



Green shipping: Marine engine pollution abatement using a combined catalyst/seawater scrubber system. 1. Effect of catalyst [☆]



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ABSTRACT

A marine engine pollution abatement system was constructed and tested on a 1.5 MW auxiliary marine engine. The integrated system, designed to abate all of the currently legislated emissions from marine engines, consisted of a monolithic Pt/Al₂O₃ oxidation catalyst and a seawater scrubber, both of suitable dimensions for the engine size. The test results obtained showed the general validity of the approach adopted, as significant abatement of emissions was achieved. However, under the conditions used, the system showed some limitations with regard to the sulphur content of the fuel. On the basis of the results obtained, the system can be used with fuel sulphur content of up to 0.4%, while problems were encountered when a fuel with a sulphur content of 2.0% was used. Whereas the catalytic section operated satisfactorily, fine tuning of the scrubber operating conditions is necessary to improve abatement of NO_x and increase the range of fuel sulphur which can be used with the system.

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1. Introduction

Abatement of air pollution generated from mobile sources, namely automobiles and trucks, has been one of the most successful stories of catalytic science [1]. In fact, after the introduction of the catalytic converter in 1976, catalyst performance was continuously improved as legislation requirements became tighter and tighter. Compared to unregulated exhaust in the early 70s of the last century, nowadays a degree of catalytic pollution abatement well over 95% is achieved in the case of gasoline-fuelled engines equipped with the three-way catalysts (TWCs), which is a very efficient technology [2,3]. The increase of oil prices and the necessity to limit CO₂ emissions following the Kyoto protocol, together with significant engine technology improvements that occurred over the last 20 years, for example, introduction of common rail injection systems for diesel engines and development of novel lean-burn gasoline engine, favoured widespread use of these engines,

[☆] This article is dedicated to the memory of Haldor Topsøe, whose lifelong mission was to develop and transfer innovative catalytic technology to the industrial world. The subject matter of the present investigation illustrates his visionary approach: Haldor Topsøe's research laboratory addressed the issue of post-combustion abatement for ships already in 1997 (CATTECH, 1 (1997) 125), whereas stringent regulations that require novel technologies will come into force in a near future.

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particularly in light duty vehicles. A major drawback of the TWC is its inefficiency in converting NO_x under lean conditions [4]. Despite more than 30 years of research in the field, no lean deNO_x catalyst capable of selectively reducing NO_x using fuel hydrocarbons has been brought to a market stage, despite the identification of a number of promising systems [5,6]. In fact, technology transfer from well-established stationary state technology [7], that is use of selective catalytic reduction (SCR) catalysts using *in situ* generated ammonia, has been successfully applied to road transport and nowadays is marketed on heavy-duty vehicles, as well as some light duty diesel vehicles [8]. As a result of these continuous improvements in emission control, considerable reduction in emissions has been achieved: for example a reduction of 46% for road transport NO_x emissions was observed in European Economic Area (EEA) countries in the 1990–2010 period. However, road emissions still accounted for ca. 40% of total NO_x emissions in 2010 [9]. It must be underlined that the ever decreasing legislation limits to emissions have represented a major driving force for innovation [10].

Surprisingly enough, sea transportation, which represents the most economic method of transportation of goods and accounts for transport of ca. 90% of all trade by volume to and from the EU-25 member states, and 80% by weight of all trade in and out of the United States [11], has not been considered until relatively recently [12,13]: Annex VI of the MARPOL 77/78 (MARine POLLution) convention of the International Maritime Organisation

(IMO), which regulates “Prevention of Air Pollution from Ships”, entered into force on the 19th of May 2005. This regulation, however, is quite relaxed compared to land transport and in fact results in strong environmental concerns in terms of overall shipping emissions, both at present and for the future (Fig. 1). Comparison of NO_x regulation is also presented in Fig. 1, highlighting the relatively lenient IMO NO_x limits.

The comparison is more striking when the sulphur content in the fuel is considered: 3.5% is currently the maximum fuel sulphur content allowed by IMO regulation (1.0% in the EU), which will be decreased to 0.5% by 2020. These limits are somewhat more stringent in the so-called SECA's (Sulphur Emission Control Area) where a sulphur content of just 0.1% will be allowed from 2015. This compares to a sulphur content of less than 10 ppm in commercial diesel fuel used for land transportation. As a result of these relaxed regulations, it is estimated that maritime emissions of SO_x and NO_x will surpass those from land-based sources by 2017 and 2020, respectively.

It is important to underline that fuel quality plays a crucial role in marine transport. Ocean shipping carriers typically burn heavy fuel oil (HFO), which is a residual product of crude distillation with an average sulphur content of about 2.7% [14]; when entering into a SECA zone, low sulphur content (0.1% from January 2015) fuel must be used, usually MDO (marine distillate oil) or MGO (marine gas oil), both being obtained from distillation of crude, which makes them more expensive by ca. \$300/ton compared to HFO (ca. \$900 vs. \$600 – September 2014). This makes the use of HFO and fitting the engine with an effective exhaust post-treatment an economically interesting option, an option which is allowed by legislation [15]. In fact, the cost of the fuel is a major contributor to the economics of marine transport.

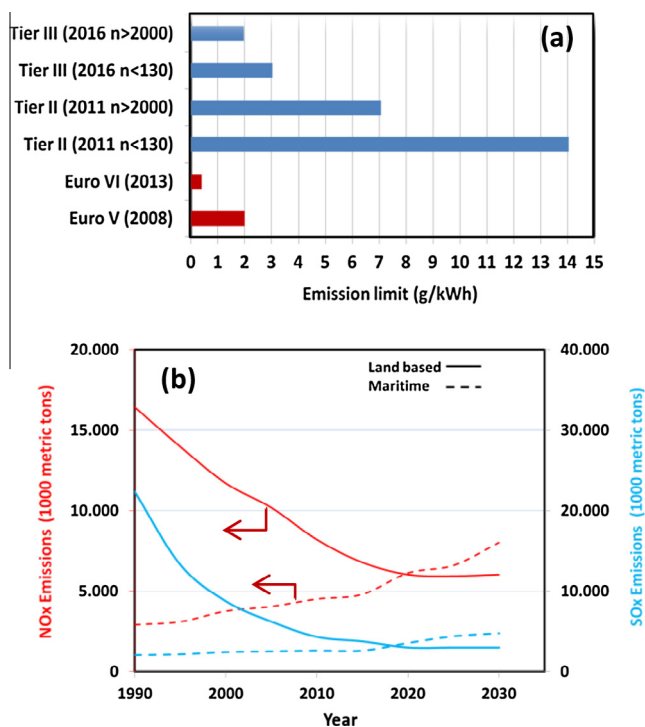


Fig. 1. (a) Comparison of legislation limits to NO_x emissions between the marine (IMO, MARPOL 77/78, Annex VI, Regulation 13) and EU Emission Standards for Heavy-Duty Diesel Engines: Steady-State Testing. For marine emissions, low- and high-speed engine limits are reported (*n*: rotations per minute (rpm)). (b) Inventories and projections of NO_x and SO_x emissions in Europe from land-based and international shipping sources. Adapted from [11].

