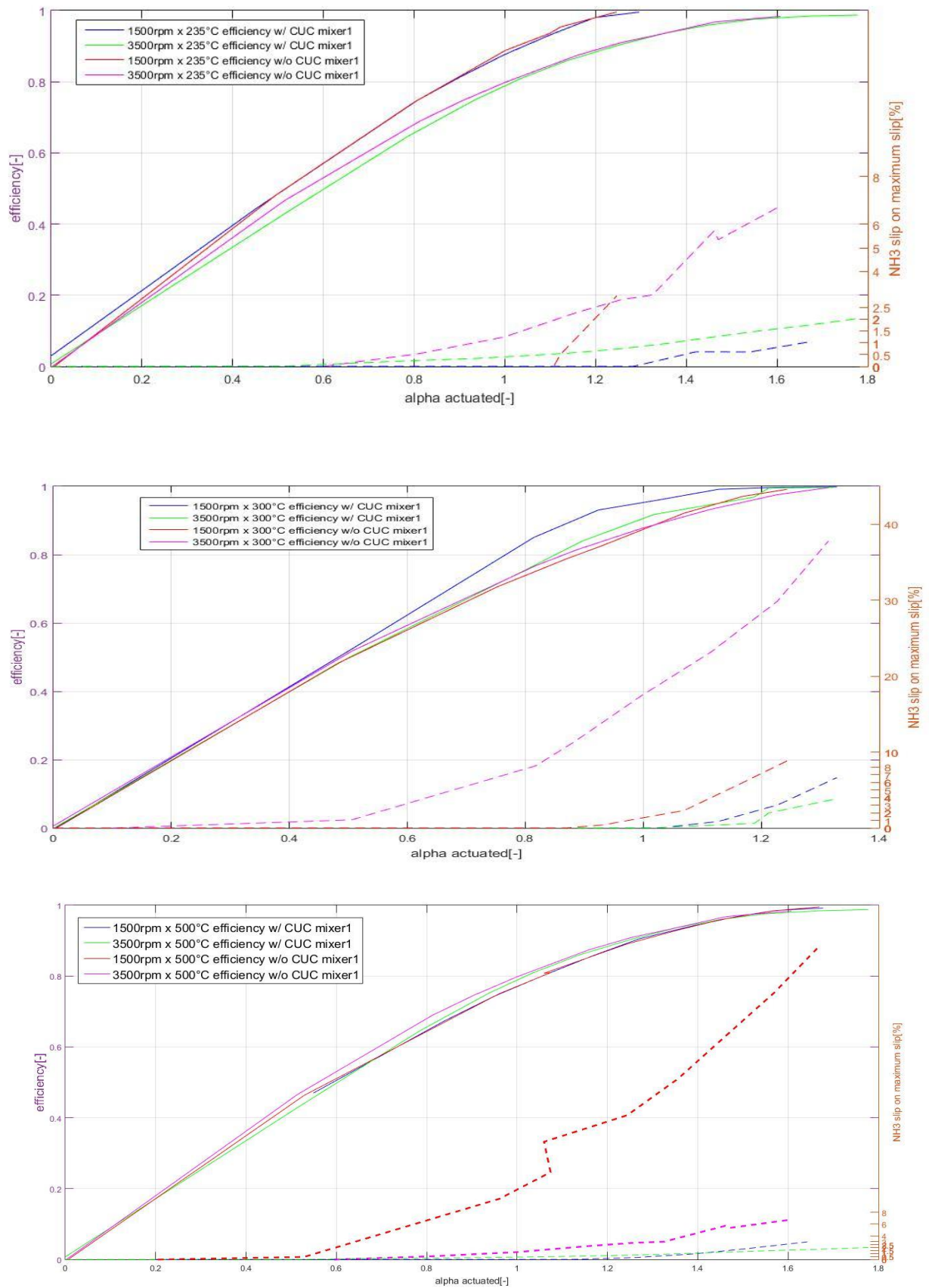


Figure 52. Efficiency-NH3 slip vs alpha actuated, comparison component CUC- no CUC at different temperature, cpsi_1 tested-reference components with mixer1

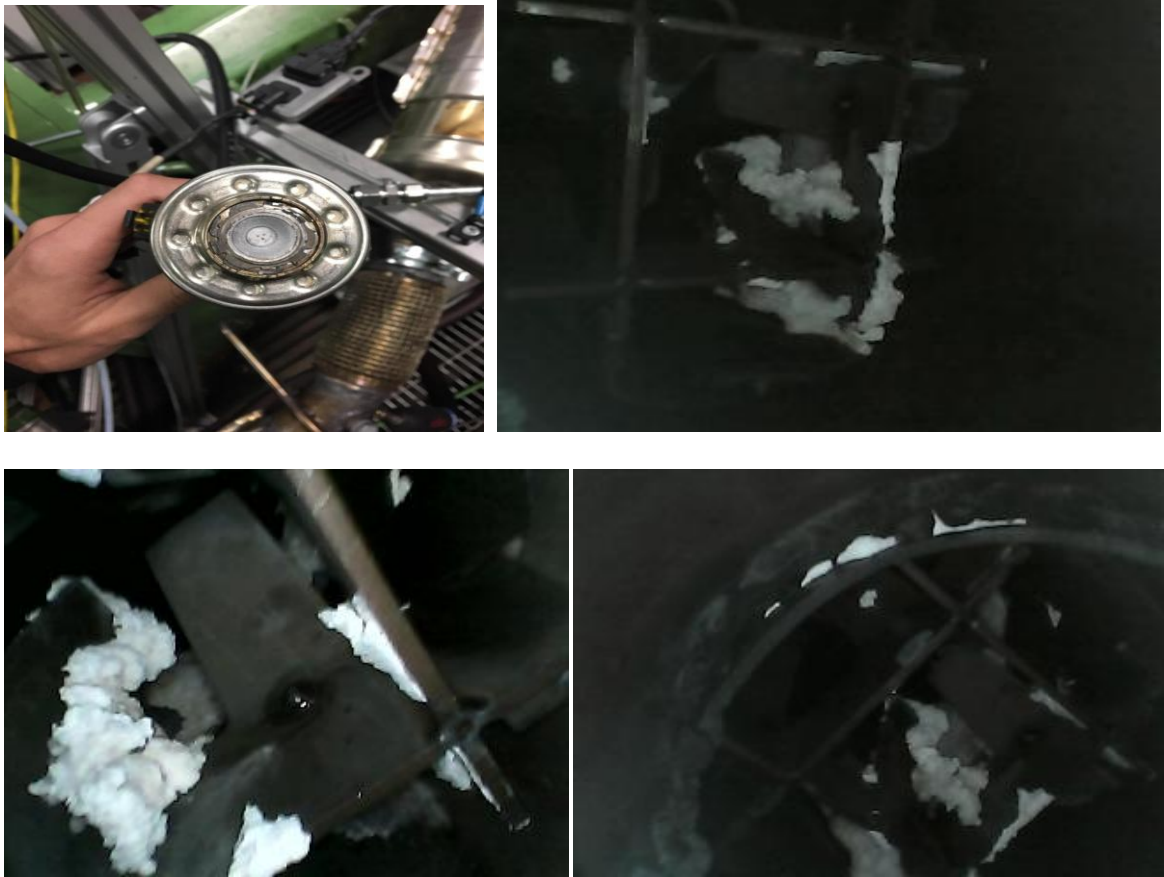


Figure 53.Urea deposits on tested component cpsi_1 mixer1 pre regeneration; end of 1500x235 alpha sweep test



Figure 54.tested component cpsi_1 mixer1 photo post regeneration; end of 1500x235 alpha sweep

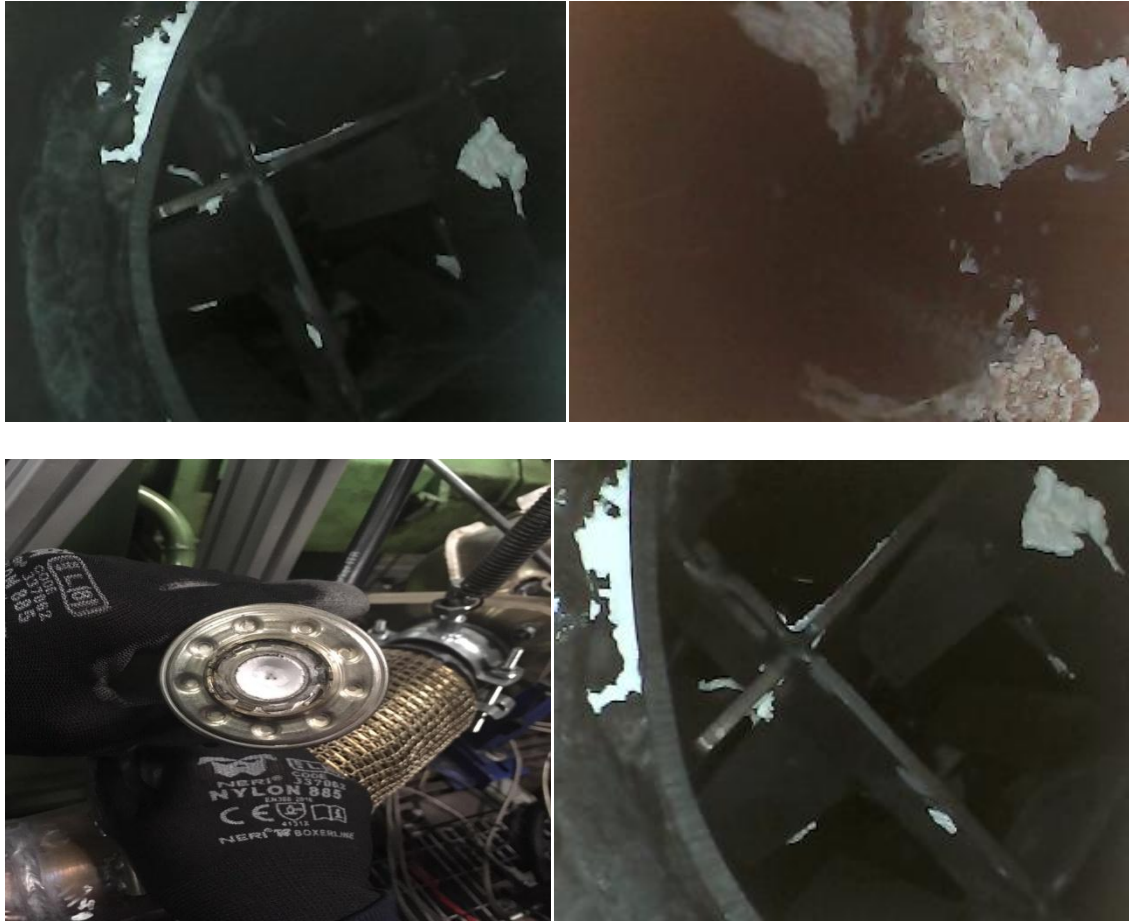


Figure 55.Urea deposits tested component cpsi_1 mixer1; end of 3500x235 alpha sweep test



Figure 56.tested component after regeneration; end of 3500x235 alpha sweep test

5.2 Load-Unload test

Major informations for the characterization of an SCR and future activities comes from the load-unload tests; a valid calibration is a valid trade-off between injection of Ad-Blue and loading and the capacity of the component to reduce the risk of NH₃ slip in all possible working conditions. Main result of the tests are shown below for the loading phase and then for the unloading phase. For the loading part it is shown for each working point the trend of NO_x emissions upstream SCR and downstream. For different exhaust flows the indication of time needed for the test and the time needed to have a complete load of the component is added. A complete load of an SCR component could be considered as 20ppm of slip is reached but for completeness of information a stable behavior of all the parameter under analysis was waited. Main indication parameters will be presented in the graph with indication of the efficiency reached at the corresponding loading and actual alpha used. For the unloading part it will be shown the trend of the NO_x emissions during all the time duration of the test, the reduction of efficiency trend related to the diminishing of the loading and the actual alpha of conversion related only to the design of the component and of the zeolite. For one representative test in term of phenomena, preparation and development all the graphs used for internal checks of the results will be shown to give a more complete view of the post-processing activities.

Taking in consideration the working point asked in term of upstream temperature and exhaust flow, from the knowledge from the engine map the working points are individuated. For some tests a re-arrangement of the calibration was asked so the points not shown in the table.11 are the one out of the engine map.

The sampling frequency used for the signal elaboration is 2Hz.

Emissions are calculated as percentage on the maximum recorded for each emissions species.

The green point in the graphs represents the 90% efficiency of the component. If not present a too high approximation for the estimate was needed.

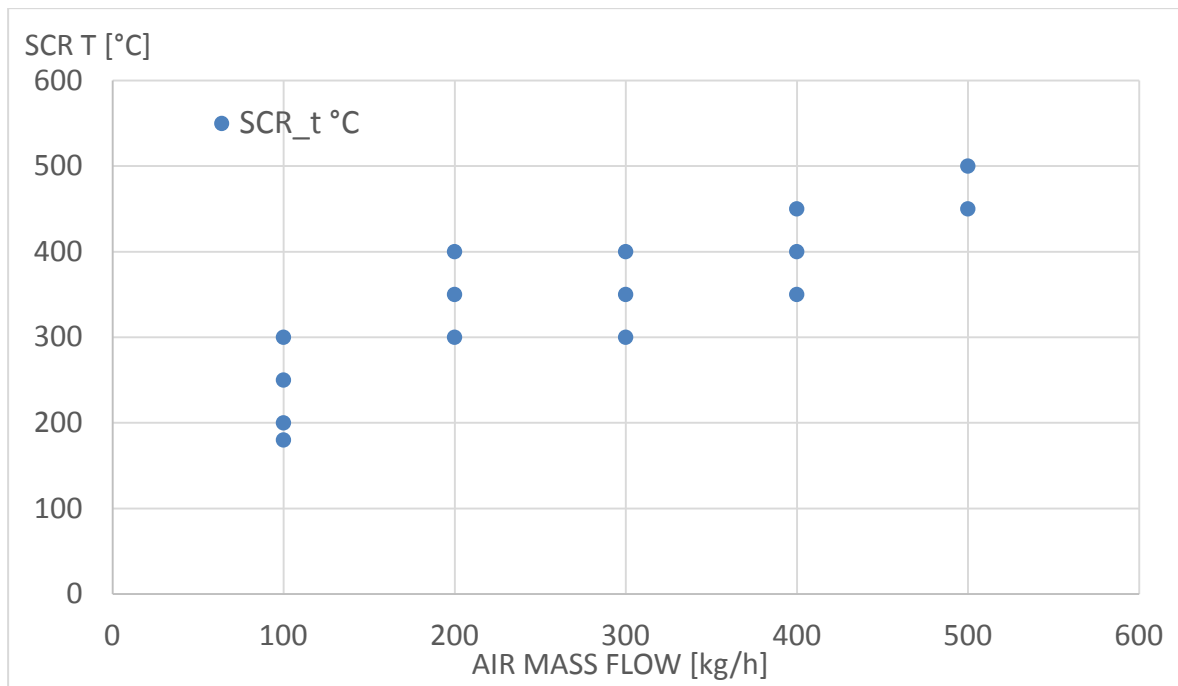


Figure 57. Loading-Unloading working points

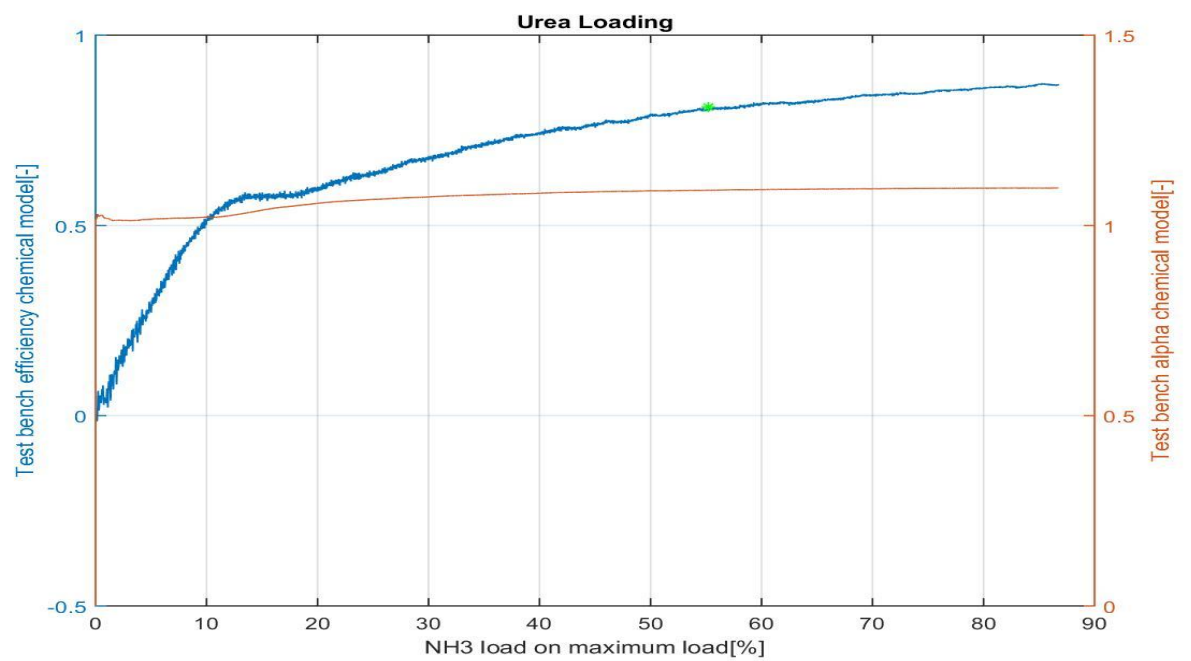
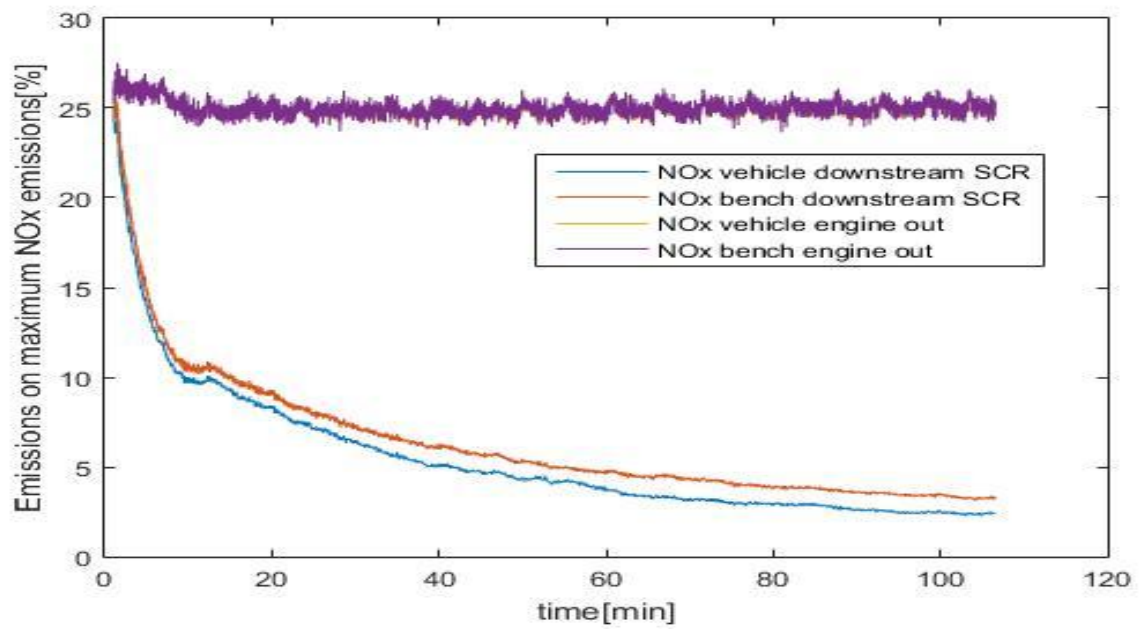
<u>Alpha</u>	<u>Rpm</u>	<u>Load[%]</u>	<u>Exhaust flow[kg/h]</u>	<u>SCR up[°C]</u>
1.25	1450	26	100	180
1.25	1100	32.2	100	200
1.25	1100	36.8	100	300
1.35	1800	45.3	200	300
1.35	1500	48.2	200	350
1.35	1350	51.4	200	400
1.35	2500	51.3	300	300
1.35	2100	59	300	350
1.35	1850	66	300	400
1.35	2700	66.3	400	350
1.35	2300	74	400	400
1.65	2200	79	400	450
1.65	2700	84	500	450

Table 12. Working points on engine map for Load-Unload tests

5.2.1 Tested component *cpsi_2 mixer2* without CUC

- 100kg/h- 180°C

Load



Unload

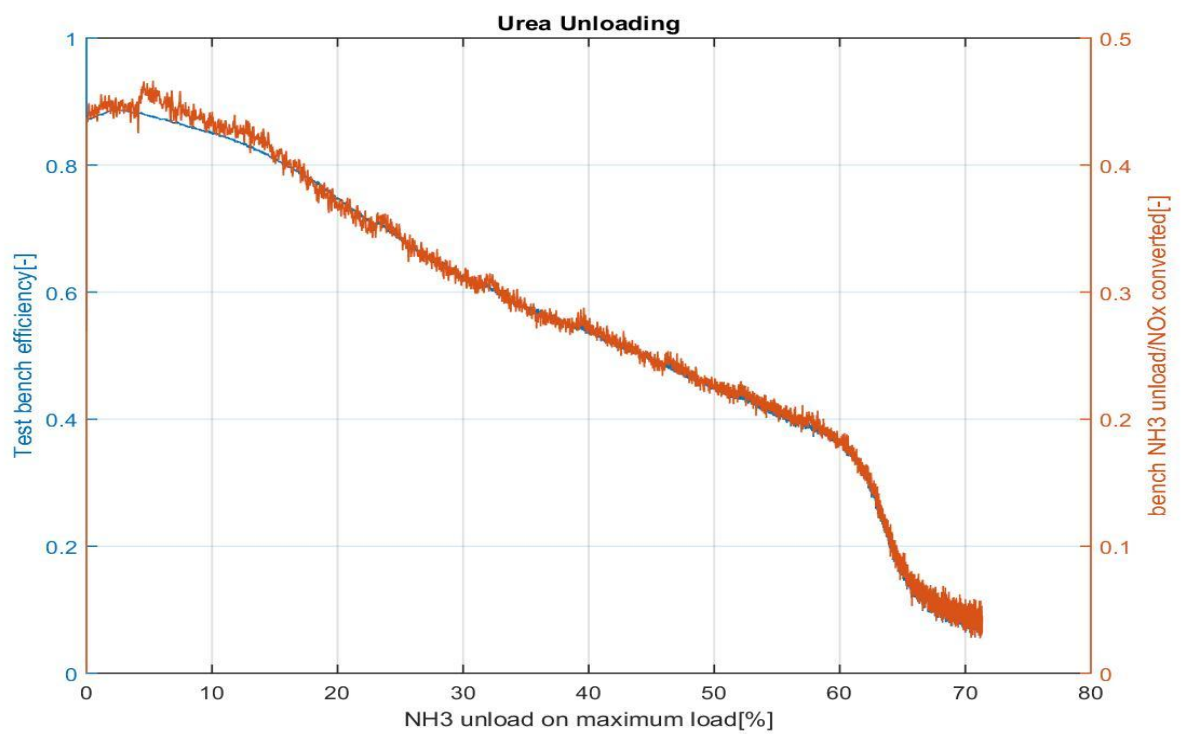
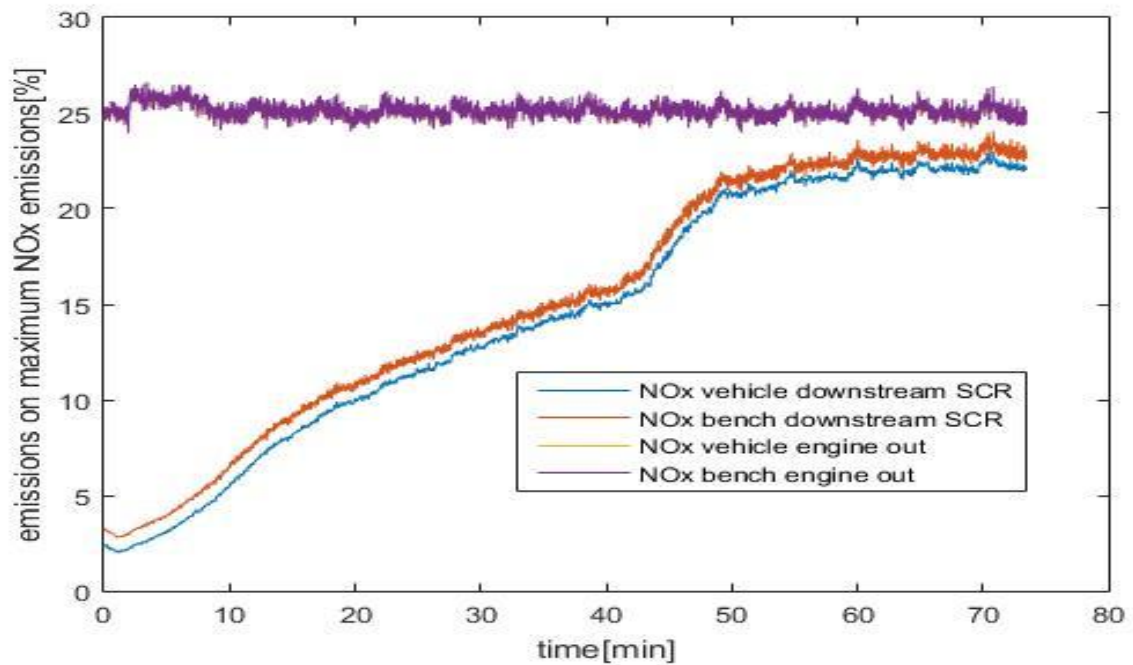
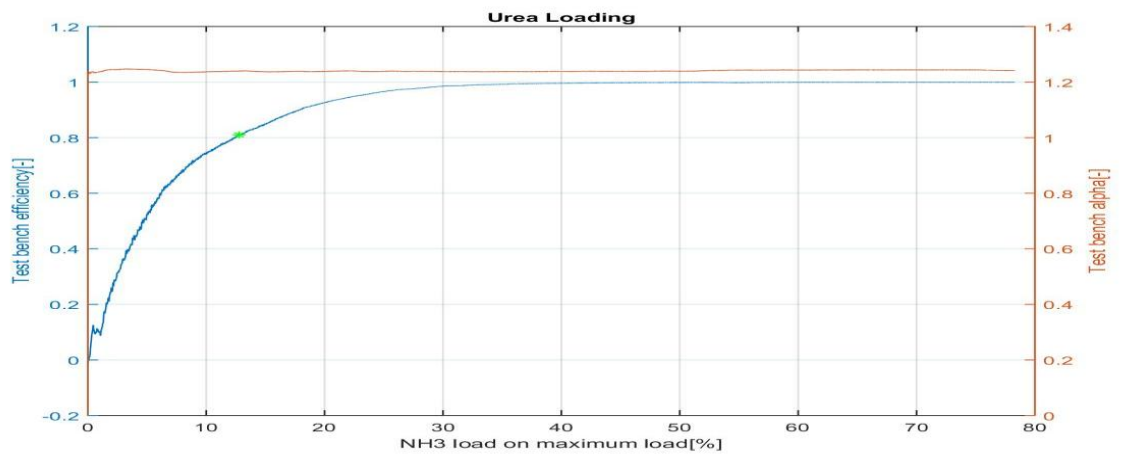
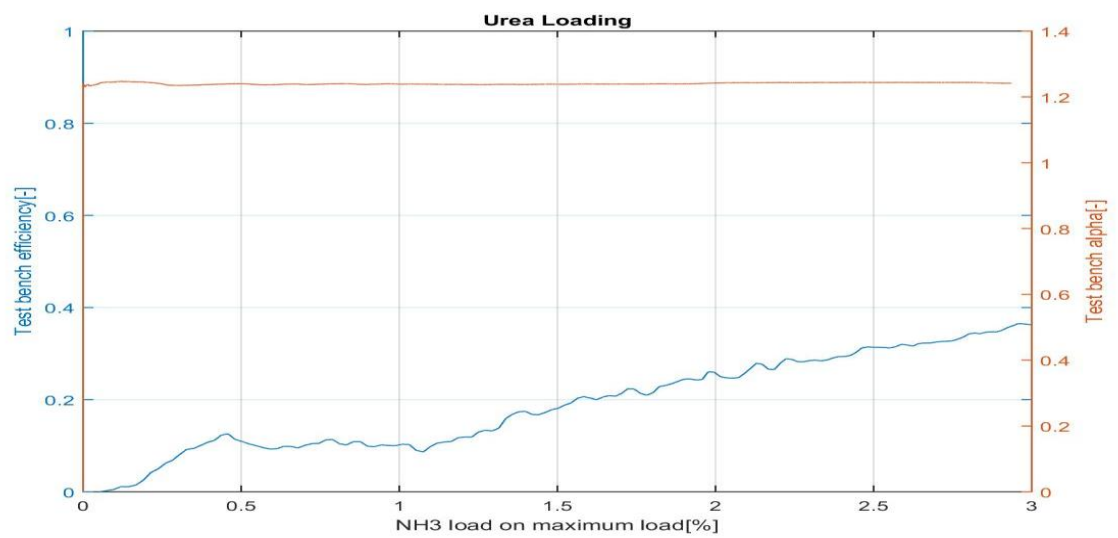
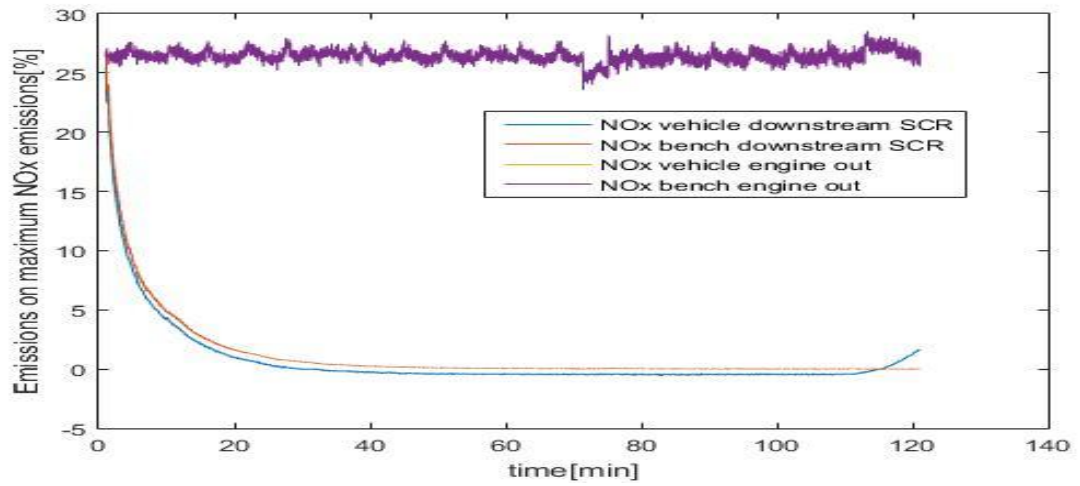


