

SCR under pressure - pre-turbocharger NOx abatement for marine 2-stroke diesel engines

ABSTRACT

Since January this year, new requirements are in place regulating the NOx emissions from ship's engine exhausts. For decades Selective Catalytic Reduction (SCR) has been an established method for NOx abatement on board seagoing vessels and SCR equipment has been installed on a large number of four-stroke diesel engines. So far, only a few large marine two-stroke diesel engines have been equipped with SCR. The exhaust gas temperatures of such two-stroke diesel engines are in general lower compared to four-stroke engines so, in order to obtain sufficient operating temperatures, the SCR can be placed upstream of the turbine (turbocharger). As a consequence, the catalyst is operating at elevated pressures and high temperatures during high loads of the engine. On the other hand, at part loads the exhaust gas is close to ambient pressure and the temperature is at the lower operating limit of the SCR.

In 2015 Winterthur Gas & Diesel conducted a series of tests on a full scale pre-turbocharger SCR to establish engine test-bed procedures, map the performance of the engine/SCR, and to demonstrate compliance with Tier III limits. Moreover, a series of laboratory and bench scale experiments were conducted in order to test the catalyst operation and, explicitly, to be able to assess the effects of temperature and pressure on the catalyst performance.

Our tests show that a modern two-stroke engine, in combination with an SCR upstream the turbocharger, presents a fuel-flexible NOx compliant solution for sea-going vessels. This paper confirms methods for predicting the operating temperature of the catalyst when using residual fuels and when operating at elevated as well as atmospheric pressures. We show that the absolute minimum temperature for long-term operation is limited by the condensation of ammonium- and sulphate-containing salts in the bulk phase and that the SCR must not run for long periods at temperatures where significant amounts of the salt can condense in the catalyst pores.

In summary, careful control of the exhaust gas temperature of the two-stroke engine enables successful SCR operation with low sulphur fuels as well as with residual fuels containing high amounts of sulphur.

INTRODUCTION

Ships engine's emissions are regulated by the International Maritime Organization (IMO) [1,2]. MARPOL Annex VI [1] applies in respect to the emission of sulphur oxides (SOx) and nitrogen oxides (NOx), both globally and in designated geographical areas denoted as emission control areas (ECAs). The IMO limit on SOx emissions is correlated to the sulphur content of the fuel. Currently, the global limit is set to 3.5% sulphur and it will change to 0.5% sulphur in the year 2020, provided that such fuels are proven to be available for the industry by that time. The limit of sulphur fuel content that can be used in a sulphur emission control area (denoted as SECA) is 0.1%. An alternative to sulphur content limited fuel is to use secondary emission control technology for capturing sulphur oxides from the exhaust gases. In this context, wet flue gas scrubbers are used as a standard sulphur capturing technology.

IMO regulates the NOx emissions as defined under different stages or levels of control criteria denoted as Tiers. Unlike the SOx limits, the validity of the NOx relevant Tiers is dependent on the date when the vessel was constructed, or more precisely, when the vessel's keel laying was done. Vessels whose keel was laid later than 2011 need to comply with Tier II globally. Vessels with keel laying after 1 January 2016 and sailing in a NOx emission control area (denoted as NECA) need to comply with the most stringent level -

Tier III. At the time of writing this paper, North America and the US Caribbean are the only NECA's and for any new NECA's the Tier III limit will only apply for ships constructed after the date of adoption (of the new NECA by the Marine Environment Protection Committee or later when specified in the application of the new emission control area). The numerical value of the NO_x limits depend on the rotation speed of the engine (RPMs) and a test cycle at different load points is defined. For a main engine, typically a low-speed two-stroke engine with variable speed, the NO_x limit is 3.4 g/kWh, as averaged with weighting factors over the load points 25, 50, 75, and 100% load. An auxiliary engine running at 1800 rpm, on the other hand, has a lower Tier III limit of 2.0 g/kWh. Auxiliary engines with constant speed additionally need to prove the emission performance at a lower load of 10%. Table 1 shows geographical areas with their corresponding NO_x and SO_x emission limits as applied to a typical two-stroke ship propulsion engine.

