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Use of Catalytic Converter for Achieving Efficient and Economic Emission Reduction

Hare Ram Hare[1,*], Vikash Sinha[2], Nakshatra Sah[3]

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ABSTRACT

Stringent international emission rules according to MARPOL ANNEXURE VI have made, finding more economical ways to fight emissions, an immediate need of the hour. A major step in this direction can be taken by the inclusion of a catalytic converter which has proven time and again to be of immense use in reducing harmful emission gases upto a considerable level. Despite its use of expensive metals like platinum and palladium, the method is researched upon for its economical use in the shipping industry versus the conventional method already being used, i.e., the selective catalytic reduction (SCR). The catalytic converter inter-alia occupies less space for the same operation as a SCR plant.

1. Introduction.

In 1975, the EPA's regulations on reducing toxic emissions led to the widespread introduction of catalytic converters in American production vehicles. The Clean Air Act of 1975 mandated a 75 percent reduction in emissions for all new vehicles manufactured after 1975, which had to be achieved through the use of catalytic converters. Vehicles produce hydrocarbons, carbon monoxide, and nitrogen oxide without catalytic converters. The majority of ground-level ozone, which contributes to smog and is harmful to plant life, comes from these gases. The plan now is to use the catalytic converter on ships and take it to a whole new level. A catalytic converter is a straightforward device that uses fundamental redox reactions to reduce engine emissions. It has a ceramic honeycomb-like interior with insulating layers in a metal housing and reduces the amount of harmful gases produced by an automobile engine by approximately 98%. A washcoat of aluminum oxide covers the thin wall channels that make up the interior of this honeycomb. This coating has more surface area, is porous, and contains precious metals like palladium, rhodium, and platinum. This makes it possible for more reactions to take place. A single converter for a car engine can only hold between 4 and 9 grams of these precious metals. A ship's engine, on the other hand, will need more, but the ratio will be determined by the ship's power and capacity [1].

2. What is NOx, and where does it come from?.

NO_x pollution occurs when fossil fuels are burned at high temperatures and nitrogen oxides are released as a gas into the atmosphere. These nitrogen oxides consist mainly of two molecules, nitric oxide (NO) and nitrogen dioxide (NO_2) along with a few others that occur in much lower concentrations. These molecules- Nitrous oxides are a significant greenhouse gas that plays an important role in Global Climate Change. When oxygen and nitrogen from the air interact during a high-temperature combustion event, nitrogen oxides are formed. Internal Combustion Engines and electricity plants powered by fossil fuels both experience these conditions. Each marine diesel engine installed on a ship with a power output of more than 130 kW is subject to the NO_x emission limits set forth in Regulation 13 of MARPOL Annex VI. Any reciprocating internal combustion

[1]Assistant Professor, Department of Marine Engineering, Indian Maritime University, Mumbai Port Campus, Mumbai.
[2]Faculty, Mechanical Engineering, Department of Marine Engineering, Indian Maritime University, Mumbai Port Campus, Mumbai.
[3]B. Tech Cadet (Marine Engineering), Department of Marine Engineering, Indian Maritime University, Mumbai Port Campus, Mumbai.
*Corresponding author: Hare Ram Hare. E-mail Address: hareram@imu.ac.in.

engine that runs on liquid or dual fuel is considered a marine diesel engine. Two exceptions exist: engines that are only used in emergencies and that are on ships that only operate in the waters of the state where they are flagged. The later exception only applies if these engines are subject to an alternative NO_x control measure. According to Table 1, diesel engine NO_x emission limits are determined by the engine's maximum operating speed (n, rpm). The limits for Tier I and Tier II are applicable worldwide, whereas the Tier III standards only apply to NO_x Emission Control Areas.

Table 1: MARPOL Annex VI NOx emission limits.

Tier	Date	NO_x Limit, g/kWh		
		n < 130	130 ≤ n < 2000	n ≥ 2000
Tier I	2000	17.0	45 · n-0.2	9.8
Tier II	2011	14.4	44 · n-0.23	7.7
Tier III	2016†	3.4	9 · n-0.2	1.96
† In NO_x Emission Control Areas (Tier II standards apply outside ECAs).				