In line with the above discussed technology transfer, use of scrubbers for SO_x removal and urea-SCR for NO_x removal has also been addressed in the marine sector [15,16]. However, it must be considered that to achieve IMO TIER III NO_x target (Fig. 1), use of urea-SCR technology is considered necessary [10,17]. This adds complexity to the problem: both scrubber and urea-SCR reaction should be placed at the engine outlet. Use of scrubbers for desulphurisation is an assessed process with efficiencies over 90% [18,19]. However, use of urea-SCR for NO_x abatement in exhausts with high content (500–1000 ppm) of SO_x is prone to difficulties due, *inter alia*, to oxidation of SO₂ and formation of ammonium sulphates, particularly below 300 °C [7]. An exception, *cited with pleasure in this dedicated volume*, is the Haldor Topsøe “Sulphur and nitrogen removal – SNOX™” process designed for stationary plants, which, besides simultaneously removing all the pollutants, transforms waste into a valuable product, that is sulphuric acid [20].

Notably, the issue of effects of high SO_x content on the urea-SCR of diesel exhausts is usually not considered by researchers [21]. On the other hand, placing the SCR reactor after the scrubbing section would require reheating the exhausts which is energetically unacceptable. Thus, development of a single compact device capable of efficient and simultaneous abatement of SO_x, NO_x and particulate matter (PM) is highly desirable.

As indicated above, desulphurisation of exhausts by seawater scrubbing has been used for stationary plants [22] and this technology has indeed been transferred to the marine sector: major marine engine producers do offer technology for SO₂ abatement using either open-, closed- or hybrid-loop scrubber systems [23]. As is well known, NO_x are mostly emitted as NO and, due to its poor solubility, wet-adsorption must be promoted by adding an oxidant that forms NO₂, thus promoting NO_x solubility [24–27]. Whereas such an approach is in principle possible, it must be noted that on-board storage of chemicals is undesirable due to both space/volume constrains and security issues.

We have addressed the issue by combining catalytic and scrubber technologies to achieve a “single compact” device for simultaneous abatement of PM, NO_x, SO_x, CO and hydrocarbons (HC). The concept has been investigated both at laboratory- and pilot-scales [28], using real exhausts generated from diesel engines run on low and high sulphur content fuels, within the framework of the ECOMOS project.¹ The laboratory micro-plant was employed to assess the feasibility of the project and to provide information for dimensioning of the pilot plant, which used an Isotta Fraschini V1716T2TE 1.5 MW marine engine. The results obtained on the pilot plant are presented here, focussing the catalytic aspects, whereas those on the micro-plant will be detailed elsewhere. To our knowledge, NO oxidation under such harsh conditions has not been addressed as previous studies have focussed either model feed or low sulphur content fuels.

2. Experimental

Realisation of the current project necessitated the construction of a pilot plant at the Fincantieri Shipyard, Riva Trigoso, Italy. This consisted of an Isotta Fraschini V1716T2TE, used as an on-board auxiliary engine; an oxidation catalyst, assembled on commission by Opitergina Marmitta di Nespole Renzo & C (S.N.C.); and a seawater scrubbing system, obtained from EcoSpray Technologies S.r.l. The main engine and catalyst characteristics are listed in Table 1. It should be noted that the catalyst and scrubber were dimensioned on the basis of a preliminary laboratory investigation [28] and taking into account the engine emissions and exhaust flows provided by the manufacturer.

¹ See acknowledgments for the ECOMOS project.

Table 1
Engine and catalyst characteristics.

<i>Engine</i>	
Model	Isotta Fraschini V1716T2TE
Nominal power	1500 kW @ 1650 rpm
Number of cylinders	16
Engine displacement	67 dm ³
Nominal speed	1800 rpm
Fuel used	DMA ISO 8217
Average consumption	205 ± 3% kg h ⁻¹
<i>Catalyst</i>	
Diameter	847.9 mm
Length	90 mm/monolith
Volume	50.818 cm ³
Number of monoliths	2
Cell density	200 cpi
Washcoat grade	KD2
Pt loading	40 g/cft

The catalyst consisted of a metallic monolith, onto which a Pt/Al₂O₃ active phase was wash-coated. As with analogous catalysts used for automotive application, the catalyst was housed in a container with matting to provide vibration resistance. The catalyst was divided into two equivalent sections.

The seawater scrubber contained three main abatement sections: a Venturi scrubber for PM abatement and two tray towers to promote intimate contact between the gas phase and the scrubbing water. The first of these towers was designed mainly for abatement of gas phase species (SO_x and NO_x). In fact, the exhaust gas was emitted from the system at this stage, through the use of an extractor fan. The second tray tower was designed for oxidation of aqueous species, such as SO₂ dissolved in the scrubbing water, by the addition of air.

The pilot-plant set-up and piping is illustrated schematically in Fig. 2. Measurement points for various parameters – gas phase composition, temperature, pressure, gas flow and water flow – were positioned throughout the system.

The data discussed in the present work relate to the composition of the exhaust gas at various significant points throughout the system. These measurement points are indicated by full circles and are labelled P1 to P4. Various other parameters were also measured at P1 to P4, in addition to a rather large amount of data collected at the other measurement points, which are indicated by white circles. These data will not be specifically discussed here, as they mainly relate to process control parameters. However, when necessary, the information collected at these points will be used for the purposes of calculations (for example, the gas flow rates).

With regard to the gas phase composition, measurements taken at P1, P3 and P4 correspond, respectively, to the composition measured at the engine outlet, the composition after the catalyst section and the composition after the gas scrubbing section. The last-mentioned compositions therefore correspond to the composition emitted into the atmosphere. Measurements at P2 correspond to the composition between the two catalytic beds and thus allow progressive transformations over the catalyst to be investigated.