Figure 58.Load\Unload chart 100kg/h-180°C

- 100kg/h-200°C

Load



Unload

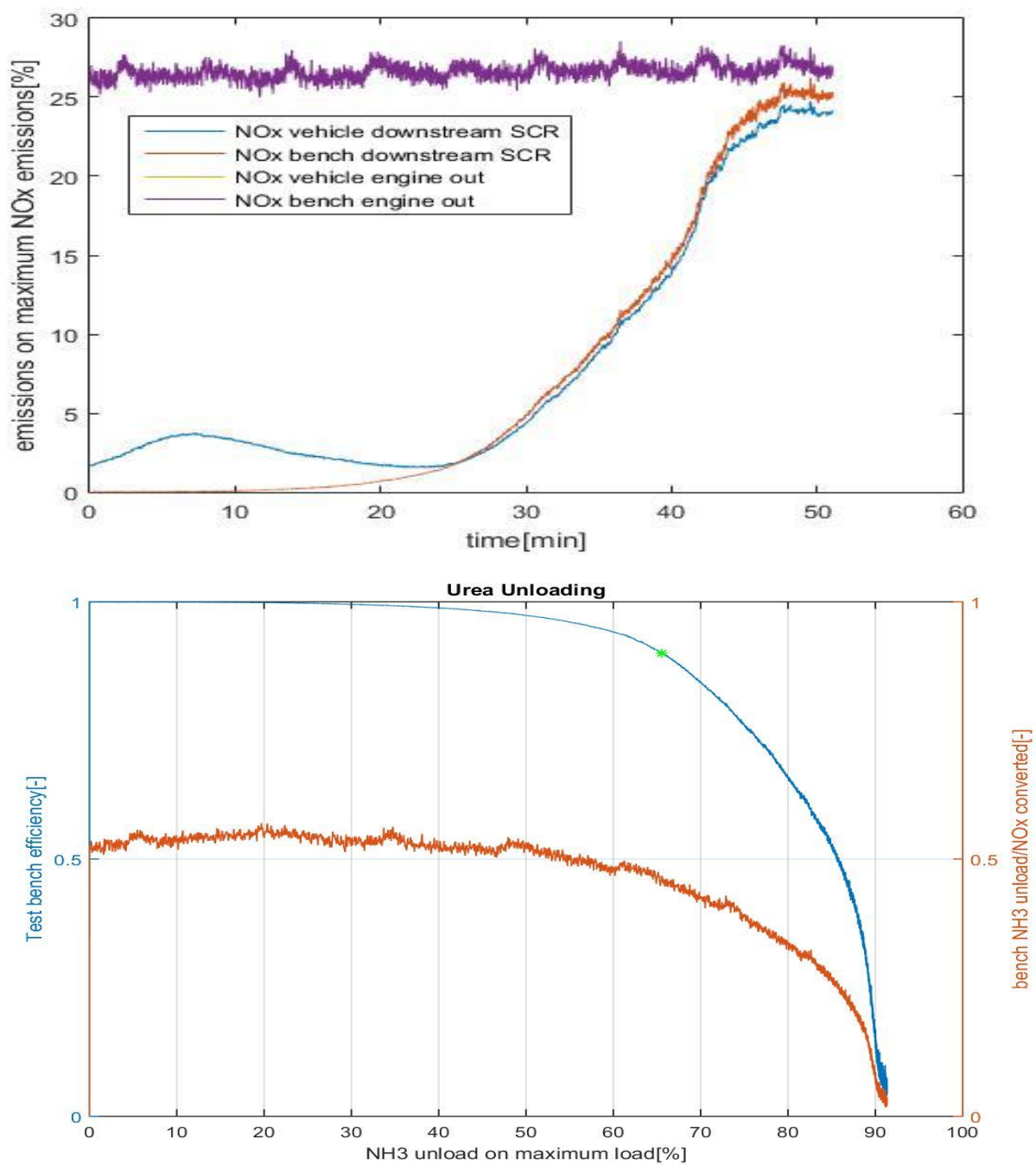
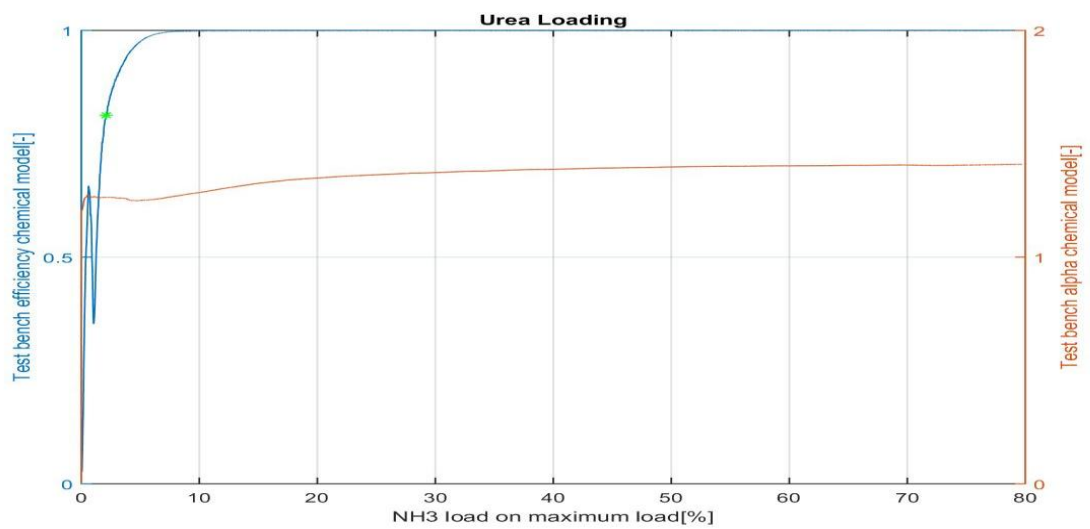
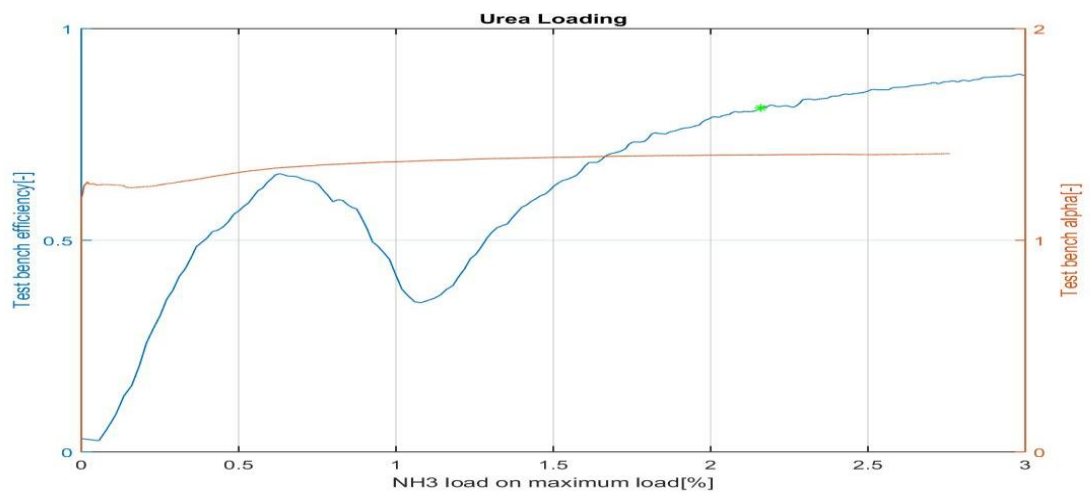
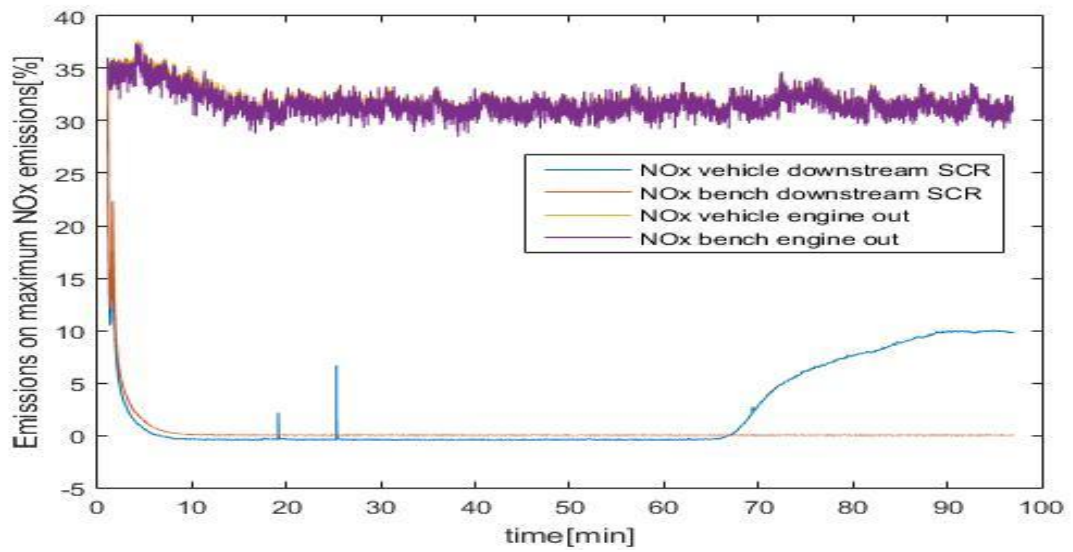


Figure 59.Load\Unload charts 100kg/h-200°C

- 100kg/h-250°C

Load



Unload

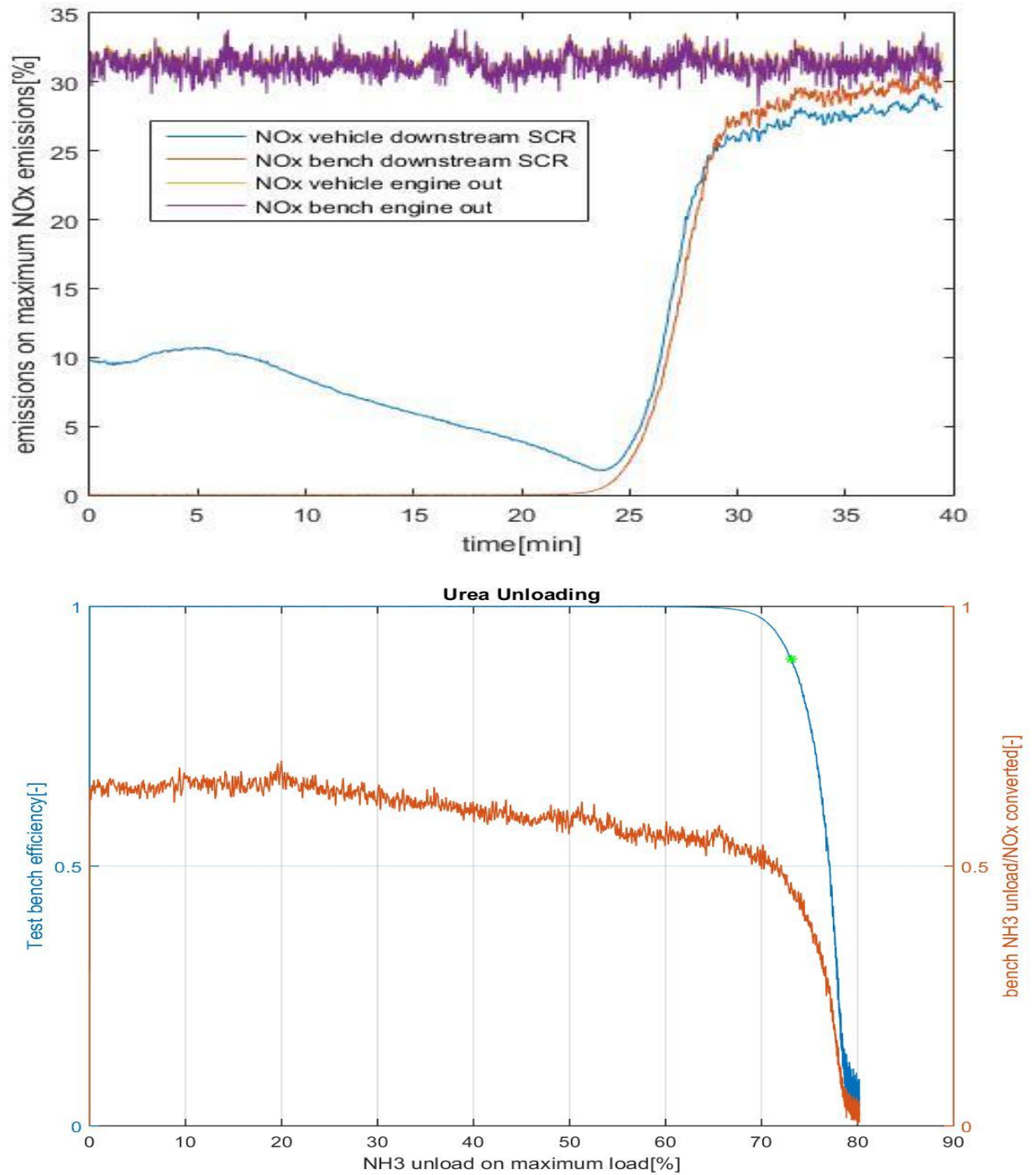
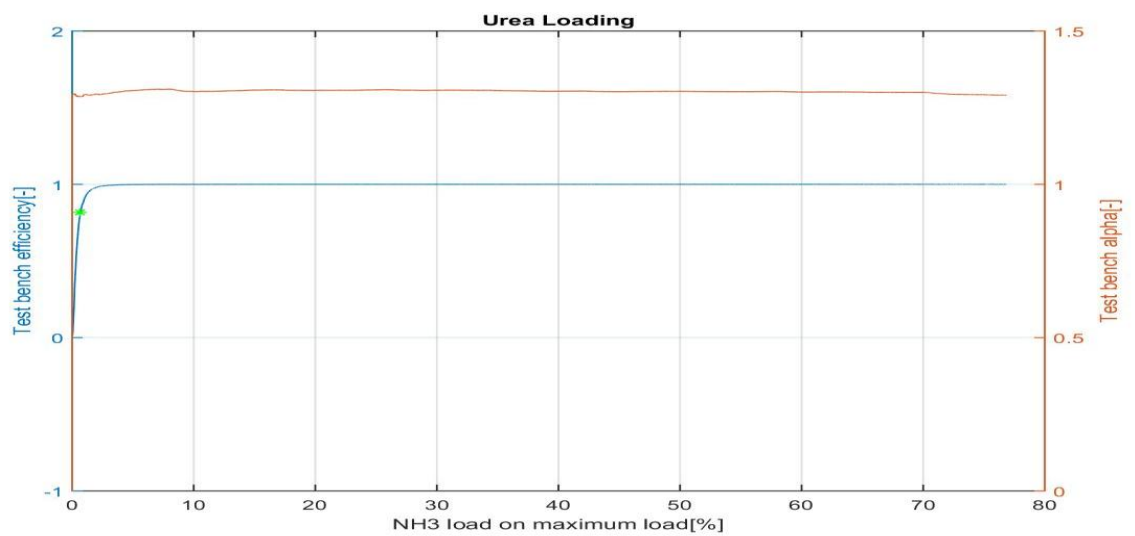
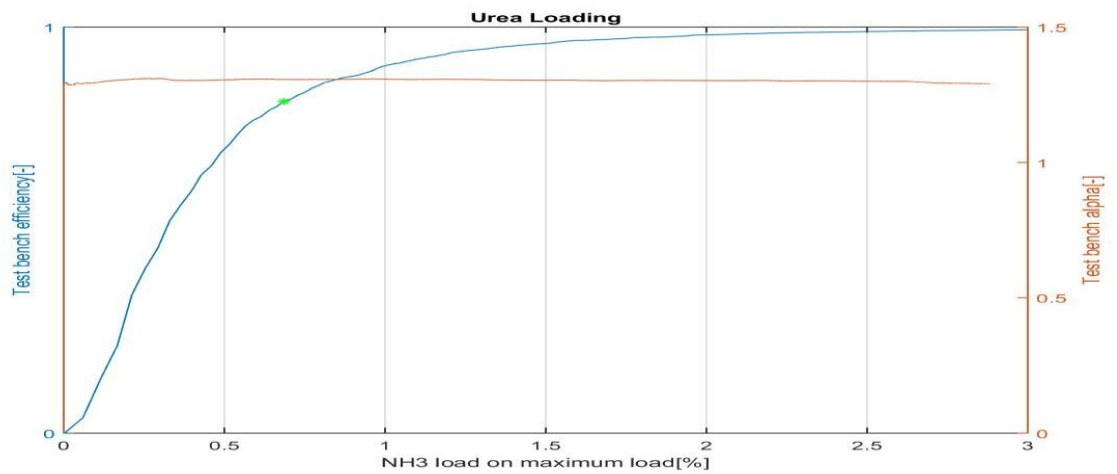
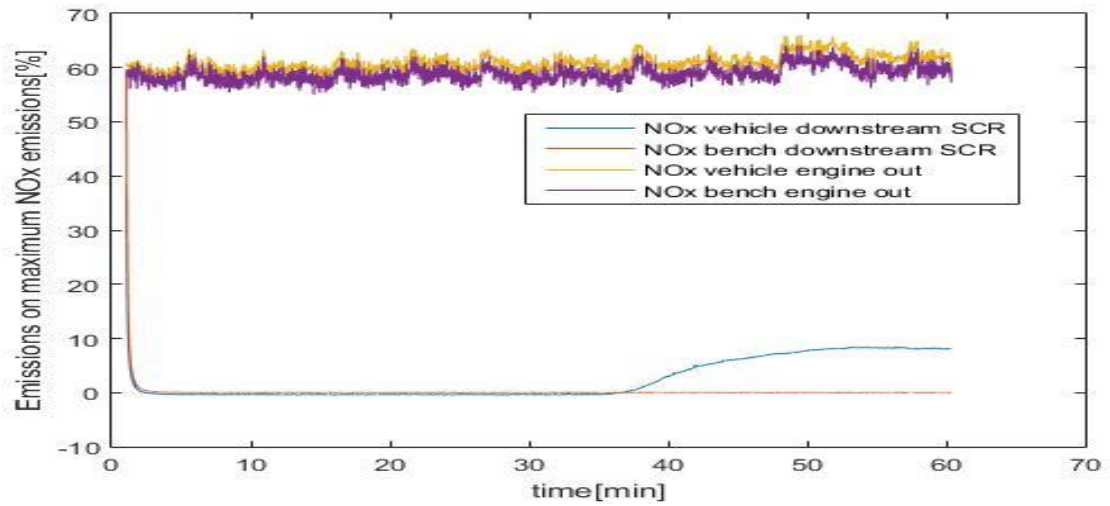


Figure 60.Load\Unload charts 100kg/h-250°C

- 100kg/h-300°C

Load



Unload

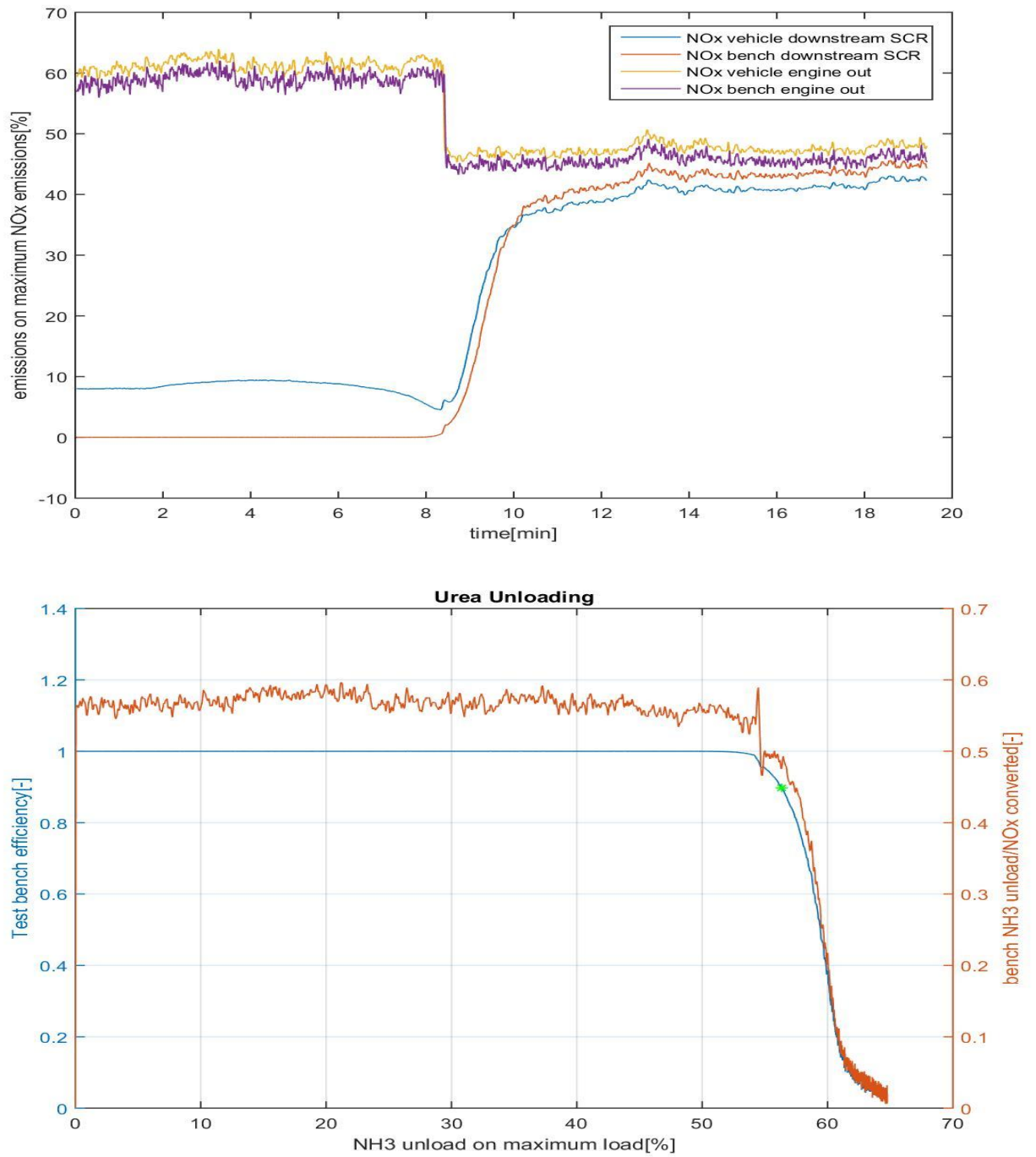
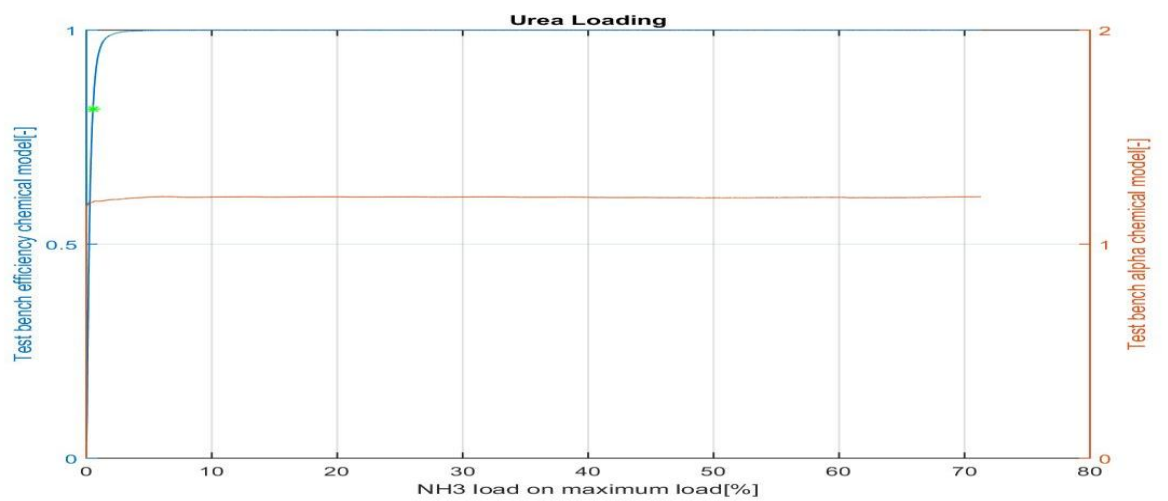
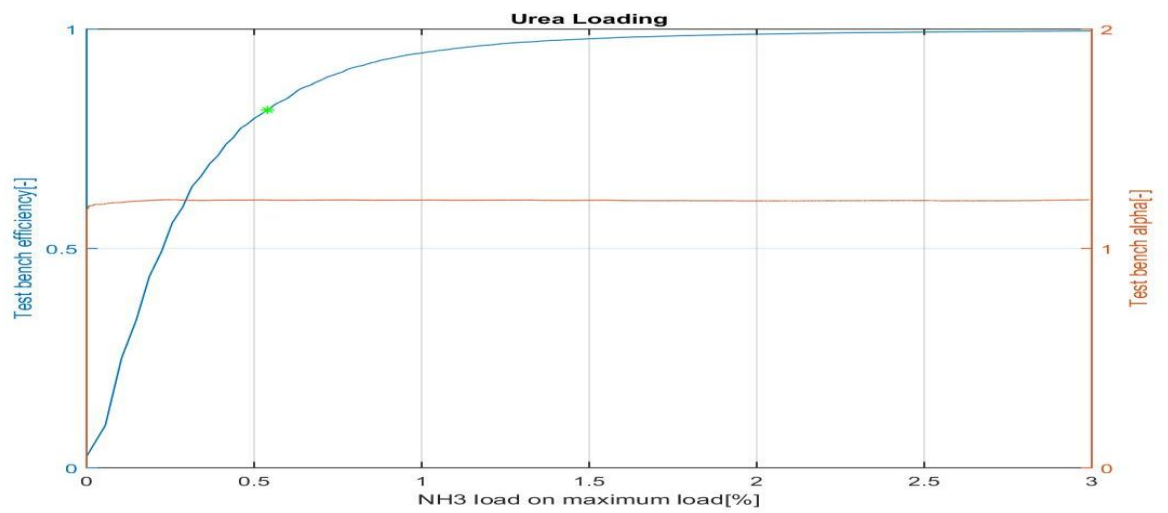
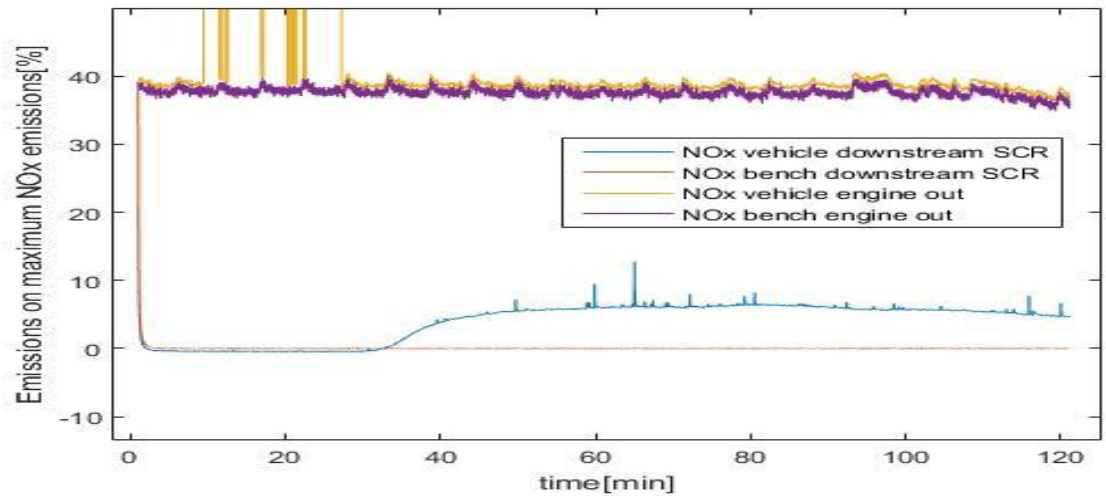


