

Investigation of SCR Catalysts for Marine Diesel Applications

Athanasios G. Konstandopoulos
CERTH/CPERI and Aristotle University

Dimitrios Zarvalis, Leonidas Chasapidis, Danis Deloglou, and Nickolas Vlachos
CERTH/CPERI

Adam Kotrba and Ginette Anderson
Tenneco Inc

ABSTRACT

Evolving marine diesel emission regulations drive significant reductions of nitrogen oxide (NO_x) emissions. There is, therefore, considerable interest to develop and validate Selective Catalytic Reduction (SCR) converters for marine diesel NO_x emission control.

Substrates in marine applications need to be robust to survive the high sulfur content of marine fuels and must offer cost and pressure drop benefits. In principle, extruded honeycomb substrates of higher cell density offer benefits on system volume and provide increased catalyst area (in direct trade-off with increased pressure drop). However higher cell densities may become more easily plugged by deposition of soot and/or sulfate particulates, on the inlet face of the monolithic converter, as well as on the channel walls and catalyst coating, eventually leading to unacceptable flow restriction or suppression of catalytic function. To assess the risk of occurrence and potential mitigation measures for such phenomena, an experimental program is conducted with a number of vanadia based honeycomb SCR substrates. A range of relevant fuel qualities and exhaust conditions were surveyed in order to better understand the relevant phenomena and improve design capabilities for marine diesel NO_x control systems.

CITATION: Konstandopoulos, A., Zarvalis, D., Chasapidis, L., Deloglou, D. et al., "Investigation of SCR Catalysts for Marine Diesel Applications," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0947.

INTRODUCTION

Although Ultra Low Sulfur Diesel has become a standard in North America and Europe in the automotive sector since 2006, it was only in 2005 when the first restriction in the sulfur content of marine fuels came into effect. In 2005, MARPOL Annex VI placed limits on the sulfur content of fuels used and NO_x concentrations in ships' exhausts. Further on, even stricter limits have been posed on ships operating in regions known as Emission Control Areas (ECAs). An overview of the history of fuel sulfur limits and NO_x emissions limits for marine engines is presented in [Tables 1 and 2](#) respectively [1, 2].

Table 1. Limits for sulfur content of fuels used inside and outside SECAs

Entry into force	Sulfur content of fuel (% m/m)	
	Outside ECA	Inside ECA
19 May 2005	4.5	1.5
1 July 2010		1.0
1 January 2012	3.5	0.1
1 January 2015		
1 January 2020	0.5	

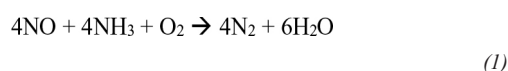
Table 2. Limits for NO_x emissions in ships' exhaust

Ship Construction date	Total Weighted cycle emission limit (g/kWh)		
	rpm < 130	130 ≤ rpm ≤ 1999	rpm ≥ 2000
1 January 2000	17.0	$45 \cdot rpm^{-0.2}$	9.8
1 January 2011	14.4	$44 \cdot rpm^{-0.23}$	7.7
1 January 2016	3.4	$9 \cdot rpm^{-0.2}$	2.0

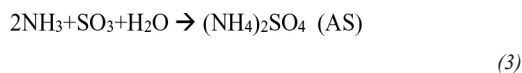
In ships, as in heavy duty road vehicles, the established technology for the abatement of NO_x emissions is the ammonia-based selective catalytic reduction (SCR). There are now hundreds of marine SCR systems installed worldwide. Besides the known challenges that automotive SCR systems face, marine SCR systems are further challenged by two additional factors: soot and ammonium sulfate deposits. While in automotive applications, SCR components are placed downstream of the Diesel Oxidation Catalyst (DOC) and the Particle Filter (DPF), this is not the case in marine applications where the focus of regulatory authorities is NO_x and standard DOC technologies would not survive in the high sulfur environment of the

ship's exhaust. Moreover, fuel sulfur content is orders of magnitude higher for typical marine fuels compared to automotive diesel fuels. Therefore, vanadia (V_2O_5) based SCR catalysts (VSCR) are commonly used in the marine sector since such catalysts exhibit significant sulfur tolerance which is not the case for Cu or Fe-zeolite based SCR formulations [3]. VSCR is actually V_2O_5 on high surface area anatase (TiO_2), optionally with tungsten trioxide (WO_3) which provides stabilization of TiO_2 at higher temperatures. The VSCR optimum window of operation is 250 - 450 °C [3].