NO_x CONTROL WITH DIFFERENT FUELS

The selection of fuel and emission control technology depends on many factors. Rational drivers are naturally the capital investment costs as well as operation costs, together with the process limitations of the technology of both the main- and auxiliary engines of the ship. The combination of the emission control areas, the rules and limits of NO_x and SO_x emissions and the ship's sailing pattern, make the selection of the abatement technology a complicated equation. At present, all NECA's are also sulphur control areas. New regions that would limit only NO_x and omit the SECA obligation seem less likely. As a consequence, the NO_x abatement technology is operating with a <0.1% sulphur fuel, typically being a distillate light fuel oil. Still, the use of high sulphur content fuels, such as the predominant residual fuel with a sulphur content of up to 3.5%, in the combination with a flue gas sulphur capturing technology, is interesting in terms of allowing greater flexibility in choice of fuel, especially for vessels that operate for a large proportion of their time in SECA's. Vessels sailing between Asia and Europe may have around 100-200 hours of time in a SECA per trip. When assuming 6 round-trips per year, this adds up to between 600 and 1200 SECA hours per year. On the other hand, vessels sailing between Asia and the USA may have substantially more running hours in SECA's because they may make more port calls per trip and sail longer in the emission control area. For large two-stroke engines, low pressure selective catalytic reduction (SCR) or even the concept of exhaust gas recirculation might be a possible emission control technology. However, for fuel flexible solutions, high pressure SCR is the established method [3].

Table 1 Emission standards, geographic areas and emission limits that apply to low-speed two-stroke engines.

Pollutant	Area	Rule	Geographic area	Limit
NO _x	NECA	Marpol Annex VI Reg. 13, Tier III	North America US Caribbean	3.4 g/kWh
SO _x	SECA	Marpol Annex VI Reg. 14	North Sea Baltic Sea North America US Caribbean	0.1 % Sulphur fuel

Recently, oil companies have developed economic alternatives to the <0.1% sulphur distillate fuels. The properties of these fuels are often similar to those of residual fuels, yet still providing the low sulphur content that enables the ship to sail in SECA's without installation of sulphur capturing equipment.

SCR FOR SHIPS

SCR is a proven method to reduce NO_x emissions from ships. It has been used for three decades and the total number of vessels with SCR installed exceeds 500 [4,5]. The majority of the SCR systems have been installed on four-stroke diesel engines. So far, a fairly low number of large marine two-stroke engines were equipped with SCR and the industrial experience is less established. For such low-speed engines, the exhaust temperature is in general lower compared to a four-stroke engine, so in order to obtain an appropriate operating temperature at the catalyst, the reactor housing can be placed upstream of the turbine (turbocharger). As a consequence of this arrangement, the two-stroke engine SCR is operated at elevated pressures and high temperatures during high power. On the other hand, at part loads the exhaust gas is close to ambient pressures and the temperature will be close to or under the operating limit of the SCR, especially when running on fuels with a higher sulphur content. The exhaust gases of pre-turbine SCR installations has, in addition, a wider temperature range compared to an SCR placed after the turbine. When placing the SCR upstream of the turbine it is often called "high pressure SCR" in the technical literature of the two-stroke diesel industry. When the equipment is downstream the turbine it is denoted as "low pressure SCR". A critical examination of the design parameters (temperature and pressure) of two-stroke high pressure SCR systems is the principle focus of this paper. Particular attention is paid to high sulphur heavy fuel oils and the exhaust temperature requirements to make use of this fuel.

