



Grant Agreement No.: 955413

Project acronym: ENGIMMONIA

Project title: Sustainable technologies for future long distance shipping towards complete decarbonisation

Call (part) identifier: H2020-EU.3.4. - Smart, Green And Integrated Transport

Thematic Priority: LC-MG-1-13-2020 - Decarbonising long distance shipping

Starting date of project: 1st May, 2021

Duration: 48 months



WP4 – “Development of the exhaust aftertreatment system (EATS) for the ammonia engine”

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

Due date of deliverable

30 April 2024

Actual submission date

24 May 2024

Deliverable version

1.0

Organisation name of lead contractor for this deliverable: AUTH

Dissemination Level	
CO	Confidential
PU	Public

Executive Summary

This deliverable was prepared within the framework of Work Package 4, entitled ‘Development of the exhaust aftertreatment system (EATS) for the ammonia engine’ and it corresponds to Task 4.1 (T4.1).

The objective of this deliverable is to describe the approach followed for modelling the processes that take place in the catalytic devices installed in the exhaust line of the ammonia dual-fuel (DF) engine. The main target of the exhaust aftertreatment system (EATS) of the ammonia engine is the control of the N-species, i.e., NO_x (nitrogen oxides), N₂O (nitrous oxide) and NH₃ (ammonia). The first species, NO_x, is a by-product of fuel (ammonia) combustion with air and is formed in the cylinder. The second species, N₂O, originates from two sources: ammonia combustion in the cylinder and formation in the catalytic devices depending strongly on their exact formulation. Finally, NH₃ can be emitted as a result of incomplete in-cylinder combustion and untreated amounts of dosed NH₃ quantities for the EATS operation. The EATS of the NH₃ DF engine is expected to comprise a deNO_x catalyst and, if necessary additional deN₂O and/or NH₃-slip catalysts.

The first step for the development of the EATS of the NH₃ engine is the experimental investigation of the catalytic activity of small-scale samples of V-SCR, Cu-SCR, Pt-based oxidation catalyst and Fe-SCR. The test campaign provides useful insight concerning the reactions taking place in each catalytic device, supporting the adoption and/or modification of the appropriate reaction scheme to be incorporated in the simulation models. Based on the test observations, the chemical reaction scheme for the V-SCR and Cu-SCR systems consisted of the commonly used SCR reactions (standard/literature model). On the other hand, in the case of the Fe-SCR catalyst, particular modifications of the chemical reaction scheme were necessary in order to accurately describe the occurring processes (Engimmonia model). These modifications were:

- modification of the Standard SCR reaction stoichiometry,
- inhibition of the modified Standard SCR reaction by NH₃ at high NH₃ inlet concentrations and low temperatures (inhibition term added to the reaction rate),
- promotion of NH₃ oxidation to N₂ in the presence of N₂O (promotion term added to the reaction rate),
- addition of the typical Standard SCR with N₂O both in the reactants and products,
- inhibition of the direct N₂O reduction by NH₃ at high inlet concentrations of NH₃ (inhibition term is added to the reaction rate).

The adoption of the appropriate chemical reaction scheme resulted in the development of accurate simulation models, capable of describing the phenomena occurring in the catalytic devices. This was particularly critical for the Fe-SCR, where processes and phenomena further to the well-known ones were observed. Indicatively, the following diagram presents the experimental and model results of N₂O conversion for various NH₃ inlet concentrations, where introduction of an inhibition term is critical for the model fit to the experimental data.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

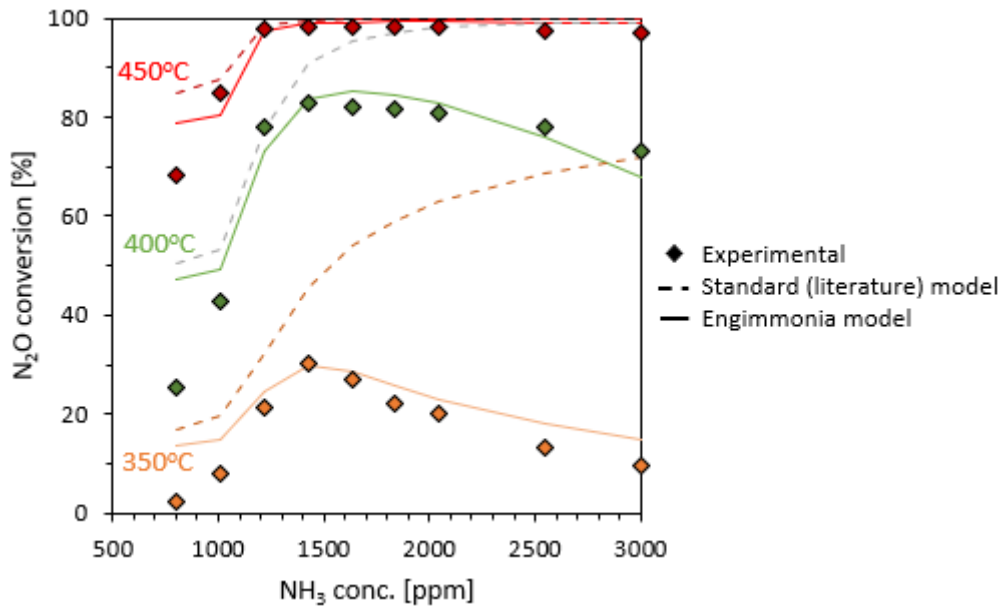


Figure 1. N₂O conversion at the Fe-SCR under various NH₃ inlet concentrations, based on the experimental data (symbols) and the model (solid and dashed lines) before and after the modifications on the reaction scheme.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

Table of Contents

Executive Summary	2
1. Introduction	7
2. Modelling of catalytic processes in the flue gas of ammonia dual-fuel engine	9
2.1 Catalytic processes in the Vanadium-based SCR.....	9
2.1.1 Test Protocols	9
2.1.2 Reaction scheme.....	10
2.1.3 Model setup and calibration	10
2.2 Catalytic processes in the Copper-based SCR.....	14
2.2.1 Test protocols	14
2.2.2 Reaction scheme.....	15
2.2.3 Model setup and calibration	15
2.3 Catalytic processes in the Platinum-based oxidation catalyst.....	19
2.3.1 Test Protocols	19
2.3.2 Reaction scheme.....	20
2.3.3 Model setup and calibration	20
2.4 Catalytic processes in the Iron-based SCR	22
2.4.1 Test Protocols	22
2.4.2 Reaction scheme.....	23
2.4.3 Model setup and calibration	23
3. Conclusion and Future Plans	33
4. References	34

List of Figures

Figure 1. Small-scale experimental set-up of synthetic gas bench (SGB).	8
Figure 2. Vanadium-based SCR catalyst sample.	9
Figure 3. Comparison of the experimental data (symbols) and the model (solid lines) of (a) NO oxidation (Feed gas: 2000 ppm NO, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance) and (b) NH ₃ oxidation (Feed gas: 1000 ppm NH ₃ , 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance) at the outlet of the V-SCR catalyst.	11
Figure 4. NO _x conversion, NH ₃ slip and N ₂ O formation at the outlet of the V-SCR catalyst under Standard SCR conditions with various NH ₃ /NO _x ratios, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH ₃ /NO _x =0.8, 1.0, 1.5, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance).....	12
Figure 5. NO _x conversion, NH ₃ slip and N ₂ O formation at the outlet of the V-SCR catalyst under Fast SCR conditions, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO _x , NO ₂ /NO _x =0.2, NH ₃ /NO _x =1.0, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance).	13
Figure 6. N ₂ O concentrations at the outlet of the V-SCR catalyst under Standard SCR conditions, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH ₃ /NO _x =1.0, N ₂ O=50, 100, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance).....	14
Figure 7. Copper-based SCR catalyst sample.	14
Figure 8. Comparison of the experimental data (symbols) and the model (solid lines) of (a) NO oxidation ((Feed gas: 2000 ppm NO, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance)) and (b) NH ₃ oxidation (Feed gas: 1000 ppm NH ₃ , 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance), at the outlet of the Cu-SCR catalyst.	16
Figure 9. NO _x conversion, NH ₃ slip and N ₂ O formation at the outlet of the Cu-SCR catalyst under Standard SCR conditions with NH ₃ /NO _x =0.8, 1.0, 1.5, based on the experimental data (symbols) and the model (solid lines).	17
Figure 10. NO _x conversion, NH ₃ slip and N ₂ O formation at the outlet of the Cu-SCR catalyst under Standard SCR conditions with NH ₃ /NO _x =1.0, and NO ₂ /NO _x =0.0; and Fast SCR conditions with	



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

NH ₃ /NO _x =1.0, and NO ₂ /NO _x =0.2, based on the experimental data (symbols) and the model (solid lines).	18
Figure 11. N ₂ O concentrations at the outlet of the Cu-SCR catalyst under Standard SCR conditions, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH ₃ /NO _x =1.0, N ₂ O=50, 100, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance).	19
Figure 12. Platinum-based oxidation catalyst sample.	19
Figure 13. Comparison of the NH ₃ , NO, NO ₂ and N ₂ O outlet concentrations for NH ₃ at the outlet of the Pt-based oxidation catalyst based on the experimental (symbols) and the model (solid lines).	21
Figure 14. Reaction rates of the Pt-based oxidation catalyst as a function of the catalyst temperature.	21
Figure 15. Iron-based SCR catalyst sample.	22
Figure 16. Comparison of the experimental data (symbols) and the model (solid lines) of (a) NO oxidation ((Feed gas: 1000 ppm NO, 10% O ₂ , 15% H ₂ O, N ₂ balance)) and (b) NH ₃ oxidation (Feed gas: 1000 ppm NH ₃ , 10% O ₂ , 15% H ₂ O, N ₂ balance), at the outlet of the Fe-SCR catalyst.	24
Figure 17. NO _x and NH ₃ conversion at the Fe-SCR catalyst under standard SCR conditions, based on the experimental data (symbols) and the model (solid lines, Engimmonia model) (Feed gas: 1000 ppm NO, NH ₃ /NO _x =1.0, 10% O ₂ , 15% H ₂ O, N ₂ balance).	25
Figure 18. NO _x conversion (a) under various ANR ratios including the inhibition term and (b) under ANR=3.0 with and without the inhibition term, at the outlet of the Fe-SCR catalyst, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 1000 ppm NO, NH ₃ /NO _x =0.7, 1.0, 3.0, 10% O ₂ , 15% H ₂ O, N ₂ balance).	26
Figure 19. NH ₃ slip and N ₂ O formation at the outlet of the Fe-SCR catalyst under Standard SCR conditions with NH ₃ /NO _x =0.7, 1.0, 3.0, based on the experimental data (symbols) and the model (solid lines).	26
Figure 20. NO _x conversion, NH ₃ slip and N ₂ O formation at the outlet of the Fe-SCR catalyst under Fast SCR conditions, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 1000 ppm NO _x , NO ₂ /NO _x =0.2, NH ₃ /NO _x =1.0, 10% O ₂ , 15% H ₂ O, N ₂ balance).	27
Figure 21. N ₂ O thermal decomposition at the outlet of the Fe-SCR catalyst, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 200 ppm N ₂ O, 15% H ₂ O).	28
Figure 22. N ₂ O reduction by NH ₃ at the Fe-SCR catalyst: (a) N ₂ O and NH ₃ conversion including the promotion term and (b) NH ₃ oxidation reaction rate with and without N ₂ O, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 200 ppm NH ₃ , 200 ppm N ₂ O, 10% O ₂ , 15% H ₂ O, N ₂ balance).	29
Figure 23. SCR reactivity in the presence of N ₂ O at the Fe-SCR catalyst: (a) NO _x and NH ₃ conversion including the Standard SCR + N ₂ O, and (b) reaction rates of the Standard SCR + N ₂ O and modified SCR in the presence of N ₂ O, and the modified SCR in the absence of N ₂ O, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 1000 ppm NO, NH ₃ /NO _x =1.0, 100 ppm N ₂ O, 10% O ₂ , 15% H ₂ O, N ₂ balance).	29
Figure 24. NO _x conversion, NH ₃ slip and N ₂ O conversion at the outlet of the Fe-SCR catalyst under Standard SCR conditions with NH ₃ /NO _x =0.8, 1.0, 1.2, 1.4, and N ₂ O inlet concentration, based on the experimental data (symbols) and the Engimmonia model (solid lines), (Feed gas: 1000 ppm NO, NH ₃ /NO _x =0.8*, 1.0, 1.2, 1.4, N ₂ O=100, 200* ppm, 10% O ₂ , 15% H ₂ O, N ₂ balance).	30
Figure 25. N ₂ O conversion, NO _x conversion and NH ₃ slip including the inhibition, at the outlet of the Fe-SCR catalyst under various NH ₃ inlet concentrations, based on the experimental data (symbols) and the Engimmonia model (solid lines), (Feed gas: 1000 ppm NO, variable NH ₃ , 100 ppm N ₂ O, 10% O ₂ , 15% H ₂ O, N ₂ balance).	31
Figure 26. N ₂ O conversion with and without the inhibition, at the outlet of the Fe-SCR catalyst under various NH ₃ inlet concentrations, based on the standard/literature model (dashed line) and the Engimmonia model (solid line), (Feed gas: 1000 ppm NO, variable NH ₃ , 100 ppm N ₂ O, 10% O ₂ , 15% H ₂ O, N ₂ balance).	32



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

Abbreviations and acronyms

ANR	NH ₃ to NO _x ratio
H ₂ O	Water
NH ₃	Ammonia
NNR	NO ₂ to NO _x ratio
NO / NO ₂ / NO _x	Nitric Oxide / Nitrogen Dioxide / Nitrogen Oxides
N ₂	Nitrogen
N ₂ O	Nitrous Oxide
O ₂	Oxygen
SCR	Selective Catalytic Reduction
SO ₂	Sulphur Dioxide

Nomenclature

A. Latin letters		
<i>A</i>	frequency factor (Arrhenius constant)	–
<i>C</i>	concentration	<i>mol/m³</i>
<i>E</i>	activation energy of reaction	<i>J/mol</i>
<i>k</i>	kinetic constant of reaction (Arrhenius)	units depend on reaction
<i>R</i>	Universal exhaust gas mixture constant	<i>J/(mol · K)</i>
<i>R_r</i>	Reaction rate	<i>mol/(m³ · s)</i>
<i>T</i>	temperature	<i>K</i>

B. Greek letters		
θ_{NH_3}	surface coverage of NH ₃	–
Ψ_S	storage capacity of storage site	<i>mol/m³</i>
ψ_{SNH_3}	surface coverage fraction of NH ₃	–

C. Subscripts and Superscripts	
<i>ads</i>	adsorption
<i>des</i>	desorption



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

1. Introduction

This deliverable was prepared within the framework of Work Package 4, entitled ‘Development of the exhaust aftertreatment system (EATS) for the ammonia engine’ and it corresponds to Task 4.1 (T4.1).