At sampling points P1–P3, the gas phase composition was measured with an MKS MultiGas™ 2020 FTIR instrument, using the in-built diesel calibration method. This method allows real time monitoring of all the expected products from diesel combustion, for example NO_x and N₂O, in addition to H₂O and CO₂ quantification. In addition, an EcoPhysics CLD 700 El ht chemiluminescence analyser and an Ersa Tec SmartFID portable flame ionisation detector (FID) were used to monitor oxides of nitrogen (NO, NO₂, and, consequently, NO_x) and total hydrocarbon (THC), respectively. PM measurement was performed using a MAHA MPM4 laser scattering particle measurement unit. Heated (180 °C) gas transfer lines were used to avoid sample condensation. With regard to the nitrogen species, only data for NO and NO₂ are considered as N₂O formation was not detected. At sampling point P4, a Semtech-D gas analyzer was used to measure CO, CO₂, THC and NO/NO₂ concentrations and an EcoPhysics fluorescence detector for SO₂.

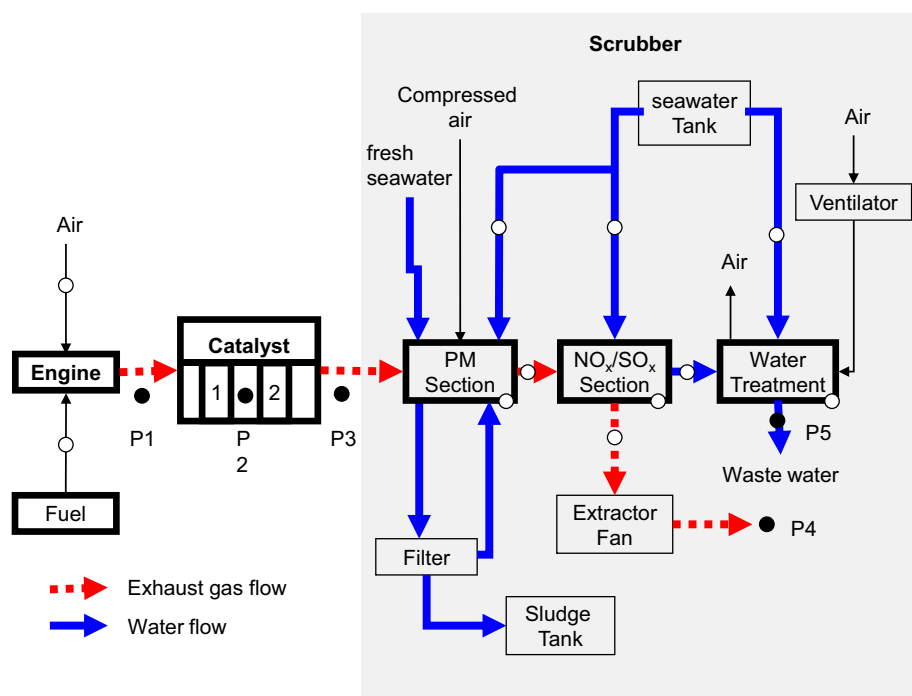


Fig. 2. Scheme of the engine/catalyst/scrubber: all the scrubber section was positioned in a smokestack (greyed) to simulate a realistic situation and size. Points P1–P4 indicate positions where exhaust composition was measured. In the PM section, a spray of water is used to mechanically remove the PM from the gas stream, followed by wet filtration.

NO and NO_x conversion are calculated respectively as
$$\text{NO} (\%) = \frac{\text{NO}^{\text{in}} - \text{NO}^{\text{out}}}{\text{NO}^{\text{in}}} \left(\frac{\text{ppm}}{\text{ppm}} \right), \text{NO}_x (\%) = \frac{\text{NO}_x^{\text{in}} - \text{NO}_x^{\text{out}}}{\text{NO}_x^{\text{in}}}$$

Since high sulphur fuel cannot be sold locally, thiophene was added to normal diesel in various amounts to simulate fuels with variable sulphur content. Thiophene is, in fact, one of the principle sulphur-containing compounds in fuel and it is normally used for the purpose of simulating high sulphur concentration. Three fuels were thus considered in the present work: normal diesel, without addition of thiophene; 0.4 wt% S; and 2 wt% S. It should be noted that the normal diesel fuel has a sulphur concentration of 10 ppm. The engine load points were chosen on the basis of the IMO NO_x technical code (MARPOL Annex VI, Regulation 13) and the SO_x regulation (MARPOL Annex VI, Regulation 14). These are as follows: 100%, 75%, 50%, 25% and 10% of total engine power for NO_x; and 100%, 50%, 18%, 5% and 0% for SO_x in our engine. These points are used for the certification of a marine engine.

All data were collected at an engine speed of 1500 rpm. On engine start-up, the speed was gradually increased to this value. The data reported in the present work are the average values measured over three-minute periods under the conditions indicated. After a change in engine operating conditions, a stabilisation period of at least 10 min was allowed to pass before the start of the three-minute data-reporting period. However, the gas phase composition was measured continuously. This allowed the transient response of the system to be monitored. The measurements were performed over a two-month period.

To conduct preliminary tests and to scale the above-described pilot plant, a laboratory-scale plant was also constructed and tested as part of the project. This consisted of a Faryman 18B-D diesel engine (cylinder displacement = 290 cm³, maximum power output = 4.0 kW, exhaust flow = 350 L min⁻¹) connected to variously dimensioned monolithic Pt/Al₂O₃ catalysts and a laboratory scale, 4 tower scrubber commissioned for the plant, with a maximum water flowrate of 100 L min⁻¹ (EcoSpray Srl).

3. Results and discussion

As discussed in the introduction, oxidation of NO to NO₂, which is the major component of NO_x emitted from diesel engines, was the first challenge of the present project. This reaction has received attention in the literature due to its relevance in lean deNO_x processes and PM oxidation [6,29,30]. Since the development of novel catalysts was not the focus of this research, the choice of the catalytic system was made on the basis of previous research. In this respect, it must be stressed that marine engine exhausts show peculiarities with respect to commonly investigated systems, that is conventional diesel or model exhausts. For example, the exhaust temperature range depends on the engine technology. Four-stroke high-speed marine engines easily experience exhaust temperatures up to 600 °C, whereas two-stroke low-speed engines hardly exceed half of this value. Furthermore, the amount of the exhaust is very high: about 3.5 kg/s of exhausts can be emitted from an 1.5 MW APU (auxiliary power unit) compared to ca. 7 × 10⁻² kg s⁻¹ from a conventional 2 L diesel engine. Last, but not least, is the amount of SO_x emitted, which can exceed 1000 ppm. For comparison: in studies carried out on fuels typically used in the 90's of the last century, for a fuel content of ca. 500–300 ppm, around 20 ppm of SO_x could be found in the exhausts [2,31]. Such harsh conditions effectively rule out any non PGM-based (platinum or precious group metal) as a potential catalyst. Despite the intensive research efforts carried out over the decades [32–34], use of perovskites or other mixed oxides appears unrealistic due to both high gas flow-rate and sulphur content of the exhausts. Among PGMs, Pt-based catalysts appear to be the most reliable [35–37]: Pt-based catalysts are routinely used as diesel oxidation catalysts