TWO-STROKE LOW-SPEED ENGINE SCR

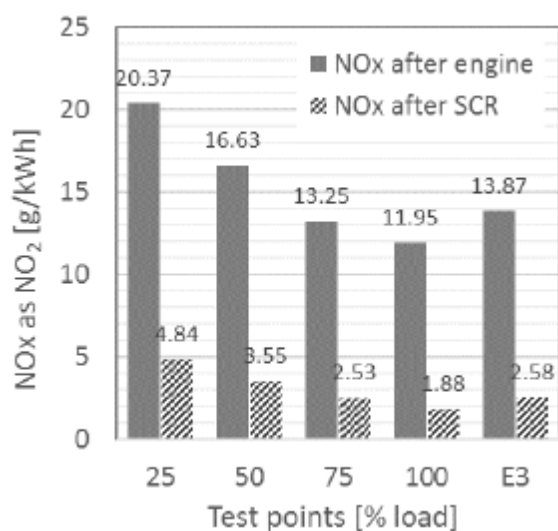
The high pressure SCR system, placed downstream of the cylinders and upstream of the turbine, consists of equipment for injecting the reducing agent, mixing the reducing agent with the exhaust gases and a housing where the catalytic material is located. Moreover, it involves several dampers or valves. The purpose of the valve system is to enable temperature management of the catalyst and to be able to by-pass it when there is a reason to exclude the use of SCR. The operation of the engine, the valves, and SCR system is conducted by dedicated control systems. Three high pressure SCR systems were installed on vessels equipped with 7RTA-52U Sulzer/Wärtsilä engines in 1999 and 2000 [6]. The next high pressure SCR delivery for a Wärtsilä engine was 15 years later and was a 5RT-flex58T-D shop-tested in January 2015 [7]. Two more W6X72 engine SCRs are delivered at the time of writing this paper. Figure 1 shows the HHM-Wärtsilä 5RT-flex58T-D SCR delivered to Ouhua shipyard for hull 667 later named Papuan Chief. Its engine was shop-tested to Tier III limits as illustrated in Figure 2.

Placing the SCR upstream of the turbine of a two-stroke low-speed engine has, however, significant design influences as compared to conventional postturbine SCR. Normally the pressure would be 1 bar and the exhaust temperature is more even over the engine load range. The most important limitation in the use of SCRs on two-stroke engines is the required minimum operating temperature. This limitation is partly due to the decreased deNO_x catalyst activity at lower temperatures and consequently the inability to reduce NO_x, but also due to a potentially increased ammonia slip which may lead to deposits on surfaces of the exhaust gas economiser/boiler, especially in the case of using residual fuels typically containing 1.0% - 3.5% sulphur. Moreover, as will be described later in this paper, low exhaust gas temperatures, typically already 320 to 360°C, may result in condensation of ammonium and sulphur salts on the catalyst surface or in the pores of the catalyst and again result in a decrease of deNO_x activity.

Figure 1 SCR system of the 5RT-flex58T-D engine.



Figure 2 NO_x emissions for the 5RT-flex58T-D engine, measured as defined by the NO_x technical code and the E3 test cycle [2].



The exhaust temperature of a modern two-stroke low-speed engine typically ranges from 250 to 500°C and the pressure is ranging from 1.0 to 4.5 bar. Figure 3 shows an example of the exhaust temperatures and pressures before and after the turbocharger of the Wärtsilä W6X72 engine as calculated using Winterthur Gas & Diesel's performance program referred to as GTD [8]. The engine parameter values shown in Figure 3 are calculated to ISO 3046-1:2002 conditions. Pressures and temperatures for the test cycle ISO8178 E3 of the same engine are shown in Table 2.

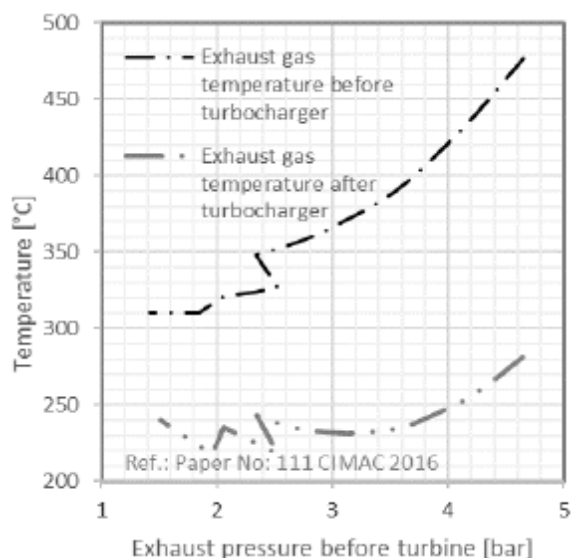


Figure 3 Exhaust gas temperatures before and after the turbocharger of a modern two-stroke low-speed engine, the Wärtsilä 6X72 engine [8].