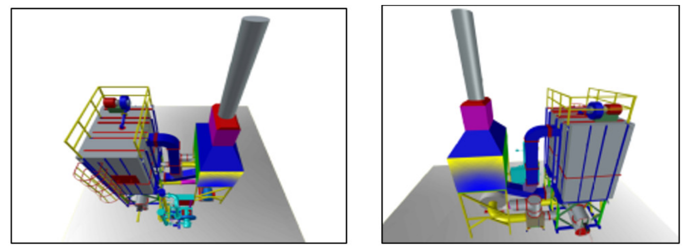
Source: Authors.

Optimizing the combustion process is expected to meet Tier II requirements. Timing of fuel injection, pressure and rate (rate shaping), area of fuel nozzle flow, timing of exhaust valve, and volume of cylinder compression are some of the parameters that engine manufacturers examine. Dedicated NO_x emission control technologies like exhaust gas recirculation or selective catalytic reduction, as well as various forms of water induction into the combustion process (with fuel, scavenging air, or in-cylinder), are expected to be required by Tier III standards. Pre-2000 Engines. Under the 2008 Annex VI amendments, Tier I standards become applicable to existing engines installed on ships built between 1st January 1990 to 31st December 1999, with a displacement ≥ 90 liters per cylinder and rated output ≥ 5000 kW, subject to availability of approved engine upgrade kit. Testing.ISO 8178 cycles (E2, E3 cycles for various types of propulsion engines, D2 cycles for constant speed auxiliary engines, and C1 cycles for variable speed and load auxiliary engines) are used to test engine emissions. The Tier III standards' inclusion of not-to-exceed (NTE) testing requirements is up for debate. NO_x emissions at each load point in the E2/E3 cycle would be subject to NTE limits that have a multiplier of 1.5. Even though residual fuels are typically used in real-world operation, distillate diesel fuels are used for engine testing. The mandatory "NO_x Technical Code," which has been adopted under the guise of "Resolution 2," contains additional technical details regarding NO_x emissions, such as methods for controlling them [2-4].

2.1. SCR used onboard ships.

Ship & Shore Environmental provides Selective Catalytic Reduction (SCR) Systems for processes that need to reduce NO_x to meet air quality regulations and low NO_x limits. Ship & Shore is able to custom engineer, design, and manufacture an SCR system that is connected to a Regenerative Thermal Oxidizer (RTO) based on the VOCs that are present during the manufacturing process as shown in Figure 1.

Figure 1: 3D Rendering of a Ship & Shore RTO (left) + SCR System (right).



Source: shipandshore.com.

The following are general components of an SCR and RTO abatement system:

2.1.1. SCR catalyst & injection grid.

The RTO stack will contain the SCR catalyst. Before entering the SCR catalyst, the RTO stack will be connected to a hot bypass to maintain a temperature of 500°F to 700°F. Through the injection grid and mixing plate, ammonia will be injected into the stack and mixed with the flow.

The catalyst media will receive the mixture of NO_x and ammonia. The SCR catalyst can be designed for up to 95% NO_x reduction efficiency and will react with NO_x and ammonia through the catalyst bed, resulting in the formation of N_2 and H_2O.

2.1.2. Ammonia vaporizor unit.

Hot air atomization will be used to vaporize the aqueous ammonia (NH_3) that will be pumped out of a storage tank. At approximately 250°F, vaporized ammonia will be delivered to injection grids. The following components typically make up an ammonia vaporizer unit: ammonia filter, electrical heater, air blower, and control system

A substitute for aqueous ammonia is either urea or anhydrous ammonia. The application of anhydrous ammonia may raise some safety concerns. The "Urea to Ammonia" equipment must be added to the Urea option. For any given process, the possibility of both options can be investigated.

2.1.3. Analyzers.

To keep an eye on NO_x or Ammonia slips at the exhaust stack, online analyzers are available. Controlling the rate of ammonia injection based on NH_3 or NO_x slip is also crucial. The rate of ammonia injection will be controlled by an analyzer signal.

