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Development of a Novel De-NO_x Technology for the Aftertreatment of Ship Exhaust Gases

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Abstract: The shipping industry is the most fuel-efficient means of transporting goods, carrying more than 90% of the global freight task. Ships generally use low quality fuel to reduce costs and, as a result, the sulfur content in the exhaust gas stream is high. Emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x) from ships represent about 13% and 12%, respectively, of the global anthropogenic SO_x and NO_x emissions. In total, 95% of the total maritime NOx emissions are NO (nitric oxide) and 5% are NO_2 (nitrogen dioxide). The present work focuses on the development and pilot operation of an advanced novel Selective Catalytic Reduction of NO_x with H_2 (H_2-SCR) technology for the elimination of Nitrogen Oxides (NO_x) emitted from ship exhaust gases. For the proper operation of the novel H_2-SCR de-NO_x unit, two additional conventional technologies were employed for the removal of SO_2 and Particulate Matter (PM). In particular, the proposed novel H_2-SCR de-NO_x technology was combined with a Sea Water Absorption (SWA) unit and an oxidative catalytic system. A pilot unit has been successfully designed, assembled and implemented on a cruise ship for the abovementioned purposes. This effort is considered to be pioneering and is here attempted for the first time worldwide. It was proven, for the first time ever, that the Selective Catalytic Reduction of NO_x with the use of H_2 as a reducing agent in combination with a suitable catalyst can be considered a suitable NO_x-pollution control technology for ships. In particular, it was found that more than 80% of NO_x (to N_2), 99.8% of SO_2 and 72% of PM can be reduced by using the present combined SWA and H_2-SCR technologies.

Keywords: H_2-SCR; ship emissions; depollution; sea water adsorption

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1. Introduction

According to Eyring et al. [1], the total emissions from transport-related annual emissions and fuel consumption in Tg/year are presented in Table 1. The contribution of each sector is presented in brackets next to the number of emissions and fuel consumption. As can be clearly seen from Table 1, the shipping industry is a major contributor in the main gas pollutant emissions globally. In January 2011, a total of 103,392 commercial ships were in service with a combined tonnage of 1396 million Dead Weight Tonnage (DWT). Looking at individual sectors, oil tankers accounted for 475 million DWT and dry bulk carriers for 532 million DWT, representing an annual increase of 5.5% and 16.5%, respectively; the containership fleet reached 184 million DWT in January 2011 (8.7% over 2010). The fleet of general cargo ships stabilized at 109 million DWT. The tonnage of liquefied gas carriers continued to grow, reaching 43 million DWT (an increase of 6.6%) [2].

During the past few years, the International Maritime Organization (IMO) has issued strict regulations in order to minimize these emissions, deriving mainly from newly constructed vessels [1–3]. The IMO has adopted these new regulations in Marine Pollution Legislation (MARPOL) Annex VI for progressive reduction of Nitrogen Oxides (NO_x), Sulphur Oxides (SO_x) and Particulate Matter (PM). The new regulations require ships to achieve a SO_x reduction equivalent to 0.1% sulfur fuel since 2015. This requirement can be met by using more expensive, low sulfur fuel or by using marine diesel scrubbers. Considering that the average age of the world fleet of propelled sea-going merchant ships of no less than 100 gross tons is 22 years and the average age of the world cargo-carrying ships is 19 years [4], it is important to implement end of pipe technologies that prevent air pollution from NO_x, SO_x and PM gases since significant modifications on these ships cannot be easily accomplished.

Table 1. Global annual emissions and fuel consumption from transport (Tg/year) [1].

	CO_2	NO_x	SO_2	PM10	Fuel Consumption
Road Traffic	4110 (74%)	27.3 (53%)	4.3 (26%)	2.1 (55%)	1320 (73%)
Aviation	654 (11%)	2.3 (5%)	0.15 (1%)	0.001 (0%)	207 (16%)
Shipping	812 (15%)	21.4 (42%)	12.0 (73%)	1.7 (45%)	280 (21%)
Total	5576	51	16.45	3.8	1807

The abatement of SO_x and particulates emitted from ships could be considered an easier task, since quite mature and technologically ready solutions are already available in the market and could be utilized for this purpose. Open- or closed-circuit scrubbers were found to achieve very high SO_x removal efficiencies, reaching up to 99%, even when using Heavy Fuel Oil with 3.5% sulfur content [5]. Moreover, under certain conditions, scrubbers were found to be also efficient towards a significant reduction in PM emissions [6]. In addition, as long as SO_x are removed from the exhaust stream, particulates can be eliminated by using oxidative catalysts or catalytic filters, similar to those already used on diesel-powered automobiles [7].