The (low) activity of the catalyst that take place at low temperatures is, however, not an SCR design limit. As such, by increasing the amount of catalyst, the NO_x abatement is achieved also at temperatures of around only 200°C. A low temperature SCR (also called "tail end") is in fact commonly used for low sulphur stationary applications. In such installations the catalyst system is designed for periodical regeneration by increasing the SCR operating temperature. A similar approach is currently being commercialised for two-stroke applications [9].

Table 2 Exhaust pressures and temperatures for the W6X72 engine [8].

Engine load	%	100	75	50	25
Pressure before turbine	bar	4.3	3.3	2.3	1.4
Temperature before turbine	°C	448	379	348	310
Pressure after turbine	bar	1.0	1.0	1.0	1.0
Temperature after turbine	°C	263	232	243	240

THE SCR CATALYST TEMPERATURE

The minimum working temperature for the SCR with respect to the condensation of ammonium- and sulphur- containing salts is determined from predicting the bulk condensation of the salt:

$$K = \frac{p_{\text{NH}_3(\text{g})} \times p_{\text{H}_2\text{O} \cdot \text{SO}_3(\text{g})}}{a_{(\text{NH}_3 \cdot \text{H}_2\text{SO}_4)(\text{cd})}} \quad (\text{eq. 1})$$

Where K is the temperature dependent equilibrium constant for bulk condensation as obtained from experimental data [10]. The thermodynamic activity of the condensed phase is denoted as $a_{(\text{NH}_3 \cdot \text{H}_2\text{SO}_4)(\text{cd})}$. Since the partial pressures of the gaseous components (ammonia gas, $\text{NH}_3(\text{g})$ and gaseous sulphuric acid, $\text{H}_2\text{O} \cdot \text{SO}_3(\text{g})$) are dependent on the total pressure, the condensation temperature of the salt increases with the receiver pressure, therefore also with the engine load. The partial pressure of ammonia is calculated based

on the theoretical amount of $\text{NH}_3(\text{g})$ in the exhaust gas and is as a consequence dependent on the amount of accessible ammonia from the injected reducing agent. The concentration of $\text{H}_2\text{O} \cdot \text{SO}_3(\text{g})$ is predicted from the gaseous sulphur with an oxidation state +VI. In practice it is calculated from the sulphur content of the fuel and the predicted share of sulphur forming $\text{S}^{+\text{VI}}$. As only fairly inconsistent data was available on the extent of $\text{S}^{+\text{VI}}$ oxidation in two-stroke engine flue gases, and because the isopropyl method for the determination of $\text{S}^{+\text{VI}}$ had shown results systematically too low, we used a modified method for the estimation of the partial pressure of gaseous $\text{S}^{+\text{VI}}$ containing components [11]. Figure 4 shows the predicted bulk condensation temperatures for different exhaust gas pressures when varying the sulphur content of the fuel. Curves are calculated for a fuel consumption of 165 g/kWh, an exhaust flow of 8.0 kg/kWh, and a $\text{NH}_3(\text{g})$ concentration of 1000 ppm. A total sulphur oxidation of 5-10% (available $\text{S}^{+\text{VI}}$) is indicated as a "grey area" for the total pressure of 1.0 bar and 4.3 bar.