Figure 61.Load/Unload charts 100kg/h-300°C

- 200kg/h-300°C

Load



Unload

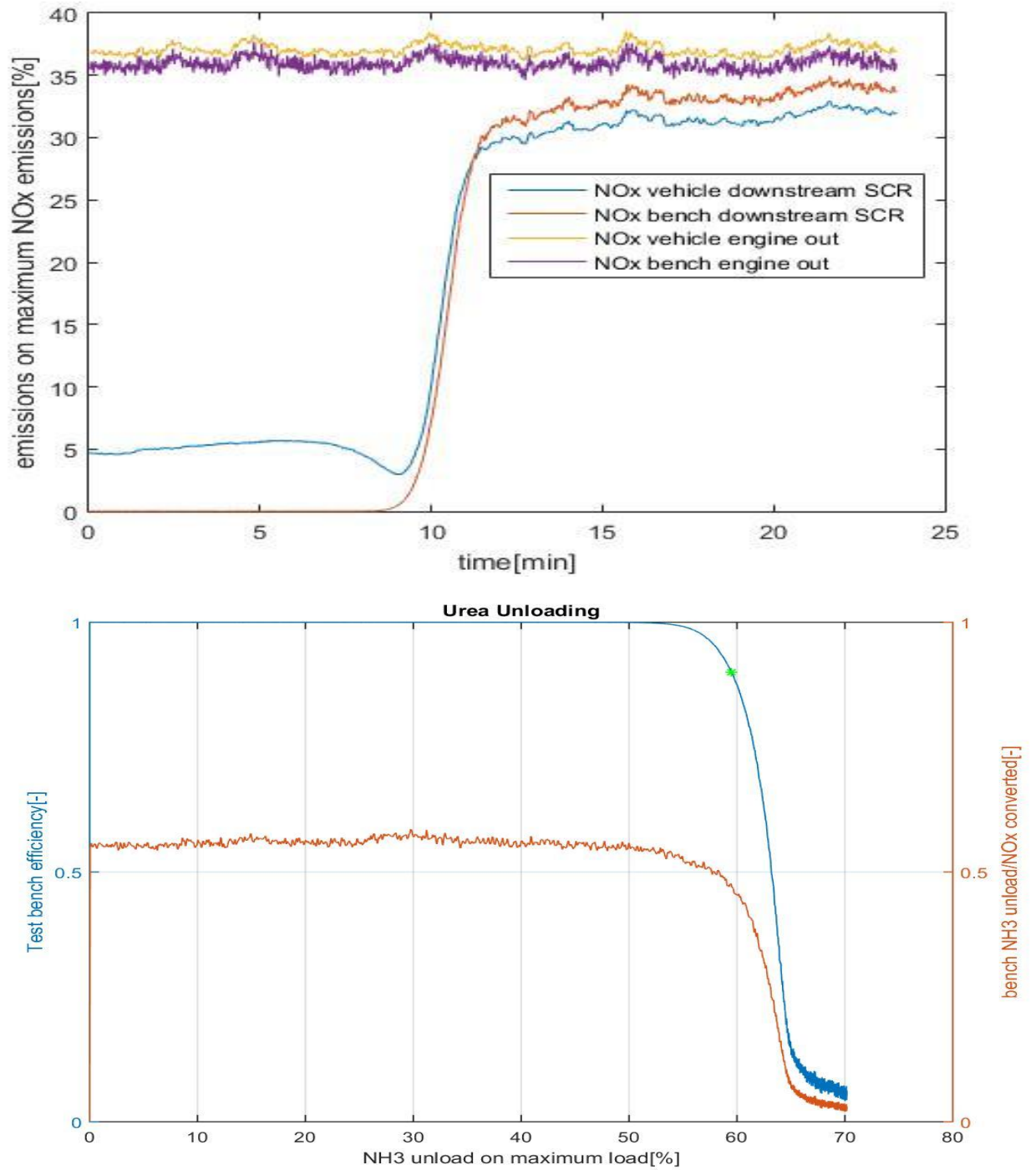
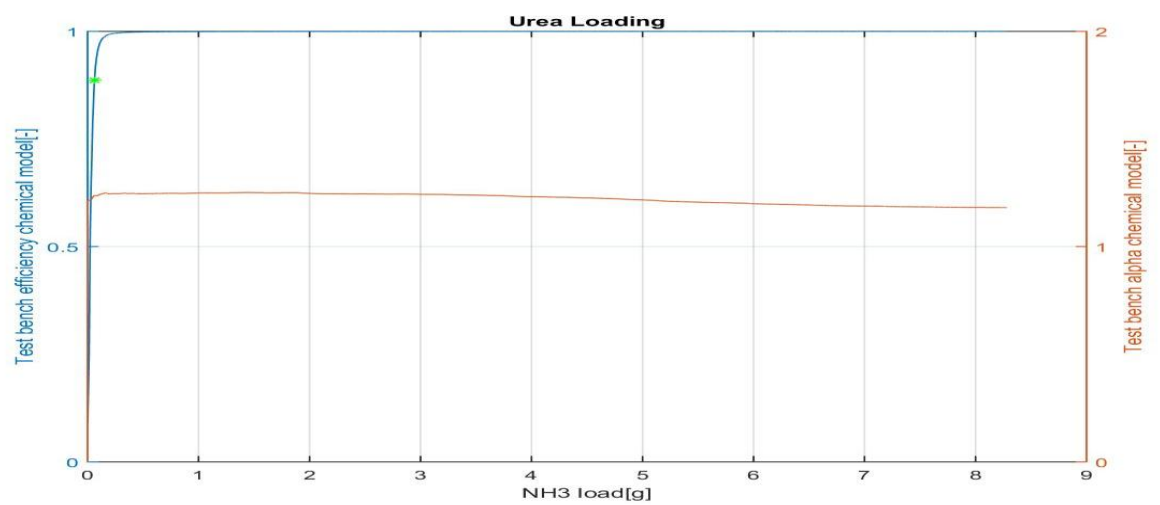
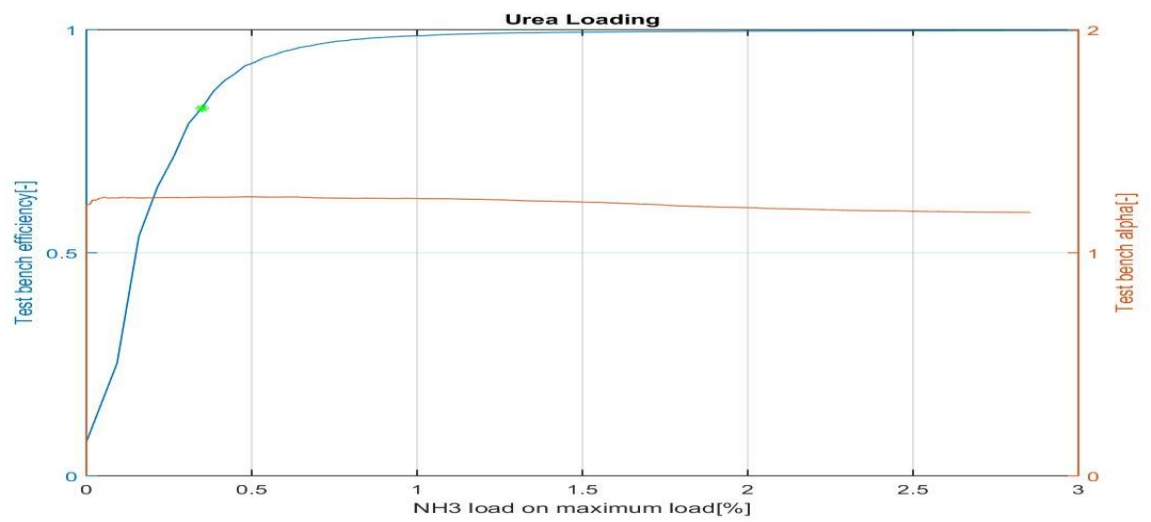
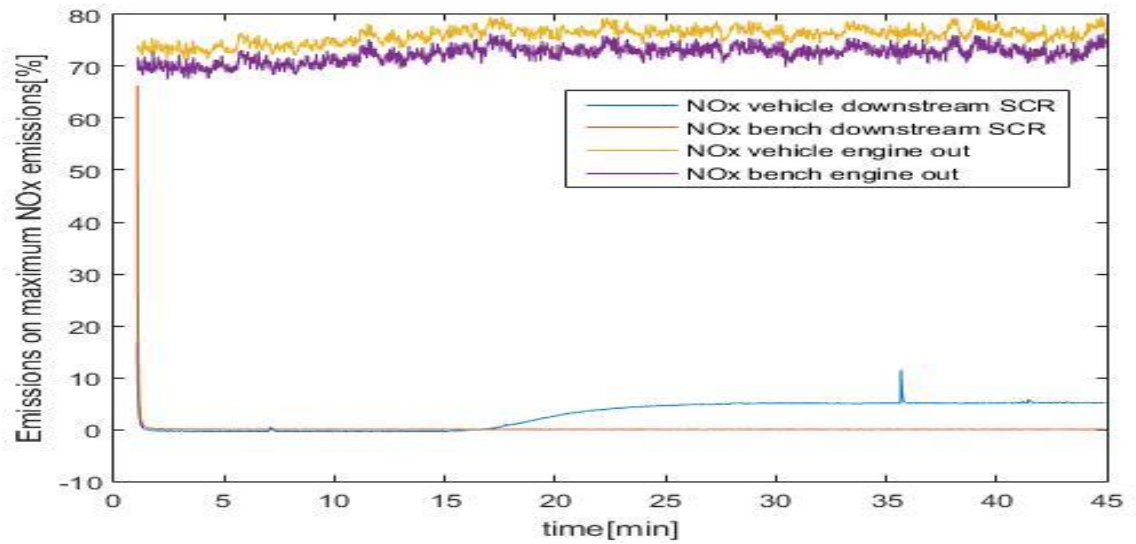


Figure 62.Load/Unload charts 200kg/h-300°C

- 200kg/h-350°C

Load



Unload

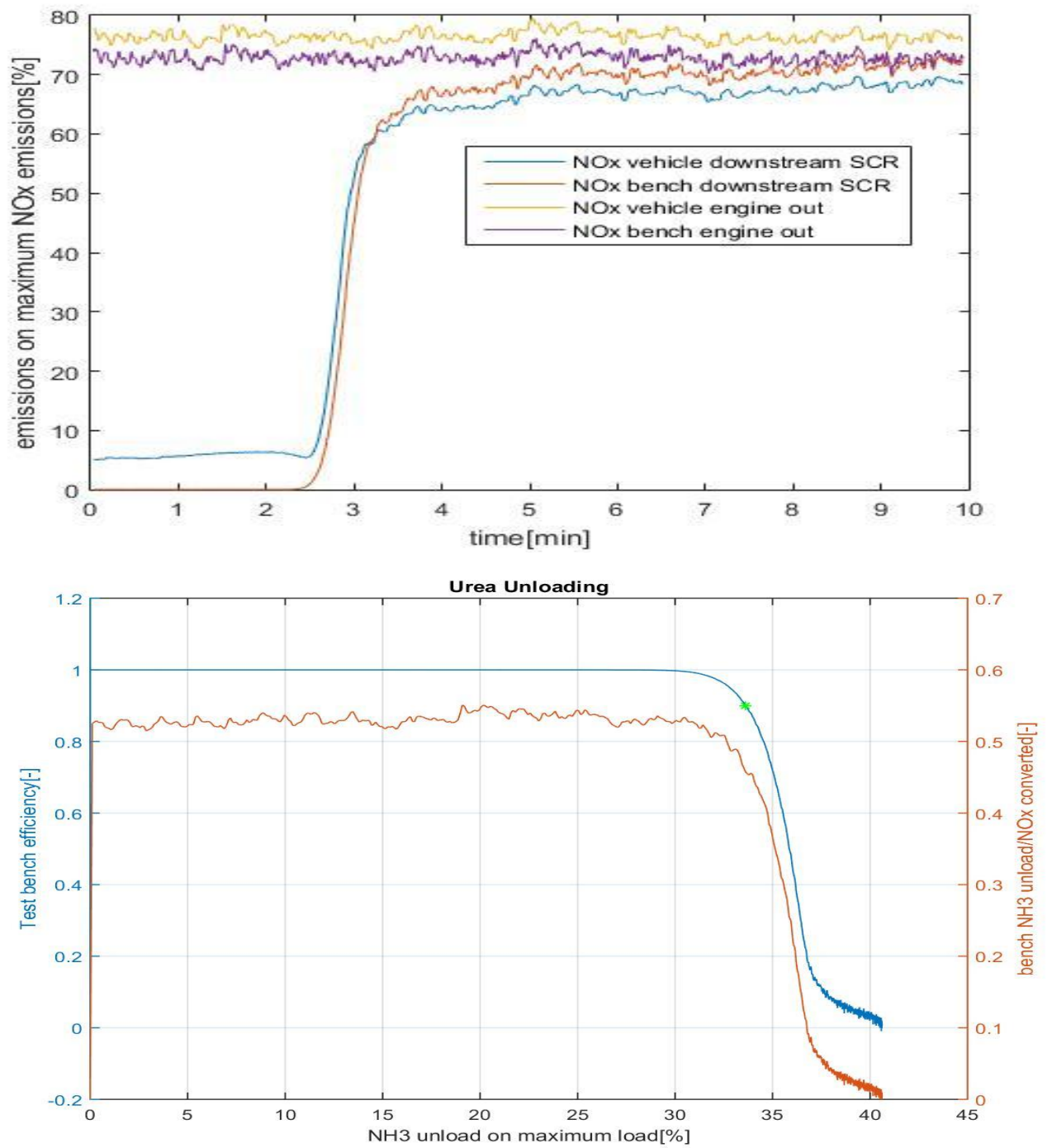
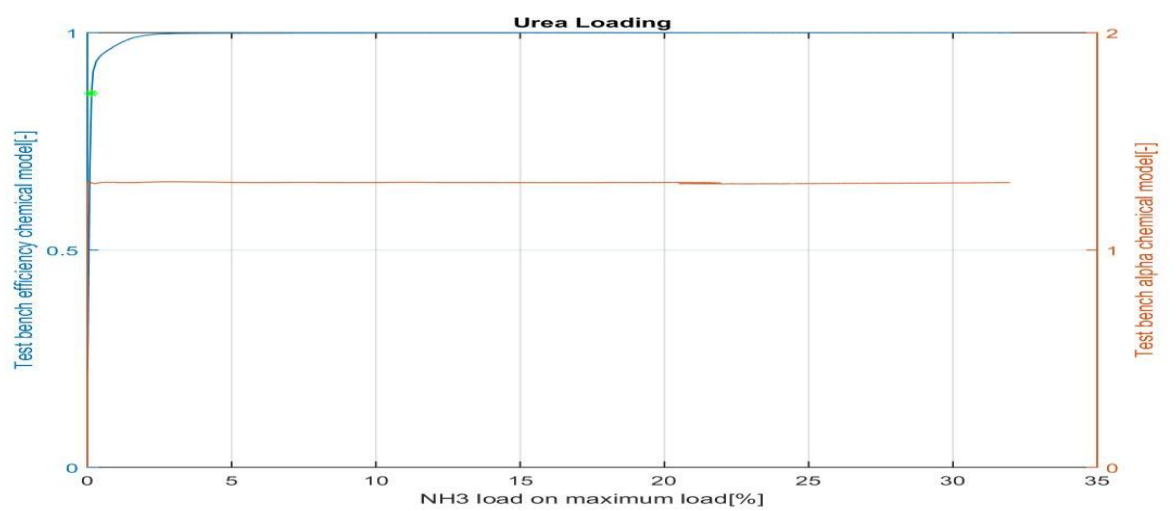
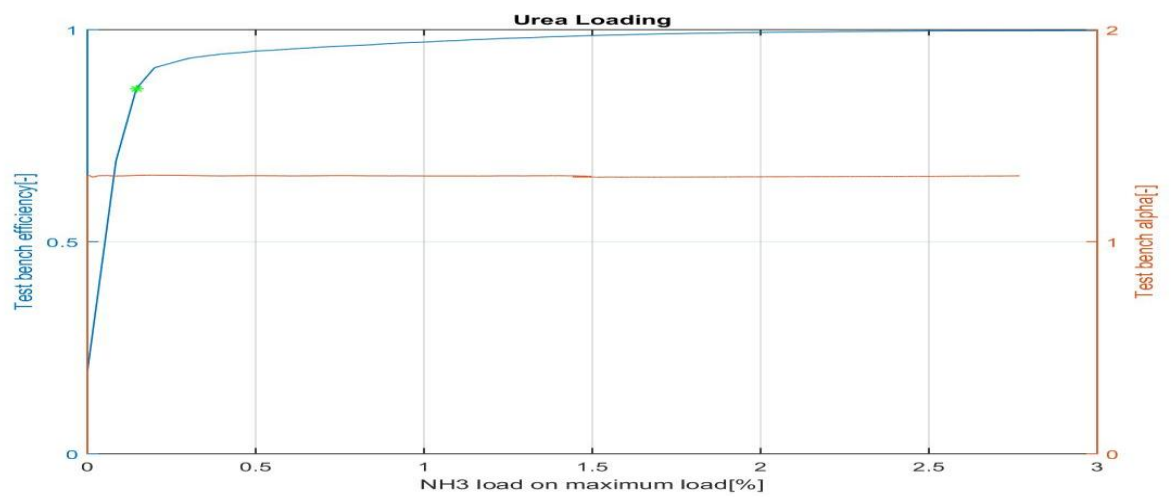
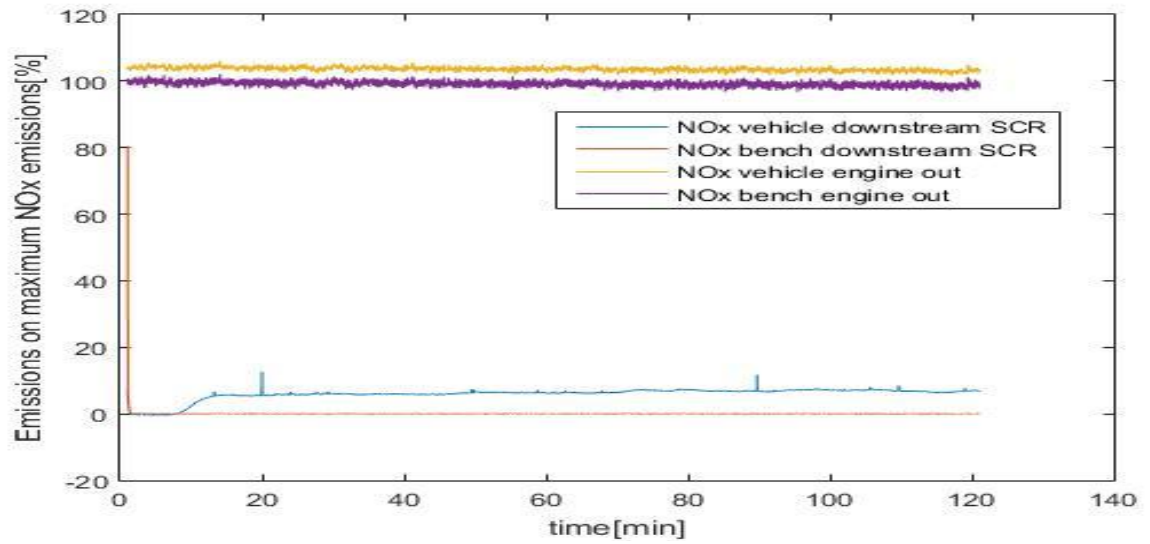


Figure 63.Load\Unload charts 200kg/h-350°C

- 200kg/h-400°C

Load



Unload

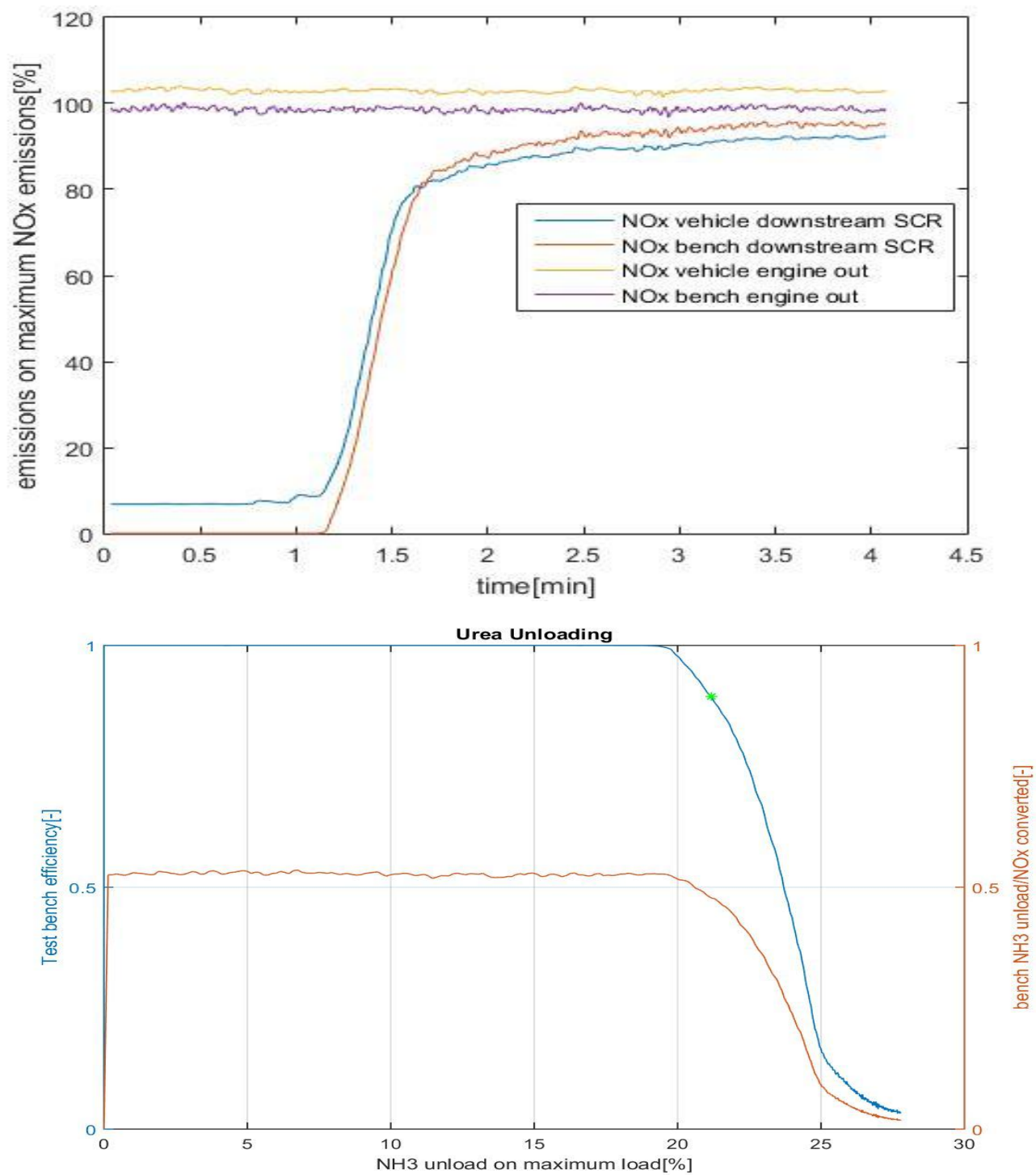
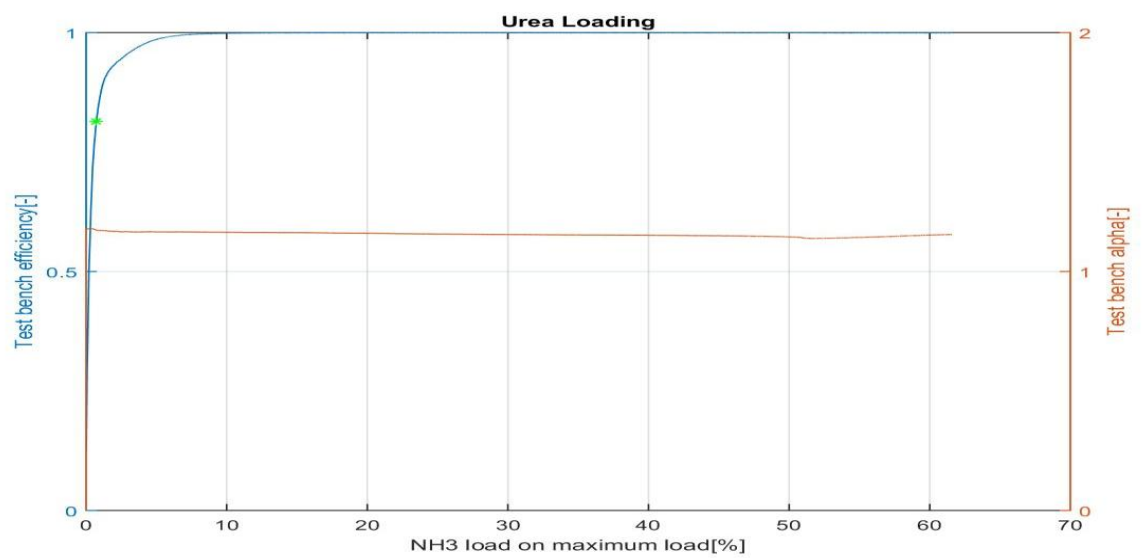
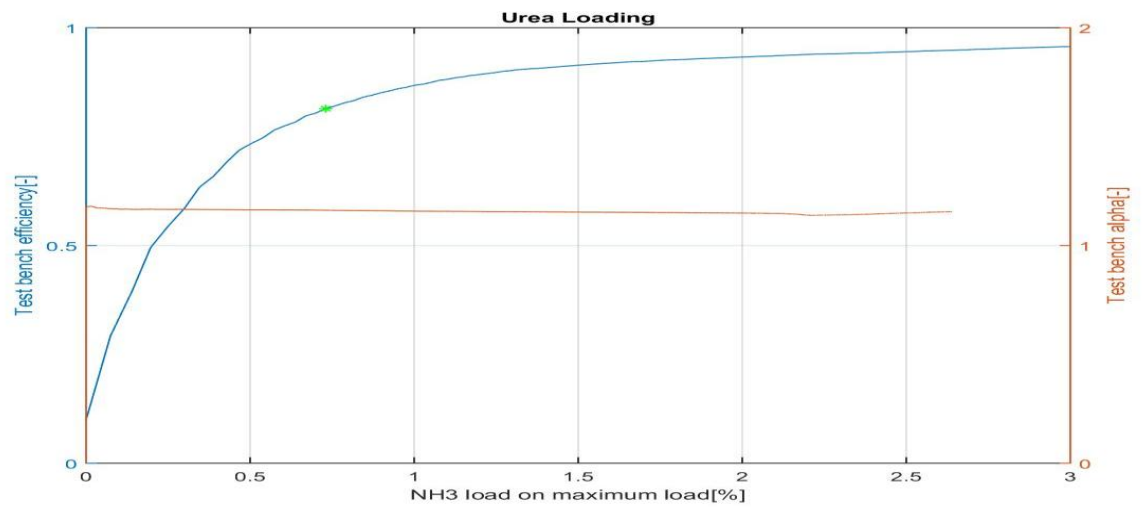
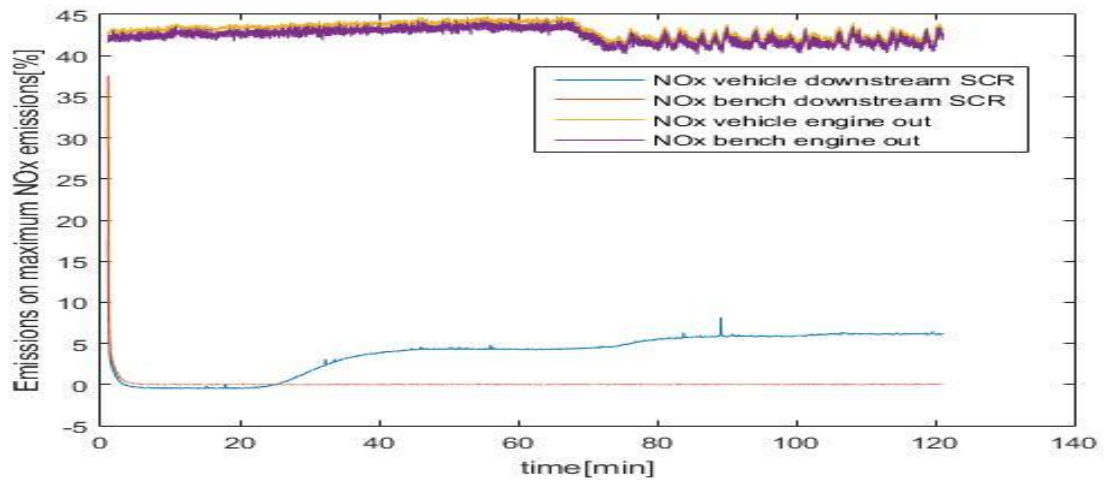