On the contrary, the abatement of NO_x from ship exhaust gases is not a straightforward task. Available commercial technologies, which have been developed for the reduction of NO_x emitted from mobile (TWC) or stationary (urea-SCR) sources, are either not suitable or cannot be easily adapted to perform equally well on ships. Selective Catalytic Reduction using urea as a reducing agent (Urea-SCR) is the only technology which is attracting some interest in terms of commercial application [8]. However, recent reviews report that deficiencies in the overall system design with a combination of technical issues (related with the use of urea), maintenance access problems and untrained operators with inadequate understanding of the SCR process have led to inefficient, costly and unsafe operations [9]. Since most of the above problems derive from the use of urea (ammonia) as a reducing compound in the SCR process, it can be claimed that an alternative reducing agent that will be less corrosive and toxic and more “friendly” to the environment (as compared to ammonia/urea) is needed.

The scope of the present work was to develop and test a pilot system for the efficient elimination of the main pollutants produced by commercial and passenger ships (NO_x, SO_2 and PM). Furthermore, this work aimed to explore the potential of the alternative Hydrogen-Selective Catalytic Reduction (H_2-SCR) process for NO_x pollution control on ships. In particular, within the present study, the H_2-SCR process was combined with conventional technologies for sea-water scrubbing of SO_2 and catalytic oxidation of soot (PM) in order to protect the de-NO_x catalyst from exposure to SO_2 and particulates. The integrated pilot unit was operated on an active cruise ship. The results obtained indicate that the proposed H_2-SCR de-NO_x process can be a suitable alternative technology to urea-SCR for the reduction of NO_x emissions from ships.

2. Materials and Methods

2.1. Technical Specifications of MS Sapphire

The MS Sapphire cruise ship (IMO number: 6513994), weighing 12,263 Gross Register Tons (GRT), has a length of 149 m and uses Sulzer CRDA 9RD 56 engines running on Heavy Fuel Oil (HFO). The qualitative analysis of the HFO, used within the present work, is reported in Table 2. As seen in Table 2, the fuel used by the vessel under study has a very high viscosity, density and sulfur and ash content, characteristics which lead to significantly high emissions of SO_2 and PM after combustion. Moreover, the high flash point of the fuel (>70 °C) is expected to lead to higher NOx emissions after combustion. MS Sapphire was a 1967 Italian built cruise ship that most recently operated for Louis Cruise Lines, once laid up at Eleusis Bay. The vessel could achieve a maximum speed of 17 knots and could accommodate 706 passengers and 240 crew.

Table 2. Fuel quality analysis for the HFO used by MS Sapphire during the experiments of the present work.

Property	Units	Value
Density @15 °C	kg/m^3	977.4
Viscosity @ 50 °C	mm^2/s	99.8
Water	vol.%	0.1
Micro Carbon Residue	wt.%	11
Sulfur	wt.%	1.47
Ash	wt.%	0.05
Vanadium	mg/kg	77
Sodium	mg/kg	20
Aluminum	mg/kg	11
Silicon	mg/kg	15
Iron	mg/kg	29
Nickel	mg/kg	29
Calcium	mg/kg	17
Magnesium	mg/kg	4
Lead	mg/kg	<1
Zinc	mg/kg	1
Flash Point	Deg. C	>70

2.2. Pilot Unit Description

The ship's exhaust gaseous stream consisted of (on average) 380 ppm SO_2, 623 ppm NO and 250 mg/m^3 of PM while its temperature (at the inlet of the sea-water scrubber) was approximately 120 °C. The pilot unit was designed in such a way in order to use an exhaust gaseous feed stream of 10 L/min (taken directly from the main exhaust pipe of the ship, after the turbocharger). The pilot unit was installed at the upper part of the funnel (top deck) of the ship. Figure 1 shows the exact position of the installed integrated pilot unit.