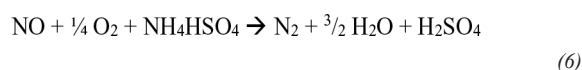
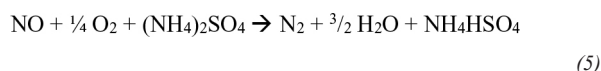
The NO_x emitted by marine engines is mostly NO since in most cases there is no Diesel oxidation catalyst (DOC) installed. Therefore, NO_x abatement mainly follows the so-called "slow SCR" reaction, described by Eq. (1) below, while there is a negligible contribution from the "fast SCR" reaction that requires NO_2 .



The sulfur in the marine exhaust, without any DOC present, exists mainly as SO_2 while SO_3 is typically less than 5 % of the total SO_x [4]. Nevertheless, the oxidation of SO_2 to SO_3 is promoted by the VSCR catalyst, despite optimization efforts which are applied to the catalyst to minimize this reaction, i.e. primarily by reducing the vanadia content of the catalyst. This factor is significant for the durability of the VSCR converter since SO_3 is the primary precursor of ammonium sulfate salts. The latter are formed by reactions shown in Eq. (2), (3), (4).



The formation and decomposition phenomena of Ammonium Sulfate (AS) and Ammonium (Bi) Sulfate (ABS) are crucial for the efficient operation of the VSCR system. It has been shown that the existence of SO_2 in the exhaust can actually have a promotional effect on the SCR activity [4, 5] and this was explained by an increasing number of Brønsted acidic sites on the catalyst surface. A key factor affecting the SCR performance in a positive way is the NH_3 storage capability [7, 8]. SO_2 -derived sulfate species can themselves lead to increased catalyst surface acidity which in turn promotes NH_3 storage by adsorption [5, 6]. Moreover, it has been shown [9] that surface AS and ABS can consume NO from the exhaust through the reactions described in Eq. (5) and Eq. (6) below.



On the other hand, excessive formation/deposition of ammonium sulfates can deactivate the catalyst via physical masking of the active catalyst sites. Whether AS/ABS deposits promote or inhibit SCR reactions seems to depend on a number of parameters like SO_2 concentration, H_2O concentration, exhaust space velocity and temperature. Moderate SO_2 concentrations, low H_2O concentration, higher exhaust temperatures and low space velocity (SV) may promote or at least demonstrate no deactivation of the catalyst. On the contrary, catalyst deactivation has been reported at temperatures below 250 °C, with a fuel of 500 ppm sulfur content and exhaust space velocity $\approx 18000 \text{ h}^{-1}$ [4]. Water increase leads to increased AS/ABS formation rate and therefore catalyst deactivation. The effect of temperature is significant since it dictates the decomposition of surface-deposited AS/ABS. Ammonium sulfates start decomposing at about 250 °C but when these are formed in the presence of water, the decomposition temperature shifts to higher temperatures by 20-30 °C [8].

With respect to the interaction of soot particles with the SCR activity, most research work performed refers to SCR on DPF systems. NO_2 plays a significant role in such systems [10, 11] but this is not relevant to marine applications where, as with ammonium sulfate deposits, the soot particles can potentially have a positive or negative overall effect on NO_x reduction. Nitrogen monoxide, which dominates the NO_x emissions, does not interact with soot while there is effectively no soot oxidation by O_2 at the temperatures of interest [11, 12]. Therefore, consideration shifts to the potential for soot deposits to inhibit SCR reactions by posing an additional mass-transfer resistance between the exhaust gas and the active catalytic sites. On the other hand, it has been shown [13] that soot provides additional sites for strong ammonia adsorption. Such an NH_3 buffering effect could promote SCR activity. Of course, soot particle matter is not just carbonaceous soot but also consists of ash particles and heavy hydrocarbons condensed on the soot particles (Volatile Organic Fraction, VOF) [14]. The organic materials on the soot particles could provide even stronger bonding with NH_3 increasing the desorption temperature thus lowering the targeted SCR activity.