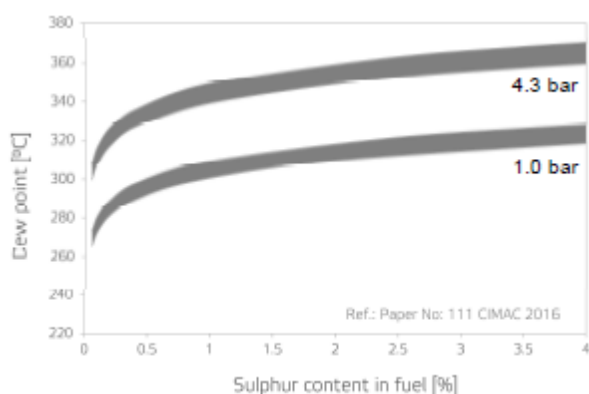


Figure 4 Bulk condensation temperatures of ammonium sulphates at exhaust pressures 1 and 4.3 bar and varying sulphur content in the fuel.

From Figure 4 we read a condensation temperature of 321°C when we assume atmospheric pressure, an $\text{S}^{+\text{VI}}$ share of 10%, and a fuel sulphur content of 2.4% (currently considered as an average sulphur content for fuels used on ocean going vessels). In the case when only 5% of the sulphur was oxidized the temperature would be 9°C lower. Besides the bulk condensation of ammonium sulphates, ammonia and sulphur also have the potential to decrease the SCR activity through condensation inside the pores of the catalyst [10]. Condensation in the pores and with it the decrease of the catalyst activity occurs at higher temperatures compared to the bulk condensation shown in Figure 4. The extent of this temperature increase is shown in Figure 5 where the relationship between the bulk condensation and the pore condensation of ammonium sulphate salts (in pores with a radius of 30 Angstroms) is predicted according to the same data. For the pore radius given above and the same log K value (same ammonia and sulphuric acid partial pressures) the pore condensation occurs at approximately 30°C above the bulk condensation temperature. Below this threshold temperature there will be a potential for severe deactivation of the SCR since a large proportion of the pores in the catalyst would be filled with ammonium sulphate salt.

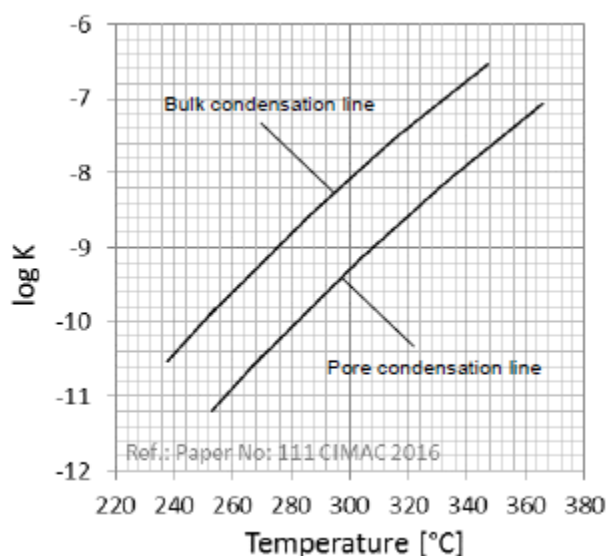


Figure 5 Relationship between the bulk condensation temperature and pore condensation temperature of ammonium sulphate salt.

Furthermore, the condensation properties are not constant for the entire catalyst bed. In the front of the bed the dew point is considerably higher due to the higher concentration of reducing agent. Downstream of the entrance section of the catalyst the reducing agent is consumed and the dew point temperature is reduced. Figure 6 shows the bulk dew point change along the flow direction of a catalyst when running on 2.4% sulphur residual fuel and injecting 1200 ppm ammonia.