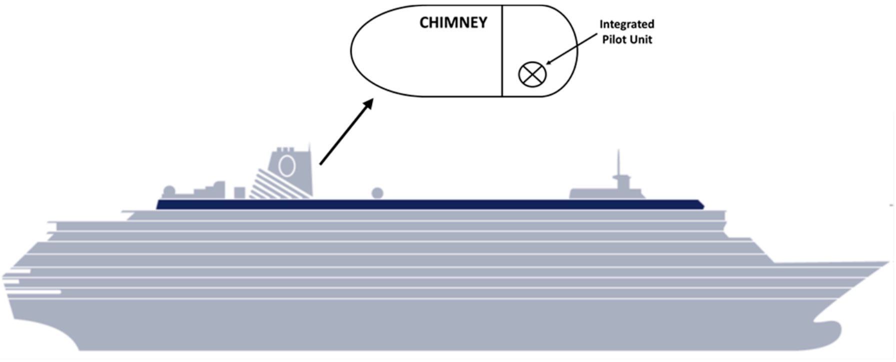

Figure 1. Position of the pilot-unit installed on MS Sapphire.

Figure 2 presents a flowchart of the treatment units used for the ship's gaseous stream. As can be seen in Figure 2, the ship's exhaust feed stream is lead to the first stage of gas treatment which is the Sea Water Absorption (SWA) unit. The purpose of this unit is to remove SO_2 from the feed stream. The unit's operation is considered to be of great significance since SO_2 is considered to be a strong catalytic poison, as it chemisorbs irreversibly on the catalytic active sites blocking the supported metals for further reaction.

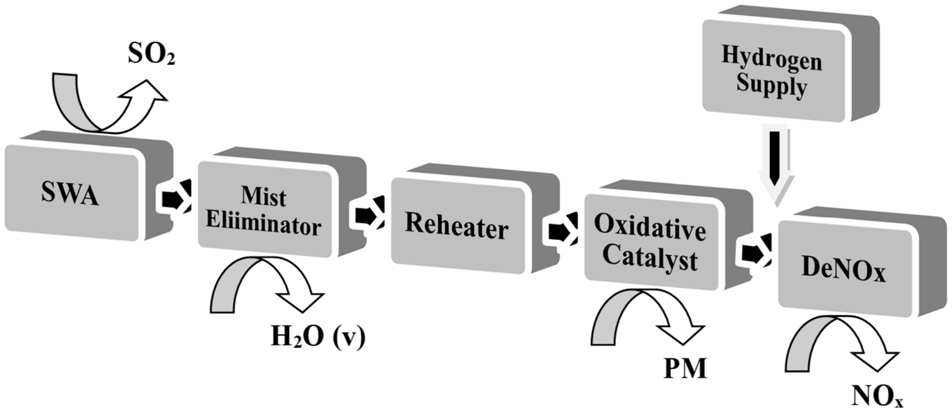

Figure 2. Flowchart showing the separate sub-units used for the complete depollution of examined ship's gaseous emissions.

A schematic representation of the SO_2 scrubber (SWA) unit used in the present work is shown in Figure 3.

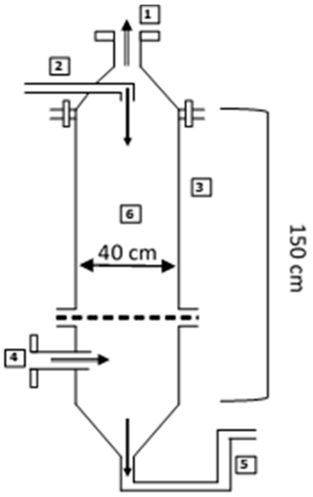

Figure 3. Schematic representation of the scrubber (Sea Water Absorption (SWA) unit), used on board for the reduction of SO_2. (1) Exhaust gas stream outlet, (2) sea water inlet, (3) the SWA tower, (4) exhaust gas stream inlet, (5) sea water outlet, (6) filling material.

After the SWA treatment, the gaseous stream is lead to a mist eliminator where the removal of water vapor occurs. The stream is then reheated to 300 °C (with the use of heating tapes) and led to the third stage of gaseous treatment which involves the removal of PM with the use of an oxidative catalyst (a metallic universal oxidation catalyst provided by "Cats & Pipes Ltd.—Holywell, UK"). The removal of PM from the feed stream is an important step in order to protect the catalytic surface (de-NO_x catalyst) from the deposition of particulates (mainly soot) and thus maintain a high catalytic activity.