The objective of this deliverable is to describe the approach followed for modelling the processes that take place in the catalytic devices installed in the exhaust line of the ammonia dual-fuel (DF) engine. The main target of the exhaust aftertreatment system (EATS) of the ammonia engine is the control of the N-species, i.e., NO_x (nitrogen oxides), N₂O (nitrous oxide) and NH₃ (ammonia). The first species, NO_x, is a by-product of fuel (ammonia) combustion with air and is formed in the cylinder. The second species, N₂O, originates from two sources: ammonia combustion in the cylinder and formation in the catalytic devices depending strongly on their exact formulation. Finally, NH₃ can be emitted as a result of incomplete in-cylinder combustion and untreated amounts of dosed NH₃ quantities for the deNO_x system operation.

The EATS of the NH₃ DF engine is expected to comprise a deNO_x catalyst and, if necessary, additional deN₂O and/or NH₃-slip catalysts. The initial development of the individual devices, as well as of the complete EATS, is heavily based on small-scale testing and modelling. The design of emission control devices via full-scale testing is prohibitive in view of the huge testing costs on a large two-stroke marine engine. It is therefore necessary to develop accurate and predictive models of the aftertreatment system that will be applicable in a wide range of conditions to ensure the coverage of all possible scenarios to be expected in a real NH₃ engine exhaust.

In this context, the developed simulation models will support the improvement of existing SCR systems when these are operating with the flue gas of either diesel or ammonia fuelled engine (Task 4.2), while they will be also used for the design and evaluation of the deN₂O system that will be developed in Tasks 4.3 to 4.6. The accurate development of the models for both systems will be supported by test data from the respective experimental activities conducted within WP4, with appropriate input received from WP3.

In order to determine accurately and confirm the exact reaction scheme that is used in the model for each catalytic device, targeted tests were conducted in the Synthetic Gas Bench (SGB) of AUTH. This small-scale testing features full control of the feed gas able to replicate the time-resolved real exhaust gas conditions (flow, temperature, composition) on the one hand, while on the other hand permits the isolation of individual phenomena and reactions by modifying accordingly the feed gas composition.

The catalytic activity of the examined samples is evaluated with small-scale tests on the SGB, indicative pictures of which are presented in Figure 1. The flow and composition of the mixture is controlled by the programmable mass flow controllers (MFCs). Moisture can be added to the mixture through an H₂O feed, which is heated beforehand to prevent condensation of the flue gas. The mixture is then heated to the required temperature through a pre-heater system before passing through the catalyst sample. A FTIR gas analyser (AVL Sesam i60) measures the concentrations of all species in the outlet gas. The targeted experiments performed for each catalytic technology are described in the respective sections in Chapter 2.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”



Figure 1. Small-scale experimental set-up of synthetic gas bench (SGB).

The kinetic mechanisms of the catalytic samples are then implemented into models of the *Exothermia Suite*® simulation platform (described in D2.1). The kinetic parameters of the reaction rates are calibrated in order to match model with measurement results. In particular, the pre-exponential factor (A) and activation energy (E) of the Arrhenius term (k) of the reaction rate are calibrated:

$$k = A \cdot \exp\left(-\frac{E}{R \cdot T}\right) \quad (1)$$

The main part of this deliverable is Chapter 2: Modelling of catalytic processes in the flue gas of ammonia dual-fuel engine, which is structured as follows:

- Section 2.1: Catalytic processes in the Vanadium (V)-based SCR system
- Section 2.2: Catalytic processes in the Copper (Cu)-based SCR system
- Section 2.3: Catalytic processes in the Platinum (Pt)-based oxidation catalyst
- Section 2.4: Catalytic processes in the Iron (Fe)-based SCR system

Each section follows the same structure: initially the test conditions are briefly described, then the reaction scheme is presented and finally the model setup and calibration are shown. It is noted that the definition of the final reaction scheme was a repetitive process during the setup and calibration of the model, aiming at replicating the behaviour observed in the tests.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

2. Modelling of catalytic processes in the flue gas of ammonia dual-fuel engine

2.1 Catalytic processes in the Vanadium-based SCR

2.1.1 Test Protocols

The Vanadium-Based SCR (V-SCR) catalyst sample (Figure 2) was provided by ECOSPRAY, and the properties of the catalyst are summarized in Table 1.



Figure 2. Vanadium-based SCR catalyst sample.

Table 1. Properties of the Vanadium-based SCR catalyst.

Catalyst Properties	Value
Diameter [mm]	28
Length [mm]	90
CPSI [-]	100
Wall thickness [mils]	2
Cell shape [-]	triangle
Substrate material [-]	metal

For the V-SCR, steady-state measurements were performed in a temperature range between 150°C and 500°C. The feed gas and test conditions are shown in Table 2. The phenomena of NO and NH₃ oxidation are examined first, followed by measurements concerning the investigation of the SCR reactions under different conditions, such as various ANRs (NH₃/NO_x), the composition of NO_x (addition of NO₂) and the addition of N₂O in the feed gas to examine possible deN₂O activity of the current catalytic technology.

Table 2. Vanadium-based SCR catalyst test conditions.

Phenomena	Inlet feed gas	Temperature [°C]	Space Velocity [h ⁻¹]
NO oxidation to NO ₂	2000 ppm NO, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance	150 200	20,000
NH ₃ oxidation	1000 ppm NH ₃ , 6% O ₂ , 15 % H ₂ O, 15 ppm SO ₂ , N ₂ balance		
Standard SCR under ANR ratios	2000 ppm NH ₃ , NH ₃ /NO _x =0.8, 1.0, 1.5, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance	250	
		300	
Fast SCR	2000 ppm NH ₃ , 2000 ppm NO _x (NO ₂ /NO _x =0.2), 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance	400	
		500	



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

Addition of N ₂ O	2000 ppm NH ₃ , NH ₃ /NO _x =1.0, N ₂ O=50, 100 ppm, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance		
------------------------------	---	--	--

2.1.2 Reaction scheme

To describe the SCR reactivity over the V-SCR catalyst, commonly used SCR reactions are adopted [1,2], as listed in Table 3. The Standard, Fast and NO₂-SCR reactions are considered principal between NO_x and NH₃ (depending on NNR (NO₂/NO_x)). While NH₃ is primarily oxidized to N₂, NH₃ oxidation reactions to NO and N₂O are also considered. The formation of N₂O has also been attributed to the oxidation of NH₃ and NO [3], as well as the direct reaction between NH₃ and NO₂ [4,5].

Table 3. Vanadium-based SCR catalyst reaction scheme.

Type	Reaction	Reaction Rate
NH ₃ storage/release	NH ₃ ↔ NH ₃ *	$R_{ads} = k_{ads} \cdot [NH_3] \cdot (1 - \theta_{NH_3})$ $R_{des} = k_{des} \cdot \theta_{NH_3}$
Standard SCR	$4 NH_3^* + 4 NO + O_2 \rightarrow 4 N_2 + 6 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot C_{O_2}$
Fast SCR	$4 NH_3^* + 2 NO + 2 NO_2 \rightarrow 4 N_2 + 6 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot C_{NO_2}$
NO ₂ -SCR	$NH_3^* + 3/4 NO_2 \rightarrow 7/8 N_2 + 3/2 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot C_{NO_2}$
NO oxidation to NO ₂	$NO + 1/2 O_2 \leftrightarrow NO_2$	$R_r = k \cdot C_{NO} \cdot C_{O_2}$
NH ₃ oxidation to N ₂ , NO and N ₂ O	$4 NH_3^* + 5 O_2 \rightarrow 4 NO + 5 H_2O$ $2 NH_3^* + 3/2 O_2 \rightarrow N_2 + 3 H_2O$ $4 NH_3^* + 4 O_2 \rightarrow 2 N_2O + 6 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{O_2}$ $R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot (C_{O_2}^{0.3})$ $R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{O_2}$
N ₂ O formation during SCR	$2 NH_3^* + 2 NO + O_2 \rightarrow N_2 + N_2O + 3 H_2O$ $4 NH_3^* + 4 NO_2 \rightarrow 2 N_2O + 6 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot (C_{O_2}^{0.2})$ $R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO_2}$

*Stored on the catalytic sites

2.1.3 Model setup and calibration

The reaction kinetic parameters of the V-SCR catalyst are calibrated to fit the experimental determined NO_x, NH₃ and N₂O concentrations.

The results of the NO and NH₃ oxidation tests are presented in Figure 3. Oxidation of NO to NO₂ is hardly detected even at high temperatures (Figure 3a). NH₃ is mainly oxidized to N₂ above 300°C and is almost fully oxidized at 500°C (Figure 3b). The same figures include the simulation model results after fitting the kinetic parameters. The model achieves a good agreement with the test results in the whole temperature range.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

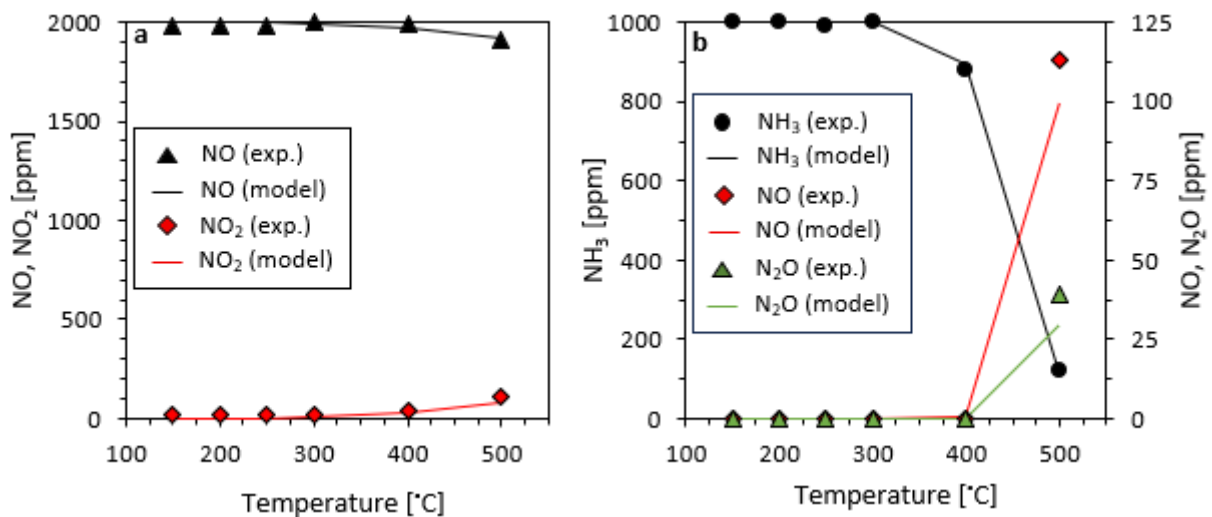


Figure 3. Comparison of the experimental data (symbols) and the model (solid lines) of (a) NO oxidation (Feed gas: 2000 ppm NO, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance) and (b) NH₃ oxidation (Feed gas: 1000 ppm NH₃, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance) at the outlet of the V-SCR catalyst.