Figure 64. Load/Unload charts 200kg/h-400°C

- 300kg/h-300°C

Load



Unload

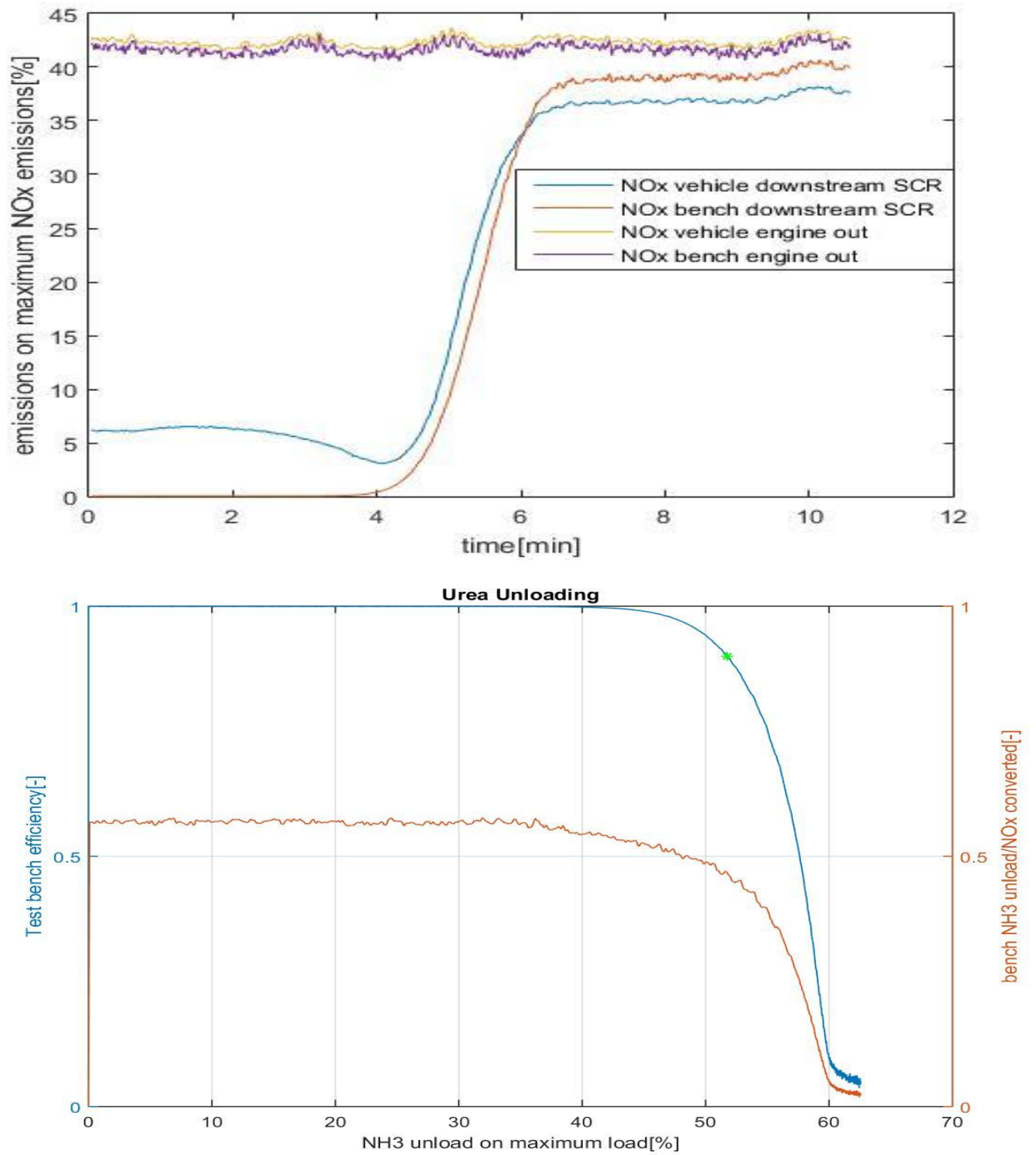
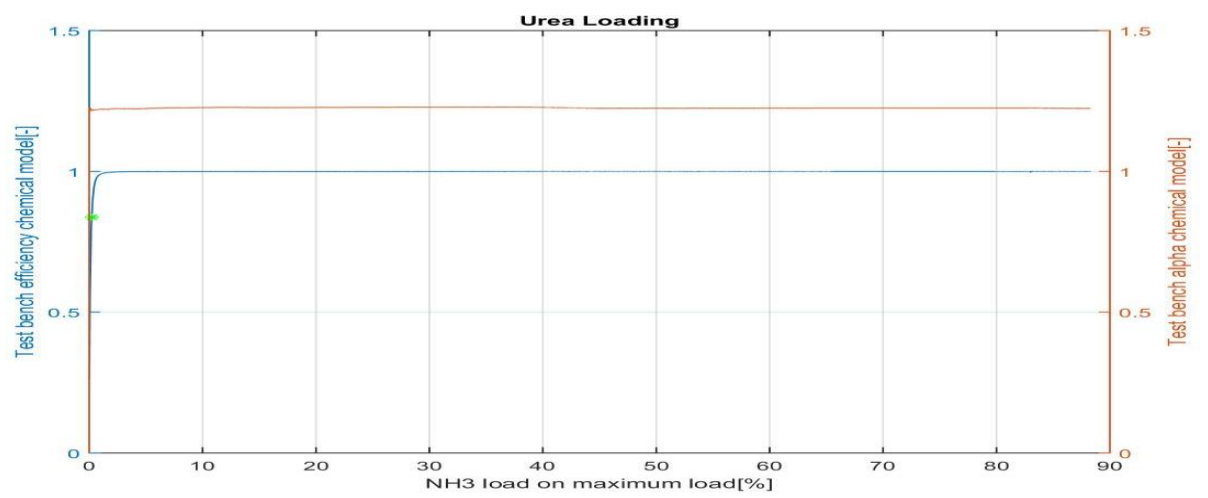
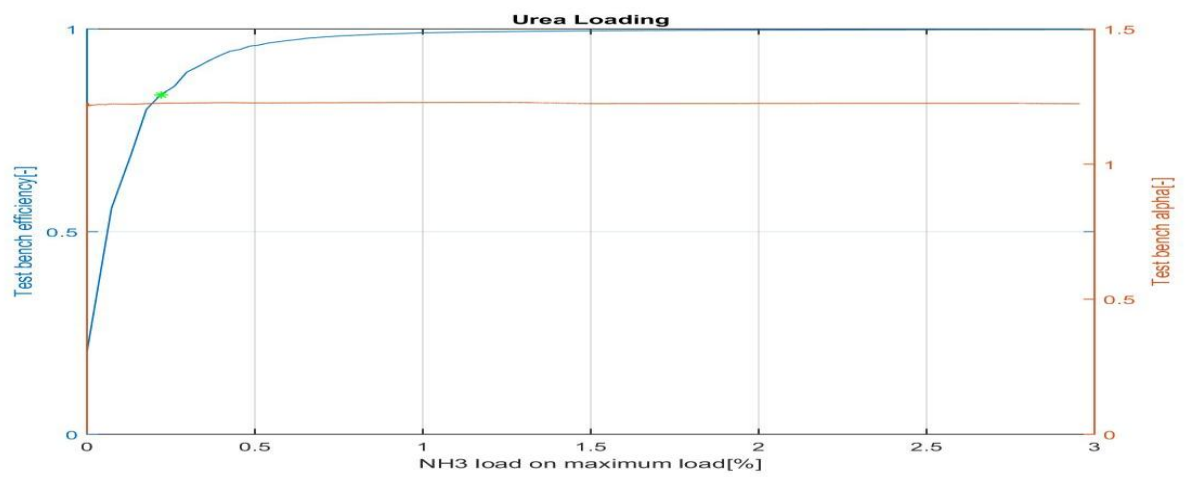
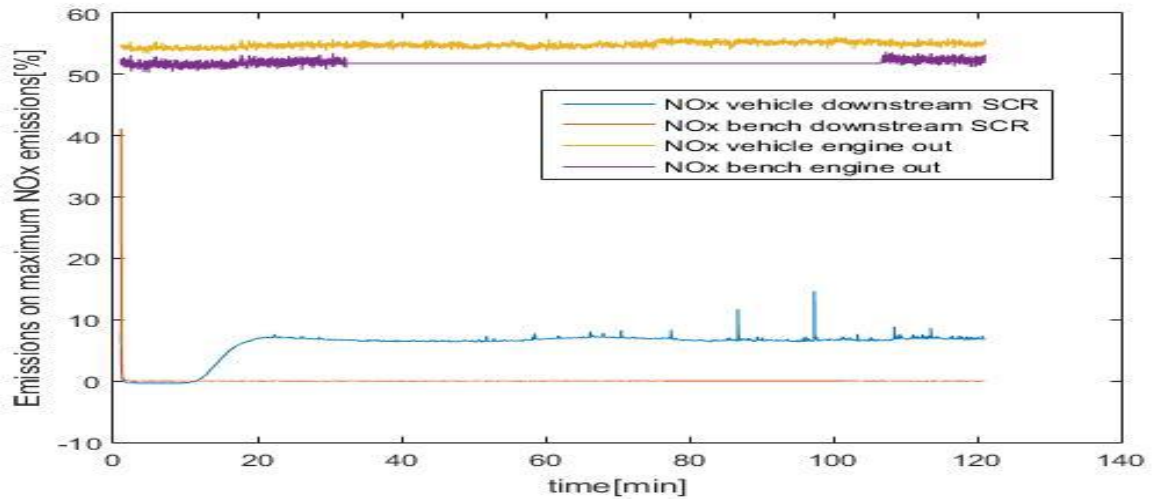


Figure 65.Load\Unload chart 300kg/h-300°C

- 300kg/h-350°C

Load



Unload

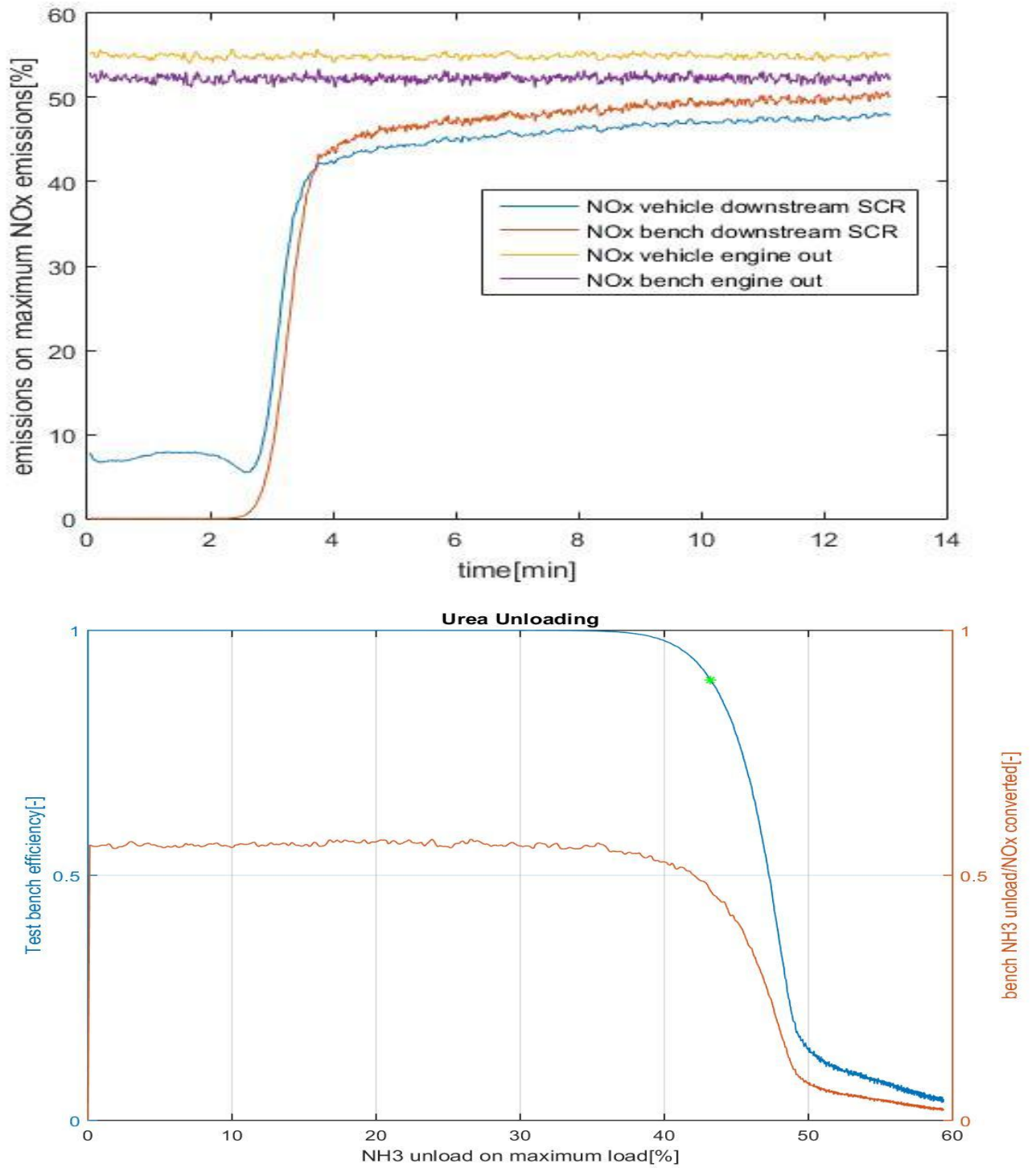
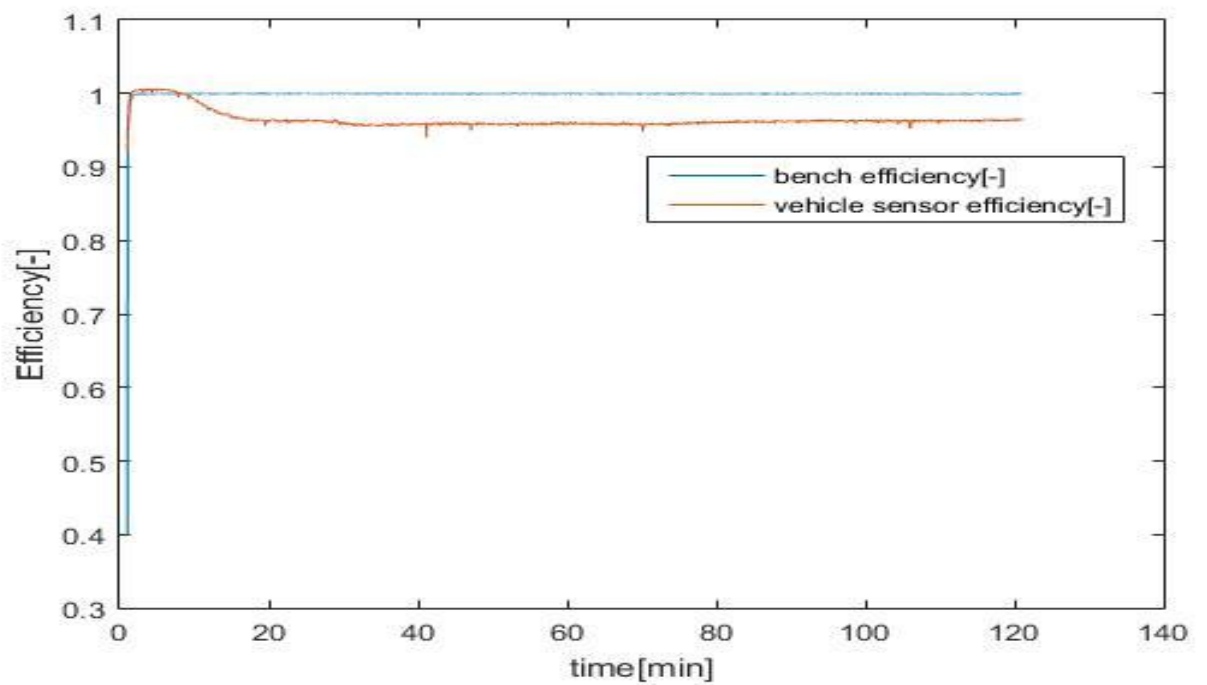
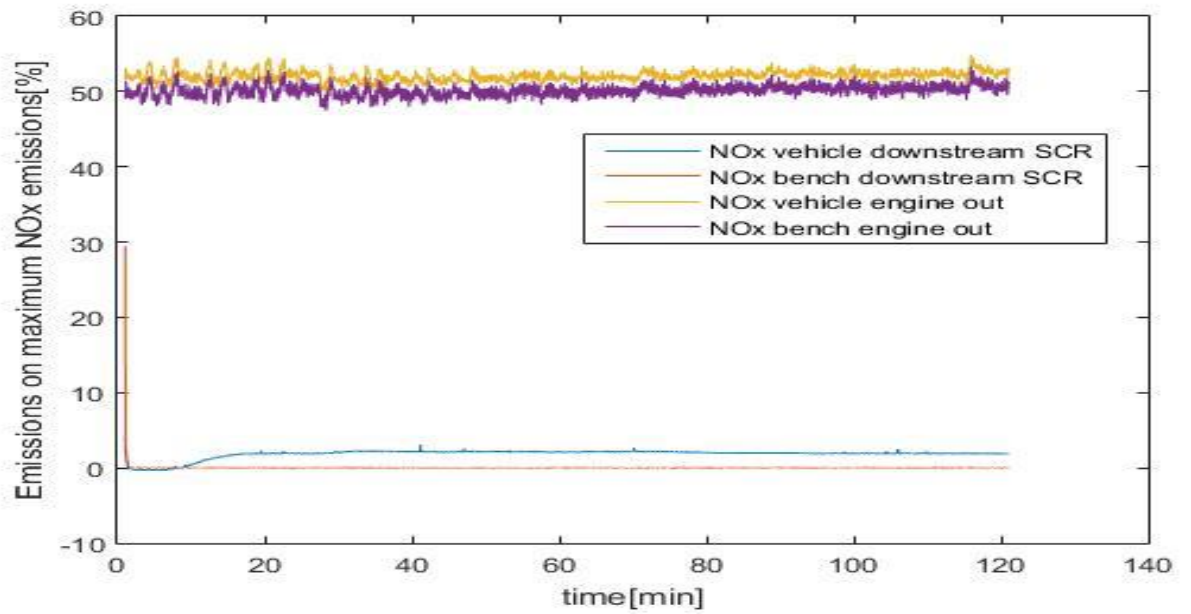
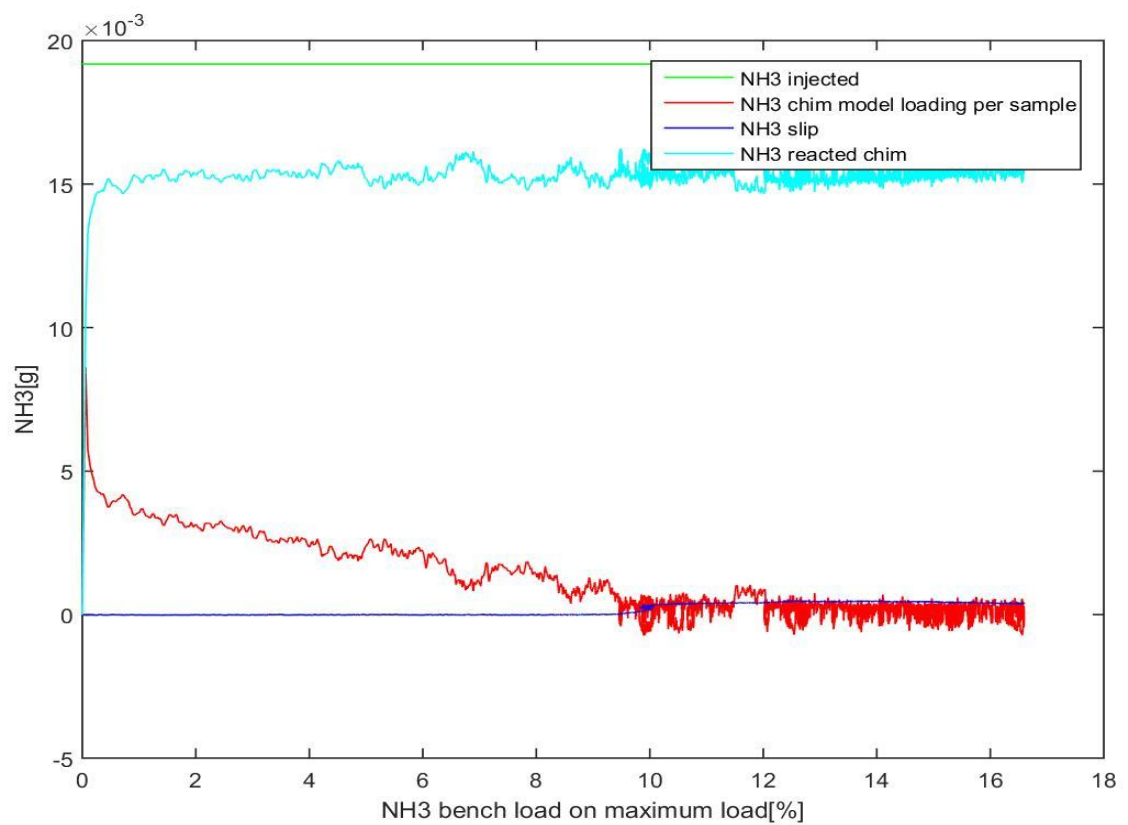
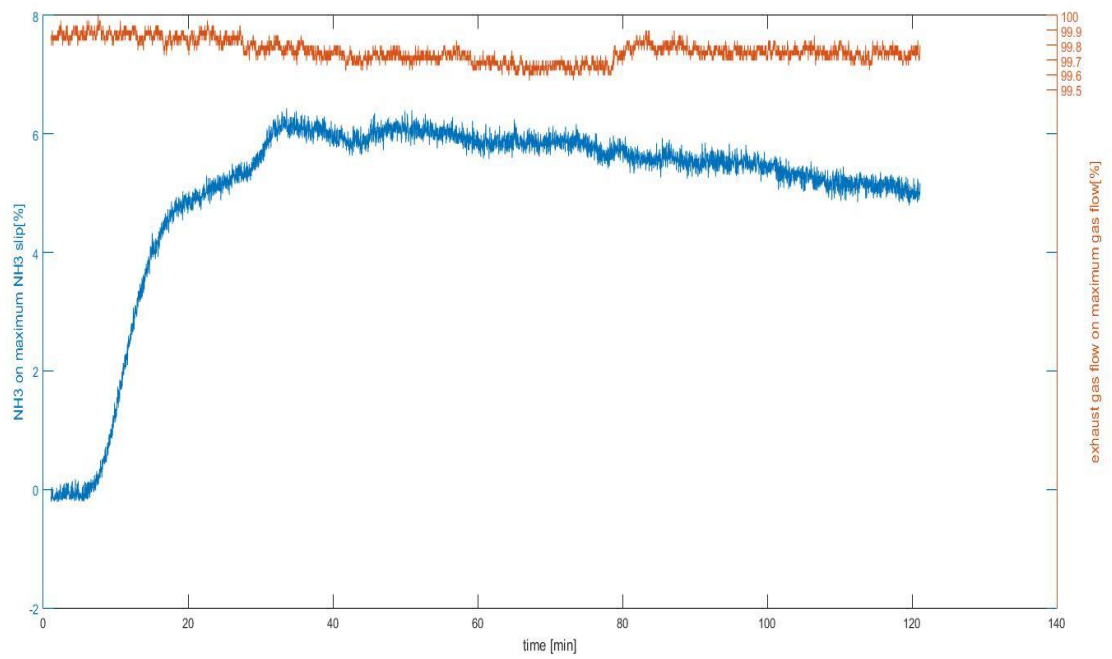


Figure 66. Load\Unload charts 300kg/h-350°C

- 300kg/h-400°C

Load





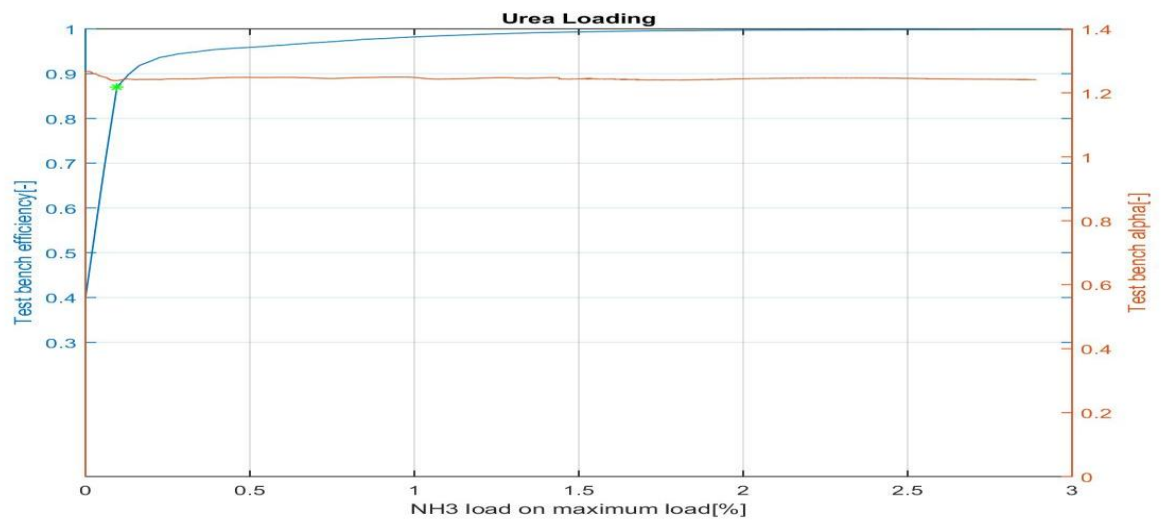
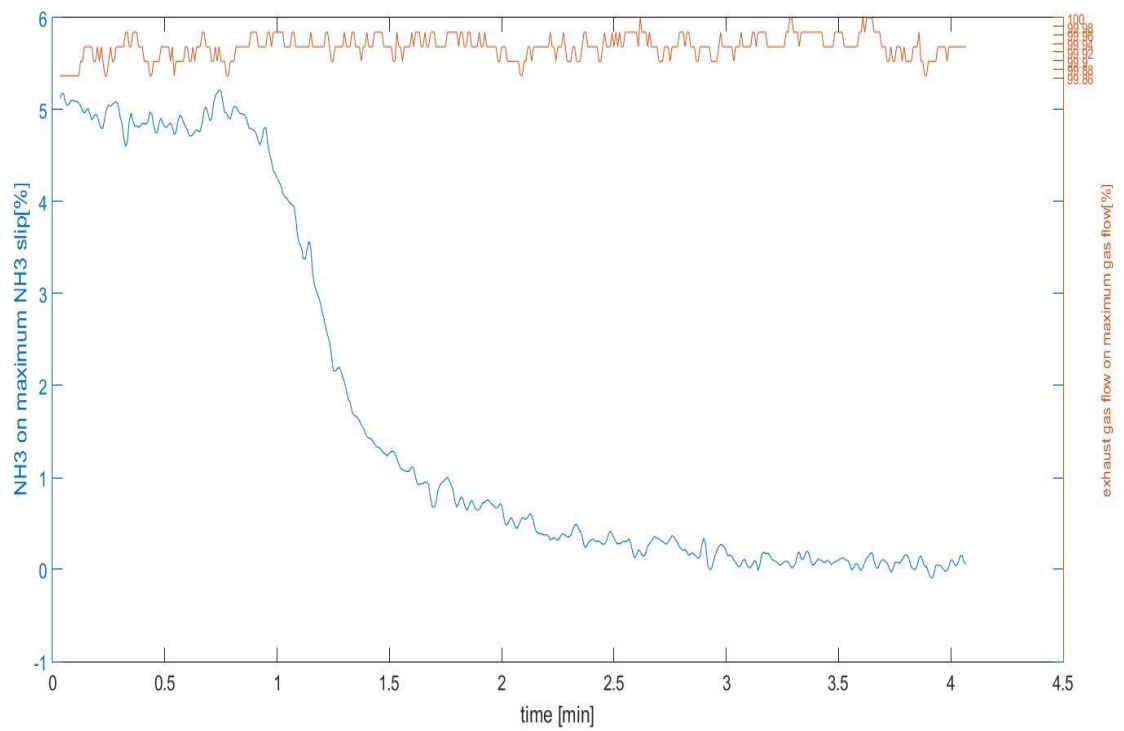
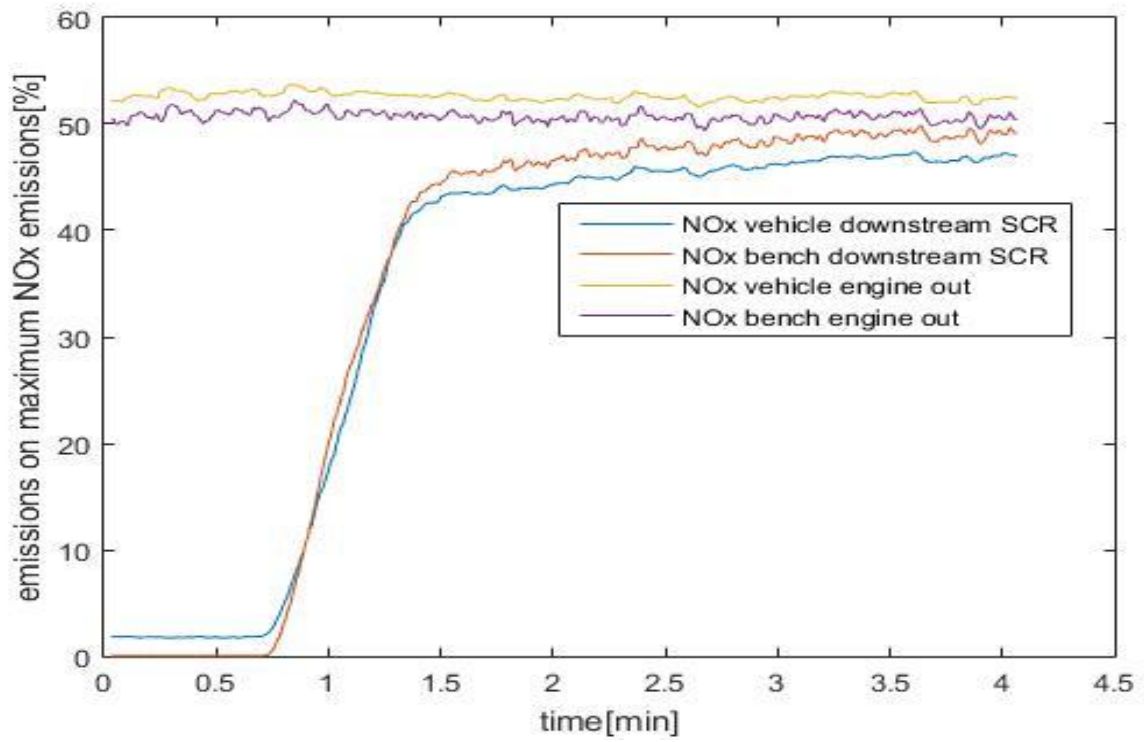