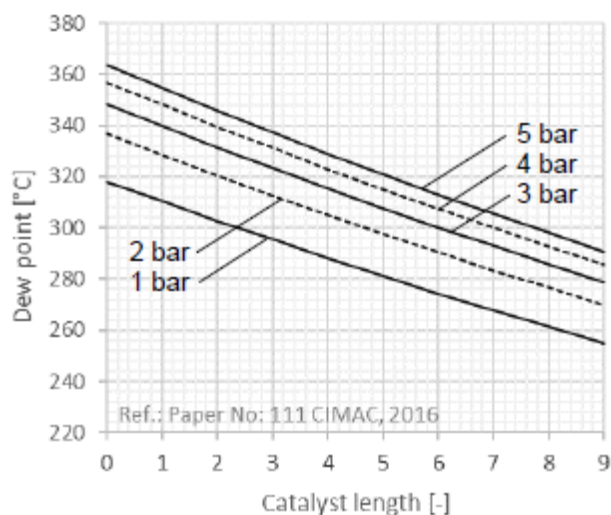


Figure 6 Ammonium sulphate salt bulk dew point change for 1, 2, 3, 4, and 5 bar total pressures as predicted along the flow direction of a catalyst when running on 2.4% sulphur residual fuel and injecting 1200 ppm $\text{NH}_3(\text{g})$.

In case the temperature is below the bulk condensation point, the catalyst system will always show a total failure with time because the condensation zone will successively shift downstream from the catalyst front. Still, in case of operation in the region of pore condensation (i.e. at temperatures above the bulk condensation point), the catalyst will deactivate but has the potential to maintain its performance providing that there is a sufficient amount of available catalyst.

The ammonium sulphate salt condensation reaction is reversible and the catalyst activity can be regained. Our investigations with a bypass stream SCR on the 6.5 MW 4-cylinder 500 mm bore size Winterthur Gas & Diesel test engine showed that total recovery can be obtained when the catalyst is operated above the bulk condensation temperature. Tests also showed that a temporary operation (short-term) of the catalyst at 15°C below the salt bulk condensation still enabled successful regeneration within a reasonable time frame and temperature profile. The tests showed, however, a very fast deactivation of the catalyst and operation under the dew point is therefore not recommended.

LOW AND HIGH LOAD OPERATION

At low temperatures, when the catalyst activity is reduced and where there is a potential for catalyst activity decline due to ammonium sulphate condensation in the pores of the catalyst, the SCR system design must ensure a sufficient catalyst reserve to safeguard the deNO_x performance and to minimize the risk of process problems. Below the ammonium sulphate salt bulk condensation point, a larger amount of catalyst will be of no help since the condensation front will migrate downstream in the catalyst until there is total deactivation and failure of the system. Ammonia and sulphur-containing salts may also deposit on the surfaces of the exhaust gas heat recovery equipment. At high sulphur content, the limiting component for the formation of ammonia and sulphate-containing deposits will be the ammonia slip. It is therefore particularly essential to minimize the ammonia slip when running with high sulphur fuels. On the other hand, when running on low sulphur fuels (<0.1%) the limiting component for deposit formation is sulphate but the potential amount of a deposit is then lower and hence the risk for harmful boiler deposits is less. To avoid excessive ammonia slip and excessive dosing of ammonia, the catalyst designer make use of slip curves obtained from laboratory tests. Figure 7 show a typical catalyst ammonia slip curve plotted as a function of the stoichiometric ratio of reducing agent to NO_x, denoted as alpha (α). The temperature of the test was set to 350°C and the pressure to 1.3 bar.

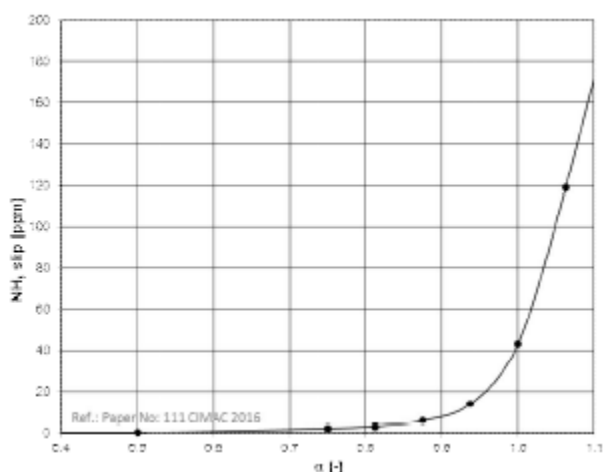


Figure 7 Ammonia slip curve plotted as a function of the stoichiometric reducing agent to NO_x ratio, α .