(DOC) and one of their required functionalities is to favour NO oxidation, which is beneficial for PM removal, as it occurs in CRT (Continuously Regenerated Trap) [38]. They also show reasonable resistance against deactivation by SO_x [39,40], which can be attributed to a less strong adsorption of SO_x over Pt surface compared to, for example, Rh: NO_x was shown to desorb from a SO₂ poisoned Pt surface at relatively low temperatures, whereas this did not occur on Rh [41]. Interestingly, there are reports that addition of SO₂ can even improve the activity of Pt catalysts [42–45]. Even though use of TiO₂ as Pt support confers a better sulphur resistance [46], the foreseen harsh conditions do not suggest use of this support due to its relatively poor thermal stability. As indicated by a referee, it should be noted that Pt/Al₂O₃ is known to form sulphates, which would shorten catalyst life by pore blockage. An interesting alternative would be the use of ZrO₂-SiO₂ as carrier. This shows higher sulphur resistance and is thermally stable. Unfortunately, it was not available at the time of constructing the plant.

On the basis of these considerations, a laboratory-scale investigation was undertaken using a small diesel engine and automotive diesel with added thiophene as fuel [28]. An example of a conversion vs. catalyst temperature curve obtained under realistic reaction conditions, using a monolith supported Pt/Al₂O₃ catalyst, is reported in Fig. 3. Even though the observed conversions of NO_x species are relatively low, both HC-SCR activity and NO oxidation were observed. The latter reaction was shown to be inhibited by the relatively high HC content of the exhausts. Thus, this initial study demonstrated the feasibility of the project, while also allowing dimensioning of the final pilot-plant catalyst. For comparison, NO oxidation activity dropped below 5% over a commercial DOC at a GHSV of 200,000 h⁻¹ when 700 ppm of sulphur was added to the fuel [39].

3.1. Catalyst performance

3.1.1. Effect of sulphur on NO_x interconversions

Before discussing the performance of the catalyst, it is important to address the issue of the catalyst temperature. Catalyst heating was achieved by contact with the exhaust gases, which in turn depends on the combustion temperature and therefore engine load. The catalyst used in the present study was rather large and, as outlined in the experimental section, it was divided into two sections: in principle, a consequence of this situation could be

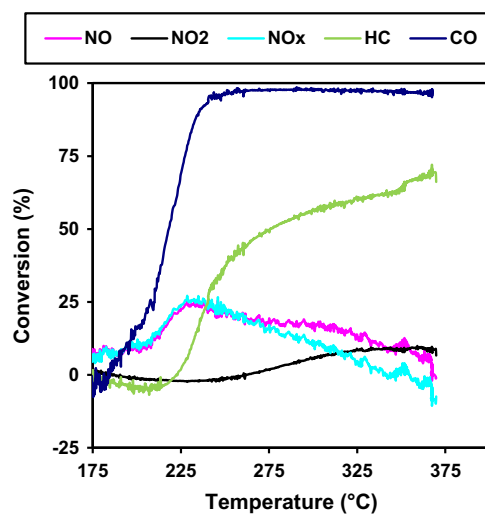


Fig. 3. Conversion curves obtained over a Pt/Al₂O₃ monolith catalyst using a Faryman 18B-D engine fuelled with commercial diesel with 1% of S (thiophene) added. HC denotes hydrocarbons. Data from [28].

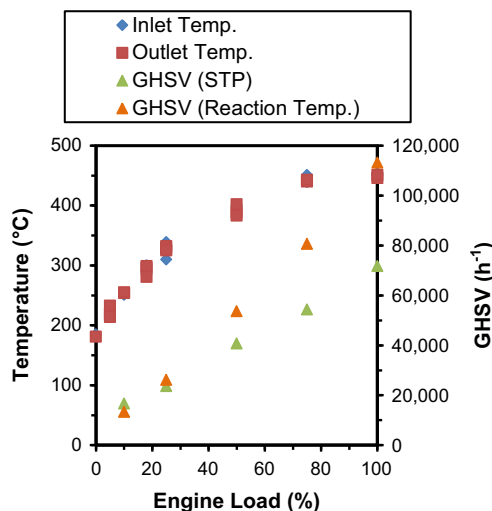


Fig. 4. Catalyst inlet (engine out) and outlet temperatures and GHSV (gas hourly space velocity) (calculated both at STP (standard temperature and pressure) and reaction conditions) vs. engine load.

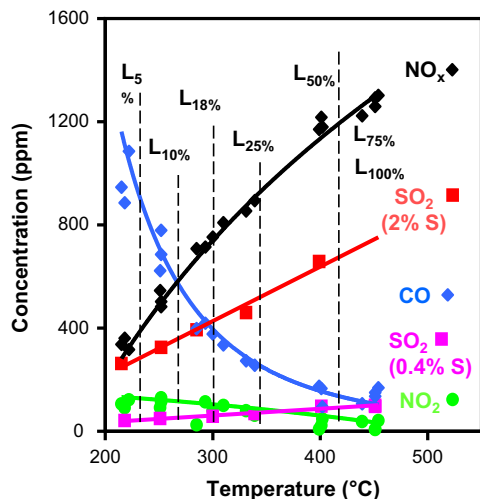


Fig. 5. Engine-out exhaust gas composition as a function of exhaust gas temperature obtained at different loads, using 10 ppm, 0.4% and 2.0% S containing fuel. The curves are present visual guides.

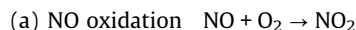
catalyst temperature inhomogeneity during tests. We monitored catalyst temperature both at the engine outlet (before the catalyst) and after the catalyst to obtain indications on potential variations in catalyst temperature along its length. The presence of gas–solid heat transfer effects cannot be discounted, nevertheless, as shown

in Fig. 4, significant variations in catalyst temperature were not observed, indicating that there were not significant temperature gradients along the catalyst beds. Finally, it is worth noting that on increasing the load and, hence the reaction temperature, GHSV increases nearly linearly, which clearly affects the conversions (*vide infra*).

The effect of sulphur addition on engine-out exhaust gas composition is shown in Fig. 5. Except for SO₂ concentration, which obviously depends on sulphur content in the fuel, all the other components follow similar trends independently of the fuel used, suggesting that the engine combustion regimes are substantially unaffected by addition of sulphur to the fuel. Thus, all the modifications of the exhaust composition after the catalyst and after the scrubber are directly linked to the performance of the system rather than to any variation in the engine regime.