Figure 67. Load charts 300kg/h-400°C

Unload



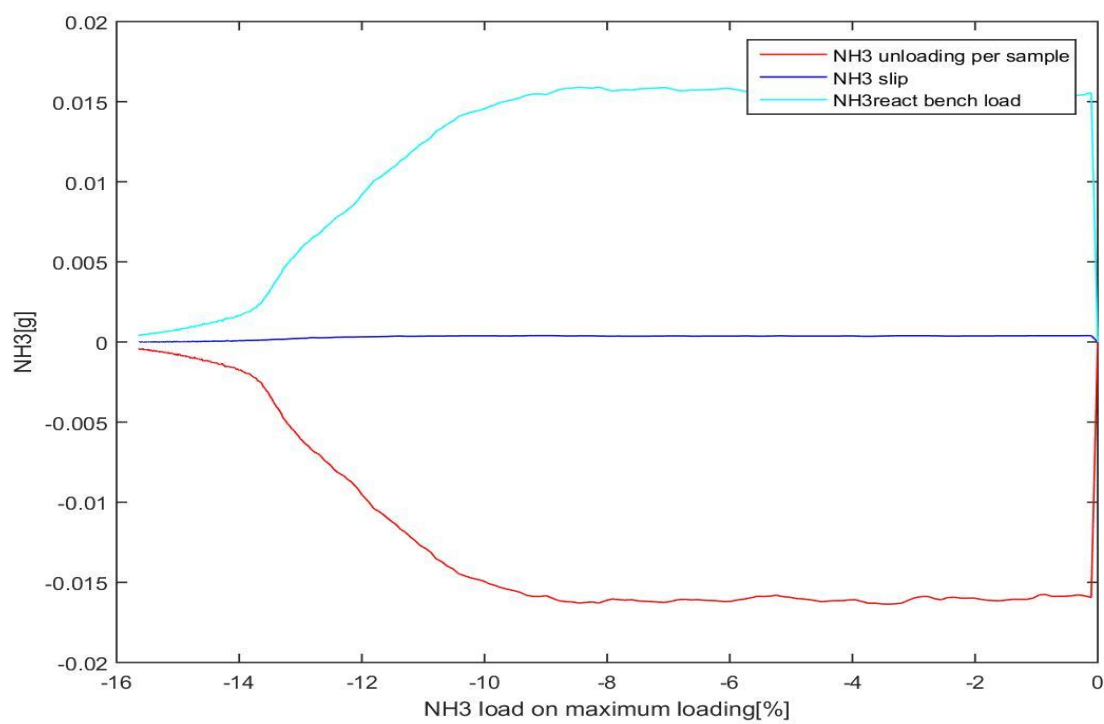
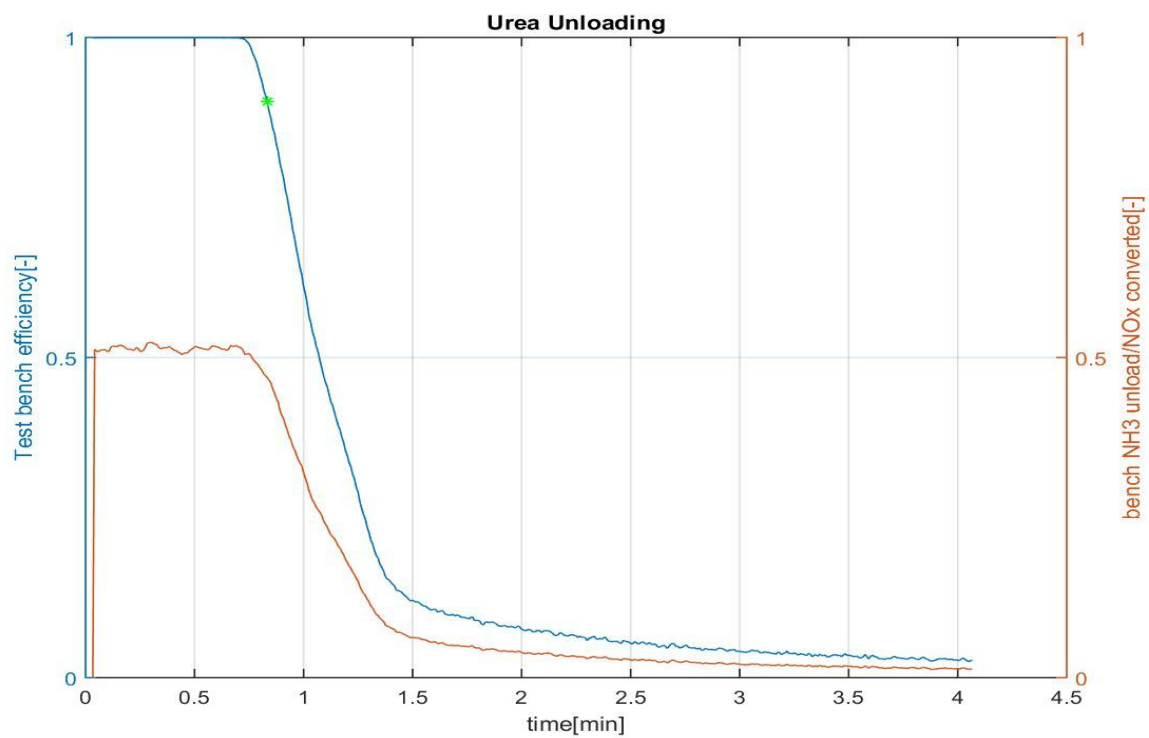
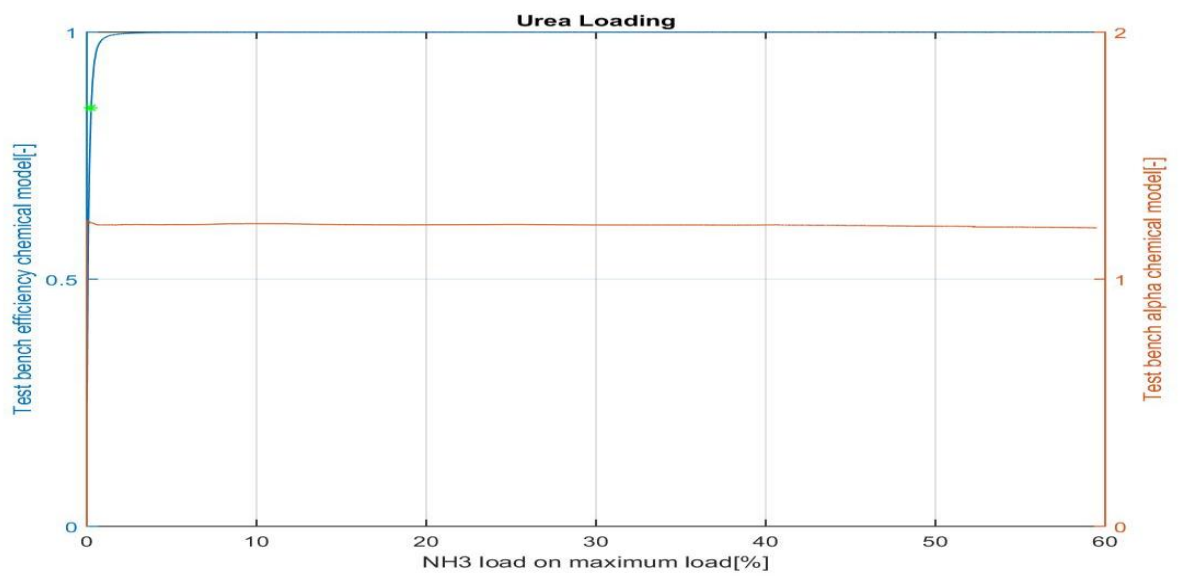
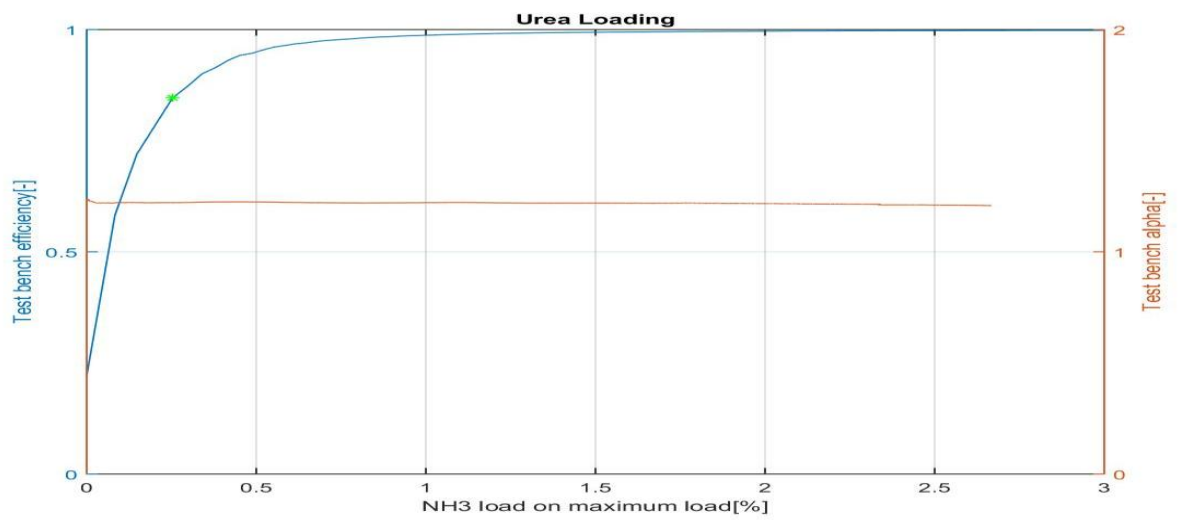
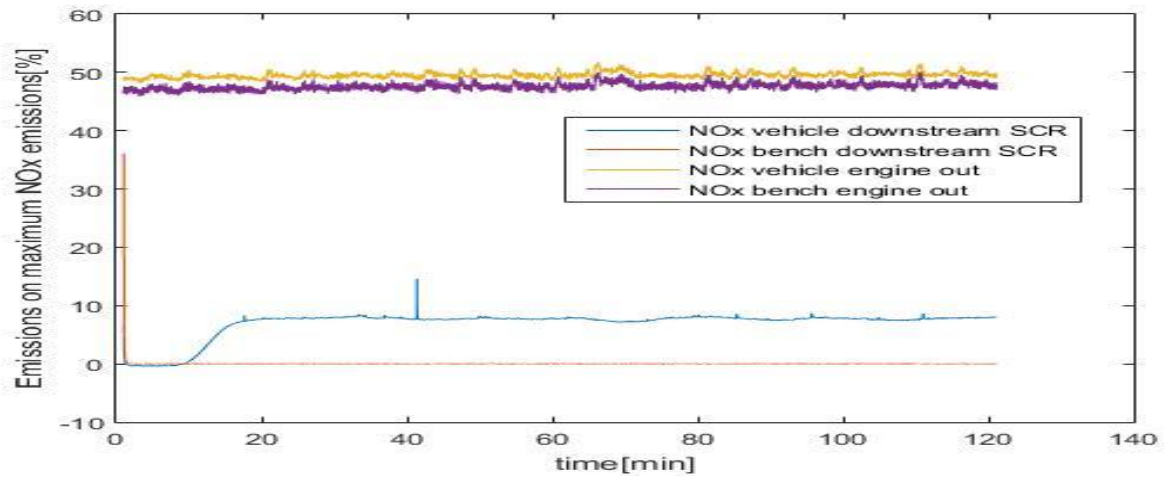


Figure 68.Unload charts 300kg/h-350°C

- 400kg/h-350°C

Load



Unload

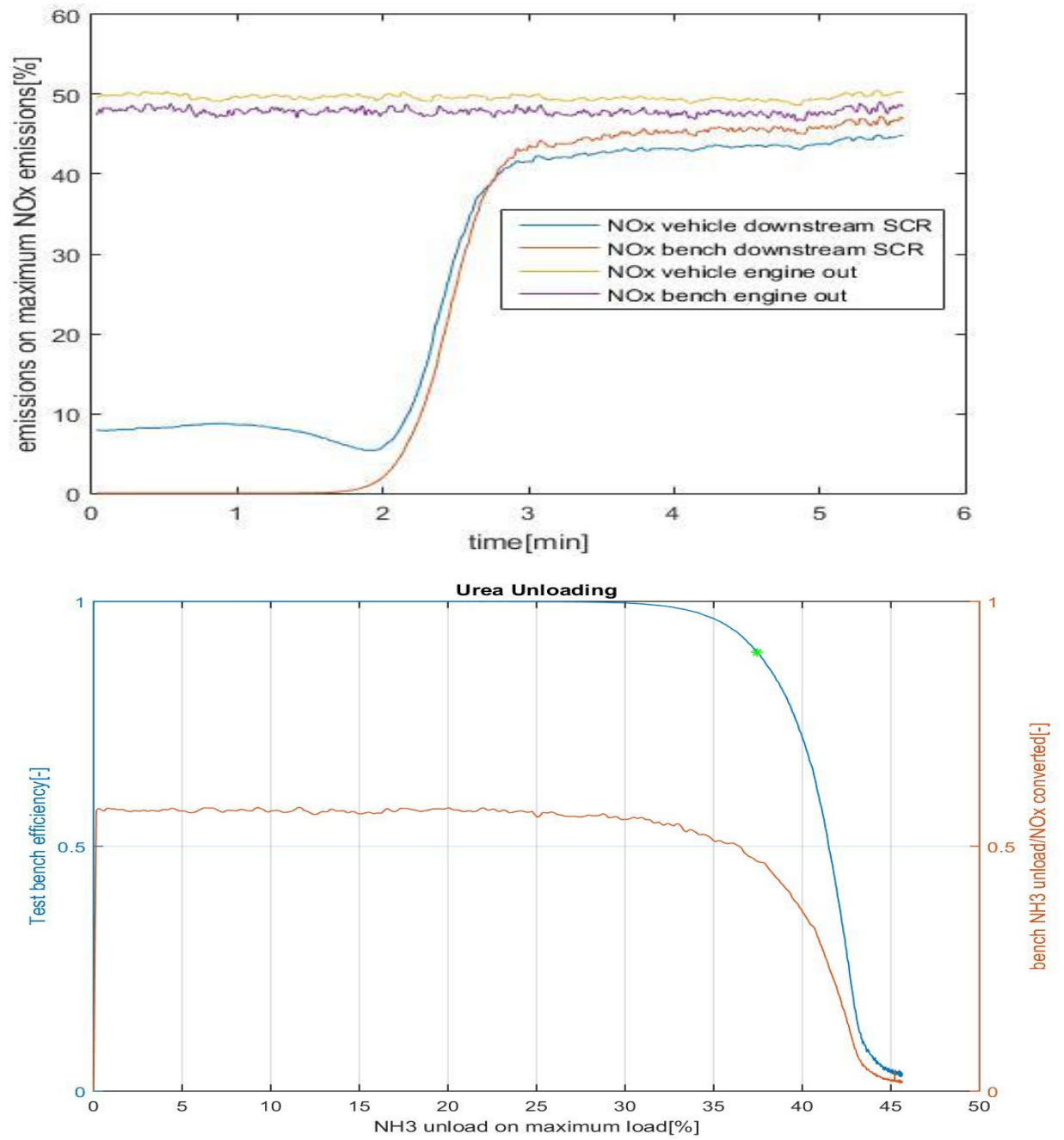
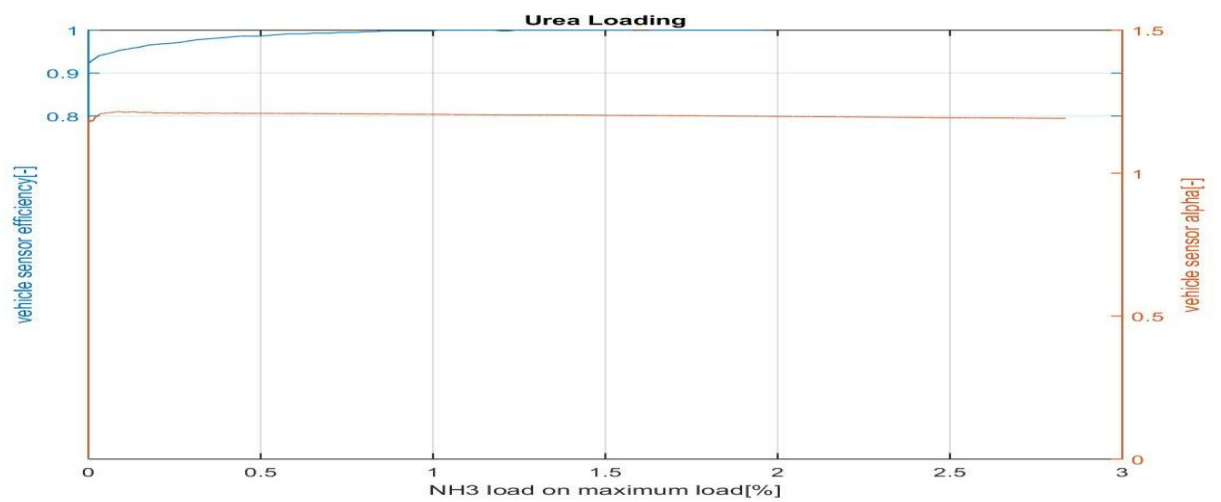
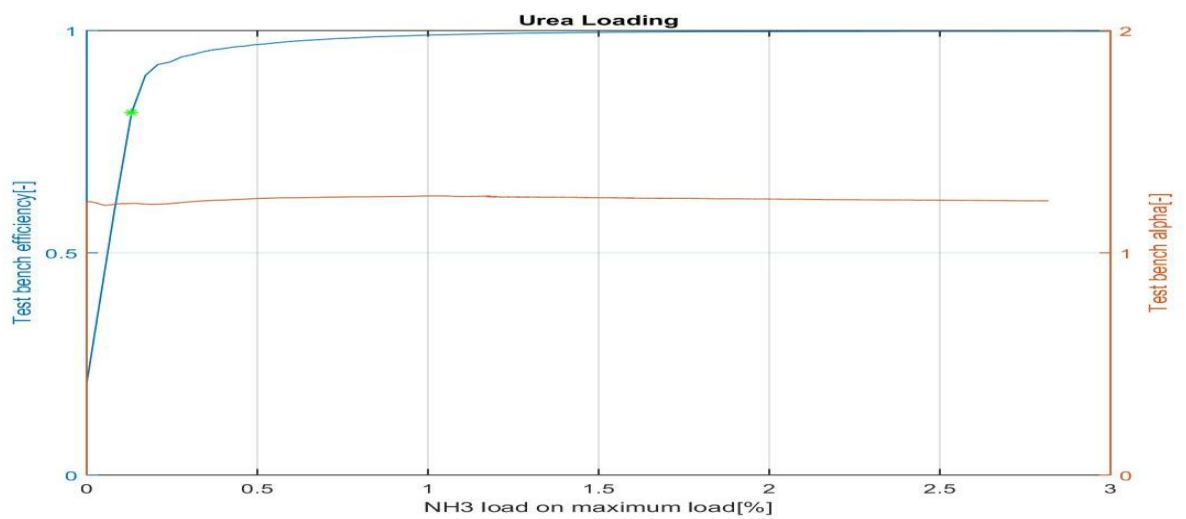
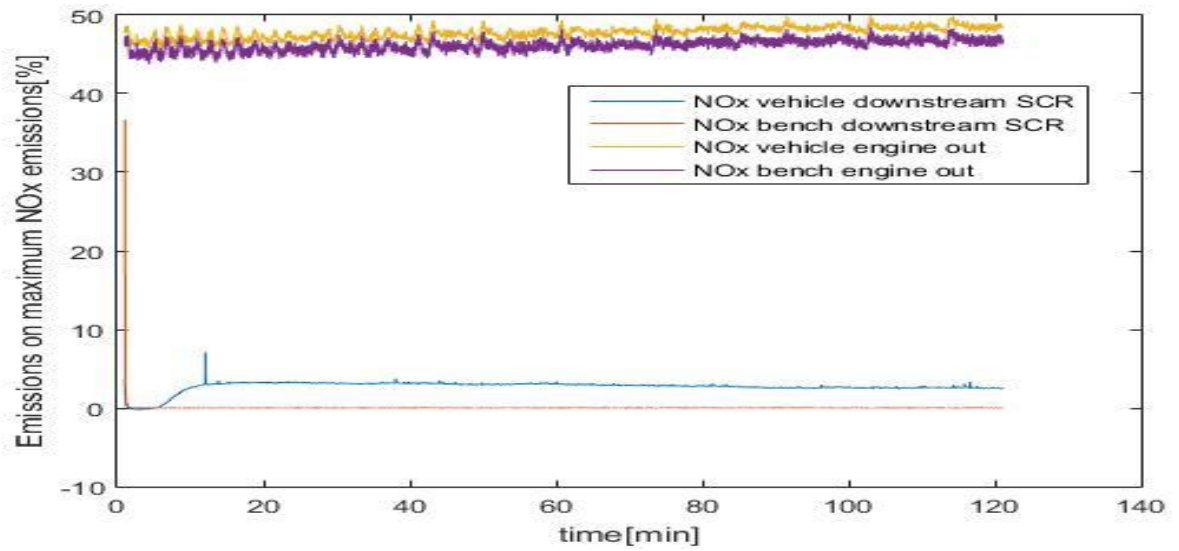


Figure 69.Load\Unload charts 400kg/h-350°C

- 400kg/h-400°C

Load



Unload

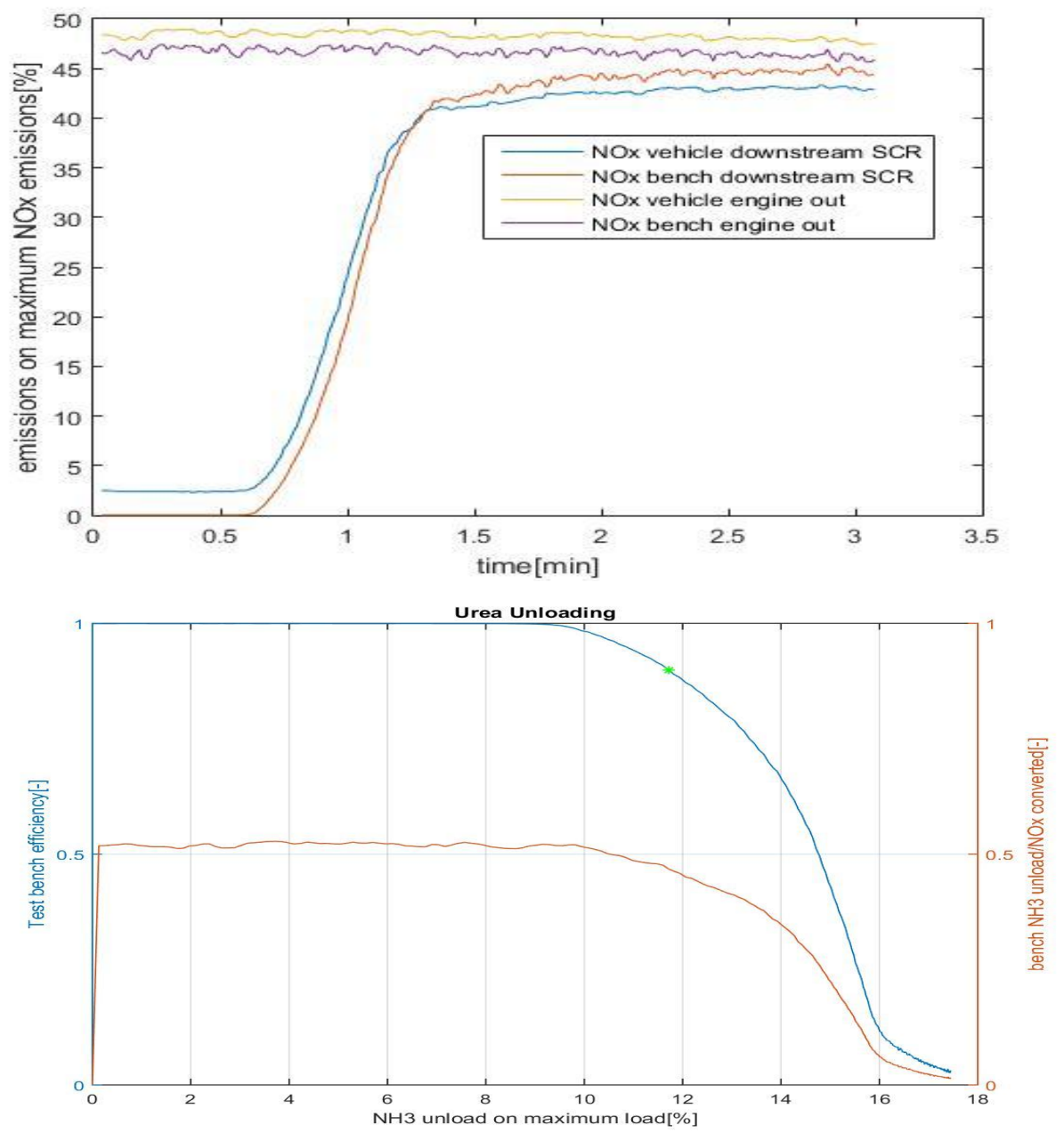
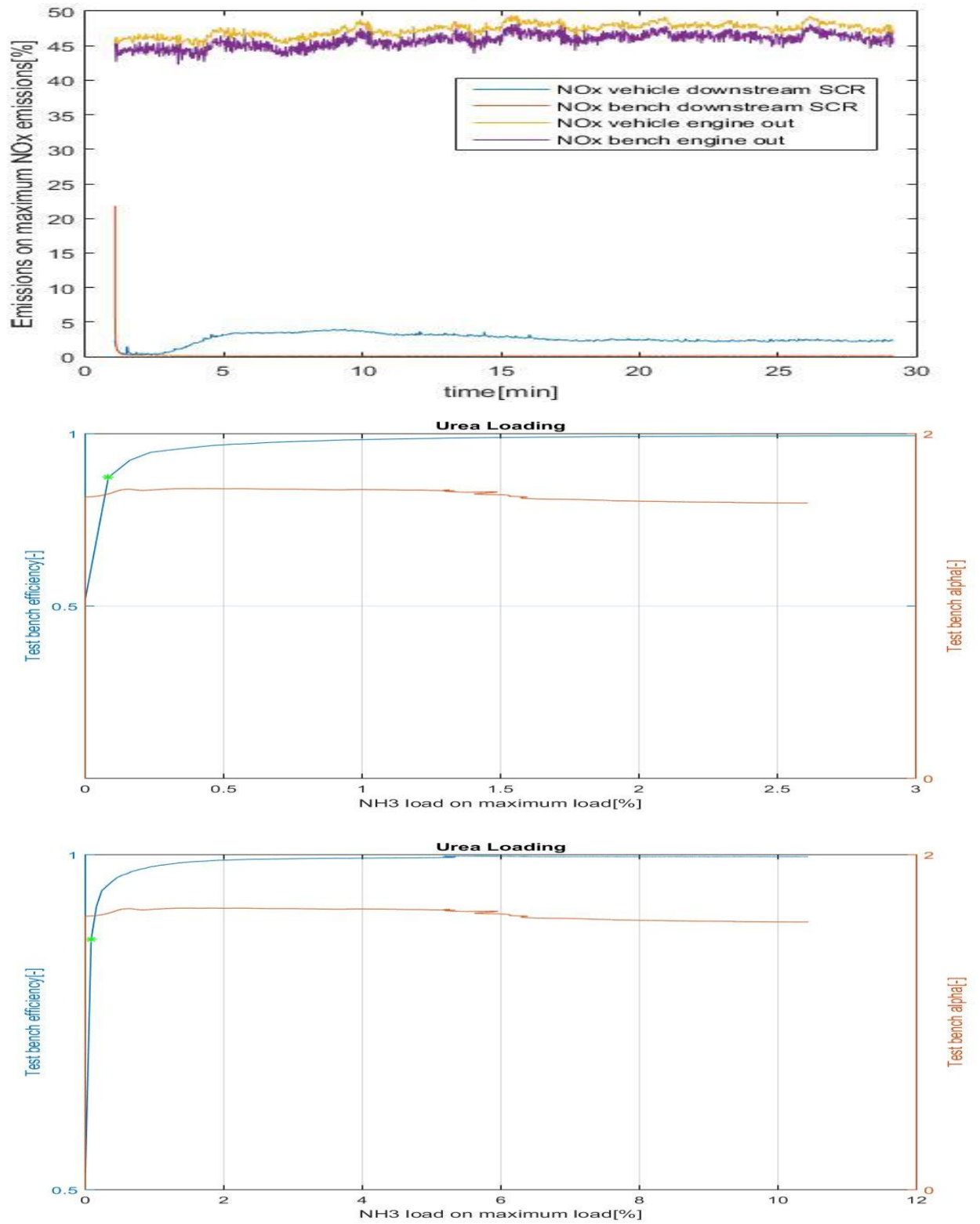