The outcome of the SCR activity presented in Figure 4 shows that the catalyst exceeds 80% NO_x conversion above 300°C. In addition, the SCR process is highly dependent on the amount of NH₃ in the feed gas. When ANR is greater than 1, NO_x is almost fully converted at high temperatures, although this leads to unreacted NH₃. When ANR is less than 1, only partial NO_x conversion is achieved as expected from the reaction stoichiometry of the Standard SCR reaction ($4 \text{ NH}_3 + 4 \text{ NO} + \text{O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}$). As NO₂ is not present in the feed gas, the Standard SCR is the dominant reaction and is calibrated to the test results for both NO_x and NH₃ outlet concentrations. Concerning N₂O, low selectivity (below 20 ppm) is observed in all conditions with a significant increase at 500°C. The kinetic parameters of the simultaneous NH₃ and NO oxidation ($2 \text{ NH}_3 + 2 \text{ NO} + \text{O}_2 \rightarrow \text{N}_2 + \text{N}_2\text{O} + 3 \text{ H}_2\text{O}$) are calibrated to fit the N₂O formation trend.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

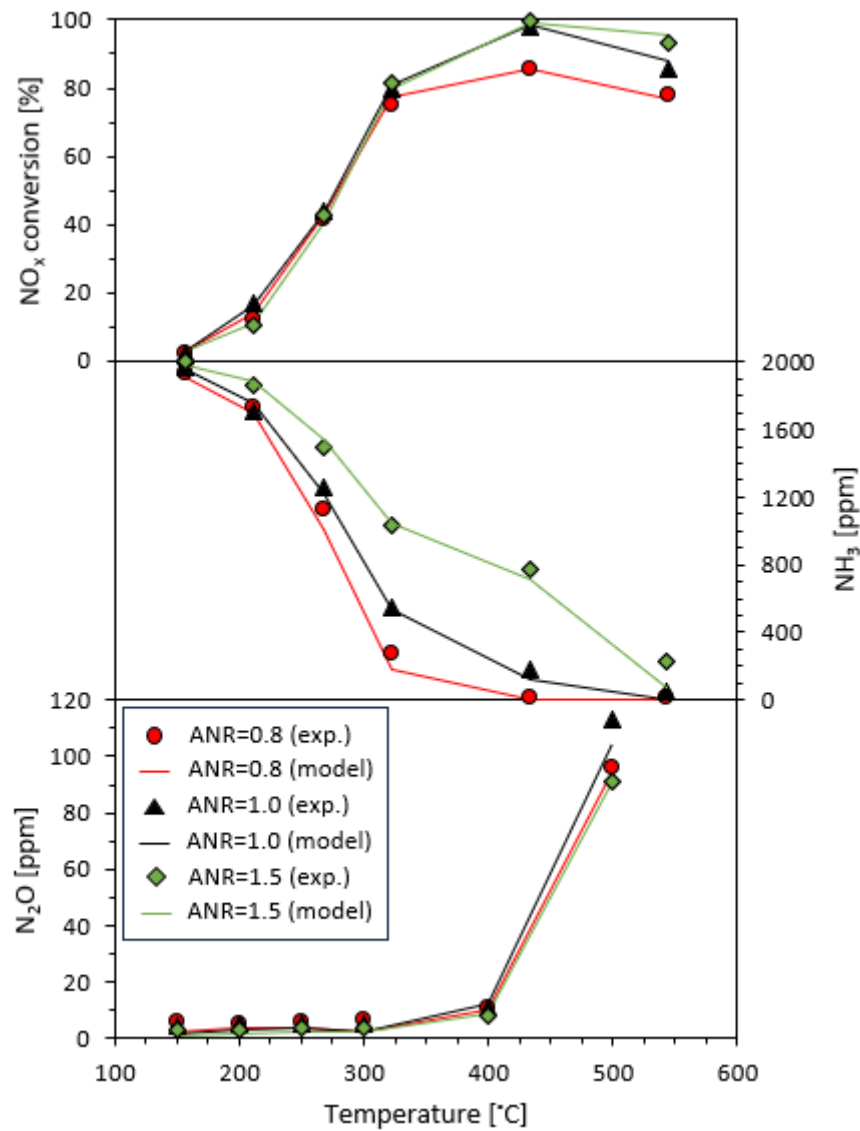


Figure 4. NO_x conversion, NH₃ slip and N₂O formation at the outlet of the V-SCR catalyst under Standard SCR conditions with various NH₃/NO_x ratios, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH₃/NO_x=0.8, 1.0, 1.5, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance).

Addition of NO₂ in the feed gas (Figure 5) enhances NO_x conversion, especially at low temperatures. Except from the Standard SCR, the Fast SCR reaction ($4 \text{ NH}_3^* + 2 \text{ NO} + 2 \text{ NO}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}$) is activated increasing the total NO_x reduction between 150°C and 300°C. N₂O formation is now attributed to both the simultaneous NH₃ and NO oxidation, and the direct reaction of NO₂ with NH₃ ($4 \text{ NH}_3^* + 4 \text{ NO}_2 \rightarrow 2 \text{ N}_2 + 2 \text{ N}_2\text{O} + 6 \text{ H}_2\text{O}$). The additional reactions are calibrated to fit the experimental data.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

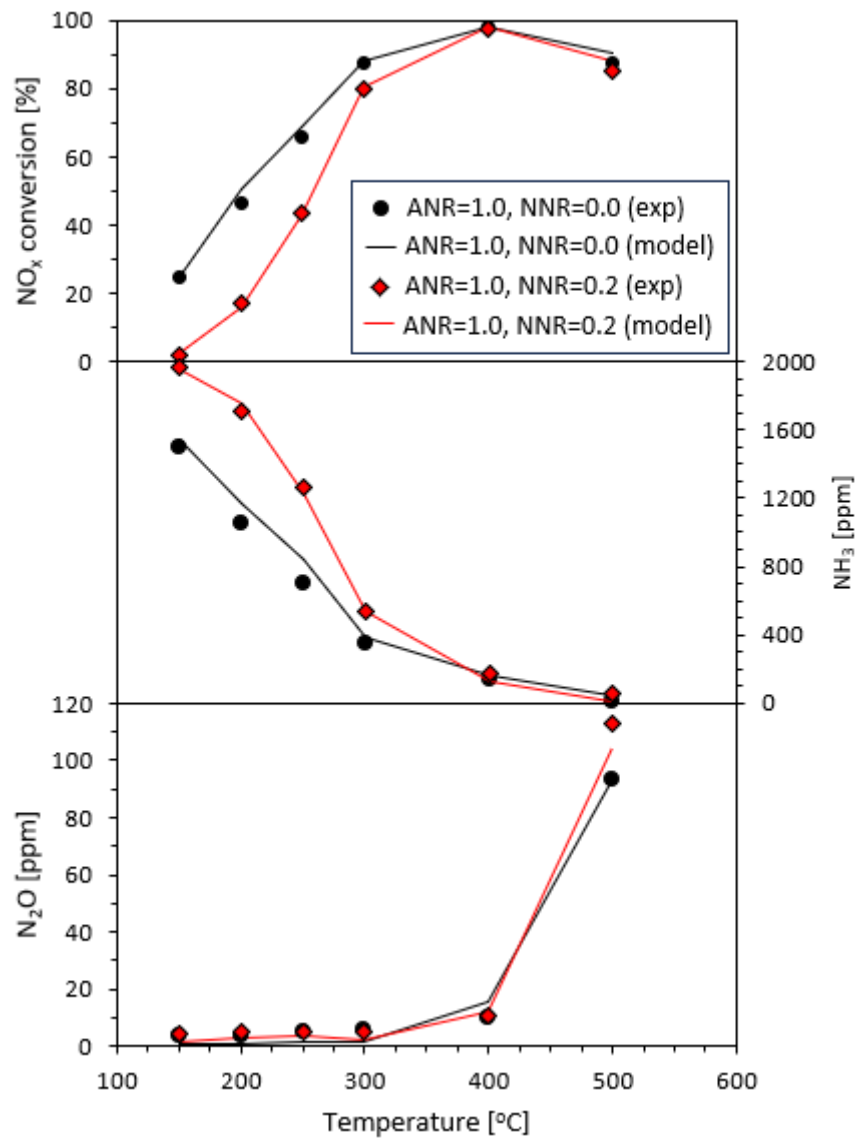


Figure 5. NO_x conversion, NH₃ slip and N₂O formation at the outlet of the V-SCR catalyst under Fast SCR conditions (compared to the Standard SCR conditions), based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO_x, NO₂/NO_x=0.2, NH₃/NO_x=1.0, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance).

In order to examine the possible reduction of N₂O along the V-SCR catalyst, N₂O was added to the feed gas (see Table 2). The results of this addition are presented in Figure 6. It is obvious that N₂O passes unreacted through the catalyst as its selectivity (Figure 6a) is not affected when it is present also in the feed gas, and only N₂O formation pathways are activated; hence the calibrated reaction scheme is able to predict the outlet N₂O levels and does not need any modifications (Figure 6).



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

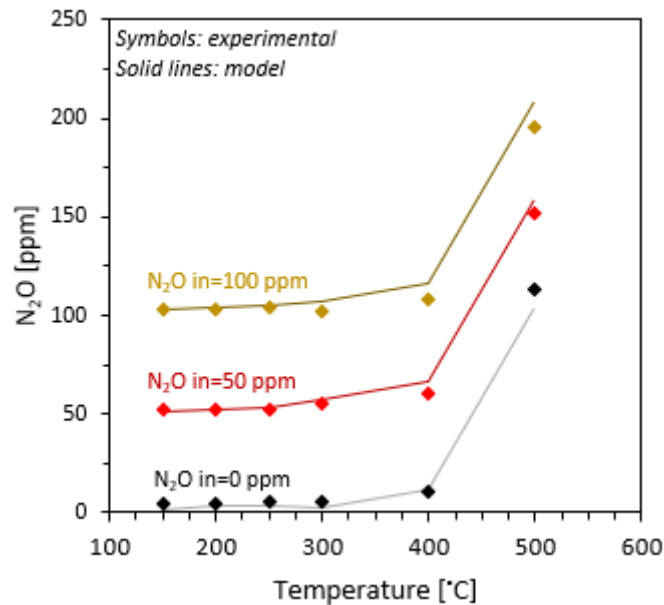


Figure 6. N₂O concentrations at the outlet of the V-SCR catalyst under Standard SCR conditions and various N₂O inlet concentrations, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH₃/NO_x=1.0, N₂O=50, 100, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance).

2.2 Catalytic processes in the Copper-based SCR

2.2.1 Test protocols

The Copper-based SCR (Cu-SCR) catalyst sample (Figure 7) was provided by ECOSPRAY, and the properties of the catalyst are summarized in Table 4.



Figure 7. Copper-based SCR catalyst sample.

Table 4. Properties of the Copper-based SCR catalyst.

Catalyst Properties	Value
Diameter [mm]	28
Length [mm]	90
CPSI [-]	100
Wall thickness [mils]	2
Cell shape [-]	triangle
Substrate material [-]	metal

For the Cu-SCR, similar test protocols to the ones of the V-SCR were performed. The inlet feed gas and test conditions are shown in Table 5. The phenomena of NO and NH₃ oxidation are examined first, followed by the investigation of SCR reactions under different conditions, such as the ANR ratio in the mixture, the composition of NO_x (addition of NO₂), etc.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

Table 5. Copper-based SCR catalyst test conditions.

Phenomena	Inlet feed gas	Temperature [°C]	Space Velocity [h ⁻¹]
NO oxidation	2000 ppm NO, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance	150 200 250 300 400 500	20,000
NH ₃ oxidation	1000 ppm NH ₃ , 6% O ₂ , 15 % H ₂ O, 15 ppm SO ₂ , N ₂ balance		
Standard SCR under ANR ratios	2000 ppm NH ₃ , NH ₃ /NO _x =0.8, 1.0, 1.5, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance		
Fast SCR	2000 ppm NH ₃ , 2000 ppm NO _x (NO ₂ /NO _x =0.2), 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance		
Addition of N ₂ O	2000 ppm NH ₃ , NH ₃ /NO _x =1.0, N ₂ O=50, 100 ppm 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance		

2.2.2 Reaction scheme

The model development of the Cu-SCR catalyst follows the same approach as the V-SCR catalyst. Commonly used SCR reactions are adopted [1,2], as listed in Table 6, to describe the reactivity. These include the Standard, Fast and NO₂-SCR reactions that are considered principal between NO_x and NH₃ (depending on NNR), NH₃ oxidation to N₂, and NO oxidation to NO₂. In addition, the formation of N₂O has been attributed to the oxidation of NH₃ and NO [3], as well as the direct reaction between NH₃ and NO₂ [4,5].

Table 6. Copper-based SCR system reaction scheme.

Type	Reaction	Reaction Rate
NH ₃ storage/release	NH ₃ ↔ NH ₃ *	$R_{r_{ads}} = k_{ads} \cdot [NH_3] \cdot (1 - \theta_{NH_3})$ $R_{r_{des}} = k_{des} \cdot \theta_{NH_3}$
Standard SCR	$4 NH_3^* + 4 NO + O_2 \rightarrow 4 N_2 + 6 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot (C_{O_2}^{0.3})$
Fast SCR	$4 NH_3^* + 2 NO + 2 NO_2 \rightarrow 4 N_2 + 6 H_2O$ $NH_3 + 1/2 NO + 1/2 NO_2 \rightarrow N_2 + 3/2 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot C_{NO_2}$ $R_r = k \cdot C_{NH_3} \cdot C_{NO} \cdot C_{NO_2}$
NO ₂ SCR	$NH_3^* + 3/4 NO_2 \rightarrow 7/8 N_2 + 3/2 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot C_{NO_2}$
NO oxidation	$NO + 1/2 O_2 \leftrightarrow NO_2$	$R_r = k \cdot C_{NO} \cdot C_{O_2}$
NH ₃ oxidation	$2 NH_3 + 3/2 O_2 \rightarrow N_2 + 3 H_2O$	$R_r = k \cdot C_{NH_3} \cdot (C_{O_2}^{0.5})$
N ₂ O formation	$4 NH_3^* + 4 NO + 3 O_2 \rightarrow 4 N_2 + N_2O + 6 H_2O$ $2 NH_3 + 2 NO + O_2 \rightarrow N_2 + N_2O + 3 H_2O$ $4 NH_3^* + 4 NO_2 \rightarrow 2 N_2 + 2 N_2O + 6 H_2O$	$R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO} \cdot C_{O_2}$ $R_r = k \cdot C_{NH_3} \cdot C_{NO_2}$ $R_r = k \cdot \Psi_S \cdot \psi_{S_{NH_3}} \cdot C_{NO_2}$

*Stored on the catalytic sites

2.2.3 Model setup and calibration

The kinetic parameters of the Cu-SCR catalyst are adjusted to fit the experimentally determined NO_x, NH₃ and N₂O concentrations. The outcomes of the NO and NH₃ oxidation tests are depicted in Figure 8. The conversion of NO to NO₂ is barely noticeable, especially at low temperatures (Figure 8a) and is activated above 300°C. NH₃ is only oxidized to N₂ above 250°C



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

and is fully oxidized at 500°C (Figure 8b). Not any NO or N₂O formation is observed during NH₃ oxidation.

The same figures also feature the simulation model results following the fitting of the reaction kinetic rate parameters. The model exhibits a strong agreement with the test results in the entire temperature window.