The gaseous stream resulted from the latter treatment process was then mixed with H_2 which was produced by a distilled water electrolysis unit (Parker Balston 100 cc/min UHP Hydrogen Gas Generator—H2PEM-100, 99.995% H_2 purity). The water consumption of the electrolysis unit was 0.75 L/week (water quality—ASTM2). The hydrogen production from the unit was 100 cc/min, which was fed to the reaction stream at the inlet of the SCR unit. The whole unit was designed in such a way so as to have the temperature of the inlet gas to the SCR unit reach about 200 °C. The H_2-SCR reactor temperature is of great importance since, according to the literature, the supported catalyst used presents the highest selectivity towards N_2 and significant NO conversion at temperatures within the range of 150–400 °C [10]. The solid catalyst used in the de-NO_x unit was in the form of pellets of 2–3 mm diameter with a total weight of 200 g. Finally, the exhaust gas stream from the H2-SCR unit returns to the exhaust gas pipe of the ship and ends up in the atmosphere.

The concentration of major pollutants was monitored in situ with the use of a Dräger MSI Compact—S/D (MSI Elektronik) portable gas analyzer. The probe of the analyzer was placed at the outlet of the catalytic reactor for the in-situ monitoring of CO_2, CO, NO_2, SO_2 and NO, while the accuracy of the concentration measurements of all monitored gases was 1 ppm [11]. The temperature and flow rate of the gas stream was also monitored with the use of the abovementioned analyzer. The analyzer was placed in a ventilated cabinet for protection against the high temperatures in the engine room (which were approximately 50 °C).

The concentration of PMs was determined gravimetrically. In particular, the solid particulates, present in the exhaust gas, were collected on a pre-weighted quartz filter which was adjusted at the end (exit pipe) of the pilot unit. The filter could be easily removed and replaced at any time for the determination of the final weight of the particles collected. The initial concentration of PMs in the exhaust stream was measured by determining the total weight of particles collected on the filter after 120 min of engine operation and while all units of the pilot system were bypassed.

Concentration measurements were also taken at the inlet and outlet of the SWA unit and the outlet of the oxidative reactor.

2.3. H_2-SCR Catalyst Synthesis

The catalyst support consisting of 50 wt. % MgO and 50 wt. % CeO_2 was prepared via the sol-gel method according to the experimental procedures reported elsewhere [10,12–14]. $Mg(EtO)_2$ (Aldrich) and $Ce(NO_3)_3.H_2O$ (Aldrich) were used as precursors of Mg and Ce, respectively. A selective pre-nitration and pre-sulfation of the mixed oxide support [15], following calcination of support in 20% O_2/He at 600 °C for 4h, resulted in a dramatic enhancement of catalyst stability (Pt/MgO–CeO_2) with time on stream in the presence of SO_2 in the feed. The pre-sulfated/pre-nitrated 0.1 wt. % Pt/MgO-CeO_2 catalyst was prepared by the incipient wetness impregnation method using $H_2Pt(IV)Cl_6$ (Aldrich) as a metal precursor. After water evaporation and drying overnight at 120 °C, the solid residue was ground and calcined in air at 600 °C for 2 h. The fresh catalyst sample was pre-treated in situ in 5% O_2/He at 600 °C for 2 h and then reduced in 10% H_2/He at 300 °C for 2 h prior to any experiment. The catalyst was formulated in pellets by Heraeus Holding GmbH (Hanau, Germany). H_2 chemisorption at 25 °C followed by Temperature Programmed Desorption (TPD) and High-Resolution Transmission Electron Microscopy (HRTEM) were used to measure Pt dispersion and particle size over the 0.1 wt. % Pt/MgO-CeO_2 catalyst (results are reported in Ref. [16]). The dispersion of Pt was found to be about 90%, while a mean Pt particle size of 1.2–1.5 nm was estimated. X-Ray Diffraction (XRD) studies revealed primary crystal sizes (use of Scherrer equation) of 10 and 12 nm for MgO and CeO_2, respectively, whereas Scanning Electron Microscopy (SEM) studies revealed a wide range (1–10 μm) for the secondary particle size of MgO and CeO_2 solid phases [17,18].