Figure 7 also shows the importance of avoiding overdosing of reducing agent. Low temperature SCR performance can to some extent be improved by making use of a catalyst with high vanadium content. However, this type of catalyst has potential (negative) design implications on the reducing agent consumption when running at high loads and high temperatures and therefore its performance needs to be checked for these conditions as

well. Figure 8 shows tests for resolving the extent of reducing agent “self-oxidation” when running at high load, resulting in a higher temperature and pressure. When operated at a high temperature, a high-vanadium SCR has an excessive reducing agent oxidation. Moreover, it has the potential to oxidize gaseous sulphur to S^{+VI} that may result in a visible bluish exhaust plume [12]. An increased amount of S^{+VI} in the exhaust also increases the risk of salt deposits in the heat recovery equipment downstream of the catalyst.

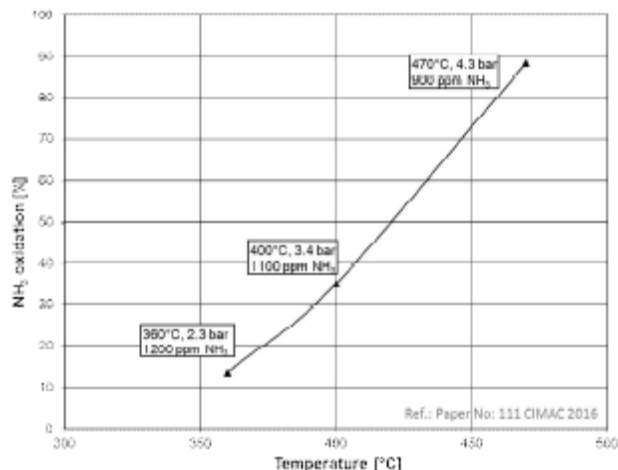


Figure 8 Extent of reducing agent oxidation when running SCR at high temperatures.

CONCLUSIONS

From January this year (2016) legislation is in place requiring new ships to meet with the new NO_x limits. This means that in practice new ships equipped with two-stroke engines, running on liquid fuels and sailing in North America or the US Caribbean, need to be equipped with secondary NO_x emission abatement. As emission control areas for NO_x are also emission control areas for SO_x, the ships are likely to run on 0.1% sulphur fuels in the designated ECA zones. However, due to the fact that operators wish to maintain fuel flexibility, some vessels may be expected to use high sulphur residual fuels as well. These vessels running on >0.1% sulphur residual fuels must be equipped with flue gas desulphurisation.

For residual fuels, two-stroke diesel engines utilise a NO_x emission control technology placed upstream of the turbine (turbocharger). This system, commonly denoted as high pressure SCR, operates under more variable conditions (temperature and pressure) compared to the unpressurized SCR equipment commonly used on four-stroke marine engines. With high sulphur fuels, the design temperatures and pressures are increasingly important for operational efficiency and for avoiding process problems with the equipment.

This paper shows that careful temperature control of the engine exhaust gases enables successful operation of the engine together with the SCR when using a high sulphur fuel. At low loads, the minimum catalyst temperature is determined by predicting the condensation point of ammonium sulphate salts from the bulk phase. These salts are also responsible for a catalyst activity decrease occurring at temperatures significantly higher than the bulk condensation. A prediction of the extent of salt condensation in the pores of the catalyst makes it possible to assess the associated decrease in catalyst activity and allows a temporary SCR use at lower exhaust temperatures. Running with high sulphur fuels at temperatures below the ammonium sulphate salt bulk condensation should, nevertheless, be avoided. Even though, our tests showed that the catalyst activity can recover, operation is risky and will eventually lead to a total failure of the SCR. Besides adjusting the engine for low load operation, the engine temperatures needs to be matched

with the catalyst to ensure a low urea consumption at high loads and to avoid potential deposits in the heat recovery system.

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 634135, HERCULES II. The authors would in addition like to thank Martin Elsener and Oliver Kröcher of the Paul Scherrer Institute for the good collaboration.

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