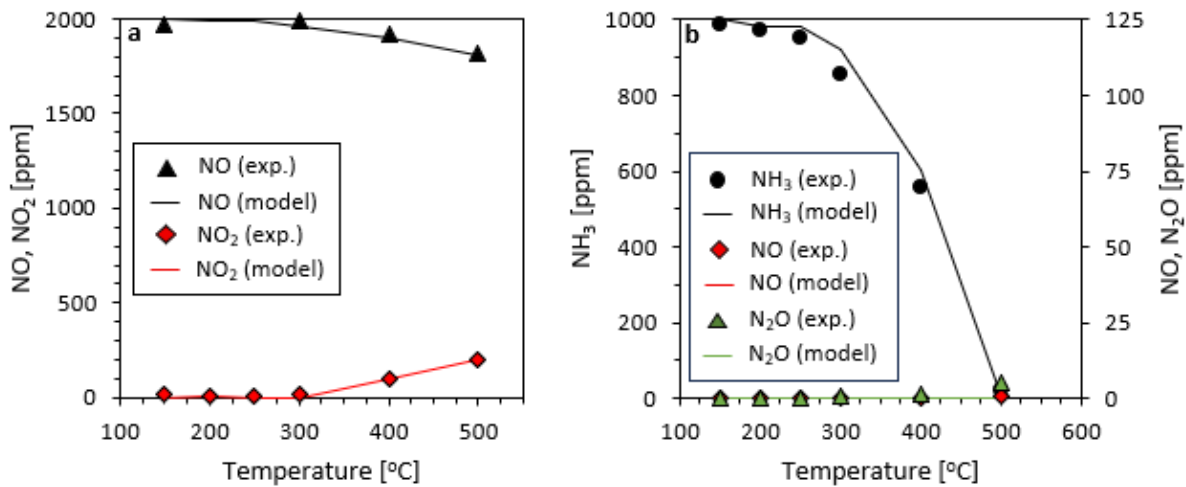


Figure 8. Comparison of the experimental data (symbols) and the model (solid lines) of (a) NO oxidation ((Feed gas: 2000 ppm NO, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance)) and (b) NH₃ oxidation (Feed gas: 1000 ppm NH₃, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance), at the outlet of the Cu-SCR catalyst.

Figure 9 shows the results of the SCR reactivity. The catalyst exceeds 80% NO_x conversion efficiency above 350°C. The SCR process is highly dependent on the NH₃ levels contained in the gas mixture. Excessive NH₃ (ANR=1.5) results in increased NO_x reduction at high temperatures, although leading to increased NH₃ slip, while shortage of NH₃ (ANR=0.8) in the feed gas results in partial NO_x conversion. N₂O formation during the deNO_x process is low with a maximum of 20 ppm at 500°C.



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

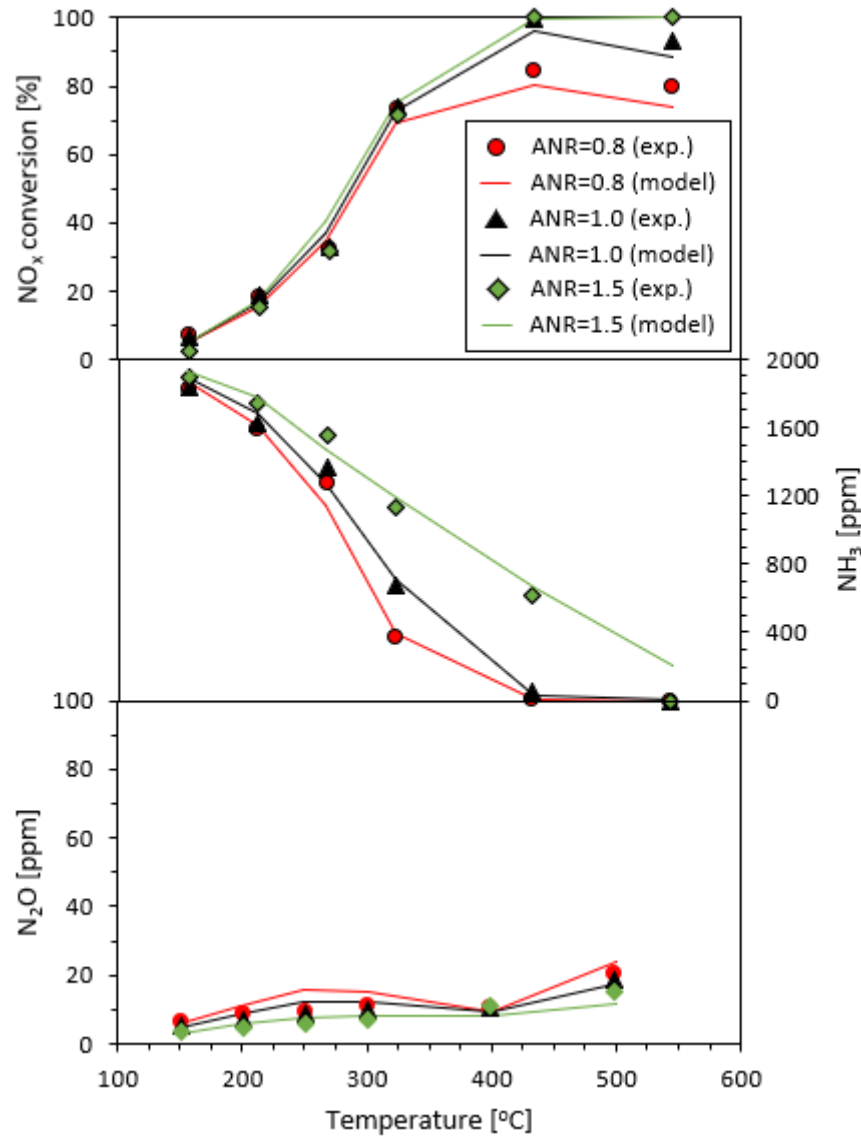


Figure 9. NO_x conversion, NH₃ slip and N₂O formation at the outlet of the Cu-SCR catalyst under Standard SCR conditions with NH₃/NO_x=0.8, 1.0, 1.5, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH₃/NO_x=0.8, 1.0, 1.5, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance).

The addition of NO₂ in the feed gas (Figure 10) increases NO_x conversion, especially at low temperatures due to the activation of the Fast SCR reaction (in the solid and gas phase) together with the Standard SCR. Therefore, NH₃ slip is decreased. Concerning N₂O, its production is slightly increased in the presence of NO₂ as NO₂ directly reacts with NH₃ to form N₂O ($4 \text{ NH}_3 + 4 \text{ NO}_2 \rightarrow 2 \text{ N}_2 + 2 \text{ N}_2\text{O} + 6 \text{ H}_2\text{O}$).

The results of the calibrated model are presented in the same figure (solid lines) with satisfactory agreement with the experimental data across the temperature range, ANRs and NNRs.



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

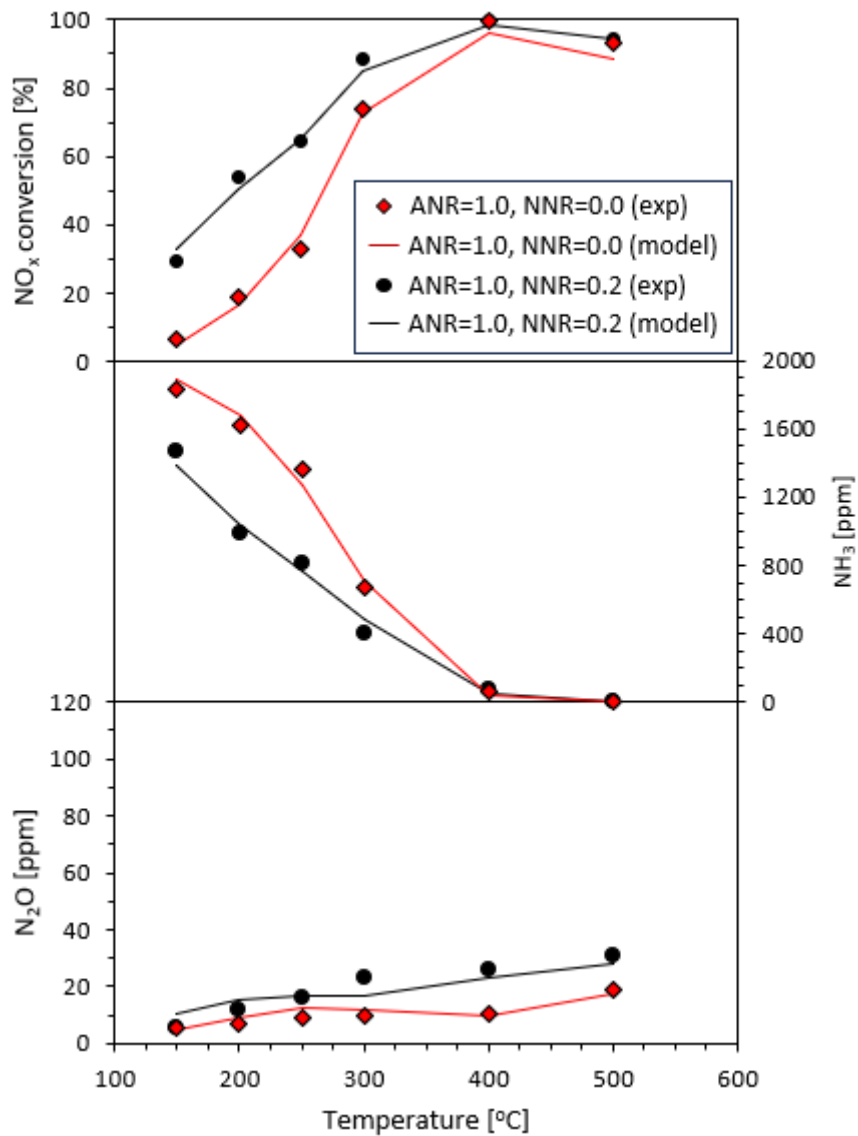


Figure 10. NO_x conversion, NH₃ slip and N₂O formation at the outlet of the Cu-SCR catalyst under Fast SCR conditions (compared to the Standard SCR conditions), based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO_x, NO₂/NO_x=0.2, NH₃/NO_x=1.0, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance).

To examine the possible reduction of N₂O along the Cu-SCR catalyst, N₂O is added to the feed gas during SCR reactivity (see Table 5). The corresponding results are depicted in Figure 11. It is obvious that N₂O does not react through the catalyst, and only N₂O formation pathways are activated; hence the calibrated reaction scheme is not affected and efficiently predicts the N₂O outlet concentrations.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

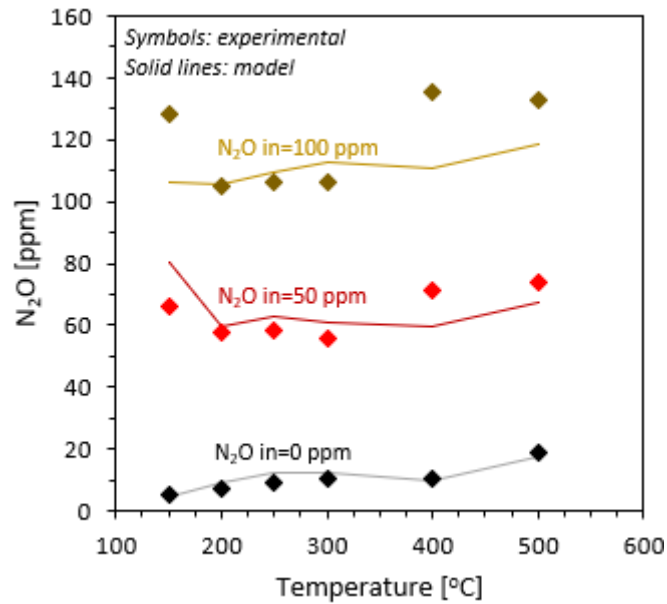


Figure 11. N₂O concentrations at the outlet of the Cu-SCR catalyst under Standard SCR conditions, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 2000 ppm NO, NH₃/NO_x=1.0, N₂O=50, 100, 6% O₂, 15% H₂O, 15 ppm SO₂, N₂ balance).

2.3 Catalytic processes in the Platinum-based oxidation catalyst

2.3.1 Test Protocols

The Platinum-based oxidation catalyst (Pt-AOC) sample (Figure 12) was provided by ECOSPRAY, and the properties of the catalyst are summarized in Table 7 Table 4.

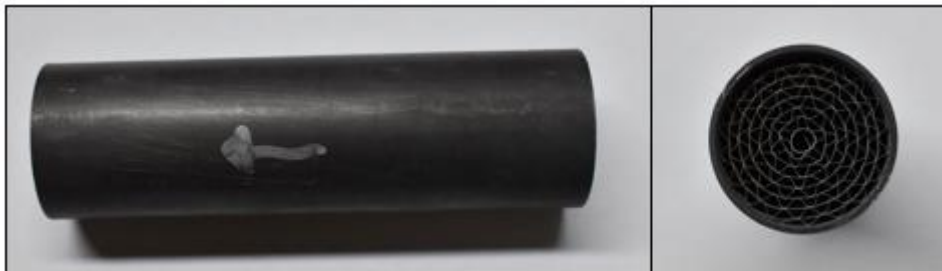


Figure 12. Platinum-based oxidation catalyst sample.

Table 7. Properties of the Platinum-based oxidation catalyst.

Catalyst Properties	Value
Diameter [mm]	28
Length [mm]	90
CPSI [-]	200
Wall thickness [mils]	2
Cell shape [-]	triangle
Substrate material [-]	metal

The oxidation activity of the Pt-AOC is tested by a temperature ramp (light-off test) from 150°C to 600°C. The feed gas and test conditions are summarized in Table 8.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

Table 8. Platinum-based oxidation catalyst test conditions.