In the relevant literature, the phenomena of soot and ammonium sulfates interaction with the VSCR catalyst activity has generally been studied under well-controlled laboratory environments using synthetic exhausts. Experimentation with the effects of real-life marine exhaust characteristics on the SCR activity is difficult and costly as it concerns large engine test cell installations. Nevertheless, the use of realistic marine diesel exhausts is necessary for achieving field-applicable optimized catalysts and structures. For example, the optimization of substrate cell density is not straightforward in the presence of real marine diesel exhaust conditions. In the more established applications of clean / low-sulfur fuels, higher cell density improves the per volume performance of the SCR reactor due to the higher available catalyst surface area. However, the effect of higher cell density in the presence of marine diesel soot and AS/ABS is questionable due to the potential for catalyst blocking and/or deactivation. For this reason, this work presents a methodology for evaluating such phenomena in a fast and cost-effective manner under realistic exhaust conditions.

In real-life applications, an aqueous solution of urea, $(\text{NH}_2)_2\text{CO}$, is employed as the source of the reducing agent (NH_3) . Urea, through a series of decomposition and hydrolysis reactions, results to ammonia usually with the help of mixers and/or catalysts that should be optimized towards maximum ammonia production at the given exhaust operating conditions. The engineering of the necessary components determines the quality of ammonia feed in the SCR catalyst and eventually affects the system's performance. In the present study, pure ammonia is used as the reducing agent to avoid any implications of the ammonia production process on the investigation of the sulfur and soot effects on the SCR performance. However, urea impurities such as potassium (K) and calcium (Ca) can impose catalyst deactivation just like fuel components (As, Ni) and lube oil ingredients (P, Zn, Ca). Regarding urea solution impurities there is evidence in the literature that K reduces the adsorption equilibrium constant of ammonia and as a consequence, small ammonia concentration in the feed is not able to provide sufficient covering of active sites [15], while when high ammonia concentration is used then ammonia emissions downstream of the SCR are increased. The effect of Ca is not that big as the one of K and moreover, it is reduced in the presence of ions like SO_4^{2-} (as in Marine applications). The proposed methodology could also cover such effects, but it was chosen to concentrate on the effects of sulfur and soot and therefore only pure ammonia was employed.

Conventional diesel-electric power generators operated with conventional low-sulfur Diesel and various grades of marine fuel were used for the exposure of VSCR samples under conditions emulating real marine diesel exhaust. The exposure conditions were varied in order to study the effect of the amount of soot and AS/ABS on the SCR performance. Particular attention was also paid in varying the VOF of the deposited soot as this may alter the overall SCR performance. The exhaust source was extensively characterized prior to the exposure study. Three experimental phases have been completed. The first concerned the effect of only the soot and the samples were exposed to near-zero exhaust sulfur. In the second phase, the combined effect of soot and AS/ABS was studied. Two extruded honeycomb cell densities were considered, namely 86 and 140 cpsi. In the final phase, exposed samples were subjected to soot blow-off tests to evaluate the parameters affecting the aerodynamic cleaning of the VSCR monoliths. It has to be noted that during blow-off tests, the flow was reversed as this is the standard procedure for cleaning the monoliths and the target was to determine the difficulty in cleaning up the monoliths by soot blowing.

Fuels

Two fuels have been considered, the characteristics of which are listed in Table 3. Low Sulfur Diesel (LSD) is the typical automotive fuel, readily available with sulfur content less than 10 ppm. Marine or Heavy Gas Oil (MGO) is a fuel with 1.3% sulfur, which is commercially available in Europe and falls under ISO 8217 classification as ISO-F-MDA.

Table 3. Analyses of the LSD and MGO fuels used

Parameter	Units	Low Sulfur Diesel (LSD)	Marine Gas Oil (MGO)
Sulfur content	ppm wt	8.7	12780.0
Viscosity (40 °C)	cSt	2.93	9.30
Density (15 °C)	g/ml	0.83	0.87
Cetane index	-	55.72	48.62
Gross Heat of Combustion	MJ/kg	45.94	45.21
Distillation (50% evaporation)	°C	277.7	349.1
Water content	% wt	0.0083	0.0190
Pour point	°C	-12.0	16

