ARISTOTLE UNIVERSITY THESSALONIKI
SCHOOL OF ENGINEERING
DEPT. OF MECHANICAL ENGINEERING

Ammonia as a Marine Fuel Towards Decarbonization: Emission Control Challenges

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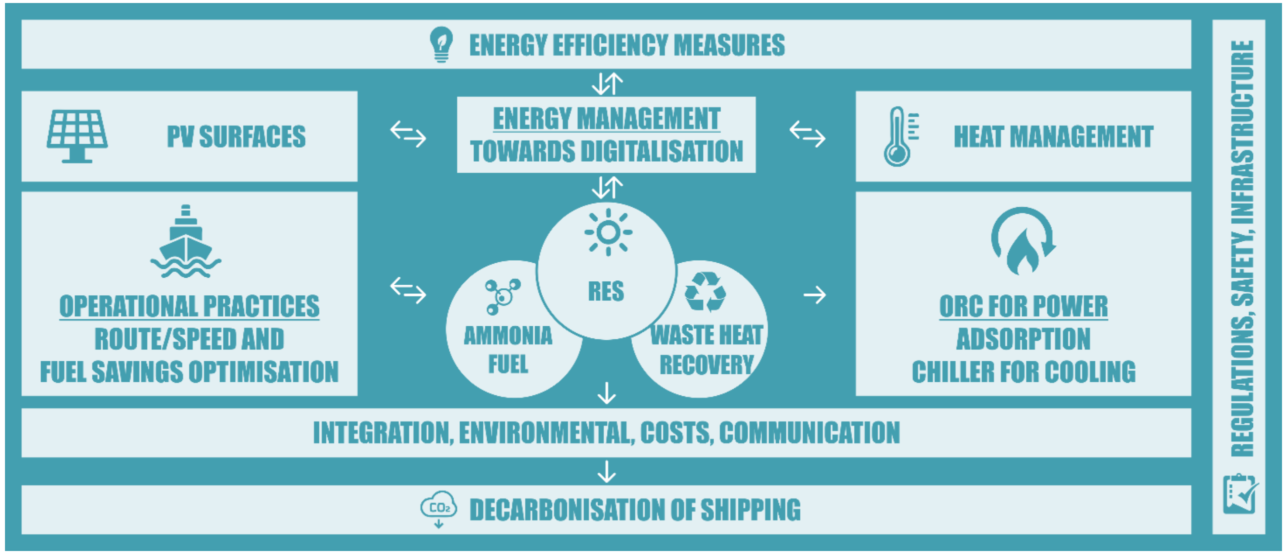
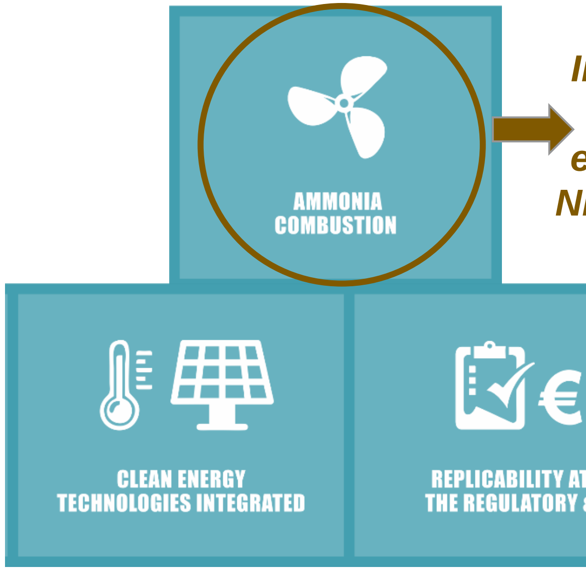
Source: EU official page

ENGIMMONIA – Sustainable technologies for future long-distance shipping towards complete decarbonization

Make Ammonia combustion fully zero emission
Bringing on board of real vessels samples of decarbonization technologie



Three main R&D Lines
Three demo vessels



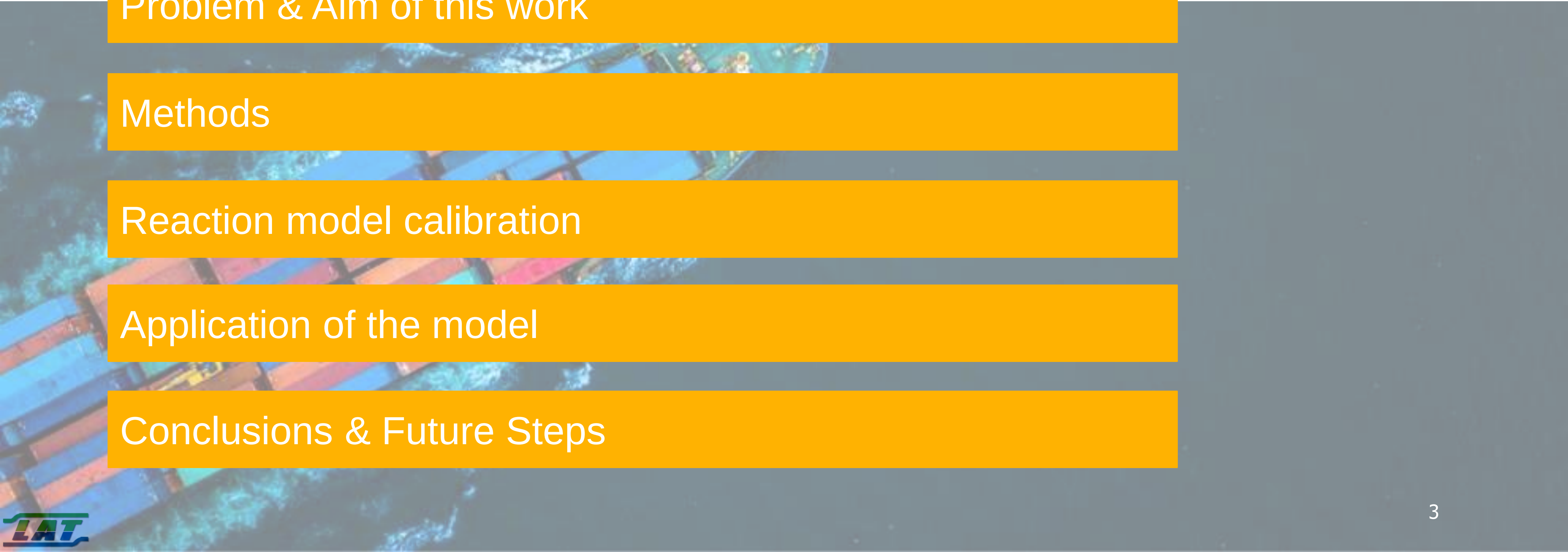
Incl. dedicated EATS for exhaust gas of NH_3 combustion