Table 2 summarises the data collected for NO_x species for the three fuel compositions tested at the various loads (temperatures), measured at the P1, P3 and P4 sampling points, that is before-catalyst, after-catalyst and after-scrubber, respectively. The NO concentration is the difference between NO_x and NO₂ values. It should be noted that the data obtained with normal diesel fuel differ from the other two in that the scrubber was not employed and the tests were mainly intended to check the baseline engine emissions and the functioning of the catalyst. In addition, a limited number of measurements were performed at P2 (compare Fig. 7 below) to investigate the “progress” of conversions across the two catalyst beds.

The conversions observed between P1 and P3 represent the overall efficiency of the catalyst. Of particular interest in this context is the ability of the catalyst to convert NO to NO₂ for potential removal through absorption in the scrubber section. The overall behaviour of the catalyst with regard to the conversion of NO_x species and conversion of NO to NO₂ over the catalyst is illustrated in Fig. 6. Analysis of the data indicates that the catalytic behaviour may be divided into three regimes (*vide infra*). Within this framework, the effect of increasing sulphur content in the fuel on the catalytic activity is also evidenced. The three catalytic regimes observed for regular diesel fuel (Fig. 6a) are as follows:



Between 18% and 100% engine load, significant conversion of NO to NO₂ was observed, with a maximum at 25% load. As the engine load also affects the combustion temperature and therefore the gas outlet temperature, and as this is the only means of heating the catalyst, it follows that the variations in NO oxidation activity are linked to changes in the catalyst temperature. The activity profile, *that is*, the volcano shape curve (NO₂ production in Fig. 6a and b), is in line with what has been reported in the scientific literature for NO oxidation over Pt/Al₂O₃ catalysts [30,35]. However, the NO₂ dissociation equilibrium does not appear to limit the yield of the

Table 2
NO_x and NO₂ emissions before and after the catalyst section.

Engine load	Diesel				0.4% S						2.0% S					
	NO _x		NO ₂		NO _x		NO ₂		NO _x		NO ₂		NO _x		NO ₂	
	P1 (ppm)	P3 (ppm)	P1 (ppm)	P3 (ppm)	P1 (ppm)	P3 (ppm)	P4 (ppm)	P1 (ppm)	P3 (ppm)	P4 (ppm)	P1 (ppm)	P3 (ppm)	P4 (ppm)	P1 (ppm)	P3 (ppm)	P4 (ppm)
100	1302	1256	42	270	1259	1160	803	7	245	145						
75	1223	1129	38	300	1292	1343	901	8	302	206						
50	1180	1028	48	362	1217		839	23	365	252	1170	1092	789	9	156	189
25	809	737	100	331	894	877	693	62	288	218	854	816	550	80	125	67
18	714	646	114	253	753	737	515	81	128	50	708	676	592	25	25	71
10	483	502	130	108	545	507	389	92	9	19	503	484	368	114	13	3
5	317	322	122	24	361		338	91	3	60	337	325	301	106	5	29

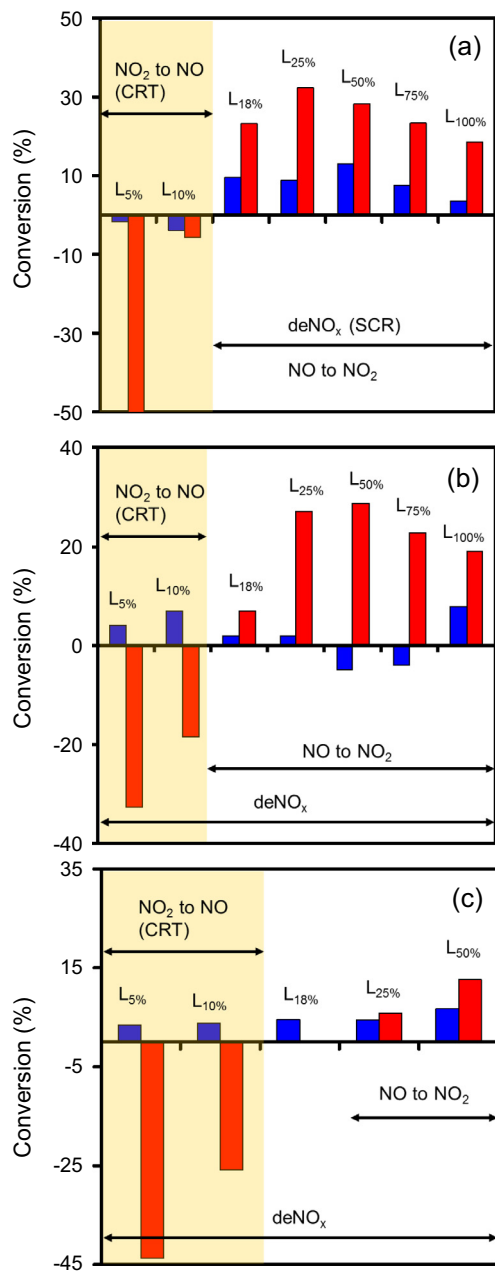
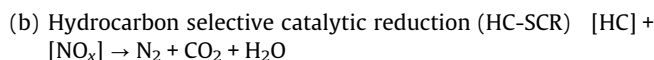


Fig. 6. NO_x conversion and conversion of NO to NO₂ over the Pt/Al₂O₃ monolithic catalyst (■ NO_x conversion, ■ conversion of NO to NO₂). Three different regions of activity are evidenced (CRT, deNO_x and NO to NO₂, compare text). (a) Regular diesel fuel (10 ppm S); (b) 0.4% S fuel; (c) 2.0% S fuel. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

desired product since at engine load of 25%, the gas/catalyst temperature is 335 °C, which is notably lower than 450–500 °C where such limitation occurs [35].



As shown by the CO₂ data reported in Table 2 and Fig. 6a, the decrease of total NO_x over the catalyst indicates some deNO_x activity, albeit to a rather limited extent. A maximum is evident at 50% engine load (ca. 400 °C). This can be attributed to direct hydrocarbon selective catalytic reduction (HC-SCR), which is symbolically represented in bold above (equation not balanced). As in the case

of NO oxidation, the volcano shape trend of deNO_x activity with temperature is a well-established observation; however, the behaviour observed here presents significant difference with previous reports for HC-SCR [47]: no N₂O was observed and the activity is observed at much higher temperatures than those at which it is observed under model feed. Direct deNO_x activity is a highly desirable property, but the conversions achieved in the present case contribute very little to overall deNO_x activity. In fact, with regard to the overall deNO_x activity, NO conversion to NO₂ is of more significance (*vide infra*).