3. Results and Discussion

3.1. Operation of Sea Water Absorption Unit

The SWA unit was set in operation first (by-passing the oxidative and SCR catalytic reactors) in order to completely remove SO_2 molecules from the ship's exhaust stream. Figure 4 presents the SO_2 concentration profile with time before and after the operation of the SWA unit. As it can be seen in Figure 4, practically complete removal of SO_2 from the feed stream was achieved after less than 60 min of operation of the unit. According to the measurements of the concentration of SO_2 at the inlet and outlet of the SWA unit, the initial concentration of the sulfur dioxide was 380 ppm, while after the unit was set in operation its concentration decreased immediately to less than 50 ppm. It is obvious that SO_2 concentration is reduced drastically (>85%) within the first five minutes (relative time) of the SWA unit's operation (Figure 3). After 30 min of the unit's operation, the concentration of SO_2 was further reduced to 10 ppm. It is well known that sulfur dioxide has the ability to absorb (dissolve) in sea water, reacting with dissolved cations such as Ca^{2+} and Na^+ forming soluble salts ($CaSO_4$ and Na_2SO_4, respectively) [19]. Based on the above, one can safely claim that the SWA unit was successful in removing SO_2 molecules from the feed stream almost immediately after is set in operation. The unit at hand was continuously operable for more than 15 h; for the trip from Limassol harbor to the Greek island of Rhodes, the concentration of SO_2 was constantly less than 0.5 ppm (not detectable) during the voyage. It was noted that during the trip from Rhodes back to Limassol, the SWA unit was set in operation before the main ship engines were initiated. In the latter case, no measurable concentration of SO_2 was found in the exhaust feed stream at any time during the trip. Based on the above, it becomes obvious that the SWA unit designed and used in the present work was capable of removing efficiently SO_2 from the exhaust gas stream from the moment the ship's engines start until they cease operation. It is important to note at this point that the main target of the present work was not to design and operate the most efficient SO_2 scrubber nor to study in detail the removal of SO_2 by seawater absorption. In this work, the only actual importance of the SWA unit was the protection of the SCR de-NO_x catalyst from exposure to high concentrations of SO_2 (>20 ppm) which may significantly affect its overall efficiency.

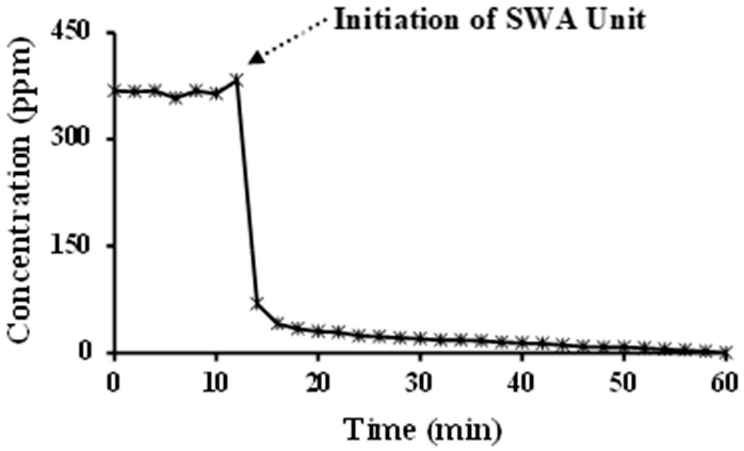

Figure 4. SO_2 concentration profile with time on stream, before and after the operation of the SWA unit (SO_2 scrubber).

It is noted that the operation of the SWA unit also achieved a small reduction of the concentration of other pollutants in the exhaust gas stream, such as NO and PM. As it can be seen in Figure 5, during the operation of the SWA unit, the aforementioned air pollutants were also slightly reduced. Although no variation in CO concentration was measured, NO concentration was found to be slightly reduced by 6% (from 623 ppm to 586 ppm), while the concentration of PMs was reduced by 15% (from 250mg/m^3 to 212 mg/m^3). According to the international literature, nitrogen oxides (NO_x), particularly NO_2, can react with water towards the formation of nitric acid (HNO_3) or with cations, such as Ca^{2+} and Na^+, towards the formation of the respective metallic salts (e.g., $Ca(NO_3)_2$, $NaNO_3$), which are soluble in water [20]. Moreover, it is well known that PM can be partially removed by wet-scrubbing [21]. As a result, a fraction of NO and PM are successfully removed from the feed stream, by the SWA unit. As shown in Figure 5, the concentration of CO was not reduced by the use of the SWA unit, since CO cannot be withheld by sea water cations or dissolved in water. Finally, a significant reduction of the exhaust gas stream temperature has been observed due to the low temperature (16 °C) of the sea water used in the SWA unit. In particular, the gaseous stream temperature at the inlet of the SWA unit was measured and found to be 120 °C, while at the outlet of the unit it was only 30 °C.