Targets

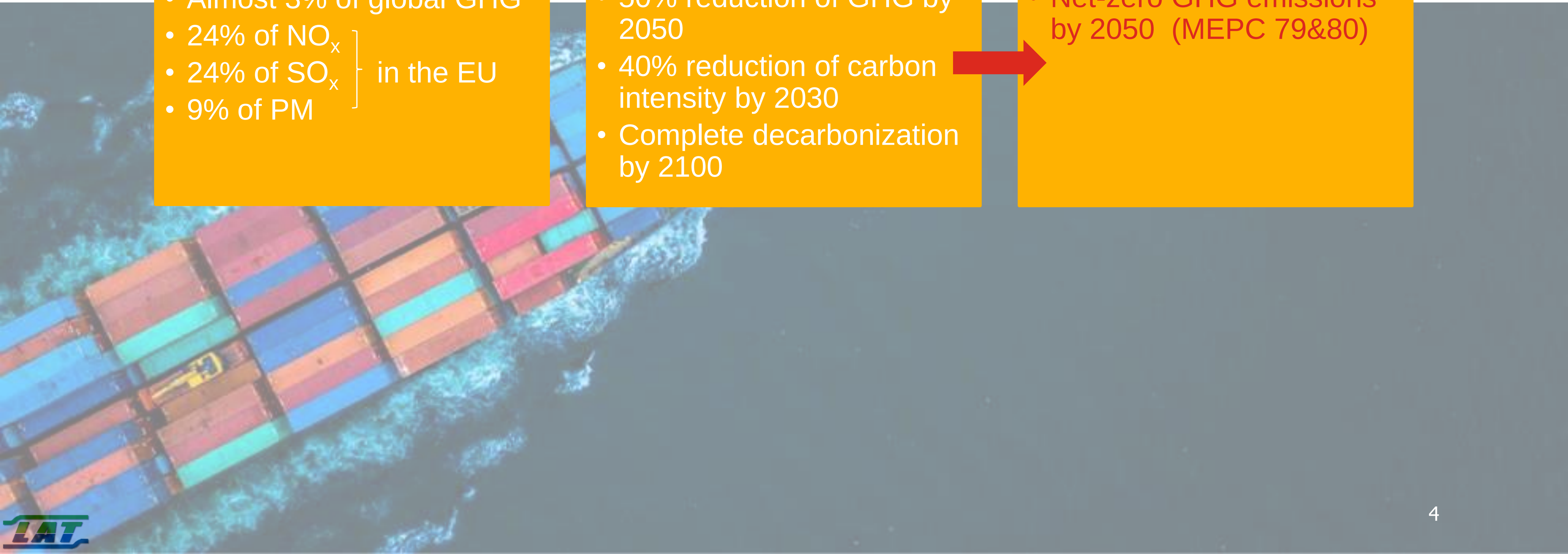
1) **promote ammonia** as the cleanest and most promising fuel for shipping sector;
2) **demonstrate clean energy solutions for on-board electricity and HVAC**;
3) **foster replicability at business, regulatory, policy and naval classification level**

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

Contents



Shipping contribution to GHG and pollutant emissions



Shipping accounts for:

- Almost 3% of global GHG
- 24% of NO_x
- 24% of SO_x
- 9% of PM

in the EU

IMO initial strategy:

- 50% reduction of GHG by 2050
- 40% reduction of carbon intensity by 2030
- Complete decarbonization by 2100

Revised strategy:

- Net-zero GHG emissions by 2050 (MEPC 79&80)

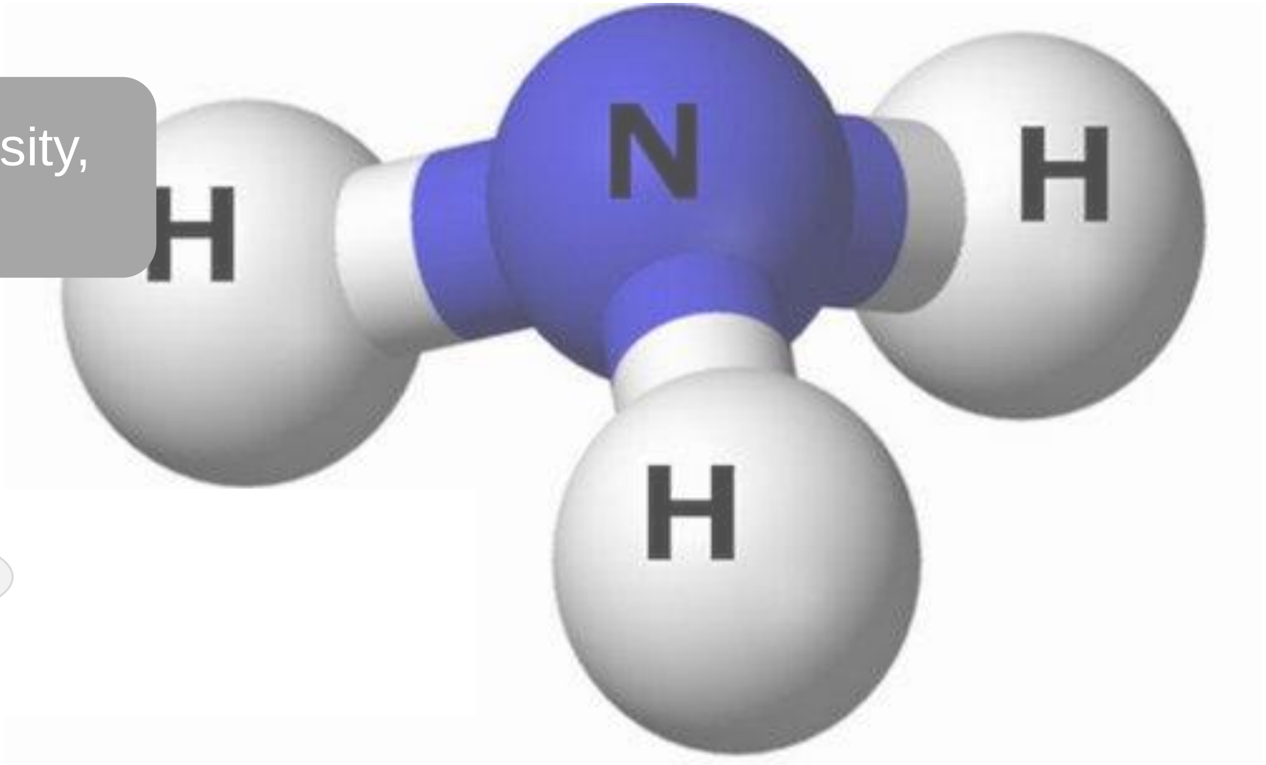
Ammonia (NH_3) as a fuel: Main emissions

Alternative, C & S free fuel, high energy density, easy storage etc.