Ammonia slip can be monitored with a laser cross-duct in situ NH_3 gas analyzer, and NO_x can be monitored with a chemiluminescent analyzer. The sampling system, probes, and analyzer enclosures are typically included in the analyzer system.

2.1.4. Ammonia tank and pump.

To transport ammonia to the vaporizer and store it, an ammonia tank and pump will be required. The tank's size can be determined by the frequency of loading and the space available. A 1000-GAL tank, for instance, will last one to two weeks at the highest NO_x concentration or three weeks at the average NO_x concentration.

3. Catalytic converter.

A catalytic converter transforms the harmful compounds in an engine's emissions into safe gases like steam in a chamber. The catalyst works by separating the hazardous molecules in car exhaust gases before they are released into the air. The catalytic converter is a big metal box that is on the underside of a vehicle. It has two pipes that come out of it. During the process of making the gases safe to be expelled, the convertor makes use of these two pipes as well as the catalyst. The vehicle's "input" pipe, which is connected to the engine, is where gas enters. Over the catalyst, these are blown, triggering a chemical reaction that separates the pollutants. The second pipe, or "output," that is connected to a car's tailpipe now transports the less harmful gases.

3.1. What is inside a catalytic converter?

So what is a catalytic converter made of? Platinum or a similar metal like rhodium or palladium is typically used to make the catalyst in a catalytic converter. Within the cat housing, a ceramic honeycomb structure allows gases to flow through it. This is lined with metals that do particular jobs that help cut emissions. There are two primary categories of catalysts that may be found in automobiles:

- **Reduction catalysts:** Helps reduce nitrogen oxide pollution by removing oxygen. Nitrogen and oxygen gases, which are innocuous on their own, are formed when nitrogen oxides are broken down.
- **Oxidation catalysts:** Used to change carbon monoxide into carbon dioxide through an opposite process of adding oxygen.

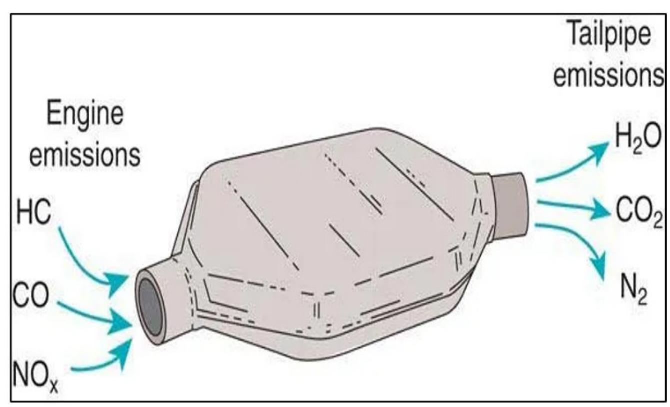
An oxygen (O_2) sensor is also close to the catalytic converter. This sensor tells the car's electronic control unit (ECU) how much oxygen is in the exhaust gases. This enables the engine to supply sufficient oxygen to the converter to complete the oxidation process, allowing a vehicle to run on a more effective air-to-fuel ratio.

3.1.1. Types of catalytic converters.

Reduction and oxidation are the two primary catalysts that can be utilized in an exhaust system to handle particular gases. There may or may not be a reduction catalyst installed, depending on the vehicle's year and type of catalytic converter. Catalytic converters can be broken down into two main categories:

- **Two-way:** Two tasks are performed simultaneously by a two-way catalytic converter: Carbon monoxide oxidation into carbon dioxide: $2CO + O_2 = 2CO_2$ Oxidation of hydrocarbons (fuel that has been burned completely or partially) into water and carbon dioxide: $C_xH_{2x+2} + [(3x+1)/2]\ O_2 \rightarrow xCO_2 + (x+1)\ H_2O$ (a combustion reaction) This kind of catalytic converter is frequently applied to diesel engines in order to lessen the amount of hydrocarbon and carbon monoxide that are released into the atmosphere. They were also installed on gasoline engines in automobiles sold in the United States and Canada until 1981. They were replaced by three-way converters because they were unable to control nitrogen oxides.
- **Three-way:** There are three simultaneous functions of a three-way catalytic converter as shown in Figure 2: Oxygen and nitrogen are converted from the nitrogen oxides: $2NOx \rightarrow xO_2 + N_2$ Oxidation of carbon monoxide into carbon dioxide: $2CO + O_2 \rightarrow 2CO_2$. Oxidation of unburned hydrocarbons (HC) to water and carbon dioxide: $C_xH_{2x+2} + [(3x+1)/2]O_2 \rightarrow xCO_2 + (x+1)H_2O$. These three reactions take place most effectively when the catalytic converter receives exhaust from an engine that is running slightly above the stoichiometric point. This point is between 14.6 and 14.8 parts air to 1 part fuel, by weight. Diesel engines employ the use of two-way catalysts, and the converters are also specifically designed to work with diesel exhausts. The converters for these types of engines try and target particulates known as soluble organic fractions. These are made from hydrocarbons bound to soot.

Figure 2: A 3-way catalytic converter.



Source: ebuyindustry.com.

3.2. Problems with catalytic converters.

So what happens when a catalytic converter fails? When the part starts to wear out, a variety of symptoms can occur due to the role it plays in the exhaust system of a vehicle.

Examples to be on the lookout for include:

- **Declining Fuel Efficiency:**A clogged catalytic converter can restrict the flow of air through your engine. Your engine might start burning more fuel than usual as a way to make up for the loss of fuel efficiency.

- **Check Warning Light:** A variety of things can cause a check engine light to come on. However, the catalytic converter can be tested by a diagnostic system on vehicles manufactured after 1996. The air-to-fuel ratio sensors may cause the warning light to come on if your converter is broken.

- **Rotten Egg Smell:** There may be internal damage to the catalytic converter that makes it difficult to convert exhaust gases. The end result might smell like sulphuric "rotten eggs."

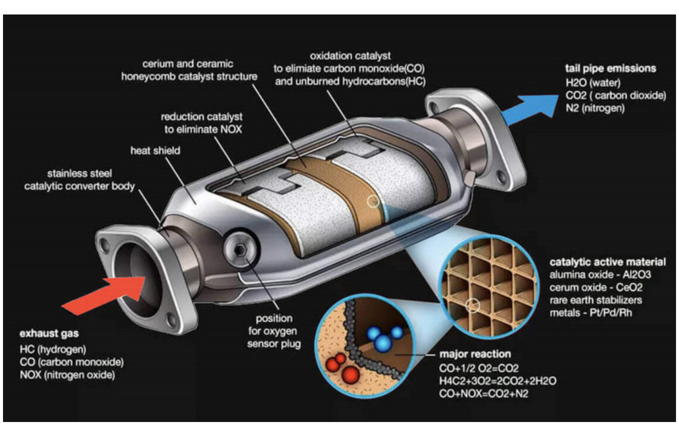
- **Issues Starting the Engine:** Your vehicle's exhaust gases must escape. As effectively, this can be prevented by a clogged catalytic converter. When you try to start your car, this can cause it to sputter or stall due to increased exhaust pressure.

- **Poor Acceleration:** The exhaust gases must again escape in some way. Acceleration might be difficult for you due to clogged converter pressure and a clogged exhaust. If you try to do so, you might notice jerking or stalling.

- **Failed Emissions Test:** Vehicle emissions testing are required by many states on a regular basis, and if yours fails, your catalytic converter may be to blame. Failure to pass this test may be accompanied by the other symptoms listed above.