Figure 70.Load\Unload charts 400kg/h-400°C

- 400kg/h-450°C

Load



Unload

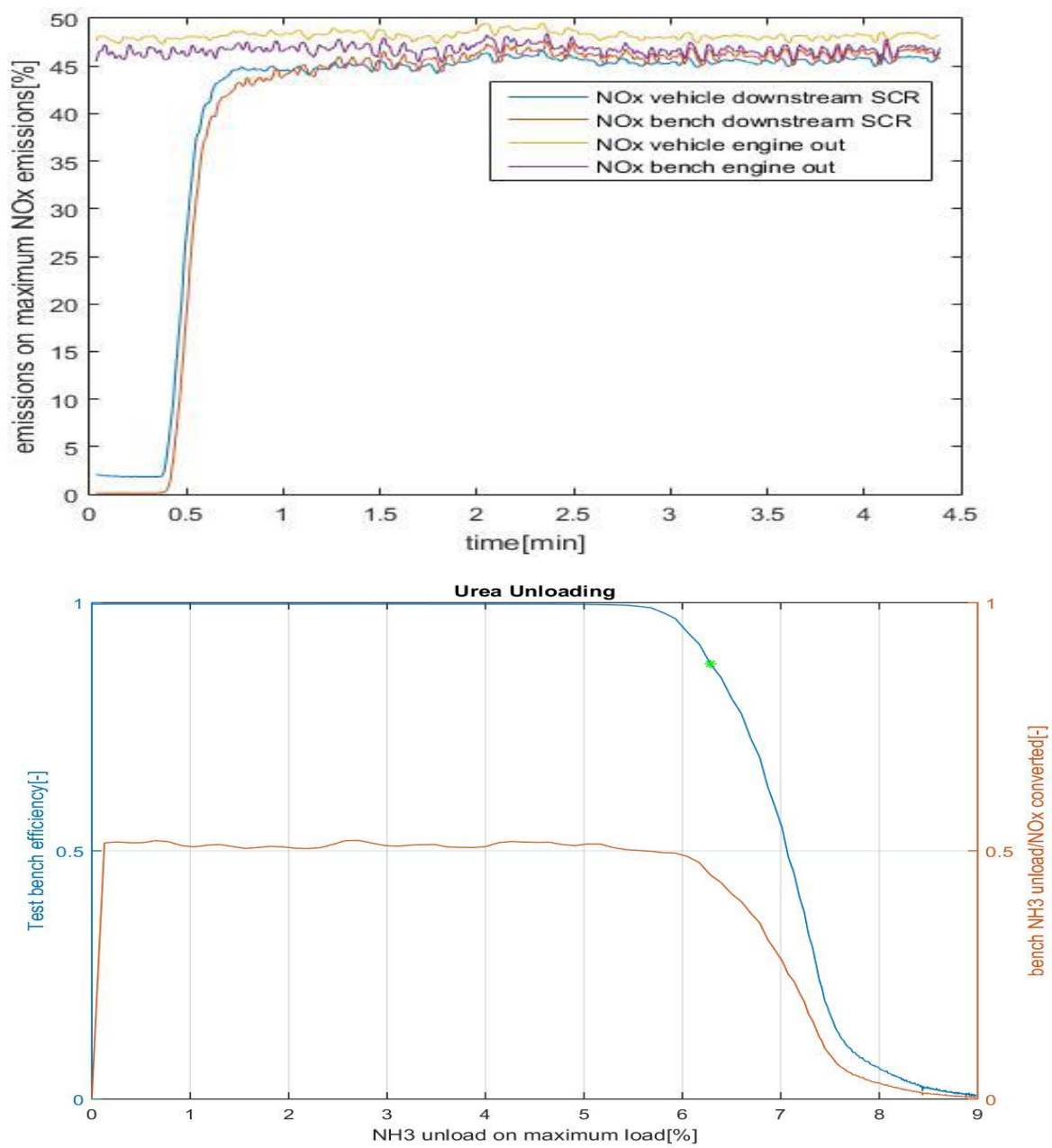
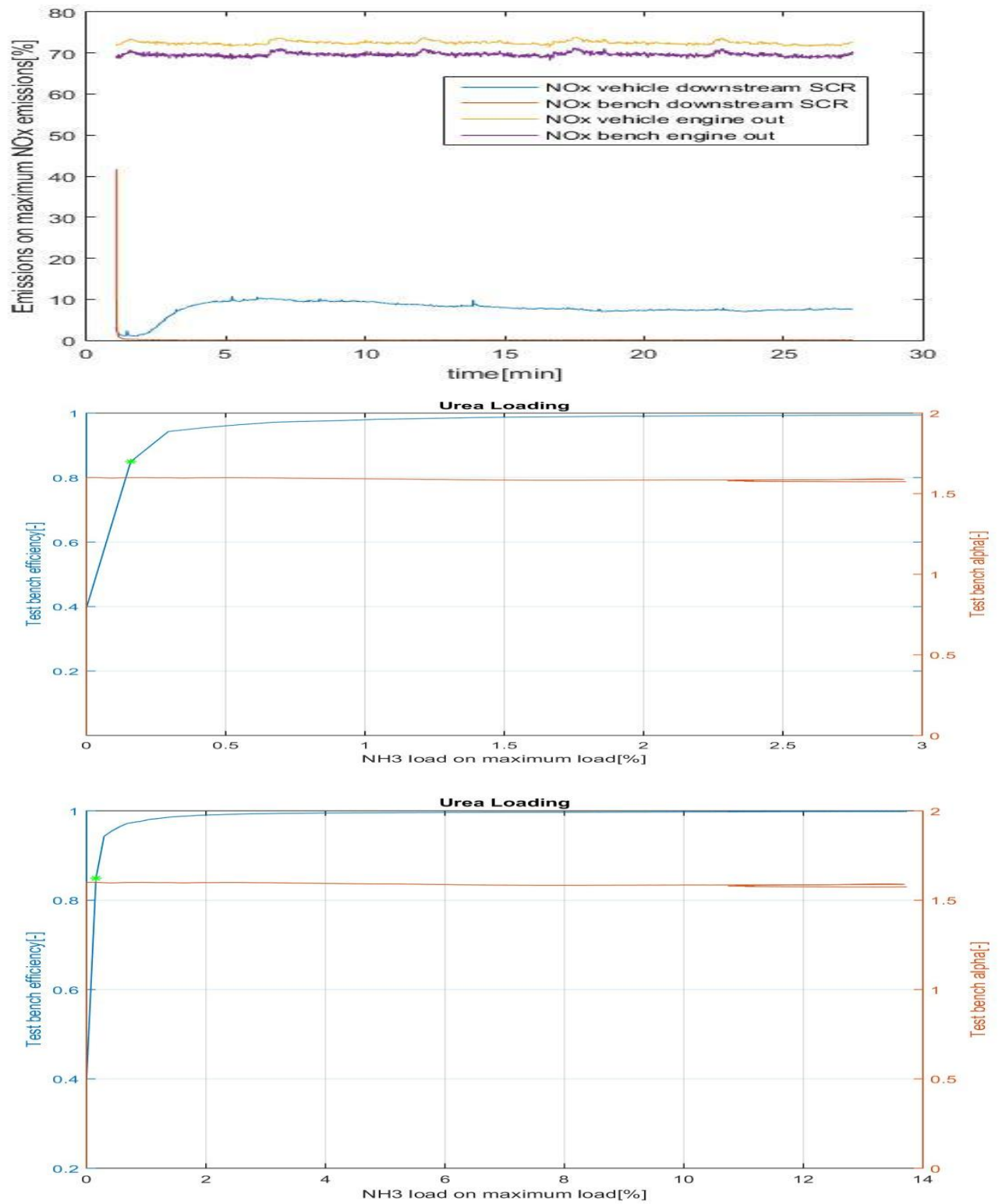


Figure 71.Load\Unload charts 400kg/h-450°C

- 500kg/h-450°C

Load



Unload

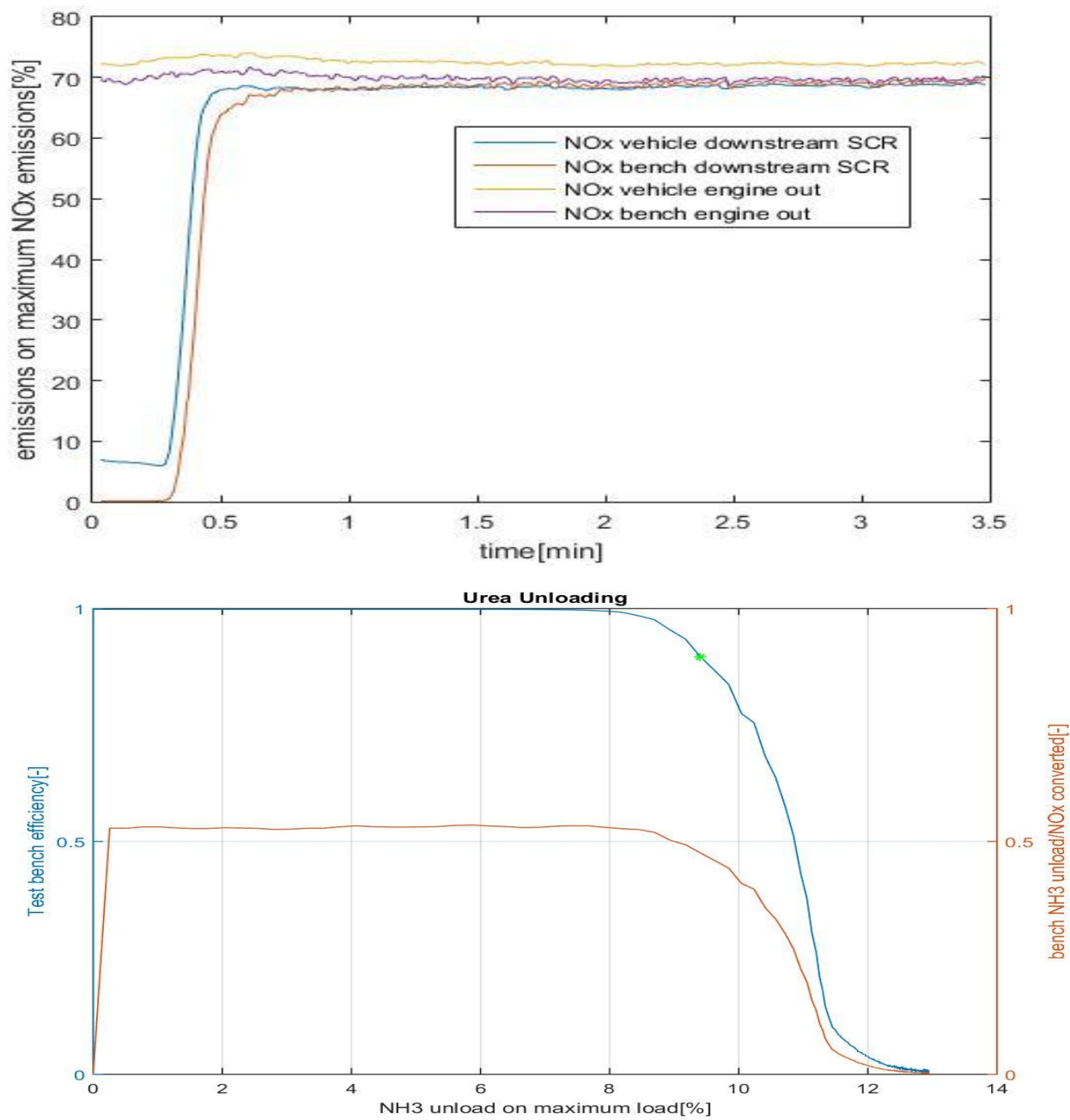
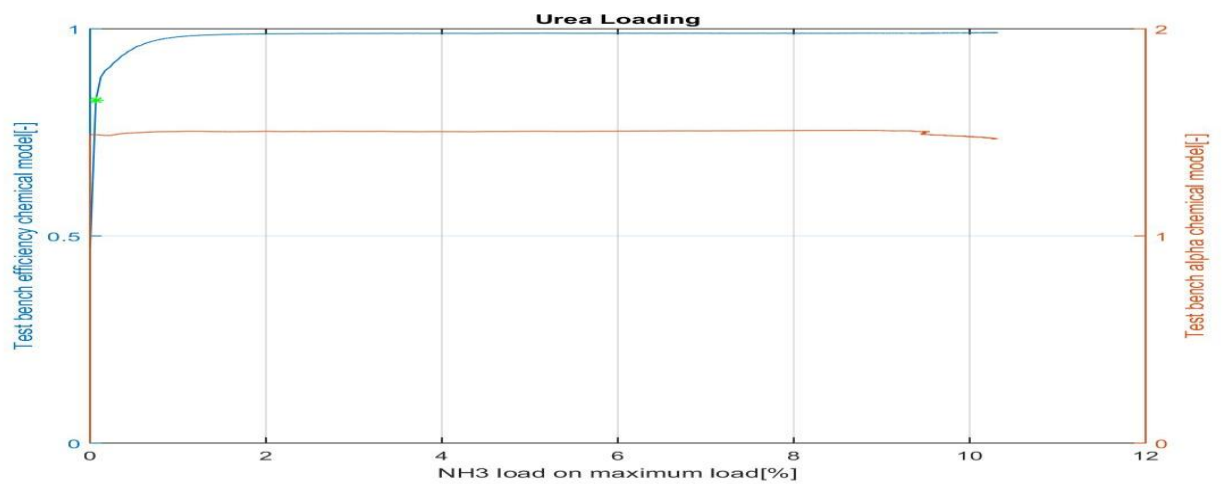
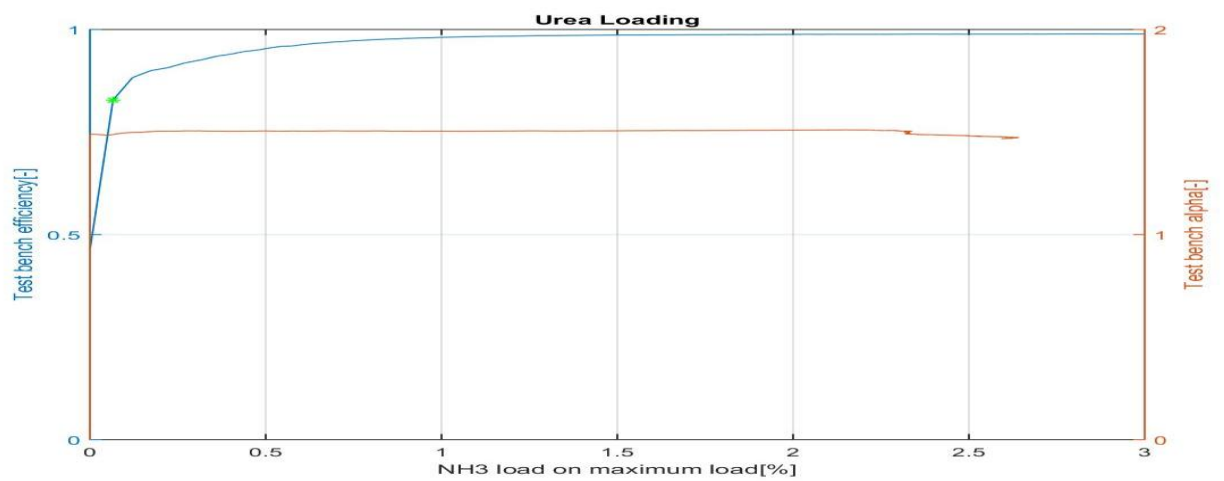
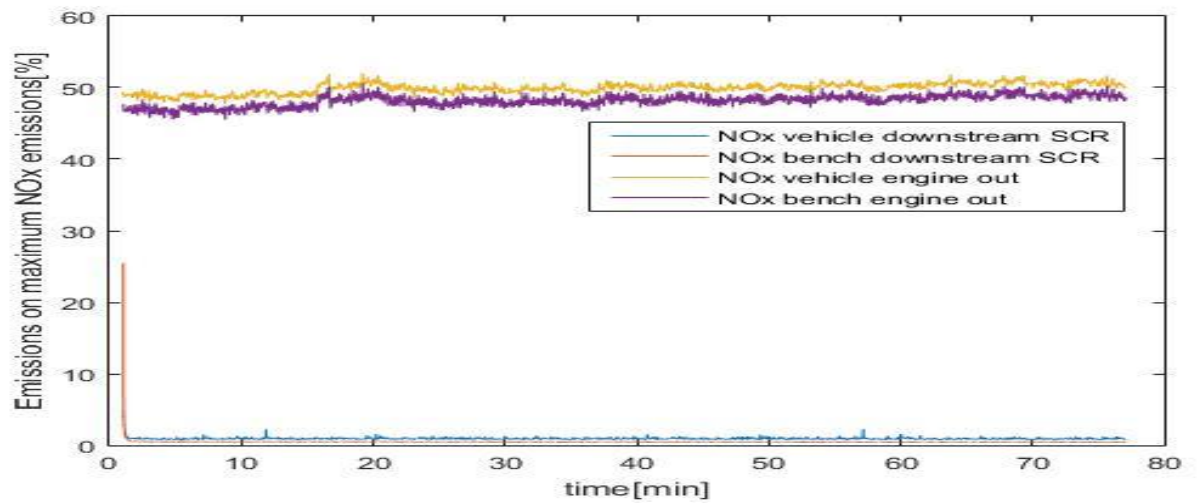


Figure 72.Load\Unload charts 500kg/h-450°C

- 500kg/h-480°C

Load



Unload

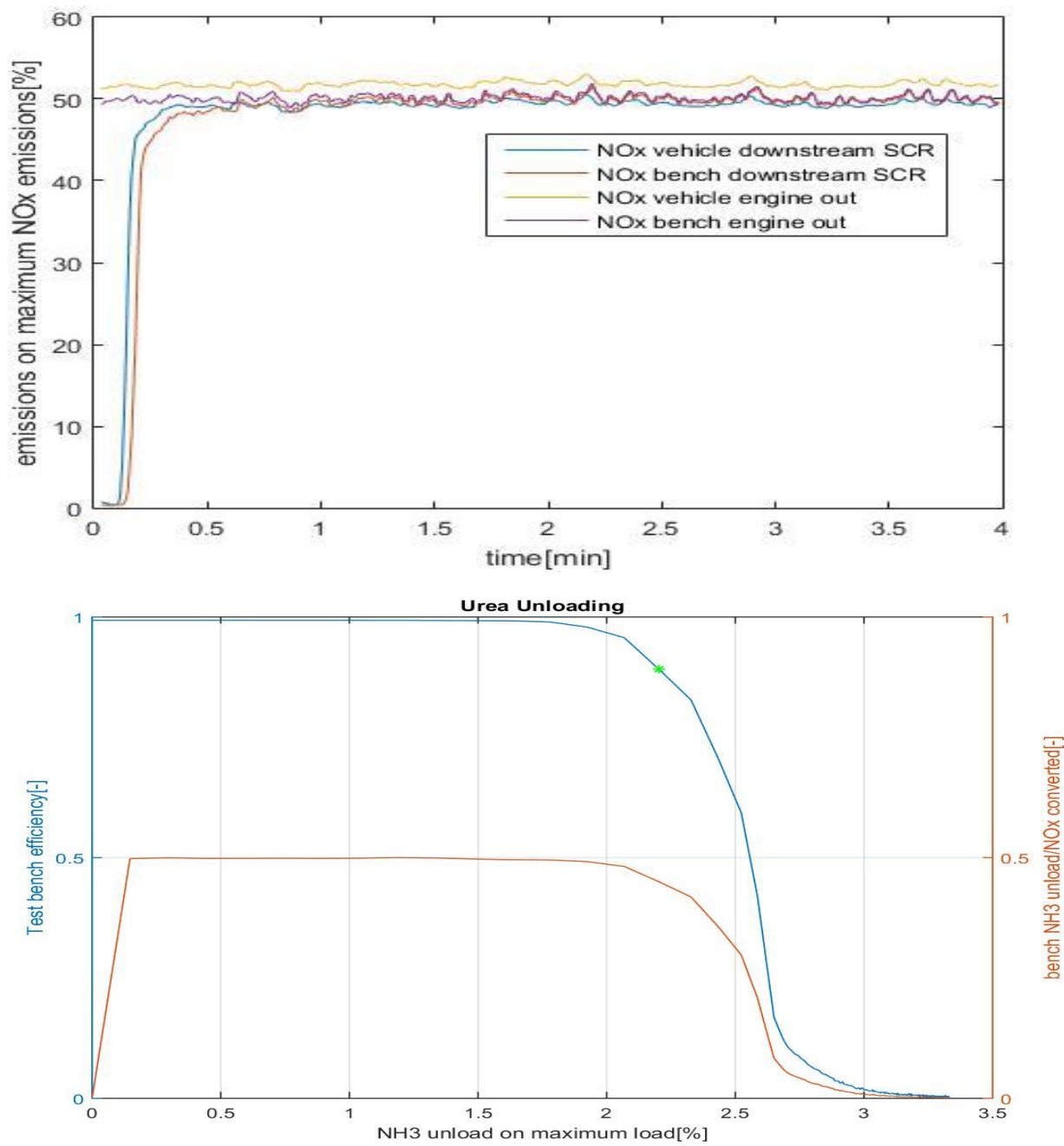


Figure 73.Load\Unload charts 500kg/h-480°C

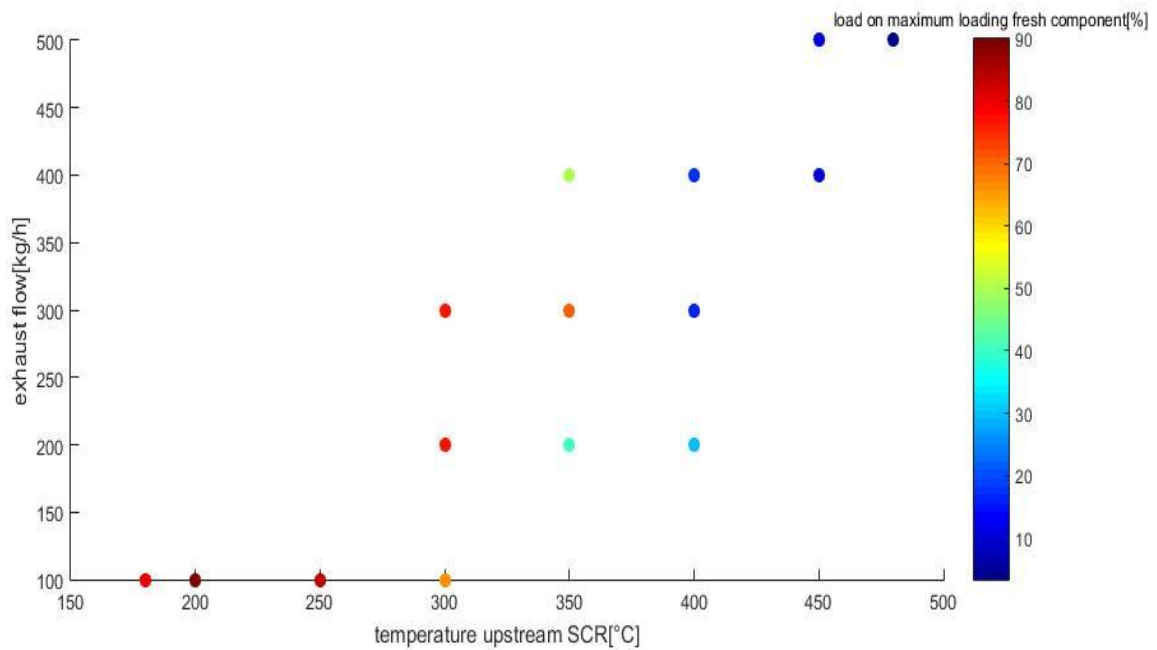


Figure 74.maximum load map

Main key points for the reading of the graphs are:

- The NH₃ conversion models, the chemical one developed internally and the most common one found in the literature, most of the times present similar behaviors but it was shown only the one between the two that is closest to the real loading.
- Real loading is considered the total unloading because external phenomena that must be considered during the loading phase can be considered negligible, the calculation is only based on the chemical quantity of NH₃ needed to reduce the NO_x quantity in that sampling and the one measured by the NH₃ laser.
- For some graphs showing the *NH₃ trans loading*, *NH₃ loading on the specific sample*, the trend is not close to zero but presents some mg of error in the total loading, this is due to some uncertainty in the measures and aleatory causes .
- It's possible to have for some tests a not perfect calculation of the loading at high speed mainly because of the oxidation model already implemented in the ECU by the customer whose logic is not transparent for us.
- In the unloading phase the trend of *bench NH₃unload/NO_x converted* is shown to well understand the reaction inside the catalyst just due to the de-loading of NH₃ stored, the conversion capacity at the variation of the slip.

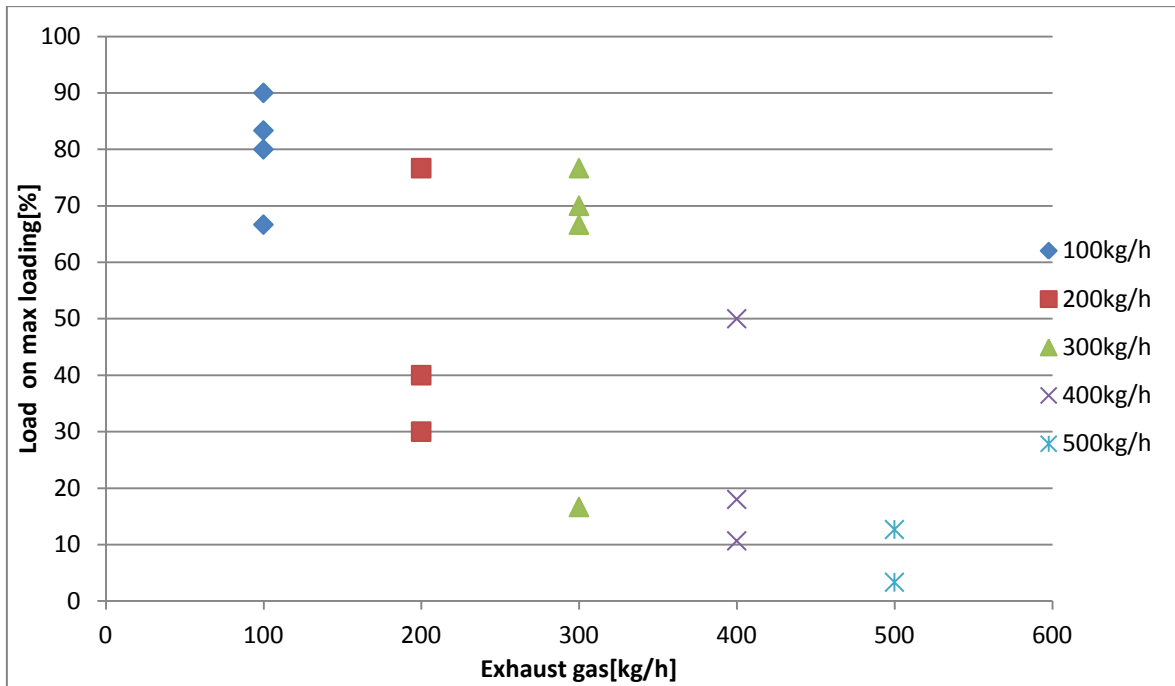


Figure 75. Exhaust gas vs total load

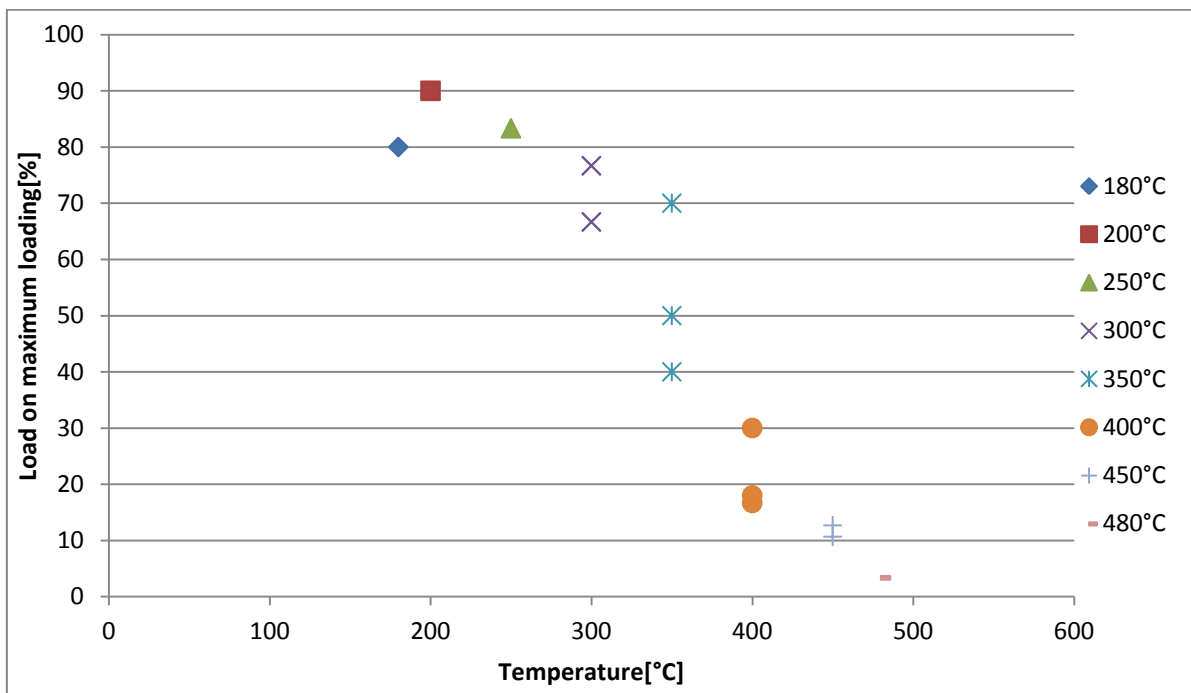


Figure 76. temperature upstream SCR vs total load

- A clear behavior of the loading is seen with figure.75 and figure.76. The major parameter affecting the phenomenon is the temperature, while the exhaust gas

affects in major way the time needed for the loading and the unloading and in minor way the quantity because of higher kinetic energy of the molecules and so lower possibilities to be trapped inside the zeolite cages. For constant exhaust flow rates higher temperatures means lower loading. For constant temperature the load behavior is not predictable but a huge influence is due to mixer design and injector position.

- After the post processing of the data for 200 kg/h of exhaust gas flow, the residues are estimated in between 4.5%-2% of the injected Ad-Blue; also for this phenomenon the mixer design is the predominant factor.
- Using the customer's oxidation model in the ECU it can be shown in figure.77 the impact of the oxidation. Taking in consideration a dummy correction factor on the Urea injection used to align the total load model to the unload for processing of the same test considering oxidation and not considering it, the factor goes to values in the range 2%-4% with the oxidation model while peaks of more than 20% can be reached without it. The impact of the model is felt for temperature higher than 350°C.

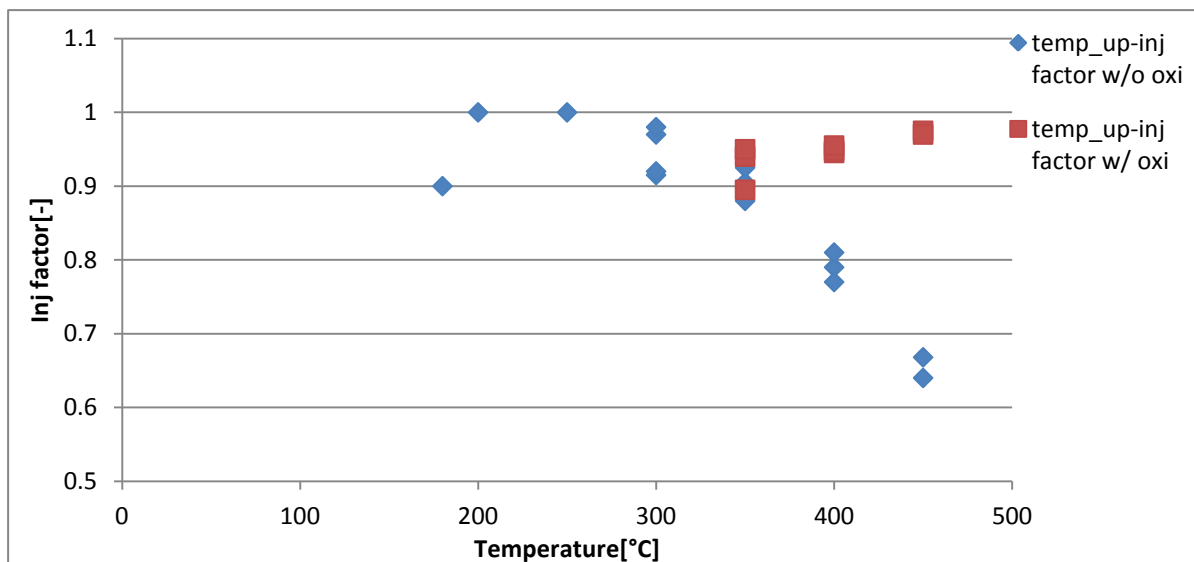
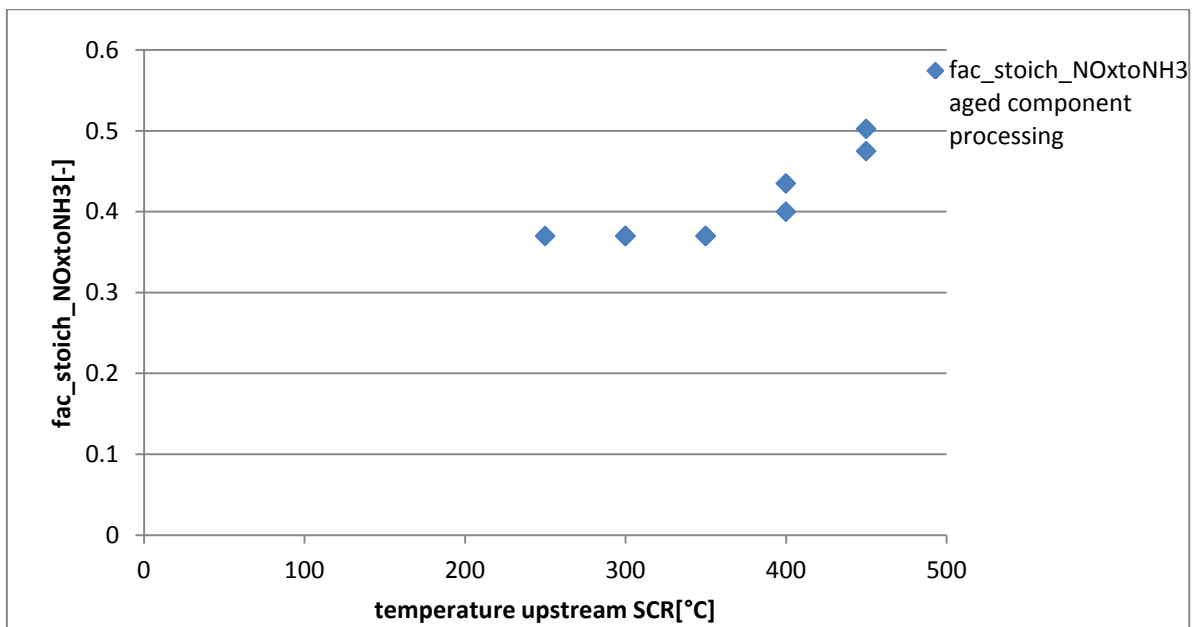


Figure 77. Temperature upstream vs injection correction for NH₃ oxidation

6 Results presentation, part II-Aged component

At 60% of the FEV customer procedures, it was scheduled some tests to check the deactivation level of the tested component. Not a big difference is expected for what concerns the conversion capability of the component but a huge difference is expected in the maximum stored NH_3 . Due to the thermal deactivation of the zeolite, subjected to high temperature, moisture and poisoning material, the capacity of storage will decrease because of the larger volume of the cages of its structure. The choice of the test was made to acquire a huge view of the behavior of the component loss of zeolite activity, while for the alpha sweep tests just few points of checking have been chosen. The processing of the data has been the same used also for the fresh component for both tests, but due to the fact that an overestimation of the oxidation was recognized for the model implemented in the ECU, it was chosen to adopt the strategy of changing the factor of conversion of NO_x to NH_3 to take in consideration of the oxidation phenomenon. The values used for this type of approximation are in the range found on the literatures or comes from previous elaboration of the fresh tests.