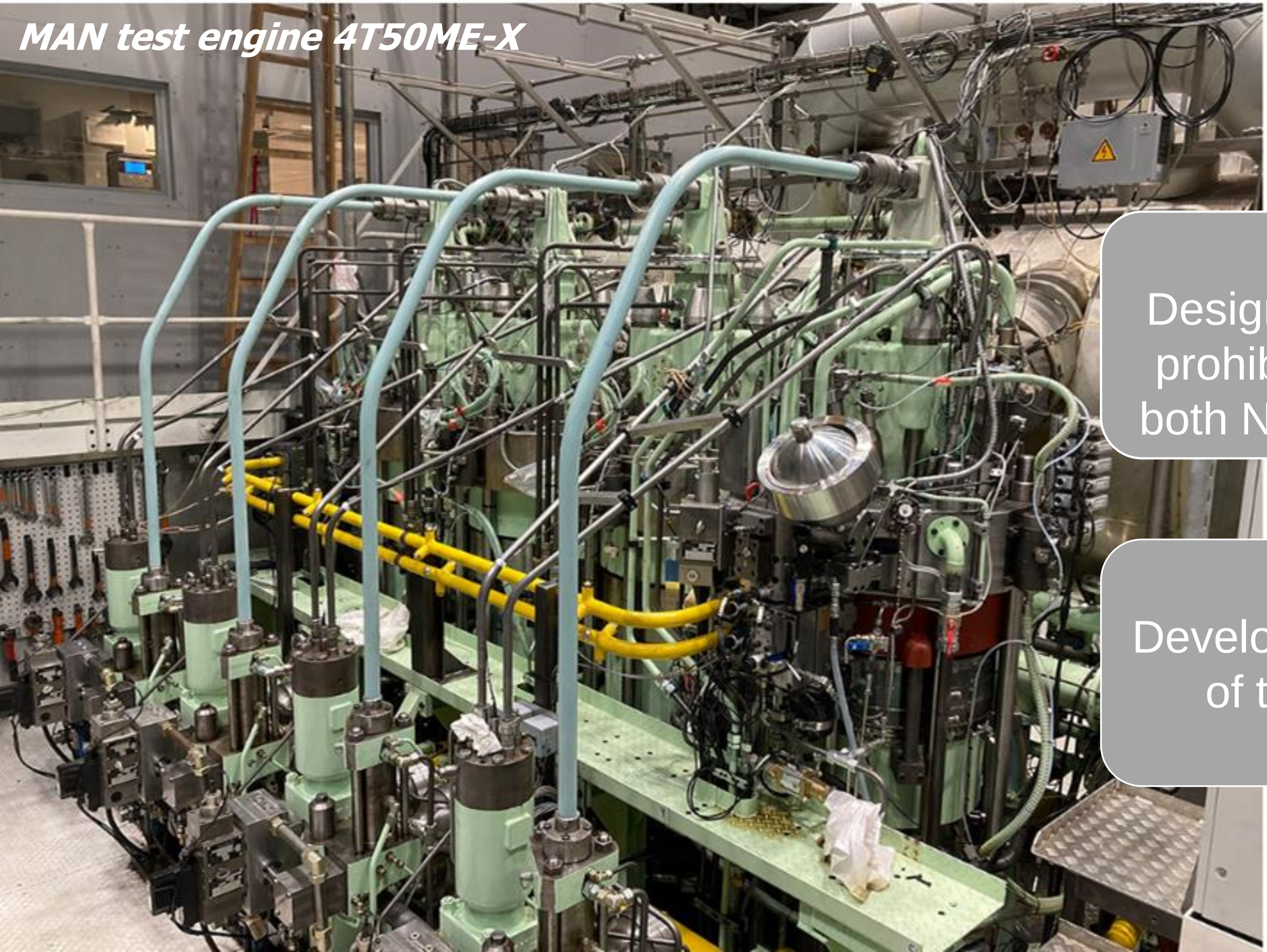
NH_3 combustion main emissions:

- Unburned NH_3
- NO_x
- N_2O →

strong GHG with 100-year GWP equal to 300.



Problem & General aim of this work


MAN test engine 4T50ME-X

PROBLEM

Design of emission control via trial and error is prohibitive in view of the huge testing costs of both NH_3 combustion & aftertreatment devices.

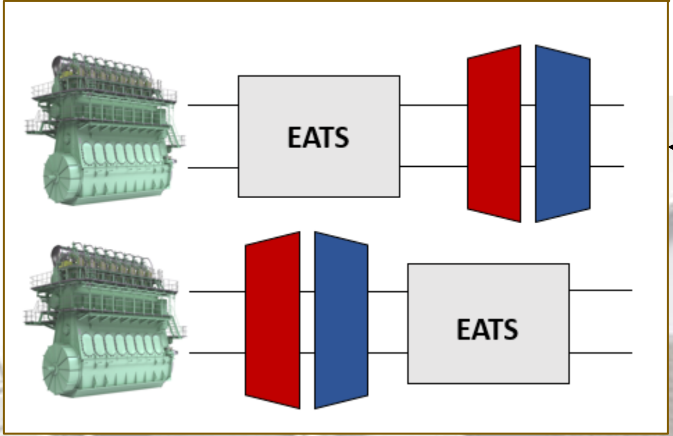
AIM

Development of accurate and predictive models of the aftertreatment system to guide the optimum design at an early phase.

Why are early-stage predictive models important…

Several parameters can be optimized

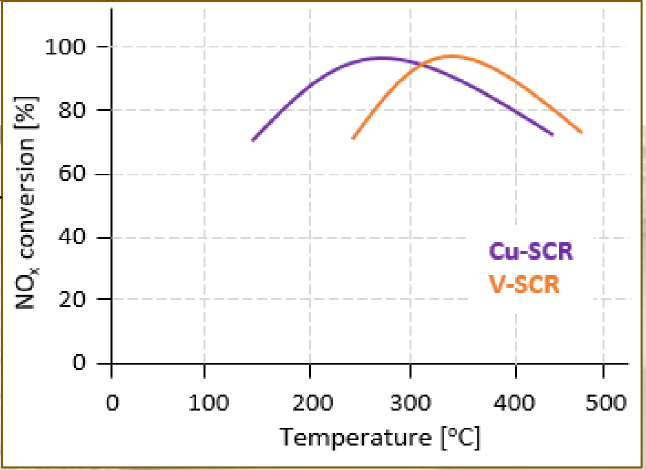
EATS position: HP vs LP EATS



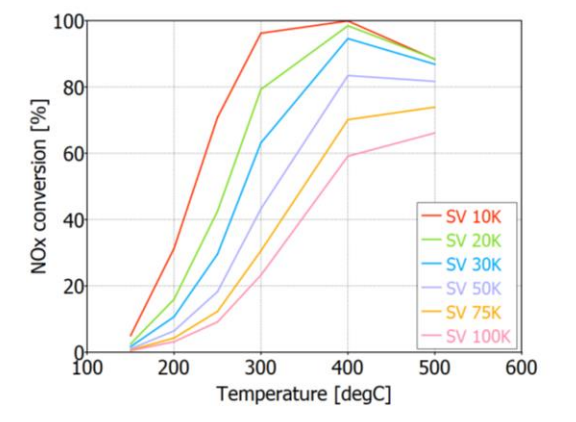
Catalyst technology

- ► SCR (deNO$_x$)
- ► AOC (NH$_3$ oxidation)
- ► deN$_2$O

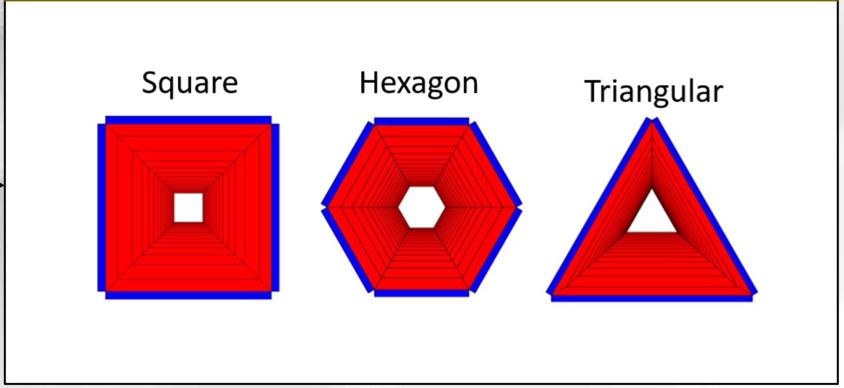
Active material: V-SCR vs Cu-SCR



Catalyst amount (loading), volume (SV)