Phenomena	Inlet feed gas	Temperature [°C]	Space Velocity[h ⁻¹]
NH ₃ oxidation	250 ppm NH ₃ , 50 ppm NO, 6% O ₂ , 15% H ₂ O, 15 ppm SO ₂ , N ₂ balance	150 → 600	20,000

2.3.2 Reaction scheme

Ammonia oxidation on the Pt-based oxidation catalyst is approached with a simple kinetic model that can give a good representation of the overall reactions [6,7]. The oxidation reactions used are listed in Table 9. These include the oxidation of NH₃ to N₂ and NO, the simultaneous oxidation of NH₃ and NO to N₂O and the oxidation of NO to NO₂ (including the reverse reaction).

Table 9. Platinum-based oxidation catalyst reaction scheme.

Type	Reaction	Reaction rate
NO oxidation	$\text{NO} + 1/2 \text{O}_2 \leftrightarrow \text{NO}_2$	$R_r = k \cdot C_{\text{NO}} \cdot C_{\text{O}_2}$
NH ₃ oxidation	$4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 5 \text{H}_2\text{O}$	$R_r = k \cdot C_{\text{NH}_3} \cdot C_{\text{O}_2}$
	$2 \text{NH}_3 + 3/2 \text{O}_2 \rightarrow \text{N}_2 + 3 \text{H}_2\text{O}$	$R_r = k \cdot C_{\text{NH}_3} \cdot C_{\text{O}_2}$
NH ₃ & NO oxidation to N ₂ O	$2 \text{NH}_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow 2 \text{N}_2\text{O} + 3 \text{H}_2\text{O}$	$R_r = k \cdot C_{\text{NH}_3} \cdot C_{\text{NO}} \cdot C_{\text{O}_2}$

2.3.3 Model setup and calibration

The experimental results compared to the simulation model of the Pt-based oxidation catalyst are presented in Figure 13. Here the focus is not only on the conversion rate of NH₃ as a function of temperature, but also on the unwanted NO_x and N₂O produced by the NH₃ oxidation reactions. It is worth noting that the calibrated model is capable of capturing these complex trends with respect to NO_x byproducts in the whole temperature range with good accuracy. The concentration of NH₃ shows a steep decrease from 200°C to 250°C and is fully oxidized around 300°C. Above 200°C, N₂O selectivity increases significantly with maximum concentration at 250°C that reaches 100 ppm. Selectivity to NO and NO₂ is favoured above 250°C while N₂O production is simultaneously decreasing.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

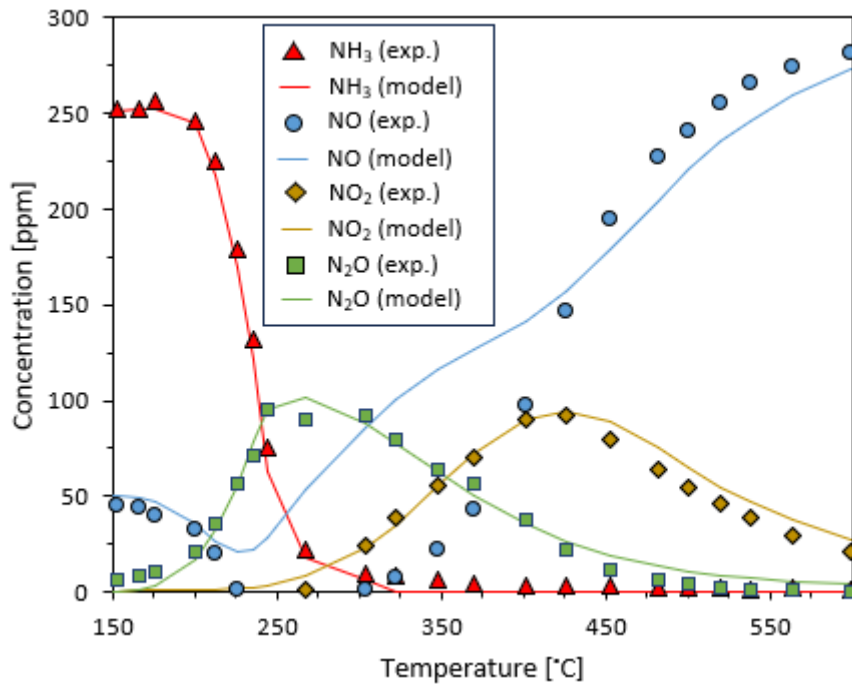


Figure 13. Comparison of the NH₃, NO, NO₂ and N₂O outlet concentrations at the outlet of the Pt-based oxidation catalyst based on the experimental (symbols) and the model (solid lines).

The trend of increased N₂O selectivity can be interpreted by referring to the reaction rates depicted in Figure 14, highlighting the competition between the reactions. Between 200°C and 400°C, the simultaneous oxidation of NH₃ and NO to N₂O is favoured, while above 250°C the oxidation of NH₃ producing NO becomes dominant; hence the availability of NH₃ towards N₂O is limited.

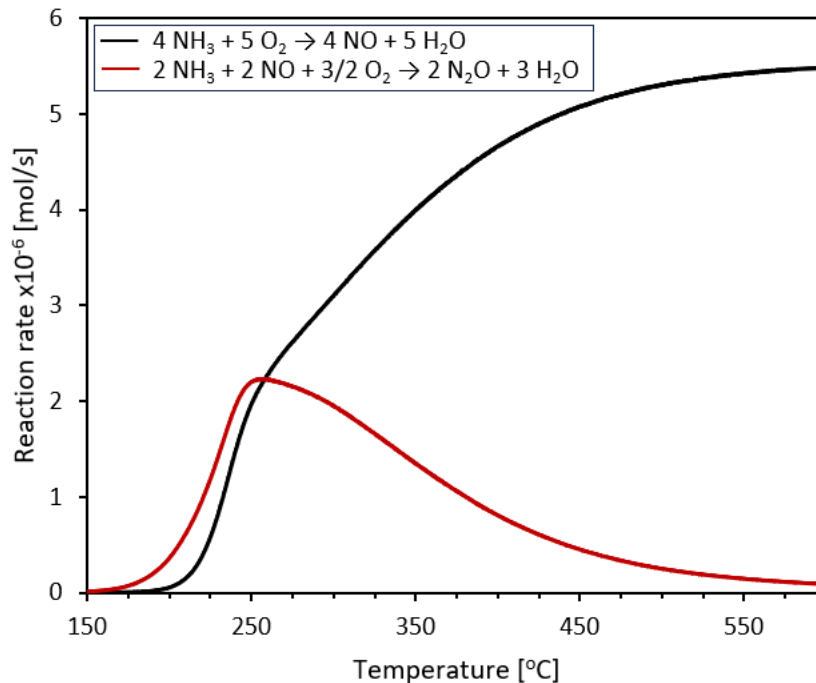


Figure 14. Reaction rates of the Pt-based oxidation catalyst as a function of the catalyst temperature.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

2.4 Catalytic processes in the Iron-based SCR

2.4.1 Test Protocols

The Iron-based SCR catalyst (Fe-SCR) sample was provided by TOPSOE (Figure 15), and the properties of the catalyst are summarized in Table 10 Table 4.



Figure 15. Iron-based SCR catalyst sample.

Table 10. Properties of the Iron-based SCR catalyst.

Catalyst Properties	Value
Diameter [mm]	28
Length [mm]	150
CPSI [-]	230
Wall thickness [mils]	9
Cell shape [-]	square
Substrate material [-]	cordierite

Fe-SCR technologies are known for the simultaneous reduction of NO_x and N₂O. For this reason, its reactivity is expected to be more complex and thus the test conditions are determined in such way so as to isolate the various phenomena prevailing in the catalyst and ultimately to facilitate the understanding of the catalyst operation for the development of the simulation model. The test protocols including the feed gas and inlet conditions are listed in Table 11.

Table 11. Iron-based SCR catalyst test conditions.

Phenomena	Inlet feed gas	Temperature [°C]	Space Velocity [h ⁻¹]
NH ₃ oxidation	1000 ppm NH ₃ , 10% O ₂ , 15 % H ₂ O, N ₂ balance	200	14,000
SCR under NH ₃ /NO _x ratios	1000 ppm NO _x , NH ₃ /NO _x =0.7, 1.0, 3.0, 10% O ₂ , 15% H ₂ O, N ₂ balance	250	
		300	
		350	
		400	
Fast SCR	1000 ppm NH ₃ , 1000 ppm NO _x (NO ₂ /NO _x =0.2), 10% O ₂ , 15% H ₂ O, N ₂ balance	450	
NO oxidation to NO ₂	1000 ppm NO, 10% O ₂ , 15% H ₂ O, N ₂ balance	150 → 600	
N ₂ O thermal decomposition	200 ppm N ₂ O, 10% O ₂ , 15% H ₂ O, N ₂ balance	200 → 600	
N ₂ O reduction by NH ₃	200 ppm NH ₃ , 200 ppm N ₂ O, 10% O ₂ , 15% H ₂ O, N ₂ balance	300	
		350	
		400	
		450	
		500	



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

SCR with N ₂ O addition under ANR ratios	1000 ppm NO, NH ₃ /NO _x =0.8 ¹ , 1.0, 1.2, 1.4, N ₂ O=100, 200 ¹ ppm, 10% O ₂ , 15% H ₂ O, N ₂ balance	250	
		300	
		350	
		400	
		450	
Effect of NH ₃ on N ₂ O	1000 ppm NO, 100 ppm N ₂ O, NH ₃ =800, 1000, 1200, 1400, 1600, 1800, 2000, 2500, 3000, 10% O ₂ , 15% H ₂ O, N ₂ balance	350	
		400	
		450	

¹When NH₃/NO_x=0.8, N₂O=200 ppm.

2.4.2 Reaction scheme

To describe the SCR reactivity over the Fe-SCR catalyst, the reactions listed in Table 12 are adopted. These include the Standard and Fast SCR, N₂O formation pathways, the oxidation of NO to NO₂ and the oxidation of NH₃ to form N₂. In addition, the global reactions of N₂O reduction by NH₃ [8,9] or by NH₃ and NO [10] and N₂O thermal decomposition [11] are added to the final reaction scheme.

In the case of the Fe-SCR catalyst, phenomena such as the overconsumption of NH₃ during NO_x reduction, inhibition of NH₃ on NO_x conversion when exposed to high NH₃ concentrations that is reduced in the presence of N₂O in the feed gas, and the promotion of NH₃ oxidation in the presence of N₂O are observed. The reaction scheme has been adjusted to take into account all the above. The behavior is further analyzed in Section 2.4.3.

Table 12. Iron-based SCR catalyst reaction scheme (Engimmonia model).

Type	Reaction	Reaction Rate
NH ₃ storage/release	NH ₃ ↔ NH ₃ *	$R_{r_{ads}} = k_{ads} \cdot [NH_3] \cdot (1 - \theta_{NH_3})$ $R_{r_{des}} = k_{des} \cdot \theta_{NH_3}$
Modified Standard SCR Standard SCR (+N ₂ O)	$6 NH_3^* + 5 NO + 2 O_2 \rightarrow 11/2 N_2 + 9 H_2O$ $NH_3^* + NO + 1/4 O_2 + N_2O \rightarrow N_2 + 3/2 H_2O + N_2O$	$R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{NO} \cdot C_{O_2} / (1 + k \cdot C_{NH_3}^2)$ $R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{NO} \cdot C_{O_2} \cdot C_{N_2O}$
Fast SCR	$NH_3^* + 1/2 NO + 1/2 NO_2 \rightarrow N_2 + 3/2 H_2O$	$R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{NO} \cdot C_{NO_2}$
N ₂ O formation pathways	$2 NH_3^* + 2 NO + O_2 \rightarrow N_2 + N_2O + 3 H_2O$ $2 NH_3^* + 2 NO_2 \rightarrow N_2 + N_2O + 3 H_2O$	$R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{NO} \cdot C_{O_2}$ $R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{NO_2}$
NO oxidation to NO ₂	$NO + 1/2 O_2 \leftrightarrow NO_2$	$R_r = k \cdot C_{NO} \cdot C_{O_2}$
NH ₃ oxidation to N ₂	$NH_3^* + 3/4 O_2 \rightarrow 1/2 N_2 + 3/2 H_2O$	$R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{O_2} \cdot (1 + k \cdot C_{N_2O})$
N ₂ O thermal decomposition	$2 N_2O \rightarrow 2 N_2 + O_2$	$R_r = k \cdot C_{N_2O}$
N ₂ O reduction by NH ₃	$2 NH_3^* + 3 N_2O \rightarrow 4 N_2 + 3 H_2O$	$R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{N_2O} / (1 + k \cdot C_{NH_3}^{1.5})$
Simultaneous reduction of NO and N ₂ O by NH ₃	$2 NH_3^* + 2 NO + N_2O \rightarrow 3 N_2 + 3 H_2O$	$R_r = k \cdot \Psi_S \cdot \Psi_{SNH_3} \cdot C_{NO} \cdot C_{N_2O}$

*Stored on the catalytic sites

2.4.3 Model setup and calibration

The kinetic parameters of the reaction rates were calibrated in order to fit the experimental data for NO_x, NH₃ and N₂O. The results of the experimental data and the simulation model for the



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

NO oxidation to NO₂ and the oxidation of NH₃ to N₂ are presented in Figure 16a and Figure 16b respectively. The oxidation of NO is detected above 200°C with maximum oxidation around 450°C. NH₃ is oxidized to N₂ above 300°C, while not any NO or N₂O formation was observed.