3.3. *Catalytic converter used in automobiles.*

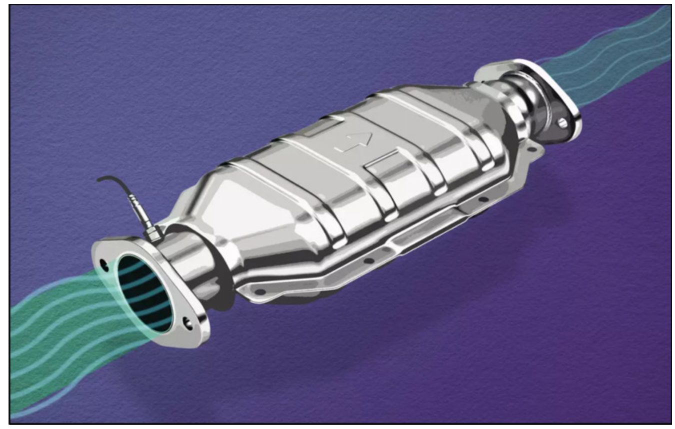
Figure 3: Design of a Catalytic Converter.



Source: catalyticconverterking.com.

It reduces the amount of harmful gases produced by an automobile engine by approximately 98%. Catalysts like palladium and platinum are used in a catalytic converter. Ceramic honeycomb or ceramic beads, which are housed in a package resembling a muffler and attached to the exhaust pipe, are coated with the catalyst. The catalyst aids the converter as it converts unwanted fumes through straightforward oxidation and reduction reactions. The engine produces the following three harmful pollutants:

Figure 4: Catalytic Converter in an Automobile.



Source: Cars.com illustration by Paul Dolan.

- Hydrocarbons (in the form of unburned gasoline)
- Nitrogen oxides (created when the heat in the engine forces nitrogen in the air to combine with oxygen)
- Carbon monoxide (formed by the combustion of gasoline).

3.4. *Parts of a catalytic converter.*

Despite their similarities, a catalytic converter and muffler serve distinct purposes in your exhaust system. Ceramic honeycomb - shaped structure is housed in the converter; This component and precious metals in the converter facilitate a chemical reaction in your vehicle's emissions. These components, which are referred to as catalysts, work to reduce harmful pollutants released by a vehicle.

Parts of a catalytic converter include:

- **Substrate** – A core made of ceramic honeycomb or metallic foil.
- **Washcoat** – Aluminum oxide, titanium dioxide, silicon dioxide, silica, alumina.
- **Catalyst** – Platinum, palladium, rhodium.

3.5. *Working of catalytic converter.*

It is possible to significantly reduce the number of harmful components in vehicle exhaust, though it is not yet possible to completely eliminate all of them. An intake pipe draws exhaust fumes from the engine into the catalytic converter when your vehicle is running. The catalysts, which are made of ceramic honeycomb and metals like palladium or rhodium, move hydrocarbons, carbon monoxide, and nitrogen oxides over them. After that, the metals start two major chemical reactions inside the converter:

3.5.1. *Reduction.*

By removing oxygen gas, this reduces the amount of nitrogen oxide in the exhaust. Pure nitrogen and pure oxygen are produced when the elements of nitrogen oxide are broken down. These components are harmless on their own.

3.5.2. Oxidation.

By adding oxygen to carbon monoxide, it becomes carbon dioxide, which is less harmful. Your vehicle's oxygen sensor is evaluating whether your fuel intake process contains sufficient oxygen for optimal performance during these conversions. Your car's computer can instruct the fuel intake process to adjust the amount of oxygen for a more effective combustion process if the ratio is found to be off. The exhaust is routed through the muffler to reduce noise after the conversion is finished, and then it exits the vehicle entirely via the tailpipe [10-12].

4. Problems and counter measures.

Few things can be incorporated before introducing this idea to the marine industry.

- Cost effectiveness of the catalytic converter in comparison to the ship-based SCR currently in use. Efficiency, as the SCR currently in use reduces NO_x emissions by 90%.
- Need of modifications to the ship required to fit the converter.
- Working temperature.
- Maintenance issues.
- Catalytic converter cleaning.