Cell structure (i.e., cpsi, shape)



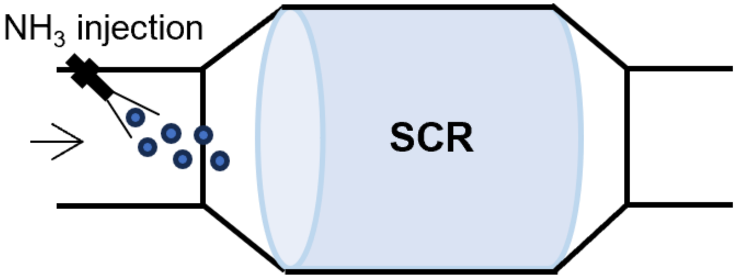
Why are early-stage predictive models important…

- Ammonia combustion is likely to result in unburned NH_3.
- Two possible scenarios of NH_3/NO_x ratio in the exhaust gas of the NH_3 engine:

$$\mathbf{4}\,NH_3 + \mathbf{4}\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O$$
$$\mathbf{4}\,NH_3^* + \mathbf{2}\,NO + \mathbf{2}\,NO_2 \rightarrow 4\,N_2 + 6\,H_2O$$

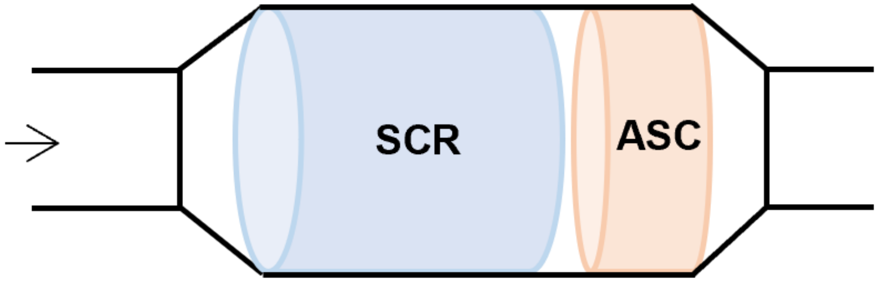
1. Lack of ammonia ($NH_3/NO_x<1$):

NH_3 injection upstream of SCR to reduce NO_x.



2. Excess of ammonia ($NH_3/NO_x>1$):

ASC placed after the SCR to handle unreacted NH_3 of the deNO_x process.

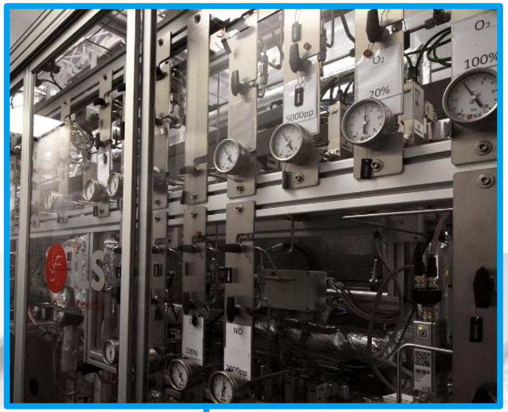


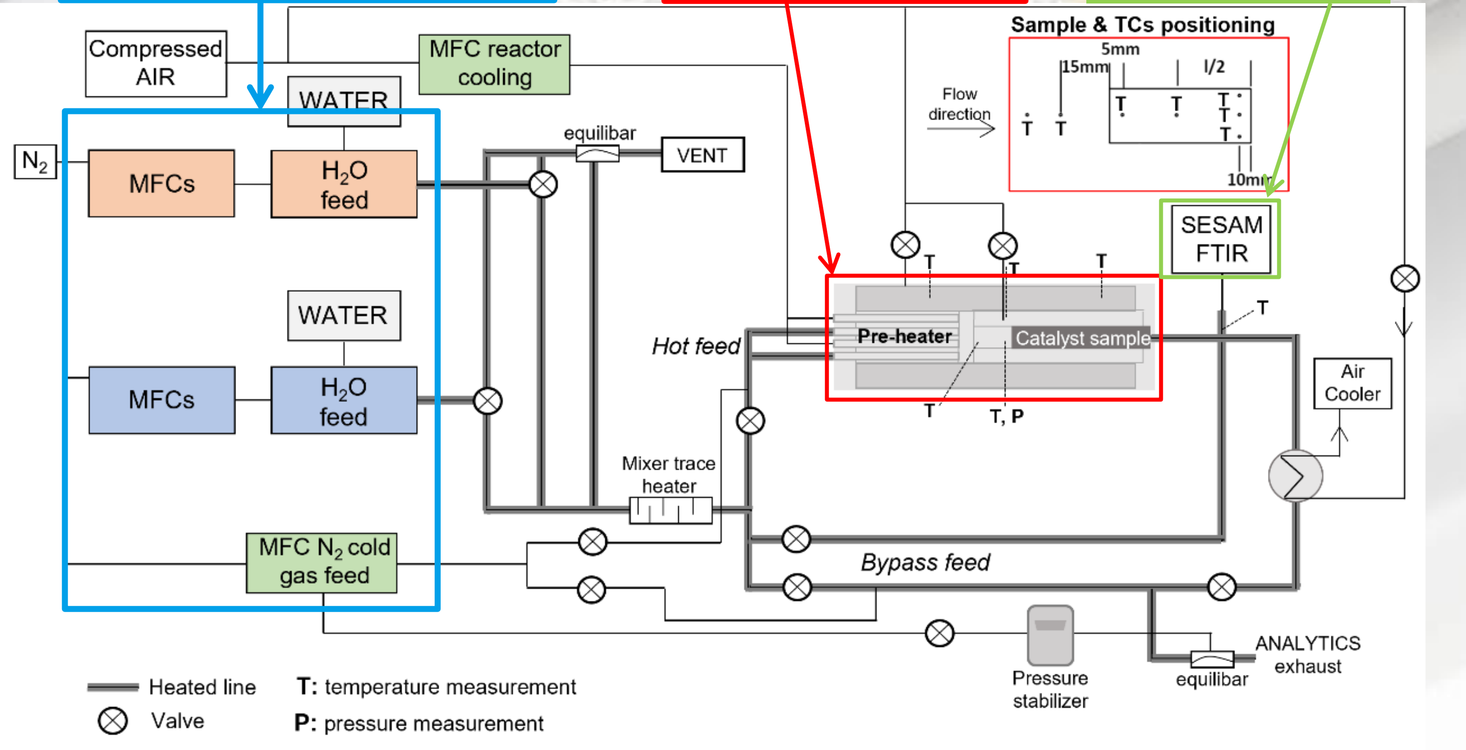
Experimental set-up

Small-scale testing in Synthetic Gas Bench (SGB)

Two commercial catalyst samples are tested:

1. Vanadium-based SCR (V-SCR)
2. Platinum-based AOC (Pt-AOC)





Model set-up: Mathematical model

“Exothermia suite” software

1D simulation approach (single channel):

- Uniform flow distribution.
- Negligible heat losses.
- Negligible internal diffusion.