Engine Conditions

Three engine operating points (engine speed, power output) were utilized within this study, denoted as "EPA", "EPB" and "EPC". In EPA and EPC both available fuels have been used while in EPB only MGO has been used. It has to be pointed out that the experiments were, by necessity, carried out with two different engines. The first set of tests were conducted with Engine 1 while the remaining tests used Engine 2. The technical characteristics of the two engines can be compared in Table 4. Switching engines became necessary after the failure of Engine 1. It was not possible to replace Engine 1 by an identical one because its production had been discontinued. Therefore, engine points EPA and EPB were conducted on Engine 1 and EPC on Engine 2 (Table 5). Both engines are single cylinder, four-stroke, air cooled and direct injection with the primary difference being the larger displacement of Engine 2. The main raw / engine-out exhaust characteristics obtained for each steady engine point are presented in Table 5. The effect of the MGO fuel sulfur content is readily apparent in the soot emissions measured. Soot mass concentration was measured using the (photoacoustic) Micro Soot Sensor instrument (MSS, AVL GmbH) while total particle number was measured with a 3022A Condensation Particle Counter (CPC, TSI Inc.). As the soot transport and deposit dynamics are of interest in this study, the exhaust particle size distributions were also obtained over the engine points and fuels matrix, as shown in Figure 1, measured with a Scanning Mobility Particle Sizer (SMPS 3080, TSI Inc.) combined with a 3025A CPC. The particle geometric mean diameter falls in the region of 100nm, except for the combination EPC/LSD which exhibits a lower diameter around 70nm and the condition EPB/MGO where a slightly larger (110nm) diameter is observed.

Table 4. Characteristics of the two engines used

Characteristic	Engine 1	Engine 2
Bore x stroke [mm]	70 x 55	80 x 69
Displacement [cc]	211	347
Engine speed (rpm)	3000 (max 3600)	3000 (max 3600)
Compression ratio	20:1	21.5:1
Rated output power [kW/rpm]	2.5/3000, 2.8/3600	4.6/3000, 5/3600

Table 5. Description of the Engine Points used

	EPA		EPB	EPC	
	LSD	MGO		LSD	MGO
T exhaust (°C)	255	255	365	321	330
Soot mass (mg/m ³)	70	240	574	32	96
Soot number (#/cm ³)	2.9E+7	5.7E+7	1.3E+8	1.1E+8	2.2E+8
O ₂ (%)	13.0	13.0	10.6	12.4	12.6
CO ₂ (%)	4.8	4.74	6.46	4.73	4.93
CO (ppm)	512	893	1679	213	419
NOx (ppm)	487	457	604	297	278

The amount of soot mass deposited on the catalyst surface is primarily affected by the engine point (EP) and the sample exposure time. The exposure time in this campaign ranged from 4 hours up to 32 hours. The VOF of the deposited soot is primarily affected by the EP and secondly by the temperature of the exposure flow. In general the higher the exhaust temperature of the EP the lower the VOF is (more dry soot). As will be described later, the temperature of the flow is set and controlled independently from the exhaust temperature with an oven housing the reactor that contains the sample. Again the higher the temperature is set for the SCR reactor the drier the soot is.

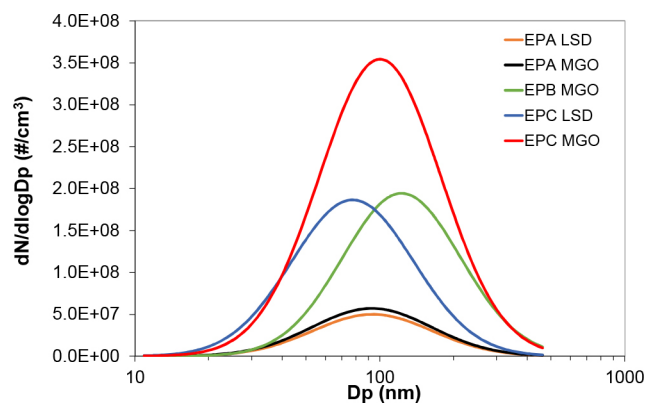


Figure 1. Particle size distribution (number basis) for all engine points EPA, EPB and EPC and fuel (LSD, MGO) combinations.

Experimental Procedure

The tested monolith samples were cut from standard full-size VSCR monoliths (6x6x20in) to approximately 35x35x53mm (WxDxL) segments. All monoliths obtained from the mid-axial plane of the monoliths after removing 1 cm from the periphery, thus avoiding inlet and outlet monoliths planes where catalyst coating uniformities could occur. The monoliths had been mounted in a canister that was then installed in a reactor. Average values of the main geometrical characteristics of the two different cell density monoliths tested, 140 and 86 c.p.s.i., are listed in Table 6.