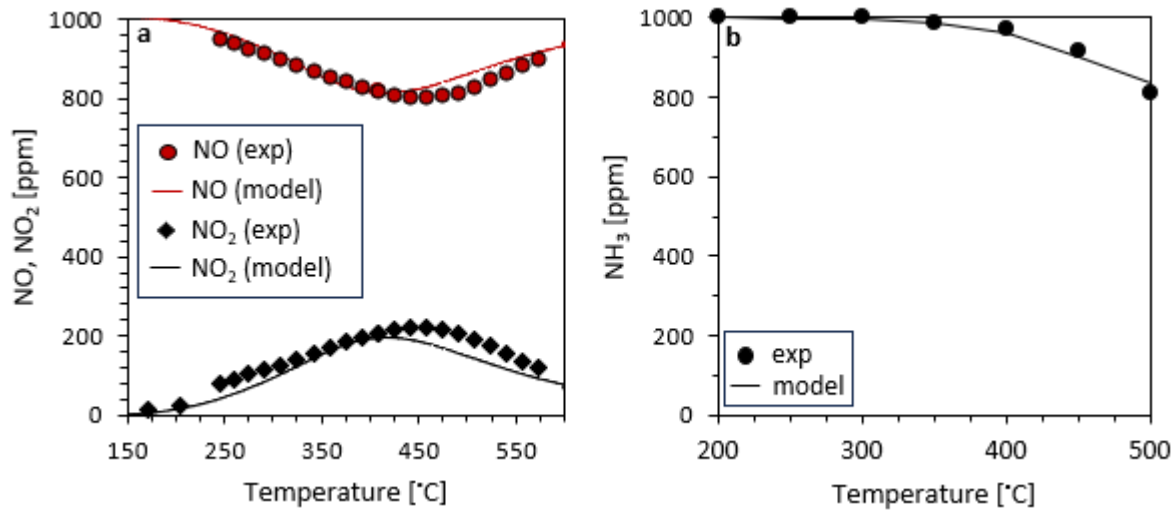


Figure 16. Comparison of the experimental data (symbols) and the model (solid lines) of (a) NO oxidation ((Feed gas: 1000 ppm NO, 10% O₂, 15% H₂O, N₂ balance)) and (b) NH₃ oxidation (Feed gas: 1000 ppm NH₃, 10% O₂, 15% H₂O, N₂ balance), at the outlet of the Fe-SCR catalyst.

Figure 17 shows NO_x and NH₃ conversion under SCR conditions. According to the commonly used SCR reaction ($4 \text{ NO} + 4 \text{ NH}_3 + \text{O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}$) equal number of moles of NO_x and NH₃ react. However, testing of the Fe-SCR catalyst revealed an overconsumption of NH₃ compared to NO_x (symbols in Figure 17). This behavior has been observed in several previous studies [12-15]. Therefore, for the development of the model, the stoichiometry of the typical standard SCR reaction has been modified as:



This modified Standard SCR reaction (Engimmonia model) is able to successfully describe the overconsumption of NH₃ (solid lines in Figure 17).



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

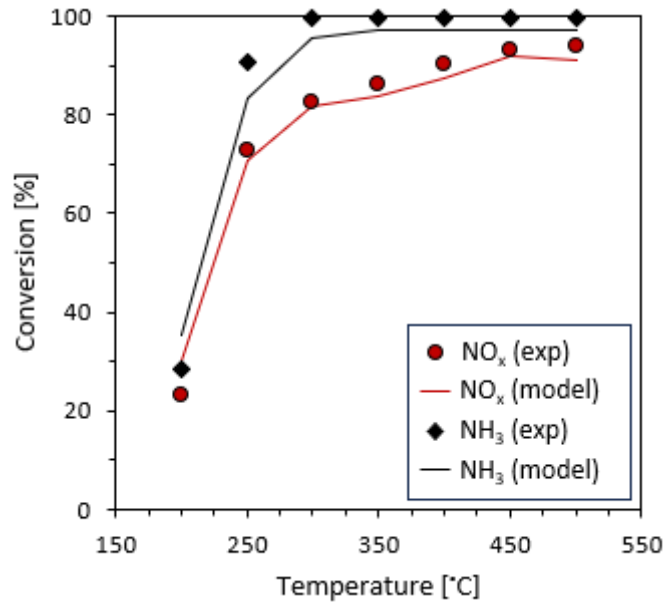


Figure 17. NO_x and NH₃ conversion at the Fe-SCR catalyst under standard SCR conditions, based on the experimental data (symbols) and the model (solid lines, Engimmonia model) (Feed gas: 1000 ppm NO, NH₃/NO_x=1.0, 10% O₂, 15% H₂O, N₂ balance).

The experimental testing is expanded to examine the dependence of the inlet NH₃ concentrations on the catalyst efficiency (NO_x conversion). The experimental outcome is depicted in Figure 18a with symbols. When ANR is less than 1, the catalyst performance is reduced due to lack of NH₃ to further react with NO_x. When abundant NH₃ is present (ANR=3.0), NO_x conversion increases at temperatures above 350°C. At lower temperatures (below 300°C) and in excessive NH₃ (ANR=3.0), NO_x conversion is significantly reduced. To simulate this phenomenon, an inhibition term $(1+k \cdot C_{\text{NH}_3}^2)$ is added to the reaction rate of the modified Standard SCR (reaction (2)):

$$R = k \cdot \Psi_S \cdot \psi_{\text{S}_{\text{NH}_3}} \cdot C_{\text{NO}} \cdot C_{\text{O}_2} / (1+k \cdot C_{\text{NH}_3}^2) \quad (3)$$

The introduction and calibration of the inhibition term results in good accuracy between the experimental data (Figure 18a symbols) and the Engimmonia model (Figure 18a solid lines). The conversion of NO_x with (Engimmonia model) and without (Standard model) the inhibition term in the case of ANR=3.0 is shown in Figure 18b. It is evident that when NH₃ inhibition is activated, the rate of NO_x conversion is reduced in the desired temperature range. Consequently, the model satisfactorily predicts NO_x concentrations at all conditions and temperatures.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

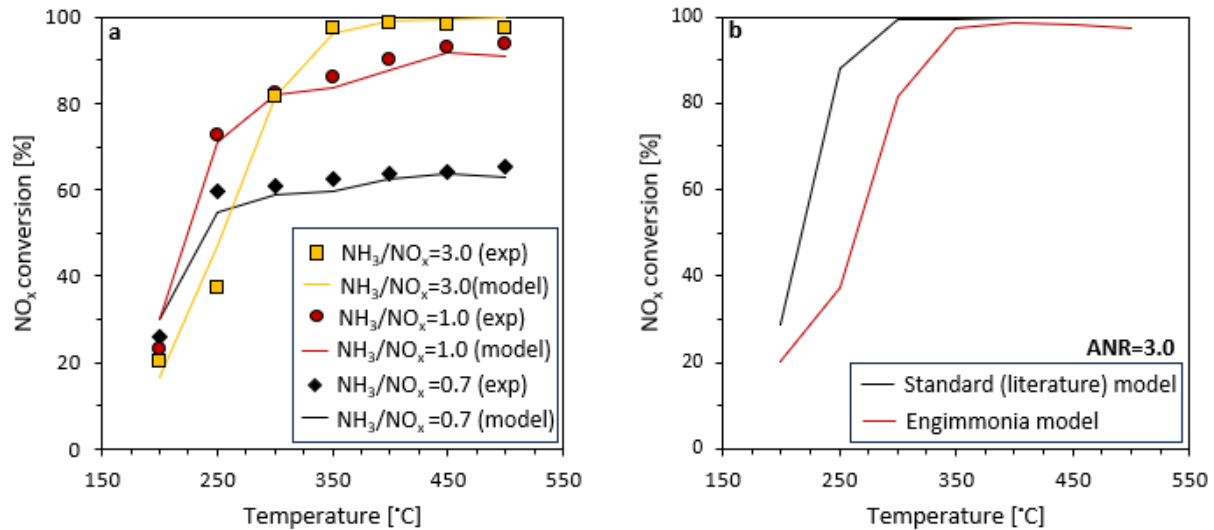


Figure 18. NO_x conversion (a) under various ANR ratios including the inhibition term and (b) under ANR=3.0 with (Engimmonia model) and without (standard/literature model) the inhibition term, at the Fe-SCR catalyst, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 1000 ppm NO, NH₃/NO_x=0.7, 1.0, 3.0, 10% O₂, 15% H₂O, N₂ balance).

Figure 19 presents the NH₃ slip and N₂O formation under various ANRs. Excess NH₃ in the mixture leads to large concentrations of NH₃ slip, while in the case of stoichiometric ANR or deficiency of NH₃, NH₃ completely reacts with NO_x (except from 200°C where the low temperature does not trigger SCR reactions). Selectivity to N₂O is maintained at low levels (<10 ppm) and it is not affected by NH₃ levels. The Engimmonia model (including the modifications) is able to predict this behaviour.

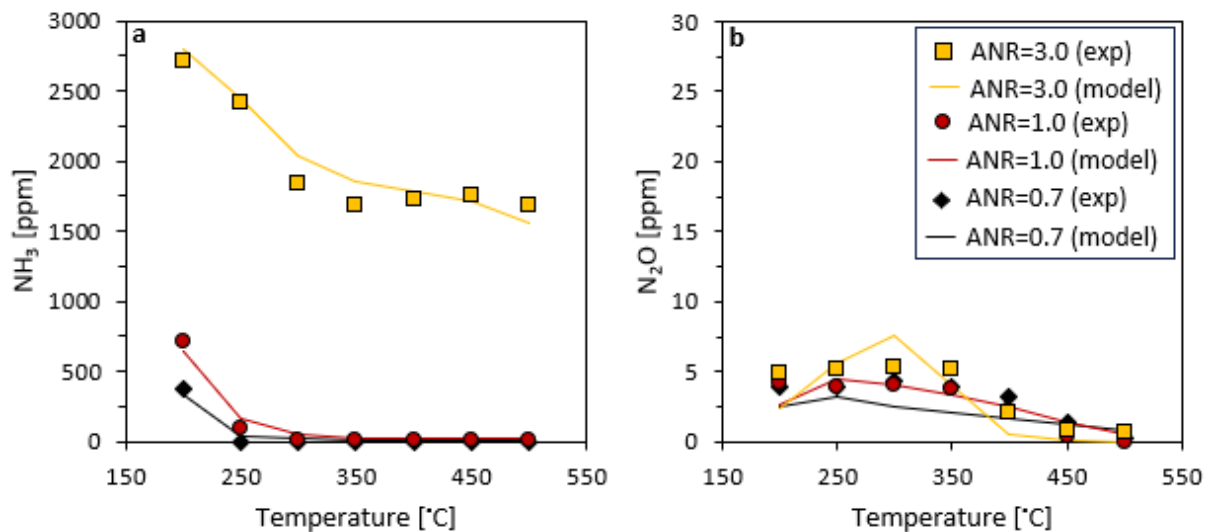


Figure 19. NH₃ slip and N₂O formation at the outlet of the Fe-SCR catalyst under Standard SCR conditions with NH₃/NO_x=0.7, 1.0, 3.0, based on the experimental data (symbols) and the model (solid lines).

The addition of NO₂ in the feed gas (Figure 20) increases NO_x conversion rate, especially at low temperatures, as the Fast SCR is activated. Low selectivity to N₂O (below 5 ppm) is observed in all conditions. The results of the calibrated Engimmonia model are presented in the same figure (solid lines). Satisfactory agreement between the Engimmonia model and the experimental data are observed within the whole temperature range, ANR and NNR ratios.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

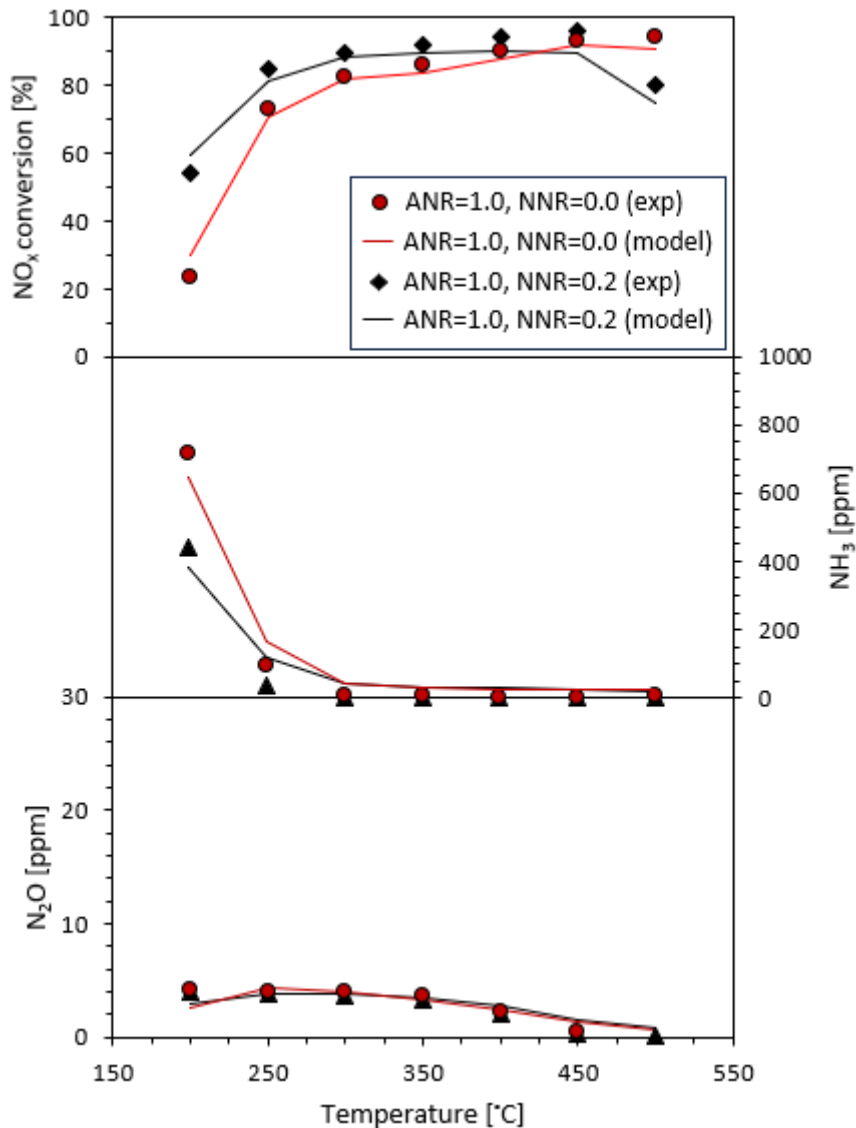


Figure 20. NO_x conversion, NH₃ slip and N₂O formation at the outlet of the Fe-SCR catalyst under Fast SCR conditions (compared to Standard SCR conditions), based on the experimental data (symbols) and the model (solid lines), (Feed gas: 1000 ppm NO_x, NO₂/NO_x=0.2, NH₃/NO_x=1.0, 10% O₂, 15% H₂O, N₂ balance)