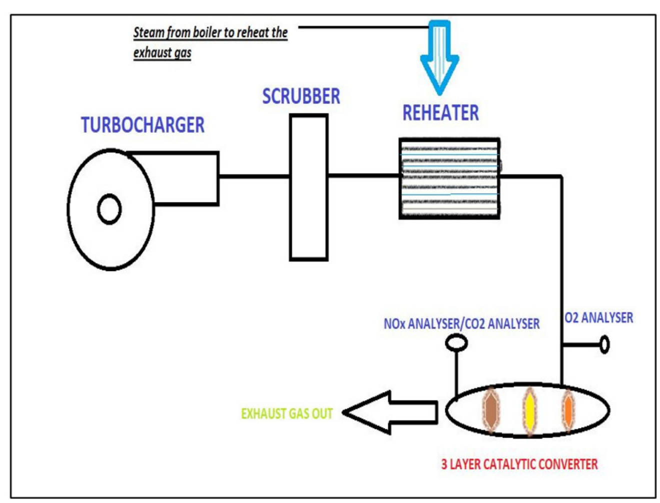
To tackle this, it is found that

- If the three-layer catalytic converter is used instead of the current selective catalytic reducer, the cost was lower than anticipated. That is provided in the headline "Economics."
- The catalytic converter in a 1400cc power car engine is 98% efficient thus by using it as a countermeasure in the maritime industry can significantly alter the situation.
- No major modification is needed to be done as this can be retrofitted with the current system.
- A clogged catalytic converter should be replaced right away if sluggish powertrain performance is noticed, decreased acceleration, the smell of rotten eggs or sulfur coming from the exhaust, dark exhaust smoke, or extreme heat coming from under the vehicle.
- Is there a way to clean a catalytic converter?
- Using lacquer thinner and water is the best technique. However, since there is no tried-and-true method for cleaning the catalytic converter in this manner, you should first look online for additive cleaners like Oxicat or Cataclean that help slowly remove carbon deposits. The time interval of replacement of a catalytic converter in automobiles is approximately 10 years continuous working.
- This works at about 600°C, so we are using a reheat system to raise the temperature to counteract this.
- To check for any deficiencies in the catalytic converter, an additional temperature sensor, oxygen analyzer, and output exhaust sensor will be installed.

5. Proposed installation.

- The catalytic converter performs best at temperatures around 600°C. Therefore, it should have been situated between the turbocharger and the exhaust manifold as shown in Figure 5.
- However, this could impede the flow of exhaust gases, reduce turbocharger efficiency, and can possibly cause turbocharger surging. Therefore, placing it after the scrubber unit would be preferable.
- The turbocharger would move the exhaust gases to the scrubber unit, with an economizer in between. After that, it would go through a reheater, which might heat the food with electricity or steam.
- The heater is provided to achieve the most efficient working temperature range, which is less than 600°C.
- The scrubber would dampen the majority of the vibrations in the exhaust gases, which may extend the catalytic converter's lifespan since platinum and rhodium now require more time to erode. This is another advantage of placing it after the scrubber.

Figure 5: Installation of catalytic converter on ships.



Source: Authors.

6. Cost analysis.

The cost analysis is shown in Table 2.

Table 2: Cost Comparison between SCR and Catalytic Converter.

SCR Unit	Catalytic Converter
Let's assume a marine diesel engine of 20 MW BHP,	Normally SUVs use a max of 7g of platinum
Since urea required would be 4-10 cubic metres per MW of engine power,	Assuming the ship to use 100g of platinum
Let's say 6 cubic metres per MW,	Average cost of platinum=$35.18/g
Urea required would be 120 cubic metres.	Cost in convertor= $35180
Density of urea is about 1.32t/m^3	About 1-2 g rhodium is used in automobiles
Amount of urea required= 1.32x120 = 158.4 tonne	Assuming the rhodium used is 20g in ship
Average cost of urea = $550/tonne	Cost of rhodium=$400/g
Cost of urea= 550X158.4=$87120	Cost in convertor=$8000
	Total cost=$35180+$8000= $43180

Source: Authors.

Conclusions.

The purpose of this research is to benefit the maritime sector by replacing the current SCR system which require a very high setup cost and too much space consuming, with an alternate system which will be cost effective, less space consuming and more effective in reducing the exhaust emissions that will be benefitting the shipping companies complying with all the rules and regulations in a very efficient manner.

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