Quasi- steady state balance equations for heat and mass transfer:

$$\rho_{\mathrm{g}} C_{\mathrm{p,g}} v_{\mathrm{g}} \frac{\partial T_{\mathrm{g}}}{\partial z} = -h \cdot \left(\frac{S_{\mathrm{F}}}{\varepsilon}\right) \cdot \left(T_{\mathrm{g}} - T_{\mathrm{s}}\right)$$

$$\frac{\partial\left(v_{\mathrm{g}} y_{\mathrm{g},j}\right)}{\partial z} = -k_j \cdot \left(\frac{S_{\mathrm{F}}}{\varepsilon}\right) \cdot \left(y_{\mathrm{g},j} - y_{\mathrm{s},j}\right)$$

Transient energy balance in solid phase (wall temperature):

$$\rho_s C_{\mathrm{p,s}} \frac{\partial T_{\mathrm{s}}}{\partial t} = \lambda_{s,\mathrm{z}} \frac{\partial^2 T_{\mathrm{s}}}{\partial z^2} + S$$

1D+1D model:

- Internal diffusion effects become important.
- Mass transfer both in the gas & solid phase.

Surface concentrations inside the washcoat: layer:

$$-D_{\mathrm{w},j} \frac{\partial^2 y_{\mathrm{s},j}}{\partial w^2} = \sum_k n_{j,\mathrm{k}} R_{\mathrm{k}}$$

Model set-up: Reaction mechanisms

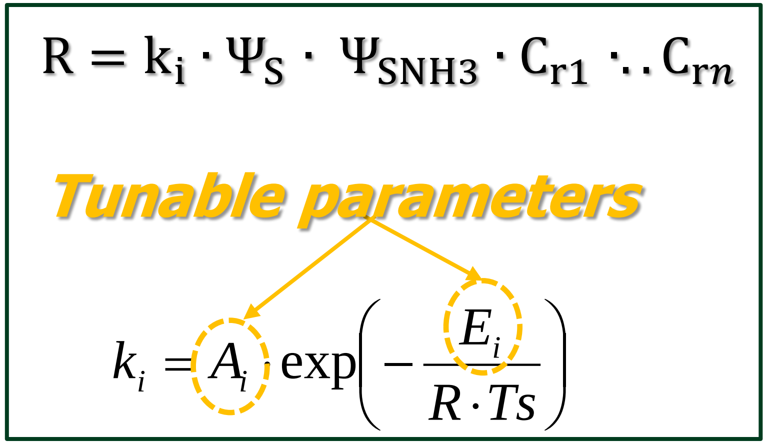
SCR reaction scheme

Type	**Reaction**
NH_3 storage/release	$NH_3 \leftrightarrow NH_3^*$
Standard SCR	$4\ NH_3^* + 4\ NO + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
Fast SCR	$4\ NH_3^* + 2\ NO + 2\ NO_2 \rightarrow 4\ N_2 + 6\ H_2O$
NO_2 SCR	$NH_3^* + 3/4\ NO_2 \rightarrow 7/8\ N_2 + 3/2\ H_2O$
N_2O formation	$2\ NH_3^* + 2\ NO + O_2 \rightarrow N_2 + N_2O + 3\ H_2O$ $2\ NH_3^* + 2\ NO_2 \rightarrow N_2 + N_2O + 3\ H_2O$
NO oxidation	$NO + ½\ O_2 \leftrightarrow NO_2$
NH_3 oxidation	$4\ NH_3^* + 5\ O_2 \rightarrow 4\ NO + 5\ H_2O$ $2\ NH_3^* + 3/2\ O_2 \rightarrow N_2 + 3H_2O$ $4\ NH_3^* + 4\ O_2 \rightarrow 2\ N_2O + 6\ H_2O$

*stored NH_3 on the catalyst sites

AOC reaction scheme

Type	**Reaction**
NO oxidation	$NO + ½\ O_2 \leftrightarrow NO_2$
NH_3 oxidation	$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 5\ H_2O$ $2\ NH_3 + 3/2\ O_2 \rightarrow N_2 + 3H_2O$
NH_3 & NO oxidation to N_2O	$2\ NH_3 + 2\ NO + 3/2\ O_2 \rightarrow 2\ N_2O + 3\ H_2O$



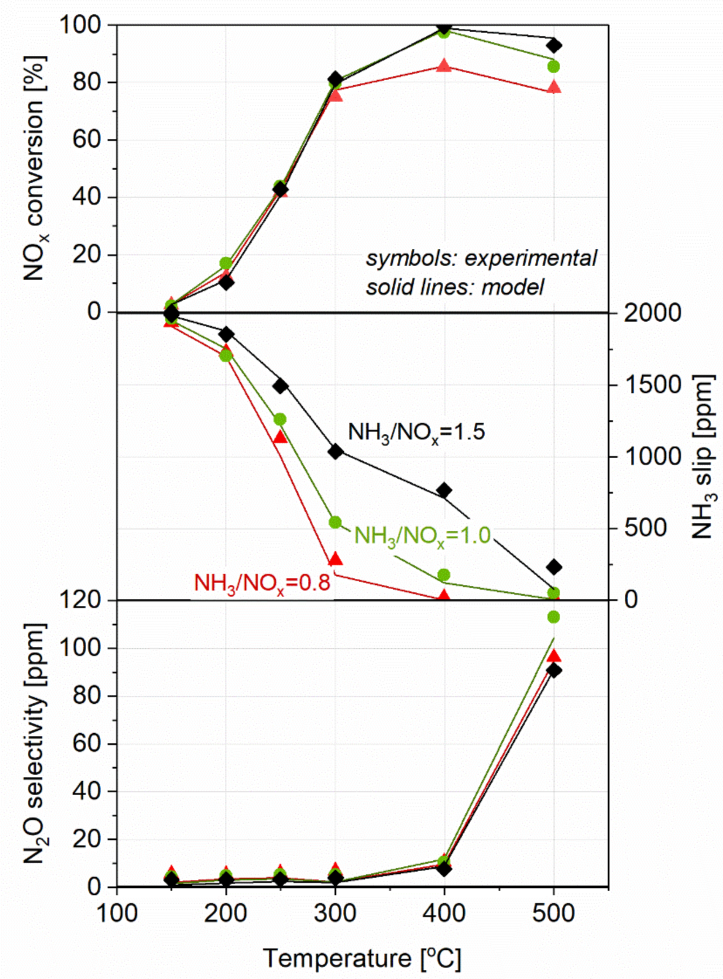
$$R = k_i \cdot \Psi_S \cdot \Psi_{SNH3} \cdot C_{r1} \cdot .. C_{rn}$$