In addition to the NO_x reduction potential, Fe-SCR catalysts have the advantage of catalysing N₂O emissions as well. Figure 21 presents N₂O conversion efficiency under thermal decomposition conditions, i.e., without any NH₃ in the feed gas. It is evident that high temperatures (above 400°C) are required to activate the N₂O decomposition reaction ($2 \text{N}_2\text{O} \rightarrow 2 \text{N}_2 + \text{O}_2$), while 80% conversion is achieved at very high temperatures (~575°C). The reaction kinetic parameters of the N₂O decomposition reaction are calibrated to accurately predict the experimental data.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

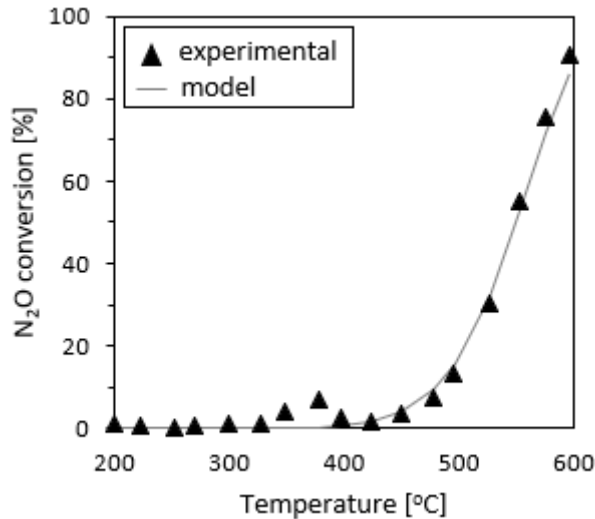
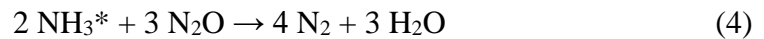


Figure 21. N₂O thermal decomposition of the Fe-SCR catalyst, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 200 ppm N₂O, 10% O₂, 15% H₂O, N₂ balance)

Figure 22a (symbols) presents the results of N₂O reduction by NH₃ with reference to the global reaction:



NH₃ and N₂O react in a ratio of 2/3. As NH₃ and N₂O levels in the feed gas are equal (NH₃=N₂O=200 ppm), a greater reduction of N₂O than NH₃ would be expected. On the contrary, at temperatures below 450°C, the conversion of NH₃ is greater than that of N₂O. This behaviour is attributed to the oxidation reaction of NH₃ to N₂ (NH₃ + 3/4 O₂ → 1/2 N₂ + 3/2 H₂O) which is enhanced by the presence of N₂O [11]. To account for this phenomenon in the Engimmonia model, a ‘promotion’ term (1+k · C_{N₂O}) was added to increase the reaction rate of the NH₃ oxidation reaction in the desired temperature window as:

$$R = k \cdot \Psi_S \cdot \psi_{\text{SNH}_3} \cdot C_{\text{O}_2} \cdot (1+k \cdot C_{\text{N}_2\text{O}}) \quad (5)$$

Following this approach, the Engimmonia model (solid lines of Figure 22a) can predict the behaviour observed in the experiment. The oxidation rate of NH₃ is enhanced between 300°C and 400°C (Figure 22b) in the presence of N₂O (Engimmonia model) and the overconsumption of NH₃ is satisfactorily determined. At temperatures above 400°C the NH₃ oxidation rate decreases resulting in an outweighing of N₂O conversion.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

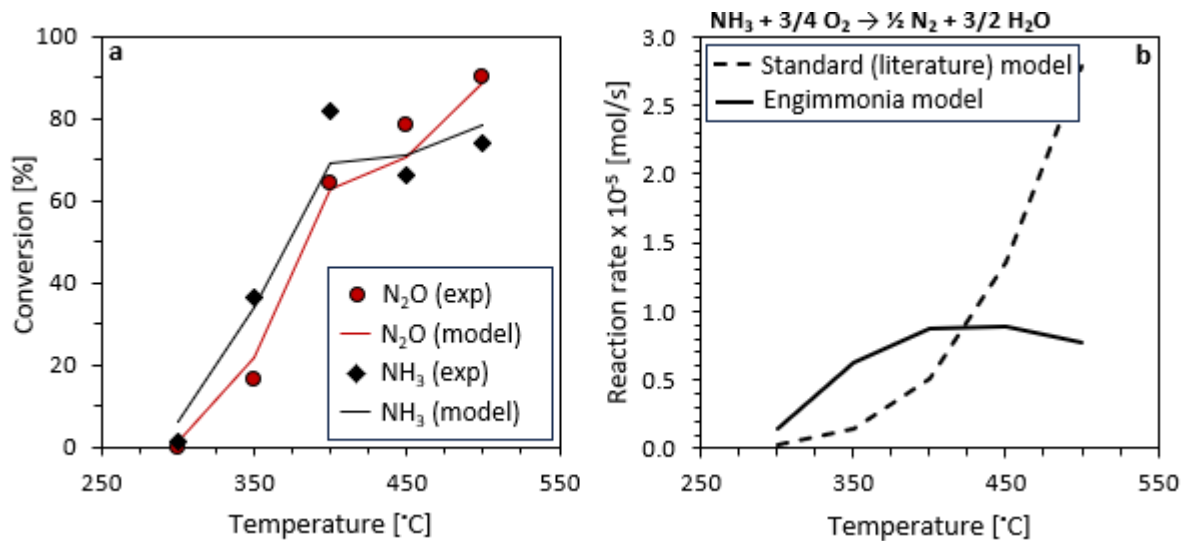
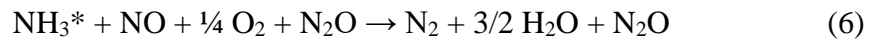


Figure 22. N₂O reduction by NH₃ at the Fe-SCR catalyst: (a) N₂O and NH₃ conversion including the promotion term and (b) NH₃ oxidation reaction rate with and without N₂O, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 200 ppm NH₃, 200 ppm N₂O, 10% O₂, 15% H₂O, N₂ balance).

Then, N₂O is added during the deNO_x process resulting in an increase in NO_x conversion and a reduction in NH₃ overconsumption (Figure 23a). To adapt the model to this behavior, the typical Standard SCR reaction is added to the reaction scheme including N₂O in both the reactants and products (Standard SCR + N₂O):



This way, the reaction is activated only in the presence of N₂O with no effect on the N₂O concentration in the exhaust gas. The addition of this reaction results in satisfactory accuracy of the Engimmonia model (solid and dashed lines of Figure 23a) and the experimental data (symbols of Figure 23a) both in the presence and absence of N₂O. Figure 23b shows that in the presence of N₂O, reaction (6) is dominant while the reaction rate of the modified standard SCR (reaction (2)) decreases due to competition between the two reactions.

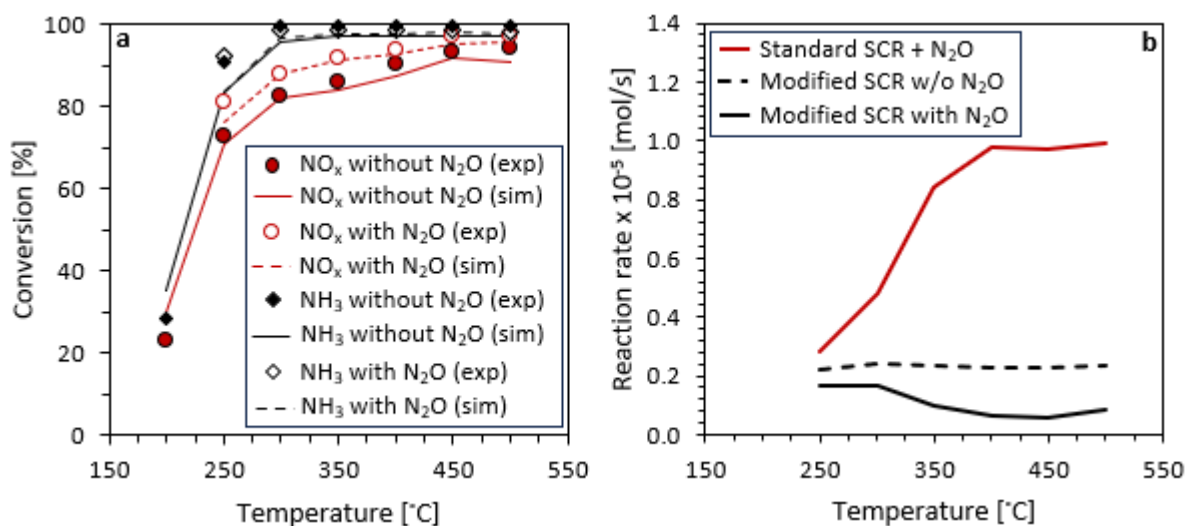


Figure 23. SCR reactivity in the presence of N₂O at the Fe-SCR catalyst: (a) NO_x and NH₃ conversion including the Standard SCR + N₂O, and (b) reaction rates of the Standard SCR + N₂O and modified SCR in the presence of N₂O, and the modified SCR in the absence of N₂O, based on the experimental data (symbols) and the model (solid lines), (Feed gas: 1000 ppm NO, NH₃/NO_x=1.0, 100 ppm N₂O, 10% O₂, 15% H₂O, N₂ balance).



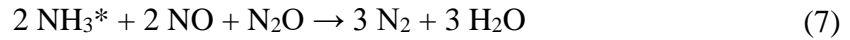
This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

The above approach gives good agreement between the experimental data and the Engimmonia model for the full range of tested ANRs (Figure 24). NO_x conversion increases at higher NH₃ levels, however with higher concentrations of unreacted NH₃ at the catalyst outlet.

Regarding N₂O conversion, the global reaction of N₂O and NO reduction by NH₃ is added to the reaction scheme:



An increase in N₂O conversion efficiency with NH₃ increase is observed, reaching 80% at a temperature above 350°C.

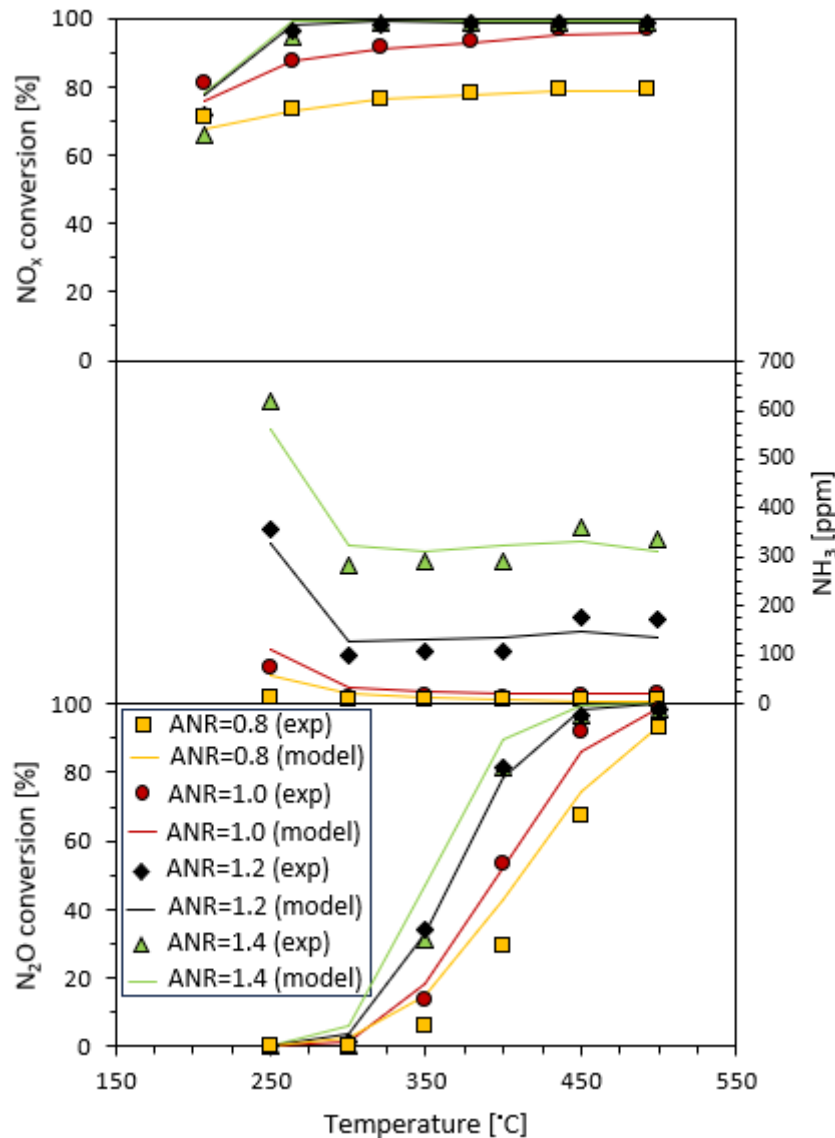


Figure 24. NO_x conversion, NH₃ slip and N₂O conversion at the outlet of the Fe-SCR catalyst under Standard SCR conditions with NH₃/NO_x=0.8, 1.0, 1.2, 1.4, and N₂O inlet concentration, based on the experimental data (symbols) and the Engimmonia model (solid lines), (Feed gas: 1000 ppm NO, NH₃/NO_x=0.8*, 1.0, 1.2, 1.4, N₂O=100, 200* ppm, 10% O₂, 15% H₂O, N₂ balance).