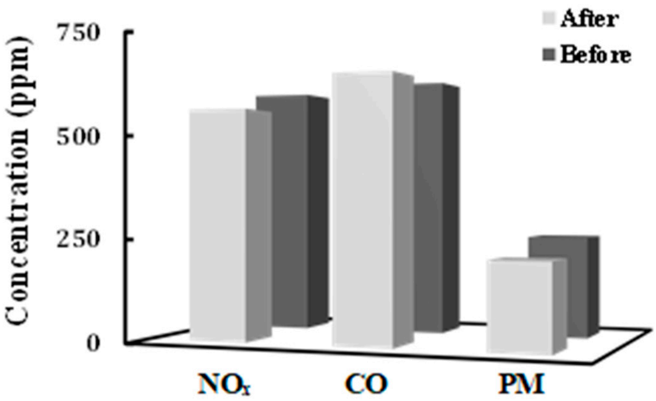

Figure 5. Steady-state concentrations of NO, CO and PM before and after the operation of the SWA unit.

Based on the above it becomes obvious that, although the SWA process can partially remove PMs, its efficiency cannot be considered sufficient, since a much higher removal efficiency of PMs is required for the safe operation of the de-NO_x unit. In particular the gas stream entering the SCR de-NOx unit must bear a concentration of PMs significantly lower than 100 mg/m^3, which is translated to a removal efficiency of at least 60% (by weight). This was the reason why a catalytic oxidation unit was used in the present work, after the SWA unit.

3.2. Operation of Catalytic Oxidation Unit

The purpose of the Catalytic Oxidation unit is to oxidize PM and CO to CO_2. The catalyst selected for this purpose (see Section 2.1) presents the highest conversion and selectivity towards CO_2 at 300 °C. Therefore, the gaseous stream after the SWA unit (30 °C) was preheated to 300 °C before entering the catalytic oxidation unit with the use of heating tapes, covering the external surface of the pipeline that leads to the catalytic oxidization reactor. The PM concentration at the outlet of the Catalytic Oxidization Reactor was measured to be 69 mg/m^3, a value that corresponds to a 67.5% reduction and a 72.4% overall reduction (before the SWA unit). In addition, during the operation of the oxidizing catalyst, the concentration of CO in the feed stream was found to be reduced from 645 ppm to 451 ppm (30% reduction). The latter results are in good agreement with the existing literature and common practice, which has shown that catalytic oxidation and/or multi-catalytic soot filtration are quite effective methods for the elimination of PM from marine exhaust streams [22].

3.3. Operation of Selective Catalytic Reduction Unit

After the successful operation of the previously mentioned units that achieved the removal of SO_2 and significant reduction of the concentration of PMs, the SCR de-NO_x unit was set in operation. The study of the novel H_2-SCR unit was the main target of the present work, and its main purpose was to reduce nitrogen oxide species (NO_x), especially NO, to N_2 in the presence of excess air and using H_2 as a reducing agent. The results obtained before and after the operation of the complete pilot unit (i.e., SWA unit, oxidation catalyst and SCR de-NO_x unit) are comparatively presented in Figure 6.

As seen in Figure 6, the operation of the integrated pilot unit resulted in the significant reduction of the concentration of all four major pollutants (NO_x, CO, SO_2 and PM), that are present in the exhaust gas stream of the cruise ship studied. In particular, the concentration of NO, CO, SO_2 and PM at the exit stream of the complete pilot unit was found to be 124 ppm, 426 ppm, 0 ppm and 69 mg/m^3. The conversion percentage of all three gaseous pollutants from the suggested combined technology is presented in Figure 7. In particular, the achieved reduction of NO_x species and SO_2 in the exhaust gas stream was found to be up to 80% and more than 99%, respectively, while the concentration of CO and PM was reduced by 34% and 72%, respectively, after the operation of the pilot unit.