At engine loads of 5% and 10% a perhaps more surprising behaviour was observed. The negative conversions of NO to NO₂ indicate that, in fact, some of the NO₂ present in the exhaust (Fig. 5) was converted to NO. It is important to bear in mind that, while the percentage conversions appear quite high, the absolute conversions are in fact modest (Table 2). This type of behaviour has been previously reported for the CRT used in diesel automotive applications, and in fact corresponds to the reaction of NO₂ with carbonaceous particulate matter (PM) [48]. It should be noted that PM concentrations were highest on engine start-up and at low loads, which is consistent with the occurrence of this phenomenon at low engine loads.

In the case of the other two fuels tested (0.4% and 2.0% S), the same three activity regimes are evident (Fig. 6b and c). The main difference is that the progressive increase in sulphur content progressively suppresses the catalytic activity observed. The only significant difference in the behaviour is that deNO_x activity is observed at all engine loads, albeit to a very small extent. Furthermore, a significant sulphur deactivation effect on NO oxidation is seen only for 2.0% S.

The increase in NO₂ concentration is due almost exclusively to the presence of the catalyst, and, as will be discussed in Section 3.2, NO oxidation promotes overall deNO_x activity across the combined system. In addition, it is clear from Fig. 6 that, from the point-of-view of the desired oxidation of NO to NO₂, an optimum temperature exists. This optimum temperature depends on the fuel used and, thus, temperature control would be advantageous to maximise the NO_x abatement observed.

Clearly the increase of sulphur content in the fuel depresses the catalytic activity; nevertheless, a significant 15% of NO conversion to NO₂ is achieved at 50% load using the 2.0% S fuel at a GHSV of 40.700 h⁻¹ at STP, which corresponds to GHSV of 53.600 h⁻¹ at the reaction temperature (cfr. Fig. 4). For the sake of comparison, a GHSV of ca. 100.000 h⁻¹ is normally employed for light duty vehicle (DOC or TWC), whereas urea-SCR catalysts work at much lower GHSVs, the catalyst volume being often three-times that of TWCs.

With regard to the overall activity of the catalyst, an interesting aspect of the overall NO oxidation behaviour is illustrated graphically in Fig. 7: most of the conversion is achieved on the first catalytic bed, indicating that there is room for significant performance improvement.

3.1.2. Hysteresis – Temperature dependence of NO conversion to NO₂

Fig. 8 shows the overall NO oxidation activity as a function of temperature for the 0.4% S fuel. A clear hysteresis loop is evident. In these tests, the engine loads were progressively increased in a step-wise manner to 100% and then decreased in a similar manner. As a consequence, the temperature also follows this trend. Hysteresis is a common phenomenon in catalysis and may be explained in a number of ways. The type of hysteresis observed in the present case, in which the activity is higher with decreasing temperature

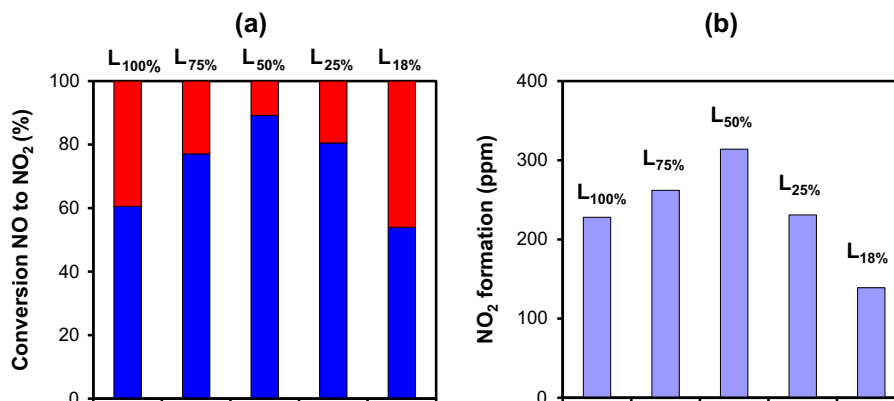


Fig. 7. (a) Relative conversion of NO to NO₂ over the first and second catalytic bed; (b) total amount of NO₂ produced at various engine loads using regular diesel fuel.

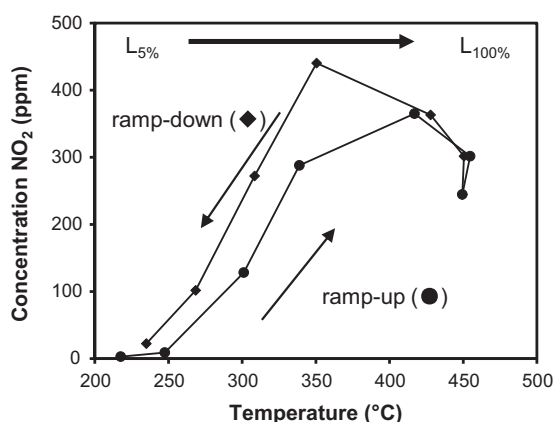


Fig. 8. NO₂ formation curves using the 0.4% S fuel: run-up and run-down parts of the cycle.

than with increasing temperature is considered as a “normal or regular” hysteresis [49]. Hysteresis phenomena have been attributed to several factors, for example thermal inertia of the catalyst multiple steady states due either to reaction exotherm or surface or inhibition due to adsorption/desorption phenomena [49], change of the state of the catalyst (oxidised/reduced) [50,51]. Evidence, however, has grown that for strongly exothermic reactions, mass and heat transfer limitations may play a dominant role [52,53]. As far as platinum catalysis is concerned, a reverse hysteresis was observed in NO oxidation under model exhaust feed [49,54,55], which was associated with an initial presence of reduced Pt species which are oxidised by NO₂ formed at higher reaction temperature. Consistently, NO₂ inhibits NO oxidation [37]. This behaviour is the opposite of what is observed here using a comparable step-wise procedure. Both the very high GHSV and the use of a metallic monolith suggest that heat and mass transfer limitations might not be operating in our case. It appears therefore reasonable that adsorption/desorption phenomena may explain the presence of hysteresis: as the temperature increases, the activity of the catalyst is inhibited by sulphur derived species, adsorbed at lower temperature (site blocking) as the bed temperature is too low for their effective desorption. On decreasing the temperature on the other hand, the surface population of such species is much reduced, if not completely absent, after the high temperature excursion of the catalyst bed and the site blocking is diminished, resulting in higher activity. Consistently, significant SO_x desorption was observed from a commercial DOC at 300–500 °C and part of the adsorbed sulphur was unstable above 250 °C [39]. A corollary

of this observation is related to the marine engine NO_x emissions certification procedure (IMO NO_x code, Regulation 13): running a ramp-down cycle during the certification provides better catalyst performance.