6.1 Alpha sweep test

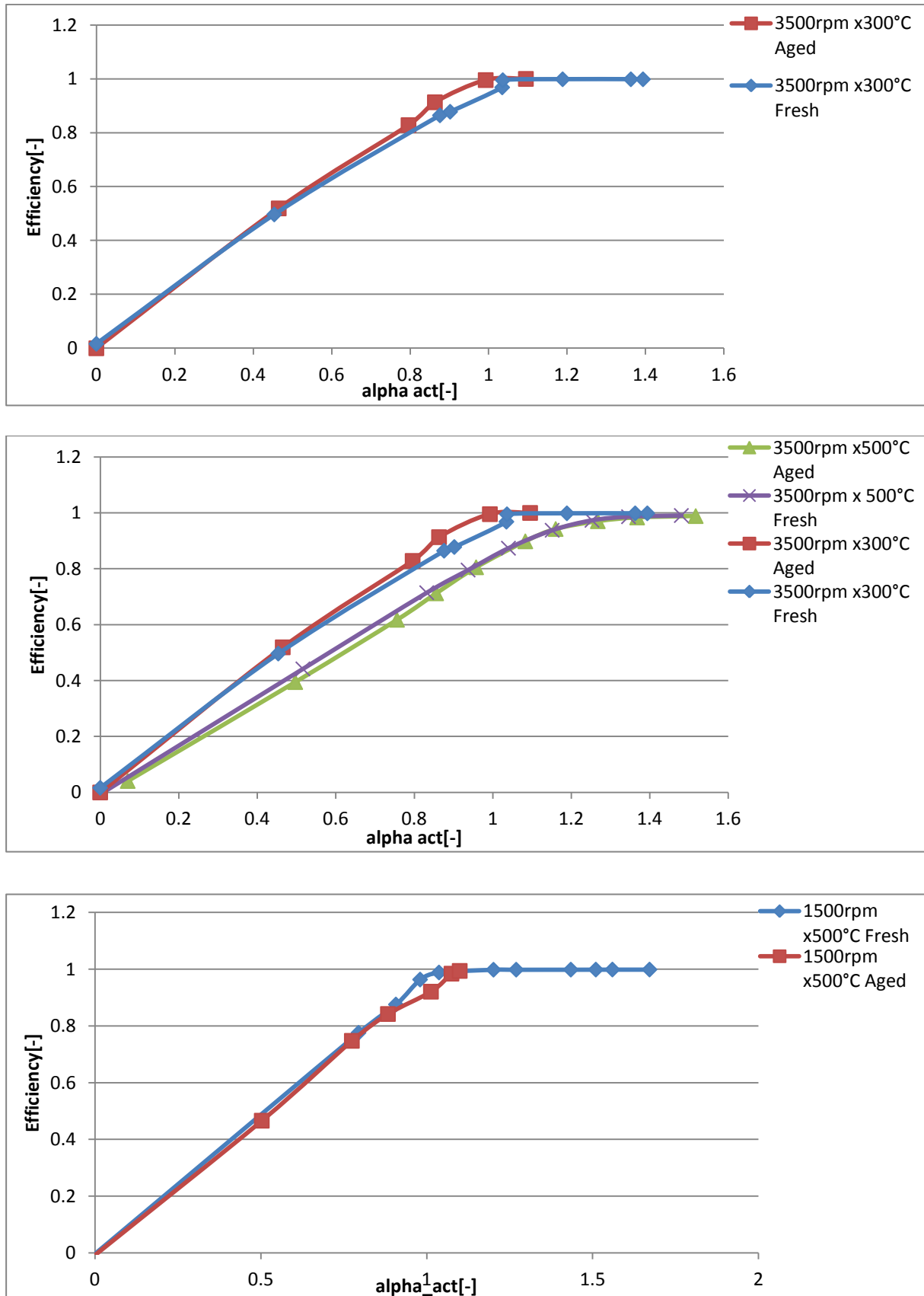


Figure 78. Alpha sweep, aged component- fresh component comparison

6.2 Load-Unload test

- 100kg/h-250°C

Load

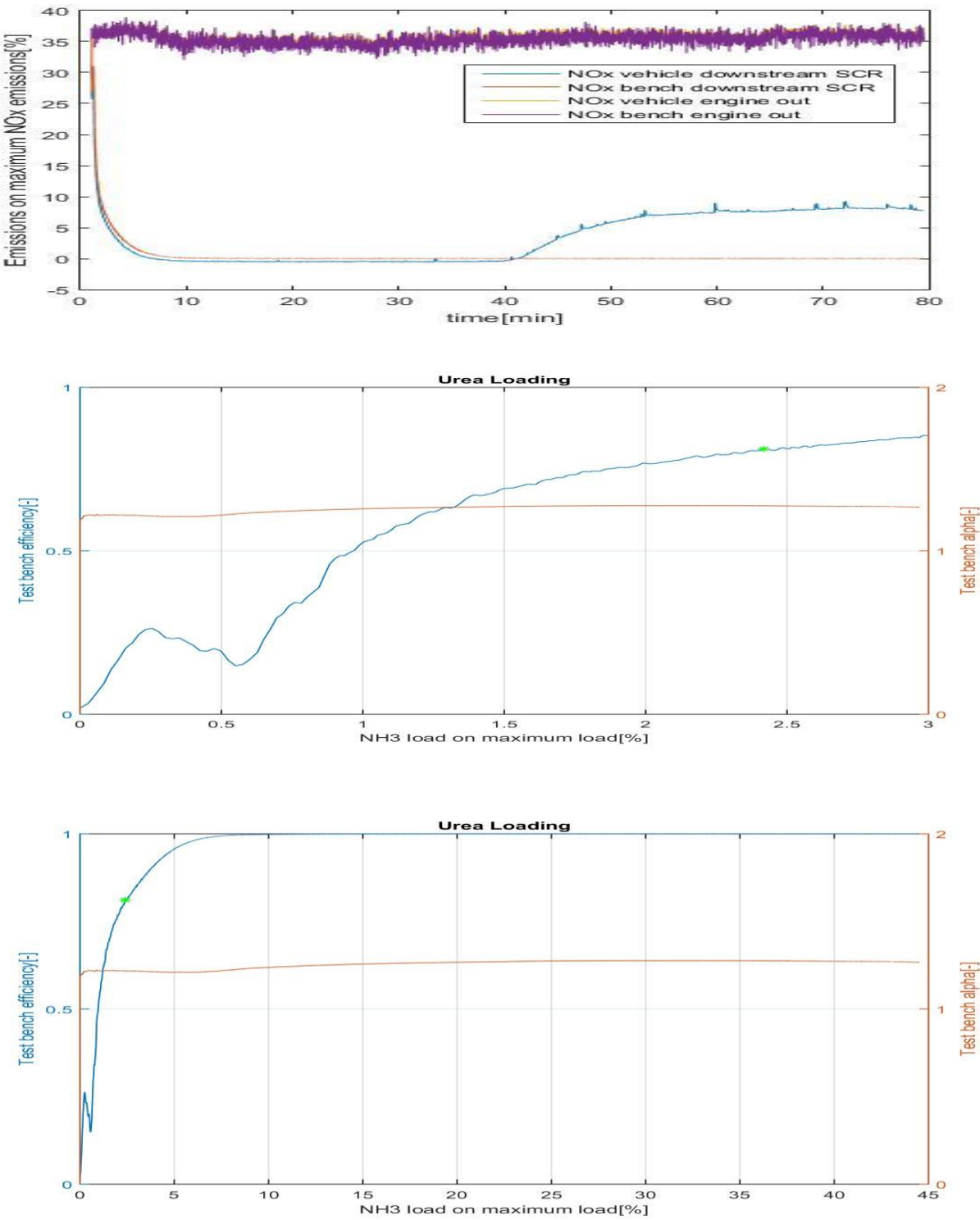


Figure 79.Loading phase, 100kg/h-250°C Aged

Unload

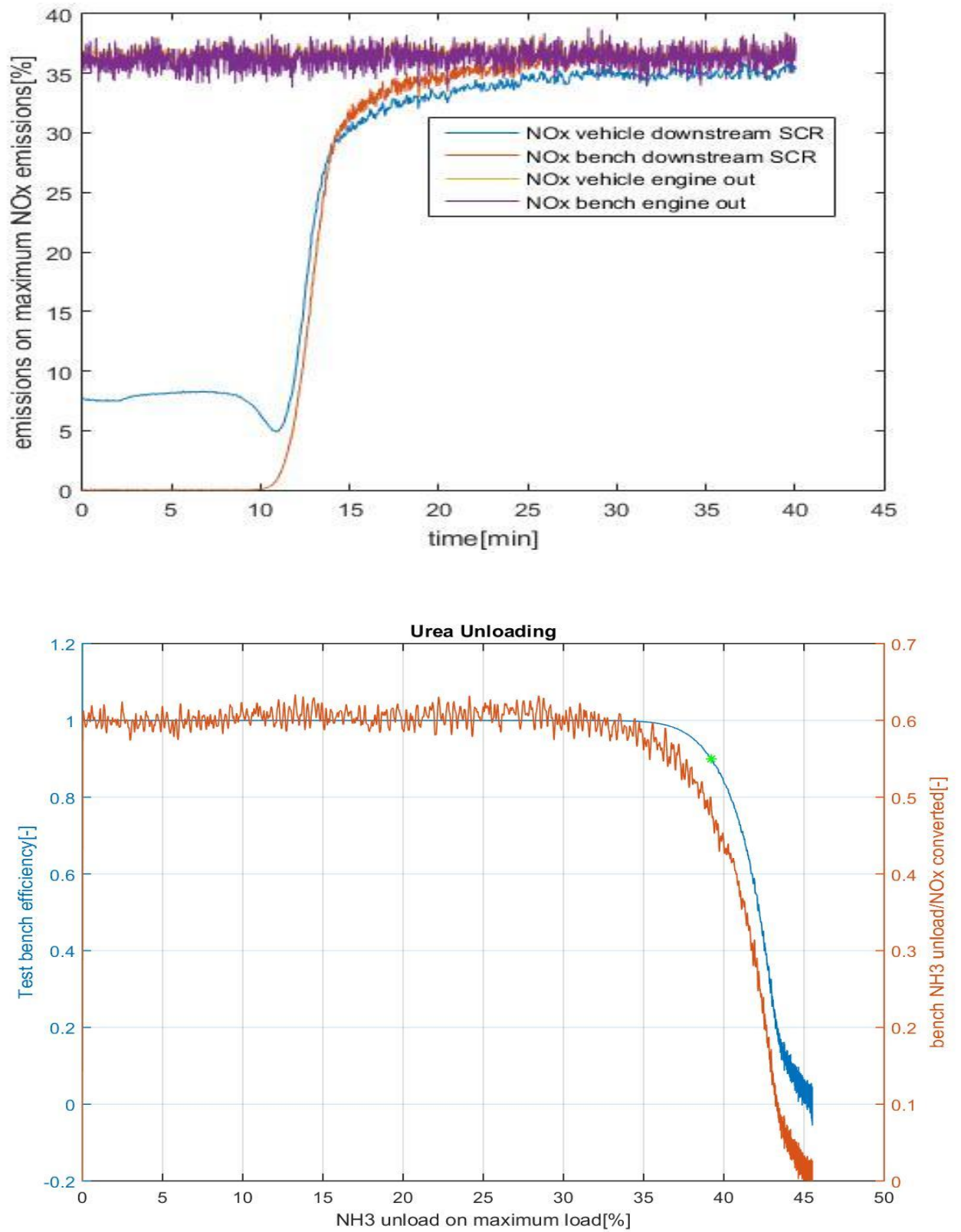


Figure 80.Unload phase, 100 kg/h - 250°C Aged

From figure81 to figure84, it will be reported only the most important results for the understanding of the conversion efficiency change due to ageing of the component. The points taken into account are chosen because are the most representative of the whole working conditions. It was chosen only to show the results for the loading phase because more affected by the deactivation, the unloading phase remains unchanged in the trends but it gets steeper.

- 200kg/h-400°C

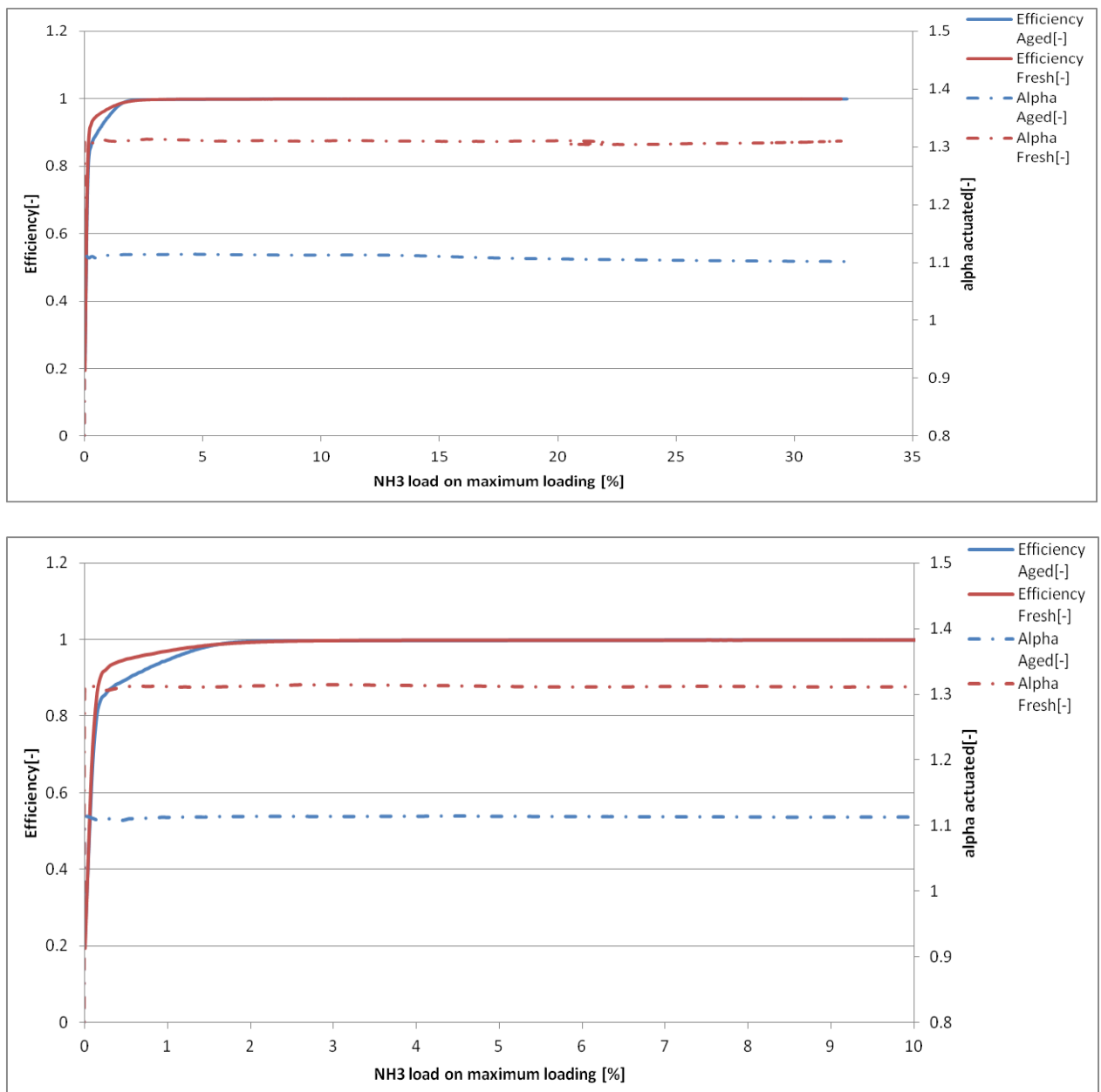


Figure 81. Load phase 200kg/h-400°C, aged

• 300kg/h- 400°C

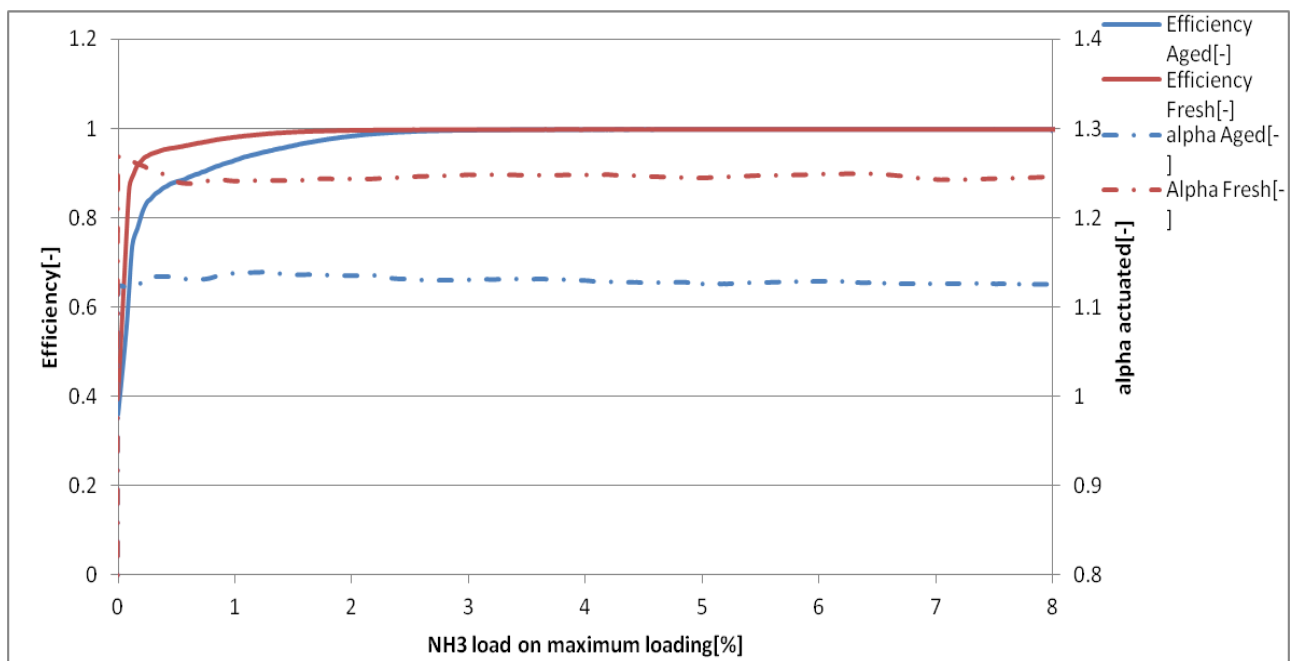
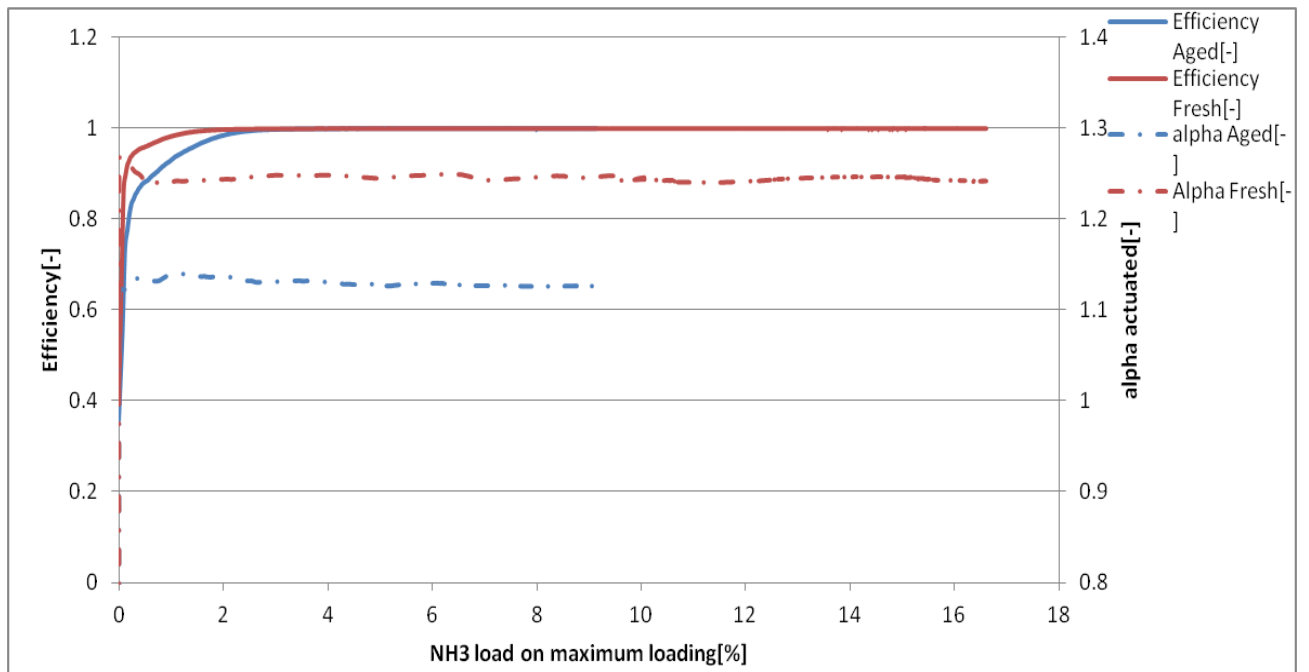


Figure 82.Load phase 300kg/h-400°C,aged

• 300kg/h-300°C

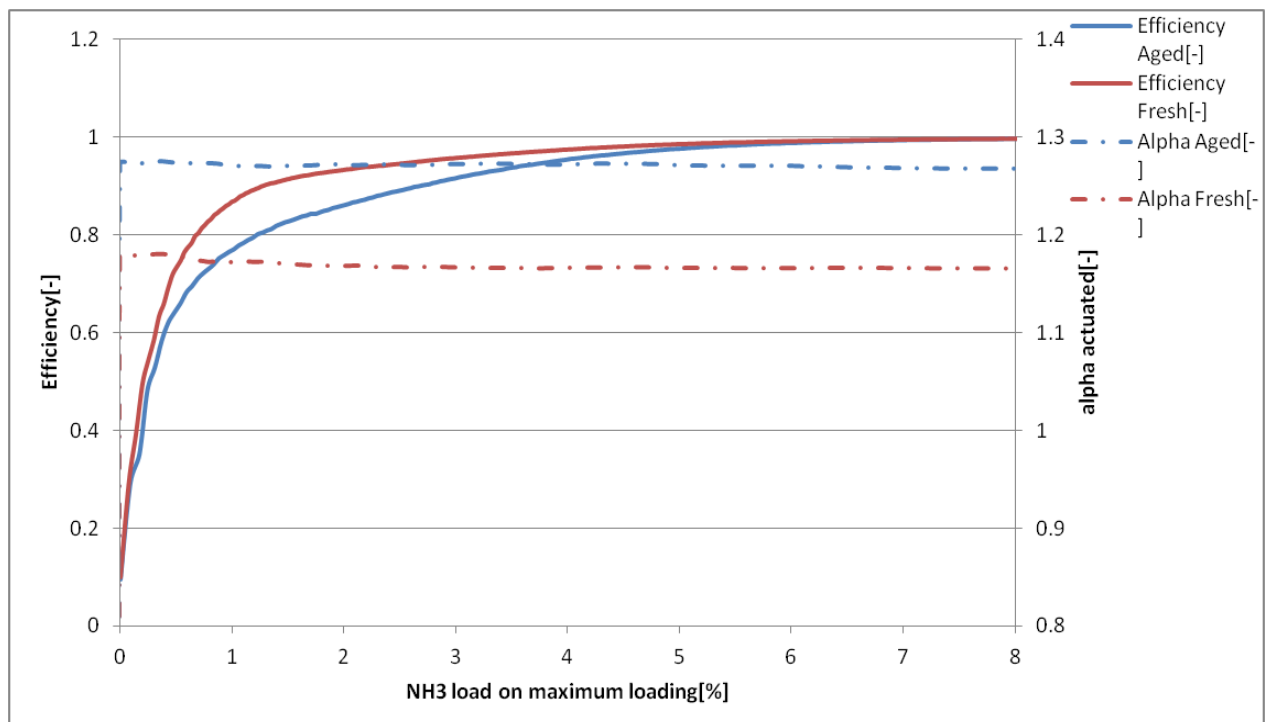
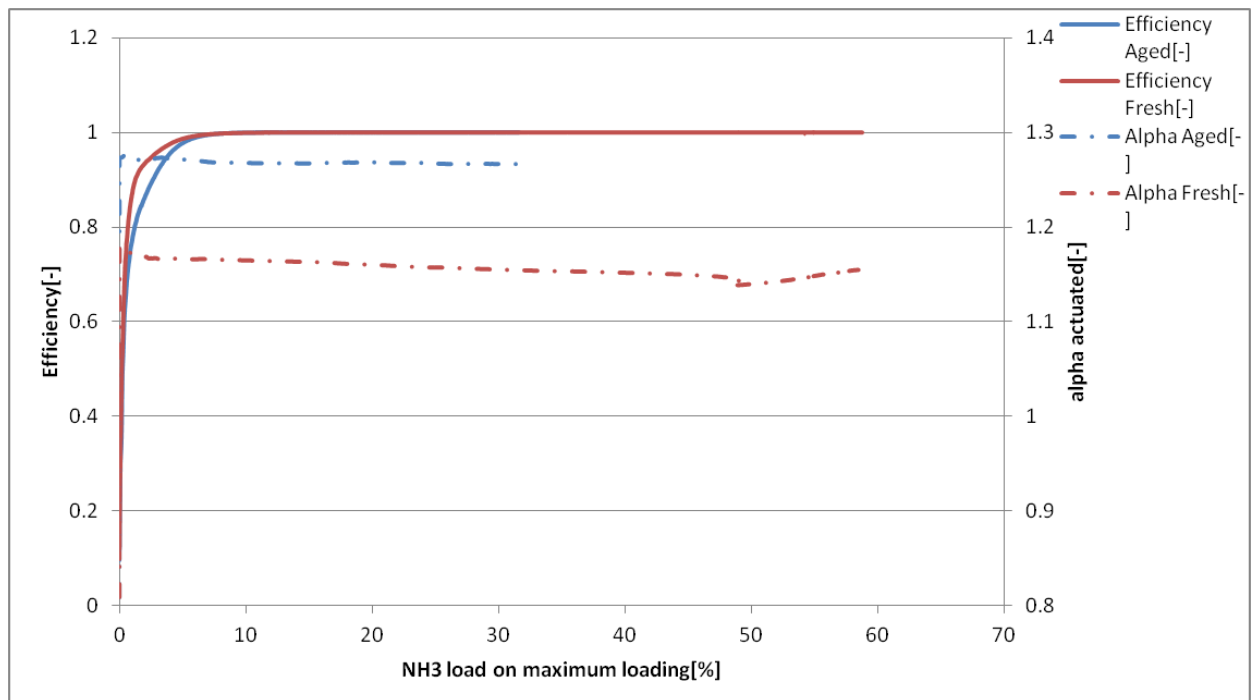