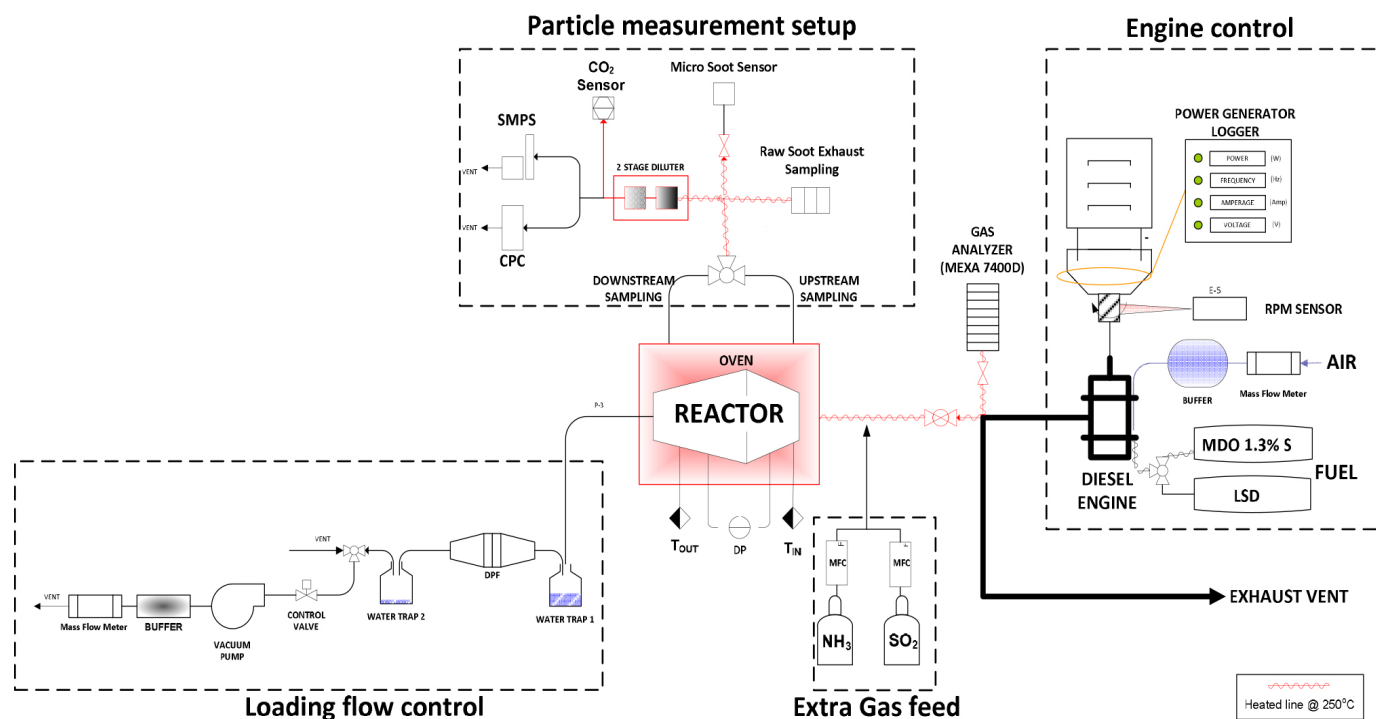


Figure 2. Process and instrumentation diagram of the experimental setup employed.

Table 6. Mean geometrical characteristics of the 140cpsi and 86cpsi monoliths tested

Monolith characteristic	140 cpsi	86 cpsi
Length (mm)	52.6	52.87
Square side (mm)	34.2	35.6
Total volume (ml)	61.6	67.1
Filtration area (m ²)	0.099	0.081
Total face area (m ²)	0.00117	0.0127
Effective face area (m ²)	0.00118	0.00127
Channel size (mm)	1.84	2.27
Wall thickness (mm)	0.285	0.435
Number of cells	256	169

All tests concerned exposure of VSCR samples to exhaust conditions for a specified time interval and then either an SCR performance evaluation test or soot blow-off test. The test campaign is divided into three phases:

- Phase 1: Effect of soot deposits on SCR performance
- Phase 2: Effect of soot and AS/ABS deposits on SCR performance
- Phase 3: Effect of exhaust conditions on soot blow-off effectiveness.