Tunable parameters

$$k_i = A_i \exp\left(-\frac{E_i}{R \cdot Ts}\right)$$

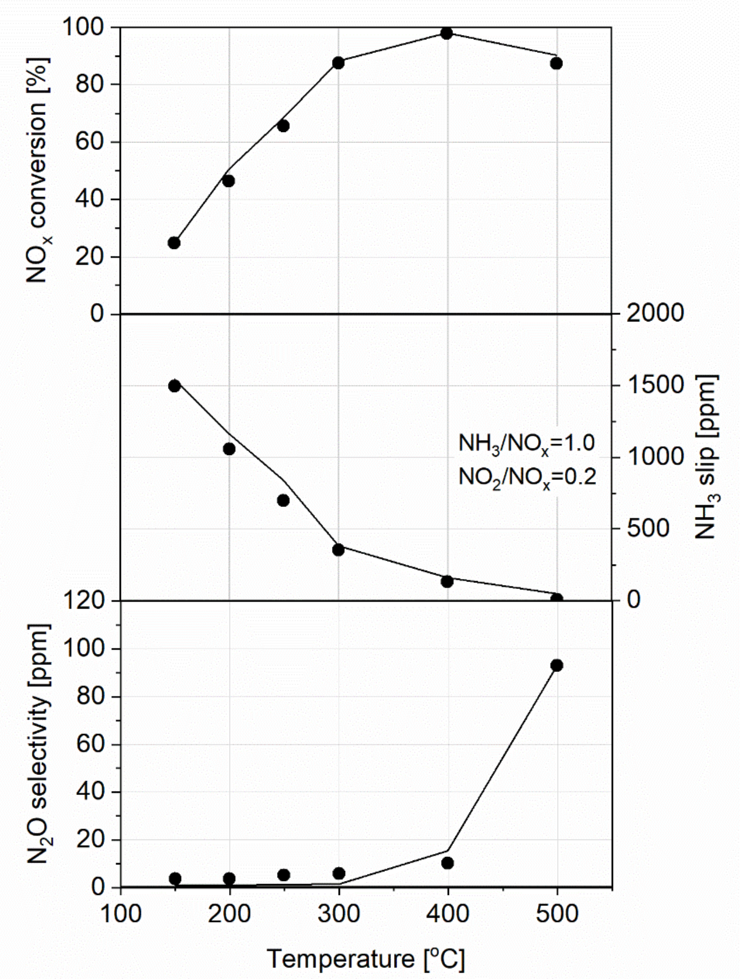
Reaction model calibration: V-SCR

Feed gas: NH_3 + NO + O_2



2000 ppm NH_3, NH_3/NO_x=0.8, 1.0, 1.5, 6% O_2, 15% H_2O, 15 ppm SO_2, N_2 balance GHSV=20,000 h^{-1}

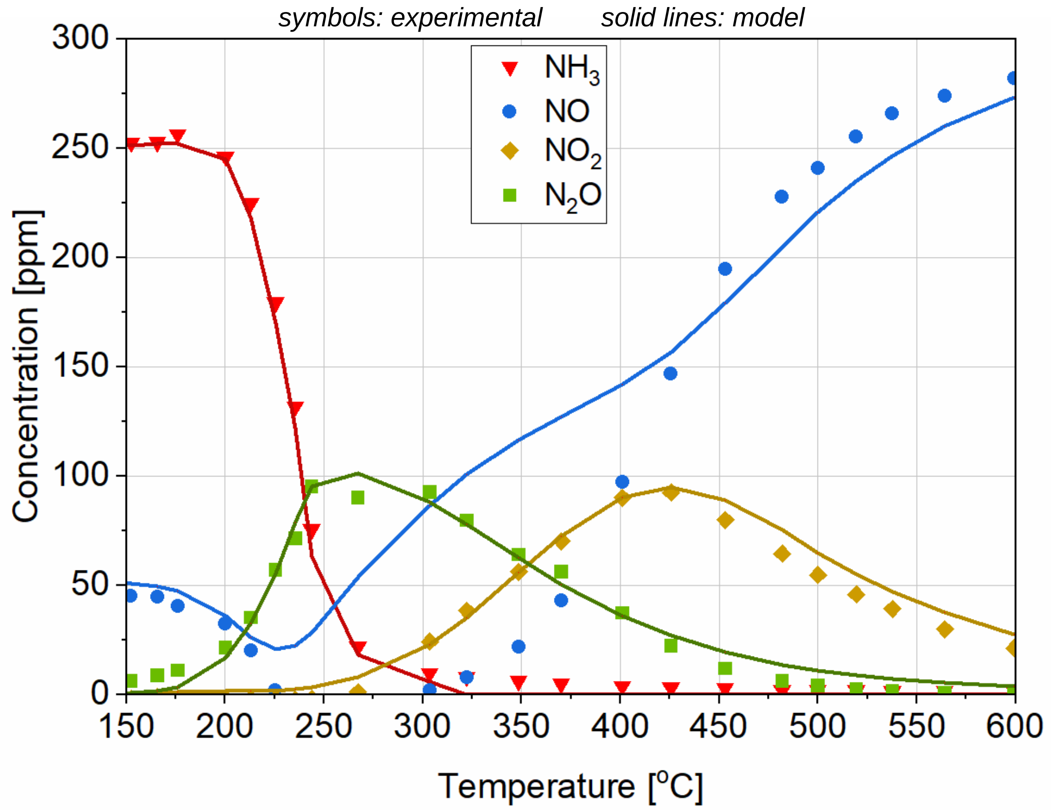
Feed gas: NH_3 + NO + NO_2 + O_2



2000 ppm NH_3, 2000 ppm NO_x (NO_2/NO_x=0.2), 6% O_2, 15% H_2O, 15 ppm SO_2, N_2 balance GHSV=20,000 h^{-1}

The model achieves a good agreement with the test results in the whole temperature range and is able to predict the reaction selectivity N_2O.

Reaction model calibration: Pt-AOC



250 ppm NH_3, 50 ppm NO, 6% O_2, 15% H_2O,
15 ppm SO_2, N_2 balance

GHSV=20,000 h^{-1}

The model achieves a good agreement with the test results in the whole temperature range and is able to predict the reaction selectivity N_2O.

Preliminary design of catalytic aftertreatment system

- Application of existing catalytic devices used in Diesel engines in NH_3 fueled engines.
- NO_x shall comply with Tier III limit of 3.4 g/kWh.
- Focus on the formation of N_2O in the EATS.

***Pre-turbo (HP)** exhaust gas conditions based on Diesel low-speed engines:

Engine load [%]	100	75	50	25
Exhaust gas temperature [ºC]	410	350	310	290
Exhaust gas pressure [bar]	4.0	3.1	2.1	1.4
SCR space velocity [h^{-1}]	40,000	32,000	25,000	10,000
ASC space velocity [h^{-1}]	140,000	115,000	85,000	40,000
NO_x [ppm]	1500-2000	1500-2000	1500-2000	1500-2000

Test cycle type E3	Power [%]	100	75	50	25
	Weighting factor	0.2	0.5	0.15	0.15

SCR volume is equal to 0.5 x engine displacement.

$$\text{GHSV}\ [h^{-1}] = \frac{\text{Volumetric flow of gas}}{\text{Volume of catalyst}}$$