Figure 83.Load phase 300kg/h-300°C, aged

• 500kg/h-450°C

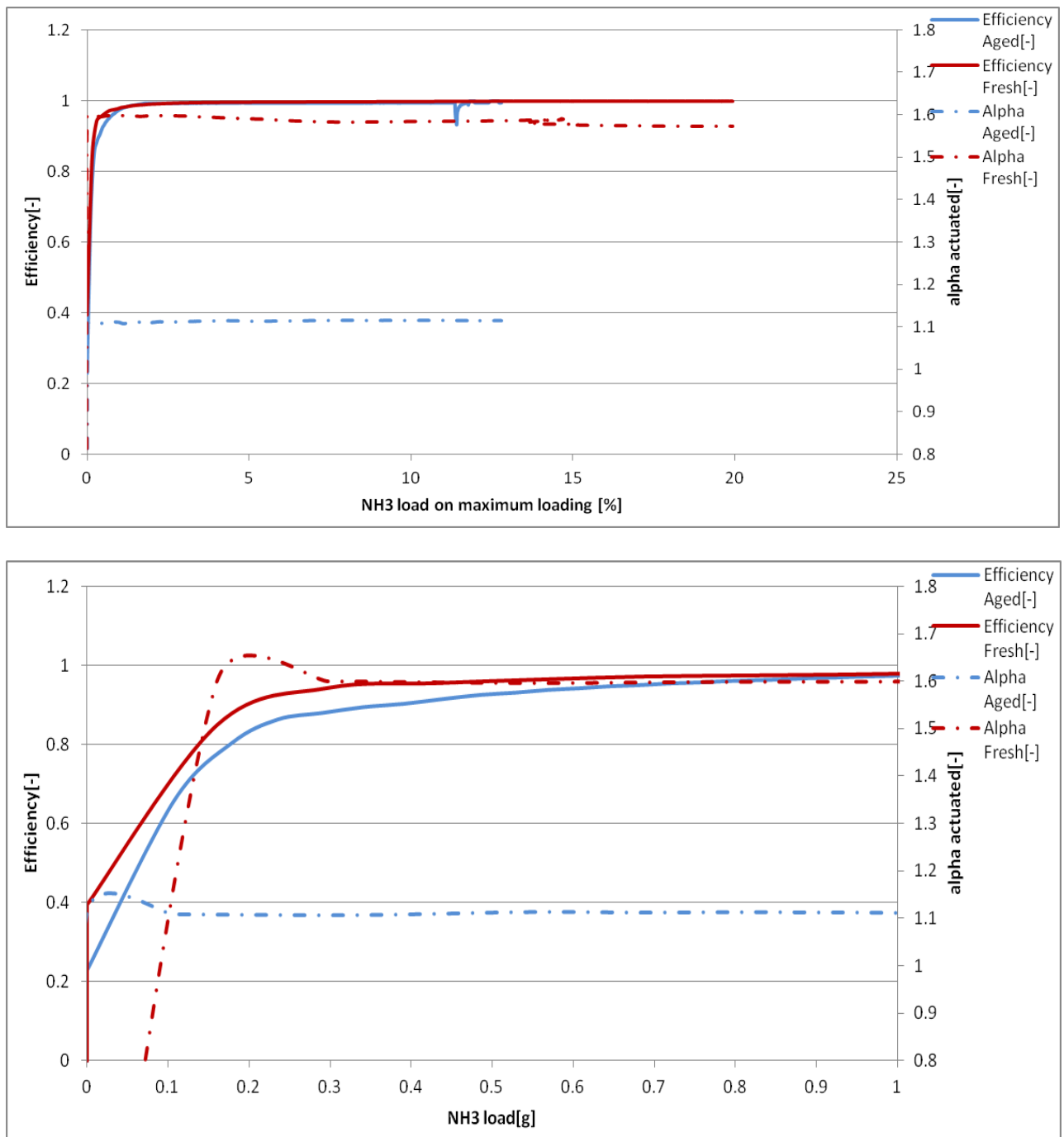


Figure 84. Load phase 500kg/h-450°C, aged

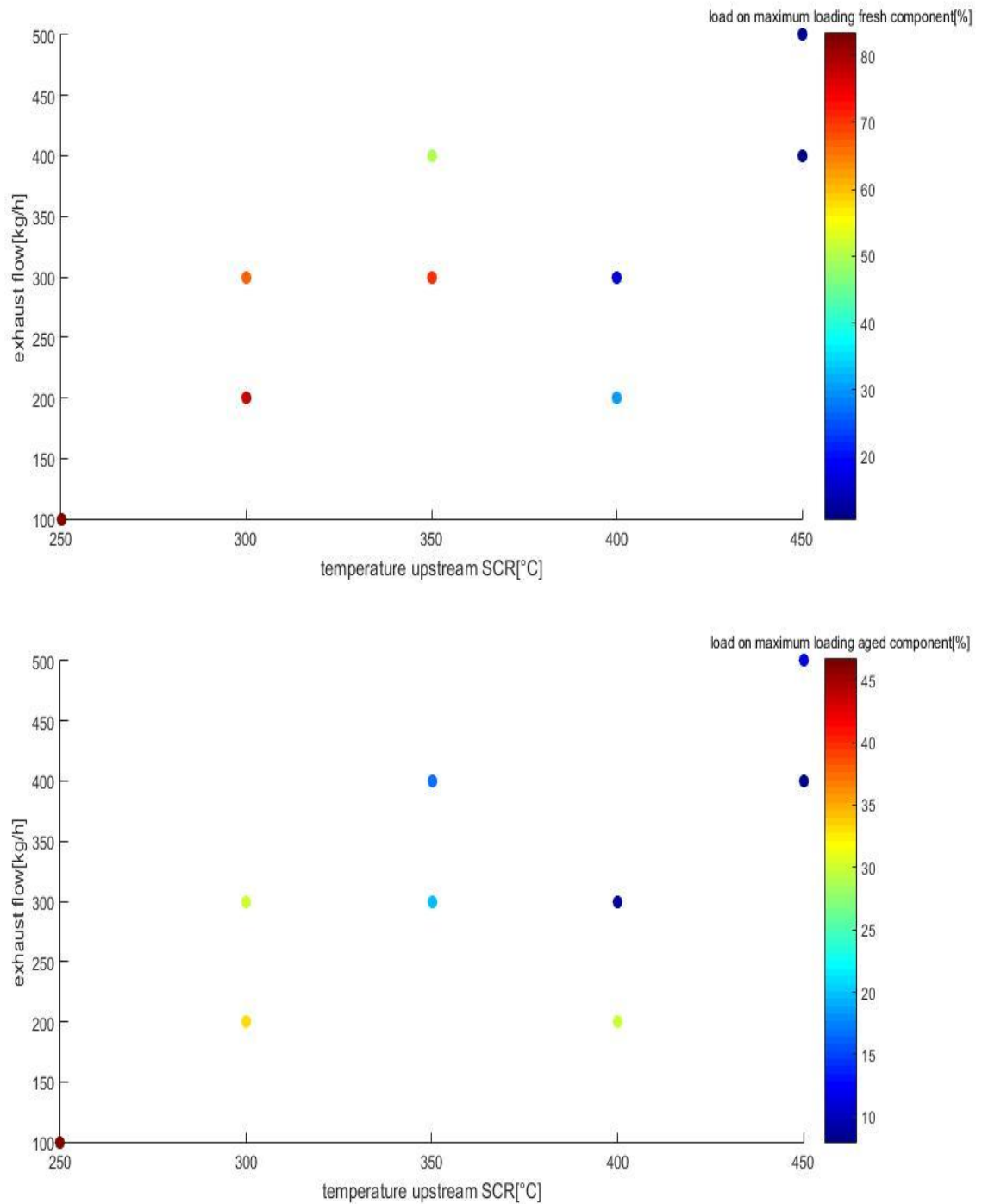


Figure 85.Fresh and aged maximum loads

The alpha sweep tests didn't present any changes to notice; the ageing procedure doesn't affect the capacity of efficiency conversion and so just three tests were chosen in accordance to the customer. Many important elements must be taken into account from the Load-unload activities. First to remark as seen in comparison of figure85, the differences of maximum load between the two is of about 30% for low and middle ranges while not

huge differences are seen for high temperatures because the phenomena of oxidation is predominant. The other remarks come from the figure81 to figure84, the trend is quite similar between the fresh and aged curves but due to the remarks of section 2.1.3, it can be notice that an efficiency of almost 100% is had with almost the same quantity of NH_3 load but the higher trend of the fresh curve can be due to an higher conversion efficiency due to many factors as for example: deterioration of washcoat in term of the position of the copper inside the zeolite or reduction of conversion efficiency of the DOC and in general of all the aftertreatment system. These types of considerations will be fundamental during the calibration phase because it will be the indication of the ageing model if chosen to calibrate and the main calibration activity developed on a fresh component or of the deterioration factors if the calibration activities will developed only on the aged exhaust system. Respect the fresh component processing of data, it was chosen for the aged phase to adopt only the conversion model using the factor *fac_stoich_NOxtoNH3*, taking in consideration of an increase of the factor in presence of high temperatures. This type of elaboration was led by the fact that with chemical model a deeper investigation on engine maps was needed also for this phase. The results of the model would tend to overestimate the loading because due to the logic behind it will tend to use more the transformations with NO_2 , still using the fresh component engine maps, that requires a lower mass of NH_3 . Due to the fact that the deterioration of the DOC has not been estimated a precise indication of the oxidation cannot be done, but the trend shown by data processing is of a decrease in the oxidation phenomena, also taking in consideration of the customer implemented ECU model response, it must be remarked that it was probably calibrated as a trade-off between fresh and aged component and it expects the use of a CUC that in the tests is not presence. It has been considered that decreasing the residence time of the NH_3 because of a lower capacity of the component to trap particles also a certain decrease in the oxidation is expected.

7 Conclusions and future studies

The thesis project was set to have a precise view of the validation process of a brand new SCR. Starting from the theoretical knowledge about the chemical and structural aspects of the catalyst, the clarification about the choice of the tests, their implementation and analysis has been proposed for the two phase of the activity, fresh and aged component. The possibility to be able to compare the theoretical aspects with a real components was of great importance because it was possible to give a weight to each aspects. The importance of the number of cells, mixer, fresh and age component, NO_2/NO_x ratio, NH_3 load have been carried out; the results shown in the elaboration of the sections 5.1, 5.2, 6.1, 6.2 can be taken as a quite precise reference of the data come from the experimental elaboration, it has not been shown all the post process phase for each tests because to avoid the discussion got too heavy but at the end the major aspects and minor phenomenon have been addressed. The results in term of precision can be considered quite sufficient, for the goals of the activity for which they were needed, starting from the new component and bringing it to the homologation. For the most precise purpose of scientific knowledge and precision weight of all the chemical and thermal reactions triggered inside the component, the results can be considered also sufficient even if some aspects could be analyzed more in deep as for example the weight of the component to have a precise indication of the residues and the introduction on the exhaust system of O_2 sensors engine out, upstream and downstream SCR. The deeper investigation activity had to be traded off with the need of the company to end the project with the right level of component validation but also in the prescribed time. As overall view the results and the procedure used and the experience carried out were the one expected. During the first period of work some studies related not only to the theoretical aspects related to the SCR but also to the phases related to calibration and homologation and the logic followed by the ECU in term of calibration maps and curves have been carried out. In this terms the aspects related the main factors concerning the catalyst, section 2.1.3, have been analyzed in sufficient way also taking in consideration of the following calibration phases on cycles and on vehicle. Another aspects to take into account in term of value of the results is the fact that it was possible during all the phases to compare the results of the bench emissions with the measure of the vehicle sensors. Comparing the two measures, inserting inside the flow charts of section 4.3.1 and section

4.3.2 the error control before urea calculation phases and triggering of injections, it was possible to add a further fundamental aspects required by the ECU logic and it is the PID controls related to the feedback of the sensors. Comparing the measure of the AMA i60 and laser measure and the one of sensors for NO_x and NH₃, after a first study of their working principles and cross sensitivity to the molecules found in the exhaust system, it will be possible to have a correct view of the aspects related to loading and unloading on vehicle.

From the results presented in the project the main aspect able to improve and that made a huge difference in term of efficiency and slip is the mixer design. As can be understood from the comparison of the results between alpha sweep tests, for the cpsi_2 components tested with mixer2, and from further internal comparison made, the mixer2 admitted same values of alpha for the same working point, respect tested component with mixer1 but with slip measured by the component with the CUC and mixer1 at the same conditions. A deeper study on the flow mixing and injector positioning would be desirable to have a further improve in term of conversion efficiency, slippage control and reduction of residual as possible. A further development is the evaluation of an ageing procedure in oven to short the procedure needed. Taking in consideration the deterioration factors during all the procedure, the tests made during procedure and the tests will be made at the end.

Appendix

Internal Combustion Engine emissions and issues related to human health and environment

The ideal combustion of hydrocarbons C_aH_b ($b/a \sim 1.85$) would transform all hydrocarbons molecules and air particles in not noxious emissions products (in addition there would be the presence of some oxygen for lean mixture), it doesn't happen for real combustion due to temperature inside chamber, time, energy of activations and chemical equilibrium of the reaction in progress during combustion; generally all processes follow the Arrhenius equation and

$$K = Ae^{\frac{-E_a}{RT}}^{16},$$

Equation 14. Arrhenius equation

produce noxious emissions, unburned hydrocarbons HC, CO, NO_x and Particulate Matter. CO₂ is not a noxious emission but is harmful from the environmental point of view. In addition to what said before, another key point for the formation of emissions and differentiation between fuel (gasoline, diesel, Natural Gas, LPG, Biofuel) is related to the molecules and to the development of the combustion and way in which combustion reaction reaches the energy of activation, (Compression Ignition or Positive Ignition), the injection system (Direct injection or Multi Port Injection), type of combustion used (homogenous combustion or stratified combustion, lean, rich or stoichiometric combustion), design of ducts and development of turbulences and parameters related to conceptual design of the engine as Compression Ratio, design of the piston, stroke to bore ratio, design of the combustion chamber and squish volume, calibration and typology of aftertreatment chosen. Major emissions for diesel engine are NO_x and PM, while low emissions, at least for most used combustion modes, are related to CO and HC.

Major issues related to noxious emissions is in the capacity of human body to filter nano particles and ultrafine particles out of the tailpipe. Smaller and smaller particles are able to

¹⁶ It must be taken into account that due to the high temperature and variation of temperature of in-cylinder gasses, it could happen to have equilibrium of reactions in both verses of the equation or freezing of formation or dissociations of combustion products.

get to the pulmonary/alveolar region with severe health effects. Related to CI engines, NO_x emissions are responsible for respiratory track irritations and are precursors for secondary noxious emissions that bring to more severe health risks. PM emissions is responsible, due to various components of which it is made: solid carbon spheres, condensed hydrocarbons, absorbed hydrocarbons, sulphates and other impurities present in the fuel or oil and resultant particles under $0.1\mu\text{m}$ at the tailpipe of severe issues related to respiratory system with mutagens and carcinogens effects.

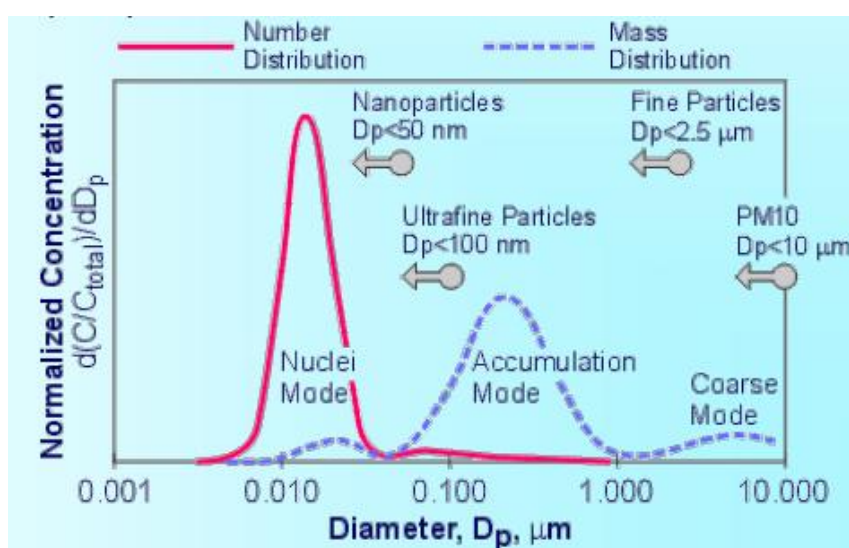
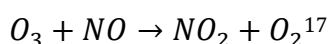
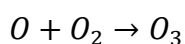
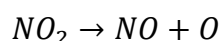


Figure 86. Mass and Number distributions of PM

Effects on environment concerns secondary reactions made by interactions of UV radiations and other particles already present in air. CO_2 emissions is one of the principle causes of the 'Greenhouse effect'; greenhouse gasses are 'transparent' for high frequency solar radiations but are 'opaque' for low frequency infrared radiations, working as glass roof of a greenhouse. NO_x is responsible for the acid rains, reacting with sulphur oxides producing H_2SO_4 and HNO_3 and when it is catalyzed by the UV radiations in reaction with O_2 it produces O_3 ;



¹⁷ last equation ideally could bring to an equilibrium in the formation of ozone O_3 but in presence of hydrocarbons the equilibrium is not reached and the formations of PeroxyAcil Nitrates PANs and additional O_3 is triggered.

Acid rains and ozone O₃ formations are not related to the presence of NO_x or ultraviolet light but their formations and levels are related also to the Volatile Organic Compounds VOC and to the interaction between each other.

Legislation framework and homologation procedures

Pollutant emissions are related to the engine working points so a test procedure must incorporate a working cycle to be performed during the homologation test within a certain tolerance in term of speed and loads and the emissions limit considering the cycle designed. During last years all major legislators Europe, US EPA, US CARB, Japan and China defined rules to have in next future convergences in term of homologation procedures, cycles and limits.

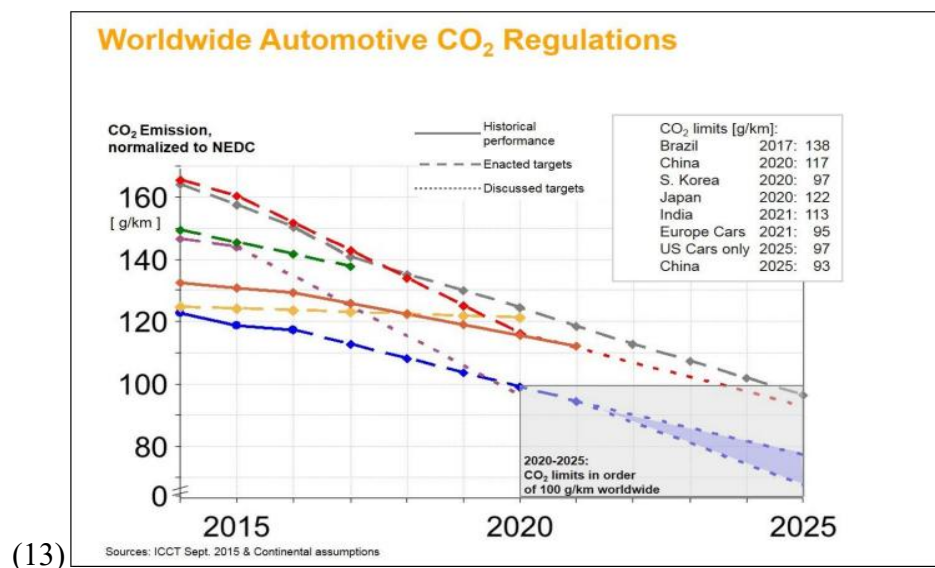
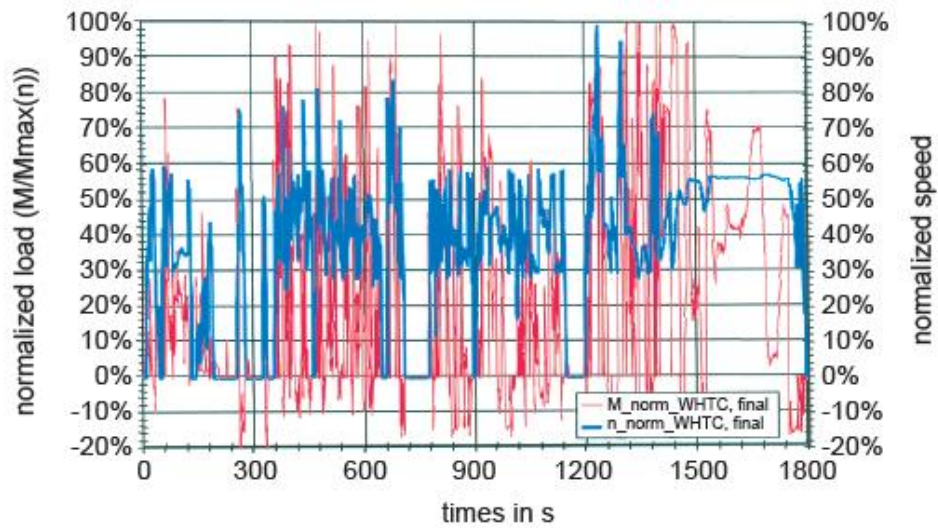


Figure 87. CO₂ emissions trends over the years

For what concerns heavy duty homologation procedures EURO VI and China VI are equivalent in term of cycles and procedures, for this reason the details of the procedures will be referred to the European regulations.

Heavy Duty homologation procedure implies three types of steps at the engine test bench.

- WHTC '*World Heavy Duty transient cycle*' is a sequence of normalized speed and load values.

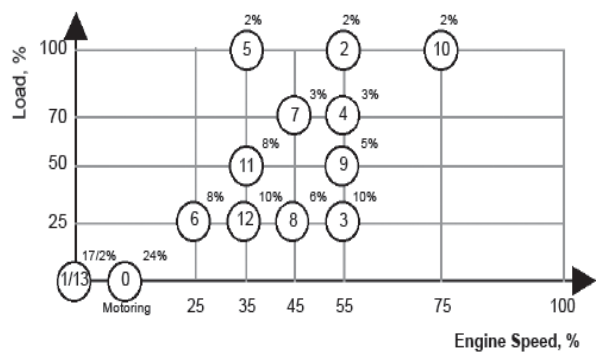


(14)

Figure 88.WHTC

- WHSC 'World Heavy Duty stationary Cycle' is a sequence of speed and loads typical of the working conditions of the HDVs.

Mode	Normalized Speed [%]	Normalized Torque [%]	Mode Length [s] incl. 20 s Ramp
1	0	0	210
2	55	100	50
3	55	25	250
4	55	70	75
5	35	100	50
6	25	25	200
7	45	70	75
8	45	25	150
9	55	50	125
10	75	100	50
11	35	50	200
12	35	25	250
13	0	0	210
Sum			1,895



(14)

Figure 89.WHSC operating points

	CO	THC	NMHC	CH ₄	NO _x ¹	NH ₃	PM Mass	PM ² Number
	mg/kWh					ppm	mg/kWh	#/kWh
WHSC (C.I.)	1,500	130			400	10	10	8.0 x 10 ¹¹
WHTC (C.I.)	4,000	160			460	10	10	6.0 x 10 ¹¹
WHTC (P.I.)	4,000		160	500	460	10	10	³

¹ Admissible level of NO_x may be defined later

² Measurement procedure to be introduced at a later date

³ Particle number limit and date of implementation not confirmed yet

(14)

Table 13.WHSC AND WHTC emission limits

- WNTE '*World Harmonized Not To Exceed Cycle*' is a sequence of 15 points chosen on the engine map belonging to three different grids in which the maps is divided. The three grid cells to be tested, the fifteen operating points, the order of testing of the grids and operating points shall be decided by the Type Approval or Certification Authority with a random procedure.

Test	CO (mg/kWh)	THC (mg/kWh)	NO _x (mg/kWh)	PM (mg/kWh)
WNTE	2000	220	600	16

(15)

Table 14.WNTE emission limits¹⁸

- Additional steps is the PEMS '*portable emission measurement system*' measurement, OBD testing, Cop testing '*Conformity of Production*', Durability testing.

For what concerns China VI here are synthesized major differences respect EURO VI

¹⁸ limits are related to PEMS emissions with a conformity factor of 1,5.

		China VI	Euro VI
Implementation year		2020 for China VI-a 2023 for China VI-b	2014
Vehicle tested		Type test, new production and in-use	Type approval and in-use
Mandated test frequency		18 months with minimum of 10,000km and then every two years	18 months with minimum of 25,000km and then every two years
Emission limits for diesel	NO _x	0.69 g/kWh (CF=1.5)	0.69 g/kWh (CF=1.5)
	PN	No limit for China VI-a 1.2x10 ¹² #/kWh for China VI-b (CF=2.0)	No
	CO	6 g/kWh (CF=1.5)	6 g/kWh (CF=1.5)
Cold start included		No	No
Driving shares (% of time duration)	Urban	20%-70%	20%-70%
	Rural	25%-33%	25%-33%
	Motorway	0%-55%	0%-55%
Test length		4x-7x work of WHTC	5x work of WHTC (4x-7x work of WHTC beginning 2018)
Payload		China VI-a: 50%-100% China VI-b: 10%-100%	50%-100% (10%-100% beginning 2018)
Ambient temperature		-7 °C - 38 °C	-7 °C - 38 °C
Altitude		<1,700 m in China VI-a <2,400 m in China VI-b	<1,700 m
Minimum power threshold		10%	15% (10% beginning 2018)
Data evaluation method		Work-based window method	Work-based window method or CO ₂ -based window method

(15)

Table 15. China VI and EURO VI summary table

Main Matlab codes used for the post processing

Chemical model developed with oxidation

```
function[NH3_react_banco_trans_chim,NH3_oxi_media,fac_stoich_NOxtoNH3_add_
_media]=NH3_react_chim_oxi(NOx_banco_1,NOx_banco_2,NO2_NOx_ratio,exhaust_
gas_1,time_1,time_2,O2_media)

NO2=NO2_NOx_ratio*(NOx_banco_1-NOx_banco_2);%ppm
NO=(NOx_banco_1-NOx_banco_2)-NO2;%ppm
NO2_1=NO2*exhaust_gas_1*46/29/3600*(time_1-time_2);%mg
NO_1=NO*exhaust_gas_1*30/29/3600*(time_1-time_2);%mg

NH3_case2=0;
NH3_case3=0;
O2_case2=0;

%case1 2NH3+NO+NO2
NO2_case1=floor(NO2_1/1.35)*1.35/1000;%g
NO_case1=floor(NO2_1/1.35)*0.88/1000;%g
NH3_case1=floor(NO2_1/1.35)/1000;%g

%case2 4NO+4NH3+O2
if (NO_1/1000-NO_case1)>0
NH3_case2=(NO_1/1000-NO_case1)*0.56;
O2_case2=NH3_case2*0.47;
end

%case3 8NH3+6NO2
if (NO2_1/1000-NO2_case1)>0
NH3_case3=(NO2_1/1000-NO2_case1)*0.49;
end

NH3_react_banco_trans_chim=abs(NH3_case1+NH3_case2+NH3_case3);

%NH3oxi 4NH3+3O2
O2_med=O2_media/100*exhaust_gas_1*32/29/3600*(time_1-time_2)*1000;%g
NH3_oxi_media=(O2_med-O2_case2)*0.708;

fac_stoich_NOxtoNH3_add_media=NH3_oxi_media/(NO2_1+NO_1)/1000;
end
```

Loop part of the code for the NH3 equilibrium calculation

```
for b=2:length(time_12)

NO2_NOx_ratio(b)=interpolazione_piano_quotato(rpm_1(b),mep_1(b),NO2_NOx_matrix,X,Y);
    eff_banco(b)=1-NOx_banco_2(b)/NOx_banco_1(b);
    eff_vehicle(b)=1-NOx_vehicle_2(b)/NOx_vehicle_1(b);
    NH3_eff(b)=NH3_1(b)*17/29*exhaust_gas_1(b)/1000*((time_12(b)-time_12(b-1))/3600);%g

NH3_vehicle_eff(b)=NH3_vehicle_1(b)*17/29*exhaust_gas_1(b)/1000*((time_12(b)-time_12(b-1))/3600);%g
    NH3_react_banco_trans(b)=(NOx_banco_1(b)-NOx_banco_2(b))*46/29*exhaust_gas_1(b)/1000*((time_12(b)-time_12(b-1))/3600)*fac_stoich_NOxtoNH3;%g
    NH3_oxi_customer(b)=...

NH3_ratio(b)=NH3_oxi_customer(b)/(UDC_des_1(b)/1000/5.425*(time_12(b)-time_12(b-1)));

    NH3_load_banco_trans(b)=UDC_des_1(b)/1000/5.425*(time_12(b)-time_12(b-1))-NH3_react_banco_trans(b)-NH3_vehicle_eff(b)-NH3_oxi_customer(b);%g

NH3_react_banco_trans_chim(b)=NH3_react_chim_copia(NOx_banco_1(b),NOx_banco_2(b),NO2_NOx_ratio(b),exhaust_gas_1(b),time_12(b),time_12(b-1));
    NH3_load_banco_trans_chim(b)=UDC_des_1(b)/1000/5.425*(time_12(b)-time_12(b-1))-NH3_react_banco_trans_chim(b)-NH3_vehicle_eff(b)-NH3_oxi_customer(b);
    NH3_react_vehicle_trans(b)=(NOx_vehicle_1(b)-NOx_vehicle_2(b))*46/29*exhaust_gas_1(b)/1000*((time_12(b)-time_12(b-1))/3600)*fac_stoich_NOxtoNH3;
    NH3_load_vehicle_trans(b)=UDC_des_1(b)/5.425/1000*(time_12(b)-time_12(b-1))-NH3_react_vehicle_trans(b)-NH3_vehicle_eff(b);

    NH3_load_banco(b)=NH3_load_banco(b-1)+NH3_load_banco_trans(b);
    NH3_load_banco_chim(b)=NH3_load_banco_chim(b-1)+NH3_load_banco_trans_chim(b);
    NH3_load_vehicle(b)=NH3_load_vehicle(b-1)+NH3_load_vehicle_trans(b);
    NH3_load_banco_diff(b)=(NH3_load_banco(b)-NH3_load_banco(b-1))/(time_12(b)-time_12(b-1));

    alpha_banco(b)=(mean(UDC_des_1(1:b-1))/1000/5.425)/(mean(NOx_banco_1(1:b-1))*46/29.*exhaust_gas_1(1:b-1)/1000/3600)*fac_stoich_NOxtoNH3);
    alpha_banco_chim(b)=(mean(UDC_des_1(1:b-1))/1000/5.425)/mean(NH3_react_banco_trans_chim(1:b-1));
    alpha_vehicle(b)=(mean(UDC_des_1(1:b-1))/1000/5.425)/(mean(NOx_vehicle_1(1:b-1))*46/29.*exhaust_gas_1(1:b-1)/1000/3600)*fac_stoich_NOxtoNH3);

    NH3_alpha(b)=(alpha_banco(b)-1)*NH3_react_vehicle_trans(b);
    NH3_rosso(b)=NH3_alpha(b)-NH3_vehicle_eff(b);

end
```


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