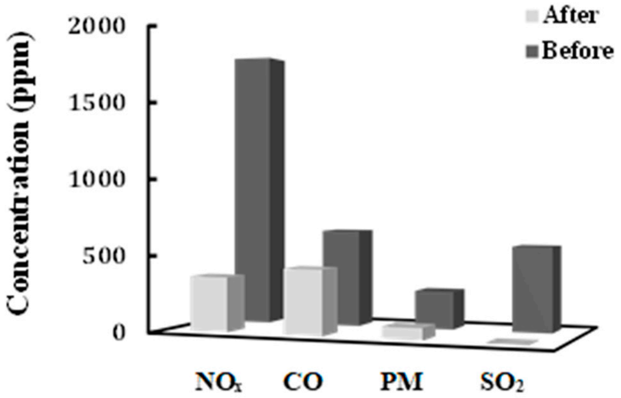

Figure 6. Steady-State concentrations of NO_x, SO_2 and PM before and after the operation of the Integrated Prototype Unit (SWA unit, Oxidative Catalyst and De-NO_x unit).

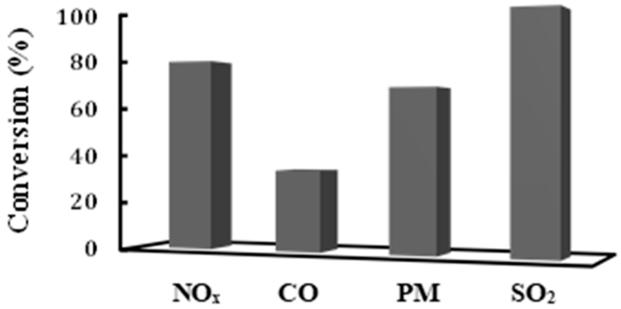

Figure 7. Final conversion (%) values of examined pollutants (NO_x, CO, PM and SO_2), as achieved by the operation of the present Integrated Prototype Unit.

The International Maritime Organization (IMO) engine NO_x limits are based on engine rated speed, with the lowest limits applicable to medium and high-speed engines. The application date of Regulation's 13 NO_x emission limits is tied to the ship construction date [23]. The restrictions introduced by Tier I were compulsory for new diesel engines constructed or installed on ships from 1 January 2000. Tier II is mandatory applicable for ships constructed after 1 July 2010 as Tier III compliance is required for ECA and 200 miles Exclusive Economic Zone of U.S. from 1 January 2016, as well as for Baltic and North Sea from 1 January 2021. Under consideration for further application area expansion are zones like Mediterranean Sea and Black Sea [24,25].

Based on the above results (Figure 7), it can be safely claimed that the novel H_2-SCR de-NO_x unit used in the present work is quite efficient for the removal (reduction) of Nitrogen Oxides emitted from ship's main engines, achieving even the strictest regulations of IMO (Tier III). Moreover, it should be noted that further improvement of the de-NO_x unit can be achieved by optimizing its overall design, catalyst mass, catalytic reactor's design (e.g., use of a monolithic reactor), etc.

4. Conclusions

The conclusions that derive from the present work can be considered of significant industrial importance, since the three different technologies used in this research are combined and implemented in a pilot unit for the first time on board a cruise ship. In particular:

- The Sea Water Absorption technology was found to be capable of practically eliminating sulphur dioxide from the exhaust gas stream. SO_2 was almost completely removed from the ships exhaust stream (more than 99% conversion), which is in full accordance with the new IMO MARPOL regulations [2].

- Moreover, a significant reduction in PM was also achieved with the use of an oxidizing catalytic converter. In the framework of the present study, it has been found that more than 70% of the PM in the exhaust gas stream of the ship was successfully removed with the use a commercial oxidation catalyst.
- Most importantly, within the present work, the H_2-SCR de-NO_x technology was examined, for the first time ever, in a real application, as a candidate technology for the reduction of NO_x present in ships exhaust gasses. It was proven that the Selective Catalytic Reduction of NO_x with the use of H_2 as a reducing agent in combination with a suitable catalyst, can be considered an effective NO_x-pollution control technology for ships. In particular, it was found that more than 80% of NO_x can be successfully reduced to N_2 with the use of the novel Pt/MgO-CeO_2 supported catalyst.

The results obtained by the present work are quite promising and can lead to a real, practical application for the complete removal of major pollutants present in ships exhaust gaseous streams, i.e., NO_x, SO_2 and PM.

Author Contributions: P.G.S. proposed the idea behind the research and had the main responsibility for the preparation of the manuscript; C.N.C. supervised the project and the experiments conducted; Y.F. had the responsibility for the construction of the pilot unit and the performance of the pilot experiments; and A.M.E. contributed to the design of the pilot unit and the interpretation of the results obtained. All authors have read and agreed to the published version of the manuscript.

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