Estimated deNO_x target = 90%

*Zhu, Li, et al., 2020; Zhu, Xia, et al.,2020

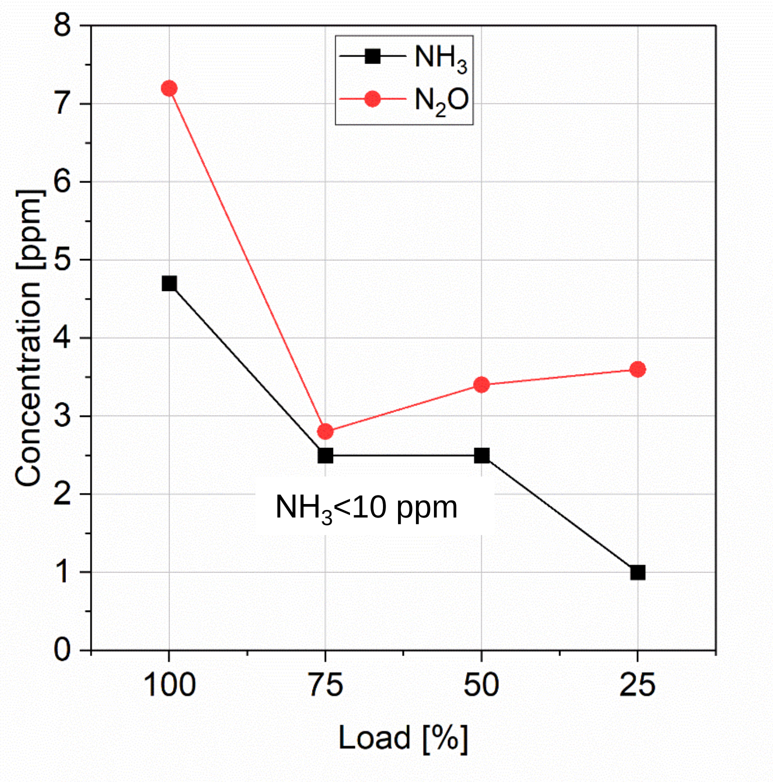
Results: $NH_3/NO_x<1$ (NH_3 injection)

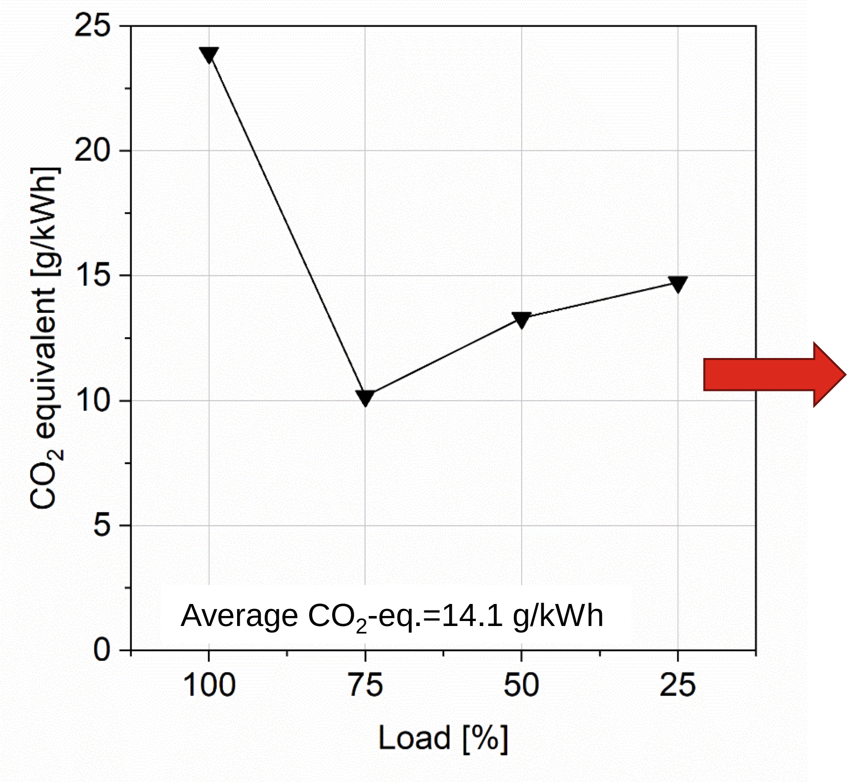
- *Optimal NH_3 injection to achieve 90% NO_x conversion at $NH_3/NO_x=0.9$*

$$\dot{m}_{N_2O} = \frac{C_{NOx} \cdot MW_{N_2O}}{MW_{exh}} \cdot \dot{m}_{exh}$$

$$\Downarrow$$

$$\dot{m}_{CO_2-eq.} = \dot{m}_{N_2O} \ x\,300$$



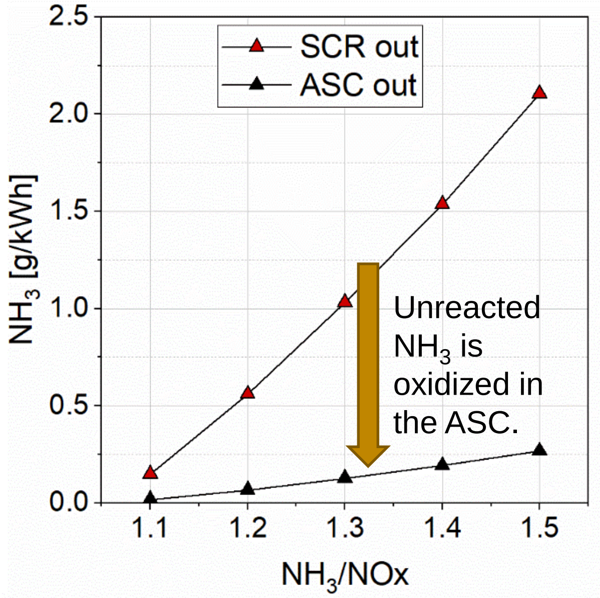


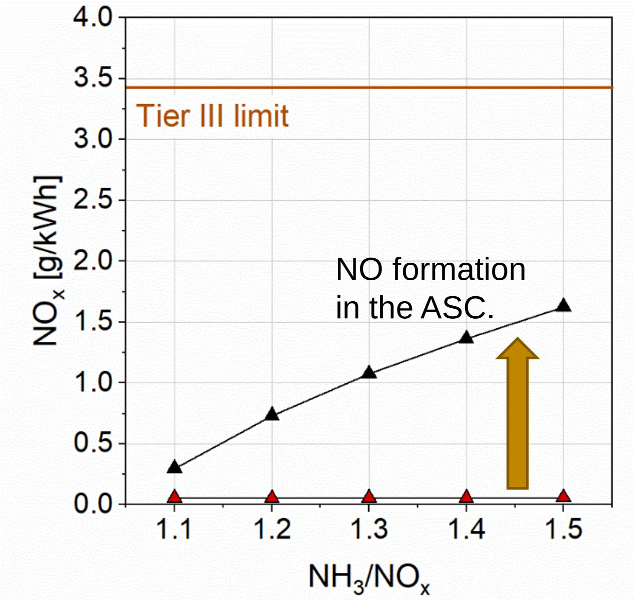
Important reduction compared to LNG operation where *CO_2-eq. emissions exceed **400g/kWh.**