Finally, the effect of NH₃ on N₂O conversion efficiency is examined by varying the inlet concentration of NH₃. Only the critical temperature range of N₂O conversion is examined (350°C, 400°C and 450°C). The experimental outcome is shown in Figure 25 with symbols. As NH₃ concentration increases, N₂O conversion also increases reaching a maximum at 1400 ppm



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

NH₃. An optimal overall efficiency is observed at 1200 ppm NH₃ where NO_x and N₂O conversions are maximized and NH₃ slip is low. Further increase of NH₃ has a negative effect on N₂O reduction especially at the lower temperatures (350°C and 400°C). To model this behaviour an NH₃ inhibition to the reaction rate of the direct N₂O reduction by NH₃ ($2 \text{ NH}_3^* + 3 \text{ N}_2\text{O} \rightarrow 4 \text{ N}_2 + 3 \text{ H}_2\text{O}$) is applied:

$$R_r = k \cdot \Psi_S \cdot \Psi_{\text{SNH}_3} \cdot C_{\text{N}_2\text{O}} / (1 + k \cdot C_{\text{NH}_3}^{1.5}) \quad (8)$$

It is evident in Figure 25 (solid lines) that by introducing the inhibition term to the reaction scheme, the Engimmonia model fits the experimental data.

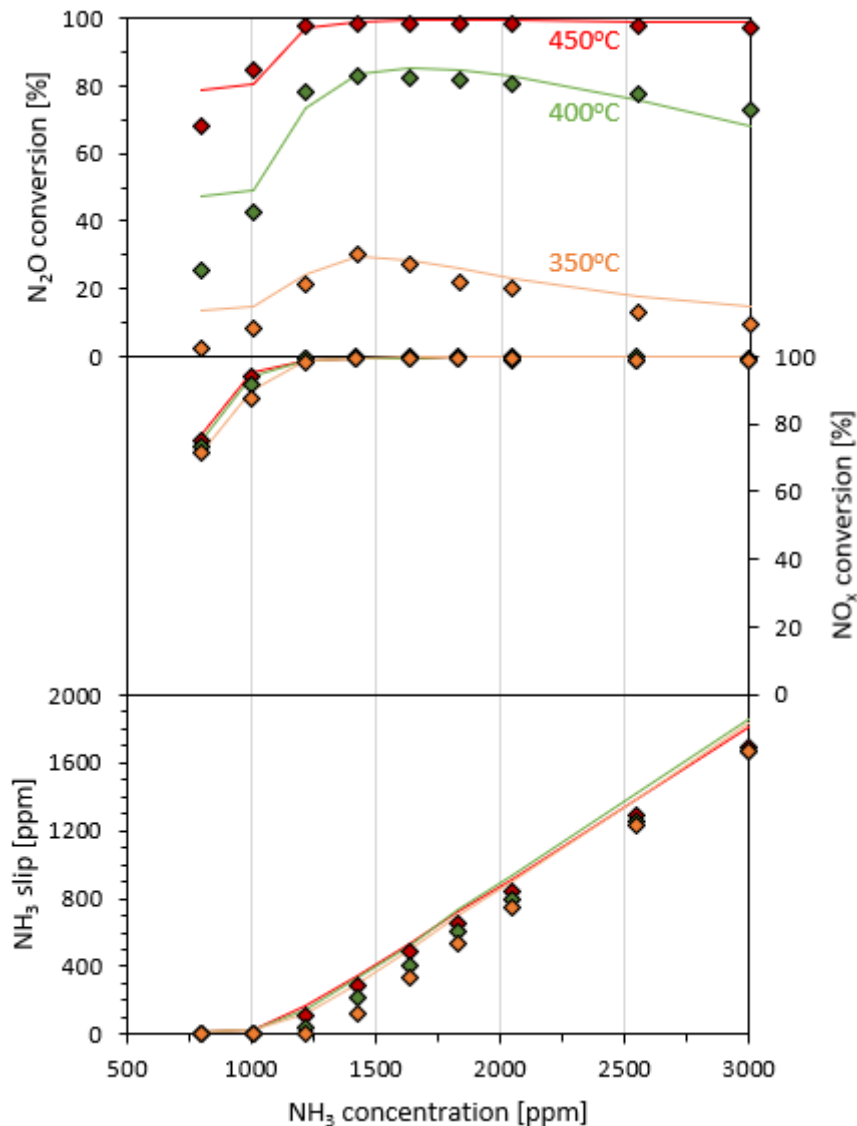


Figure 25. N₂O conversion, NO_x conversion and NH₃ slip including the inhibition, at the outlet of the Fe-SCR catalyst under various NH₃ inlet concentrations, based on the experimental data (symbols) and the Engimmonia model (solid lines), (Feed gas: 1000 ppm NO, variable NH₃, 100 ppm N₂O, 10% O₂, 15% H₂O, N₂ balance).

Figure 26 compares N₂O conversion efficiency when the inhibition term is activated (solid lines, Engimmonia model) and deactivated (dashed lines, standard/literature model). It is clear that when the inhibition is not included in the reaction, N₂O conversion increases as NH₃ inlet concentration increases.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

D4.2 – “Simulation of NO_x and N₂O catalytic processes in the flue gas of the ammonia dual-fuel engine”

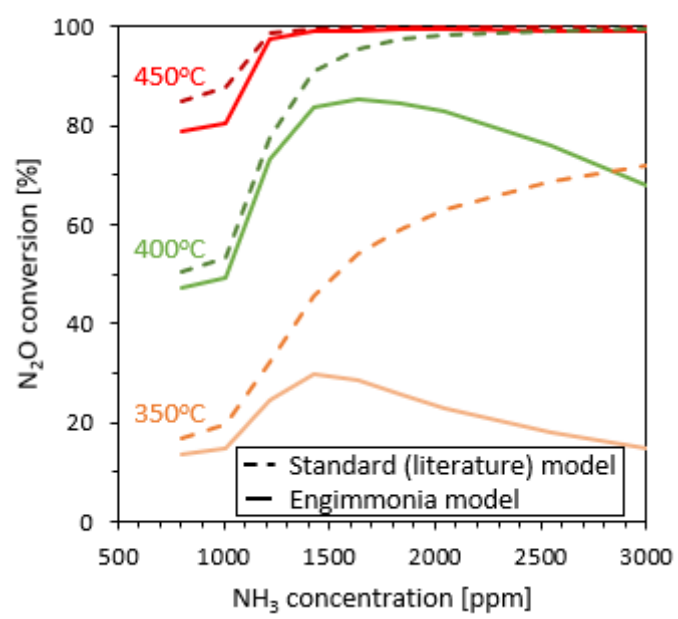


Figure 26. N₂O conversion with and without the inhibition, at the Fe-SCR catalyst under various NH₃ inlet concentrations, based on the standard/literature model (dashed line) and the Engimmonia model (solid line), (Feed gas: 1000 ppm NO, variable NH₃, 100 ppm N₂O, 10% O₂, 15% H₂O, N₂ balance).



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.

3. Conclusion and Future Plans

In the context of this deliverable, the processes taking place in the catalytic devices installed in the exhaust line of the ammonia dual-fuel (DF) engine were investigated. Starting with targeted small-scale testing, the catalytic activity of V-SCR, Cu-SCR, Pt-based oxidation catalyst and Fe-SCR systems was examined, providing useful insights concerning the occurring reactions. In turn, this supported the adoption of the appropriate chemical reaction scheme in the simulation models. Based on the test observations, the chemical reaction scheme for the V-SCR and Cu-SCR systems consisted of the commonly used SCR reactions (standard/literature model). On the other hand, in the case of the Fe-SCR catalyst, particular modifications of the chemical reaction scheme were necessary in order to accurately describe the occurring processes (Engimmonia model). These modifications were:

- modification of the Standard SCR reaction stoichiometry (eq. 2),
- inhibition of the modified Standard SCR reaction by NH₃ at high NH₃ inlet concentrations and low temperatures (inhibition term added to the reaction rate (eq. 3)),
- promotion of NH₃ oxidation to N₂ in the presence of N₂O (promotion term added to the reaction rate (eq.5)),
- addition of the typical Standard SCR with N₂O both in the reactants and products (Standard SCR+N₂O) (eq.6),
- inhibition of the direct N₂O reduction by NH₃ at high inlet concentrations of NH₃ (inhibition term is added to the reaction rate (eq.8)).

After adopting the appropriate chemical reaction scheme, the simulation models were calibrated and validated using the experimental data, providing satisfactory agreement throughout the whole temperature range that is relevant for the NH₃ DF engine. The developed models are going to be further used (in Tasks 4.2 and 4.6) in order to investigate in more detail the phenomena occurring in the examined catalytic devices, aiming at their improvement and optimization for the NH₃ DF engine. Further to the examination of the individual devices, the models will be used for the evaluation of the complete EATS, which is expected to comprise multiple catalysts to successfully control all N-species.



4. References

- [1] Klint Torp, T.; Hansen, B.B.; Vennestrøm, P.N.R.; Janssens, T.V.W.; Jensen, A.D. Modeling and Optimization of Multi-functional Ammonia Slip Catalysts for Diesel Exhaust Aftertreatment. *Emiss. Control. Sci. Technol.* 2021, 7, 7–25.
- [2] Karamitros, D.; Koltsakis, G. Model-based optimization of catalyst zoning on SCR-coated particulate filters. *Chem. Eng. Sci.* 2017, 173, 514–524.
- [3] Zhang, D.; Yang, R.T. N₂O Formation Pathways over Zeolite-Supported Cu and Fe Catalysts in NH₃-SCR. *Energy Fuels* 2018, 32, 2170–2182.
- [4] Metkar, P.; Harold, M.; Balakotaiah, V. Experimental and Kinetic Modeling Study of NH₃-SCR of NO_x on Fe-ZSM-5, Cu-chabazite and combined Fe- and Cu-zeolite monolithic catalysts. *Chem. Eng. Sci.* 2013, 87, 51–66.
- [5] Mihai, O.; Widyastuti, C.; Andonova, S.; Kamasamudram, K.; Li, J.; Joshi, S.; Currier, N.; Yezerets, A.; Olsson, L. The effect of Cu-loading on different reactions involved in NH₃-SCR over Cu-BEA catalyst. *J. Catal.* 2014, 311, 170–181.
- [6] Scheuer, A.; Hauptmann, W.; Drochner, A.; Gieshoff, J.; Vogel, H.; Votsmeier, M. Dual layer automotive ammonia oxidation catalysts: Experiments and computer simulation. *Appl. Catal. B Environ.* 2012, 111–112, 445–455.
- [7] Colomb, M.; Nova, I.; Tronconi, E.; Schmeißer, V.; Brandl-Konrad, B.; Zimmermann, L.R. Experimental Modeling Study of a dual-layer (SCR + PGM) NH₃ slip monolith catalyst (ASC) for automotive SCR aftertreatment systems. Part I. Kinetics for the PGM Component and Analysis of SCR/PGM Interactions. *Appl. Catal. B Environ.* 2013, 142–143, 861–876.
- [8] Aika, K.; Oshihara, K. Nitrous oxide reduction with ammonia over Co-MgO catalyst and the influence of excess oxygen. *Catalysis Today* (29), 1996, 123-126.
- [9] Zhang, X.; Shen, Q.; He, C.; Ma, C.; Chen, J.; Li, L.; Hao, Z. Investigation of Selective Catalytic Reduction of N₂O by NH₃ over an Fe-Mordenite Catalyst: Mechanism and O₂ Effect. *ASC Catal.* 2012, 2, 512-520.
- [10] Coq, B.; Mauvezin, M.; Delahay, G.; Butet, J. B.; Kieger, Stephane. The simultaneous catalytic reduction of NO and N₂O by NH₃ using an Fe-zeolite-beta catalyst. *Applied Catalysis B: Environmental* 27, 2000, 193-198.
- [11] Wang, A.; Wang, Y.; Walter, E. D.; Kukkadapu, R. K.; Guo, Y.; Lu, G.; Weber, R. S.; Wang, Y.; Peden, C. H. F.; Gao, F. Catalytic N₂O decomposition and reduction by NH₃ over Fe/Beta and Fe/SSZ-13 catalysts. *Journal of Catalysis* 358, 2018, 199-210.
- [12] Sjövall, H.; Blint, R. J.; Gopinath, A.; Olsson, L. A Kinetic Model for the Selective Catalytic Reduction of NO_x and NH₃ over an Fe-zeolite Catalyst. *Ind. Eng. Chem. Res.*, 2010, 49, 39-52.
- [13] Nedyalkova, R.; Kamasamudram, K.; Currier, N. W.; Li, J.; Yezerets, A. Experimental evidence of the mechanism behind NH₃ overconsumption during SCR over Fe-zeolites. *Journal of Catalysis* 299, 2013, 101-108.
- [14] Bacher, V.; Perbandt, C.; Schwefer, M.; Siefert, R.; Pinnow, D.; Turek, T. Kinetics of ammonia consumption during the selective catalytic reduction of NO_x over an iron zeolite catalyst. *Applied Catalysis B: Environmental* 162, 2015, 158-166.
- [15] Liu, Q.; Bian, C.; Ming, S.; Guo, L.; Zhang, S.; Pang, L.; Liu, P.; Chen, Z.; Li, T. The opportunities and challenges of iron-zeolite as NH₃-SCR catalyst in purification of vehicle exhaust. *Applied Catalysis A, General* 607, 2020, 117865.



This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 955413

Disclaimer: The sole responsibility for any error or omissions lies with the editor. The content does not necessarily reflect the opinion of the European Commission. The European Commission is also not responsible for any use that may be made of the information contained herein.