The space velocity of all exposure tests was 20,000 h⁻¹, consistent with typical application conditions. One test (with Engine 2) was done at 5,000 h⁻¹ to evaluate the effect of low exhaust velocity.

The soot exposure of the samples was realized in the experimental setup shown in Fig. 2. The engine control setup consisted of the engine coupled to an electric power generator. The latter was connected to an array of several electrical resistances, connected in parallel, thus giving the possibility of varying the load to the engine. The fuel selection of the engine can be made with a three-way valve from either the MGO fuel tank or the LSD fuel tank. The MGO fuel lines were heated to approximately 70°C to lower the viscosity and prevent clogging in the fuel injection system. A data acquisition system allowed the data logging of the electric load applied, the engine speed, the air consumption and the oil temperature to ensure stable engine running conditions throughout the experiment. The exhaust gasses, CO₂, CO, O₂, total hydrocarbons (THC), NO and NO_x are monitored with a multi-exhaust gas analyzer (Horiba MEXA 7400D).

The reactor containing the VSCR sample was housed in a single zone oven and heated to the prescribed experiment temperature ($T_{\text{flow}} = 250\text{ }^{\circ}\text{C}$ or $300\text{ }^{\circ}\text{C}$). This reactor is equipped with integrated particle sampling tubes upstream and downstream of the monolith sample, upstream/downstream thermocouples and pressure drop measurement ports.

At the beginning of each exposure experiment, the engine was allowed to run for 20 minutes at the desired engine point and the exhaust gasses were monitored with the gas analyzers. When stable conditions were achieved, in both the reactor and the engine operation, a sampling pump, situated downstream of the VSCR sample reactor, started drawing a controlled side-stream flow of exhaust through the test monolith. The loading flow control consisted of a vacuum pump with a control valve and a mass flow meter downstream of a buffer. Feedback control, based on the reading of the mass flow meter, was used to maintain the desired flow setpoint. In order to protect the control valve and the pump from exhaust particles, a diesel particulate filter was installed upstream of these components. This protective DPF - which was thermally cleaned offline when required - was oversized by at least a factor of 20 relative to the sample flow to avoid changing reactor conditions (pressure) as a result of soot accumulation during an experiment.

The exposure time varied, according to the test matrix, ranging up to 32 hours. During loading of the filter, upstream and downstream measurements with all the particle analyzers (CPC 3022A, SMPS 3080+3025A, and AVL Micro Soot Sensor), were conducted, every 60 minutes. This combination of particle analyzers can provide measurements of particle size distribution, number concentration and mass concentration. A two stage diluter (DEKATI, DI-1000) is used upstream of the SMPS and CPC, to lower the particle concentration within the range of the instruments, together with a CO₂ sensor to monitor in real-time the dilution ratio. Additionally, raw soot exhaust can be collected on a glass fiber filter for ex-situ analyses, such as TGA and TEM.

An extra gas feed mixture of NH₃+SO₂ was possible to be injected into the exposure flow upstream of the reactor, in order to promote the production of AS/ABS if needed.

After the soot loading, the exposed samples were first photographed and then installed into another compatible reactor for the SCR performance test.

The experimental setup for the SCR performance evaluation is shown in Figure 3. In this test rig, a synthetic gas can be prepared at the desired concentration and fed to the reactor housing the catalyst sample. The reactor can be bypassed, so upstream and downstream gas measurements can be done.

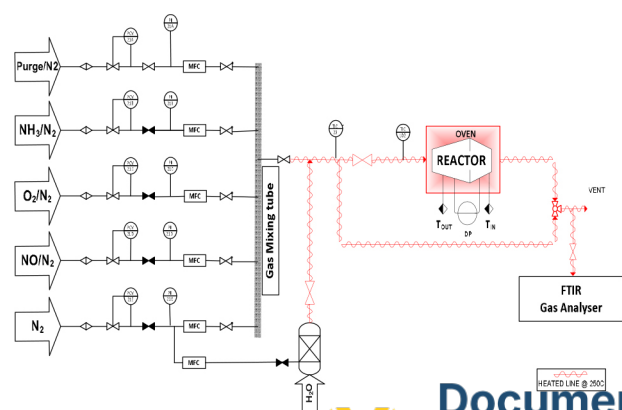


Figure 3. SCR performance test setup diagram