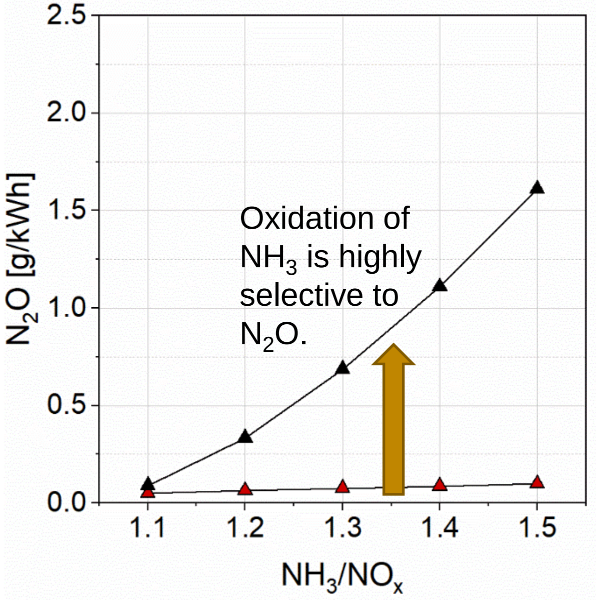
*Pavlenko, N. et al., 2020

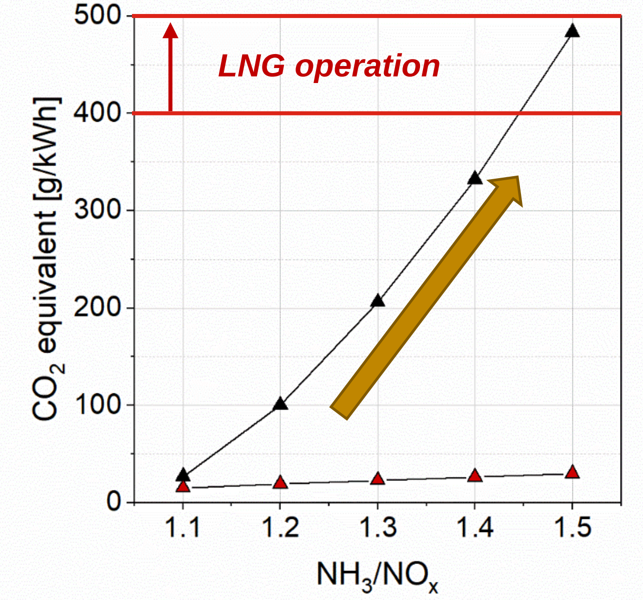
Results: $NH_3/NO_x>1$ (ammonia excess)

Average concentrations based on weighing factors of E3 test cycle at the SCR and ASC outlet.









Conclusions

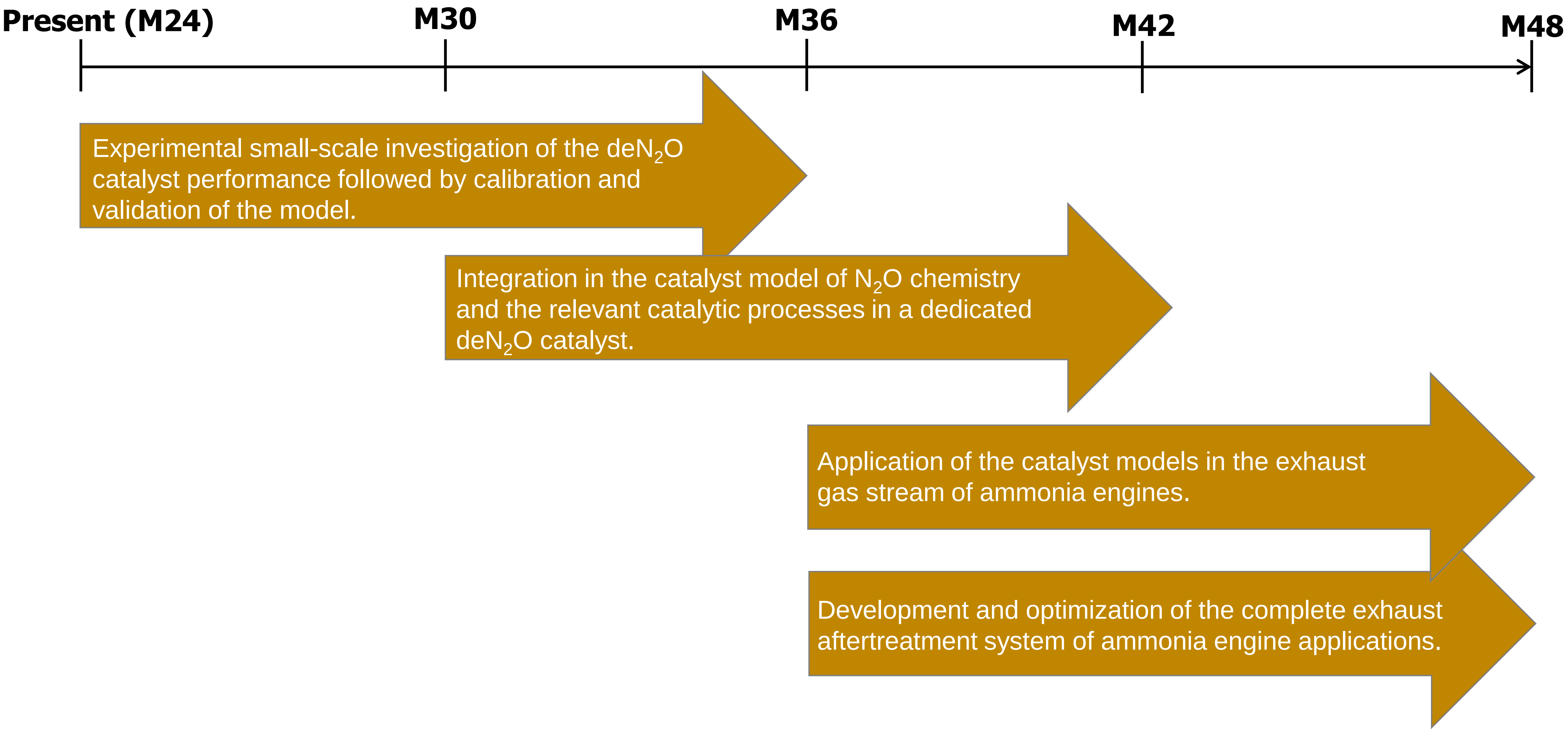
It is preferable to tune NH_3 combustion so that NH_3/NO_x is less than 1 to keep N_2O concentration formed in the EATS at low levels (ASC is highly selective to N_2O).

N_2O from ammonia combustion is expected to increase the total N_2O emissions.

High N_2O emissions may counterbalance the benefit from CO_2 reduction.

Both sources need to be considered to successfully control N_2O.

Future steps



Present (M24) M30 M36 M42 M48

Experimental small-scale investigation of the deN_2O catalyst performance followed by calibration and validation of the model.

Integration in the catalyst model of N_2O chemistry and the relevant catalytic processes in a dedicated deN_2O catalyst.

Application of the catalyst models in the exhaust gas stream of ammonia engines.

Development and optimization of the complete exhaust aftertreatment system of ammonia engine applications.

Acknowledgments

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ENGIMMONIA

Sustainable technologies for future long distance shipping towards complete decarbonisation

Funded by the European Union's
Horizon 2020 research
and innovation programme.

Thank you for your attention!