3.1.3. Effect of catalyst on CO, HC, PM and SO₂ emissions

Table 3 reports the results concerning emissions of the other main pollutants in the gas phase at the P1–P3 sampling points of the combined abatement system, that is, points related to the catalyst section. In this case, the regular diesel fuel (10 ppm S) was employed. The catalyst shows typical features of an oxidation catalyst in that CO is fully oxidised: no CO was detected after the catalyst in any of the experiments. The elimination of HC and PM was somewhat less efficient under the present reaction conditions. An important aspect, which is in line with NO_x conversion above discussed, is that all the conversion is essentially achieved over the first catalytic bed. This indicates that much higher GHSV could be employed with comparable conversion levels. Dimension and price of the catalyst are fundamental if extension of the present technology to main power engines is to be considered.

When the high sulphur fuels are considered, CO is fully converted over the catalyst (data not reported), whereas HC conversion depends on the temperature, reversible deactivation of the catalyst being observed below 350 °C if compared to sulphur-free fuel (Fig. 9). Above 400 °C comparable activities are observed both in the presence and absence of sulphur in the fuel. This is consistent with a SO₂ adsorption/desorption model in which above 400 °C the catalysts is effectively desulphated under the exhaust conditions [56].

It is well known that DOC promotes SO₂ oxidation [39]. Fig. 10 reports the data obtained for fuel with sulphur content of 0.4% S.

As would be expected, given the significant NO oxidation activity, very significant SO₂ oxidation was also observed. This can be attributed to SO₂ oxidation to SO₃. SO₃ was not directly measured, accordingly its formation was calculated from the disappearance of SO₂.

In the case of the 2.0% S fuel, the high sulphur content of the fuel means that the base levels of SO₂ are much higher. Once the engine load was increased to 50% load, a sulphuric acid mist was generated which did not allow completion of the tests. This was not the case for the fuel containing 0.4% S. As can be seen in Fig. 10, conversion of SO₂ to SO₃, that is, production of SO₃, remained below 100 ppm throughout these tests. In the case of the higher sulphur content, as already stated, the formation of the acid mist occurred on increasing the engine load to and above 50%. It is interesting to note that at 18%, while the amount of SO₂ formed is, as expected, high, conversion to SO₃ remains low due to the low temperature of the catalyst and less than 100 ppm of SO₃ were

Table 3
Effect of the catalysts on CO, HC and PM emissions using regular fuel (10 ppm S).

Engine load (%)	Temperature	CO		PM		HC			HC conversion (%)
		P1 (ppm)	P2/P3 (ppm)	P1 (mg/m ³)	P3 (mg/m ³)	P1 (ppmC)	P2 (ppmC)	P3 (ppmC)	
100	452.5	169	0	113	20	159	63	66	58
75	441	107	0	108	38	129	39	39	70
50	402	95	0	18	18	111	24	18	84
25	319	335	0	20	32	108	33	24	78
18	296	419	0	19	29	120	27	18	85
10	252	779	0	29		207	27	21	90
5	227.5	1085	0	45	7	354	51	30	92

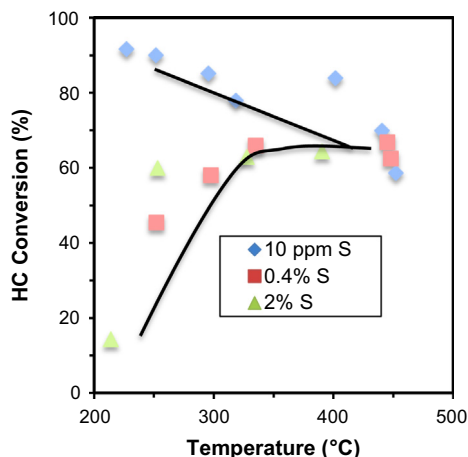


Fig. 9. HC conversion over the catalyst vs. temperature: effect of sulphur content in the fuel. The lines are reported as visual guides.

produced. On increasing the engine load to 50%, the amount of conversion increases dramatically SO_3 (>100 ppm) suggesting this value as a limit under the scrubber working conditions used.

3.2. Scrubber performance

The focus of the present work is the catalytic section, *that is*, the effect of exhausts with high sulphur content on the activity of a Pt catalyst. However, for sake of completeness, here we report some relevant result of the overall efficiency of our system, thus including the effect of the scrubber.

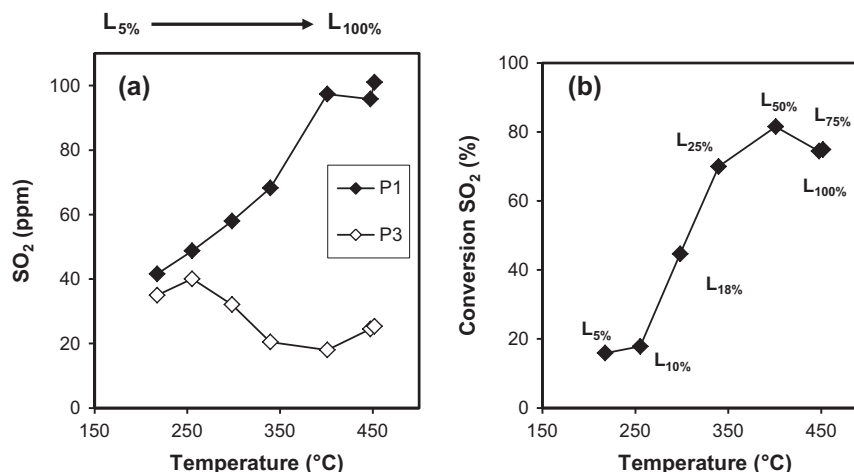
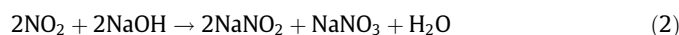
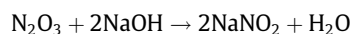


Fig. 10. Emission (a) and conversion (b) of SO_2 on the catalyst vs. temperature, fuel 0.4% S. Sampling positions P1 and P3 are indicated Fig. 2.

As already indicated, removal of SO_x by scrubbing is a well-assessed industrial technology, even though use of sea water has received less attention. As far as NO_x removal is concerned, this process is effective when wet scrubbing is carried out in alkaline solutions [57,58]. In this regard, it should be noted that seawater is in fact a buffered alkaline solution. Removal of NO alone by wet scrubbing is virtually impossible [58,59] and the presence of NO_2 is necessary to see any deNO_x activity by this method. This observation guides the basic strategy of the abatement system used here. In the present combined system, an oxidation catalyst was included to convert NO to NO_2 in order to promote its uptake in the scrubber, along with species for which scrubbers are known to be effective (especially SO_x and PM).

In the simultaneous presence of NO and NO_2 , the NO_x removal mechanism depends both on the overall concentration and the ratio of the two species. Thus, two mechanisms by which NO_x may be removed by wet scrubbing with alkaline solutions were identified:



The authors concluded that mechanism (1) predominates when NO and NO_2 are present in equal volumes, while mechanism (2) occurs to a more limited extent. If NO_2 is present in excess, it reacts according to mechanism (2); while if the ratio by volume of NO to NO_2 is greater than one, the NO equal in volume to NO_2 will react with the NO_2 (mechanism (1)), while the excess NO will remain essentially unchanged.

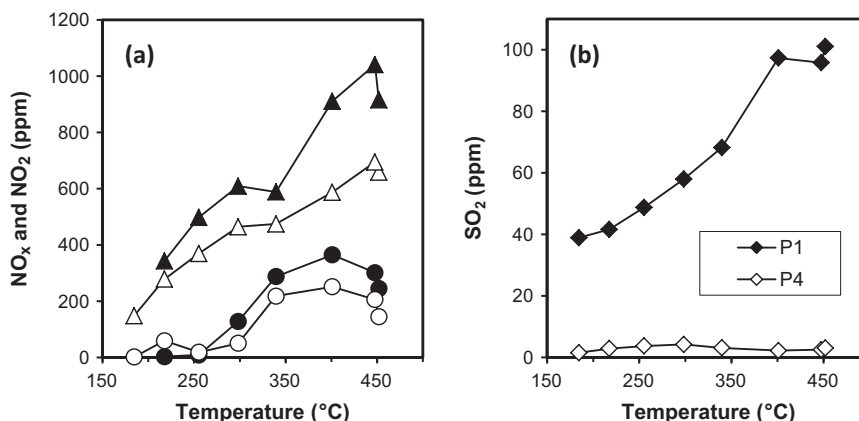


Fig. 11. (a) Effect of the scrubber on (a) NO_x and NO₂ emissions: triangles NO, circles NO₂; filled symbols P3, empty symbols P4; (b) SO₂ emissions. Fuel 0.4% S. In the case of SO₂, the abatement observed across the whole system (catalyst + scrubber) is shown. Sampling positions P1, P3 and P4 are indicated in Fig. 2.

Thus, a 1:1 NO:NO₂ ratio is suggested as an optimal composition for the scrubbing process. However, complete conversion of NO to NO₂ is desirable at low NO_x concentrations (<500 ppm) as N₂O₃ does not form in significant amounts. An important consequence of these observations is that an effective system, in principle, does not necessarily require a full conversion to the soluble NO₂ species.

To test the effective necessity of a catalyst, a number of preliminary tests were performed with the scrubber only using the 2.0% S fuel (data not reported). The data obtained showed that, in the absence of the catalyst, almost no abatement was observed for NO_x, CO and total hydrocarbon (THC), highlighting the necessity of the catalyst to efficiently remove these pollutants. On the other hand, the well-established ability of seawater scrubbing to reduce SO_x and PM was confirmed in these tests as absorption efficiencies over 90–95% were achieved.

About 90% of PM were removed independently of the fuel used, emissions at the scrubber outlet being lower than 10 mg/m³ (data not reported).

Fig. 11 reports outlet SO₂ and NO_x concentrations, thus summarising the effects of the scrubber on NO_x and SO₂ emissions of the system. For the sake of comprehension, scrubber-inlet, that is catalyst outlet NO_x and engine-out SO₂ concentrations are included.

SO_x are efficiently removed under our experimental conditions, thus confirming the efficiency of the scrubber technology for removal of these pollutants.

A perusal of the data reported in Fig. 11a discloses, however, an unexpected feature: even though significant NO_x removal could be achieved, there is also significant leakage of NO₂ from the scrubber, indicating the need of scrubber optimisation for NO_x removal. On the basis of present results, a clear mechanism of adsorption, such as that described above, does not emerge. Attempts to find a trend in the adsorption stoichiometry offered little insight since NO₂:NO adsorption ratio varied significantly.

As indicated in the experimental section, the investigation focussed on engine loads relevant to engine certification according to IMO procedures. From this viewpoint, the effects of the integrated catalysts/scrubber technology are relevant: the emissions calculated over the full test showed that NO_x emissions decreased from 6.2 g/kW h to 4.1 g/kW h, which corresponds to a 33% abatement efficiency. For our engine, a TIER III limit of 2.085 g/kW h is calculated. Consideration of the data reported in Fig. 11a reveals that if all the NO₂ were absorbed in the scrubber section, the system would be TIER III compliant. As far as SO₂ is concerned, the efficiency is high and the emissions are close to the limits defined for a SECA: 4.7% (SO₂ ppmV/CO₂ %) vs. 4.2 (SO₂ ppmV/CO₂ %), as indicated by the IMO.

4. Conclusions

As discussed in this paper, pollution generated from shipping has become a major issue which needs novel technological solutions as incoming legislation limits become tighter and tighter. There is a fundamental difference between the assessed technology used in land-based transportation and shipping, which is the “desired” use of heavy fuel oil: fuel can account for up to 80% of running costs, which means that switching to the more expensive (30–50%) low sulphur content fuel heavily affects the economics of shipping. In contrast to land transport, marine transport presents an important opportunity, which is the availability of scrubber technology for “on-board” desulphurisation. In fact, sulphates can be freely discharged to marine waters. Relevant to our technology is the fact that life cycle analysis showed “on-board” cleaning to be more sustainable compared to production of low sulphur marine fuel in the refinery [15]. This clearly opens new perspectives for catalysis community as deNO_x has necessarily to be carried out catalytically. Marine engine exhausts are more challenging to convert if compared to conventional diesel exhausts: catalysts resistant to high temperature and high sulphur content are needed [60,61]. Specifics of marine engines have also to be taken into account: exhausts of a high-speed four-stroke engine, such as that used here, are hotter compared to a low-speed two-stroke engine. Accordingly, in this case, the SCR catalyst is often located before the turbine in the exhaust outlet circuit, thus operating at high pressure (2–5 atm). Knowledge of high pressure SCR kinetics is missing.

Among these challenges, here we have shown that an alternative deNO_x technology which shows interesting potential can be implemented. As in fact, we have observed that:

- The presence of the catalyst located before the scrubber allows achievement of significant NO_x abatement in addition to deSO_x activity.
- Under tested conditions, the system shows significant abatement of all of the targeted pollutants for fuel sulphur content of up to 0.4% and TIER III requirements could in principle be achievable even for higher sulphur content.

Clearly the system is still in its infancy, improvements need to be made and other issues should also be addressed, for example more efficient catalysts, selectivity towards NO or SO₂ oxidation, treatment of exhaust waters, use of open-loop/close loop scrubber, etc.

The results also stress the importance of the use of realistic reaction conditions for catalyst investigation as findings obtained under model condition may not be strictly relevant to the real situation.

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