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FLEXibilize combined cycle power plant through power-to-X solutions using  
non-CONventional Fuels

## D2.7 – “Design of an enhanced DENOx system for the H<sub>2</sub>/nitrogenated combustion system”

Organization name of lead contractor: UCL

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## Executive Summary

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In the report deliverable (D2.7), principles and implementations of multi-stage DeNOx processes are explored. Our investigation encompasses various techniques utilized during combustion and post-combustion stages, such as narrow low NOx window, SCR, SNCR, and advanced oxidation, to synergistically enhance NOx removal. Through an extensive examination of multi-stage DeNOx processes, the report strives to offer valuable perspectives on the state-of-the-art strategies employed for NOx emissions control. By integrating these approaches, we can potentially develop improved DeNOx solutions contributing to a cleaner environment.



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Not applicable.



## Abbreviations

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GHGs Green House Gases

ER equivalent ratio

IPCC Intergovernmental Panel on Climate Change

IRENA International Renewable Energy Agency

SCR Selective catalytic reduction

SNCR Selective non-catalytic reduction



## 1 Introduction

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Human activities are causing a rise in Green House Gases (GHGs) emissions, including carbon dioxide, which is leading to climate change. The IPCC warns that if emissions continue at their current rate, the global temperature may rise by 1.5°C between 2030 and 2050 [1, 2]. Observable impacts of climate change are evident in various alterations to weather patterns. GHGs emissions exacerbate the severe weather conditions such as flooding, droughts, and heatwaves. Stronger hurricanes are happening more often and melting Arctic ice causes higher sea levels [3, 4]. Climate change affects various aspects of life, including health, jobs, food, money, water, and safety. Particularly vulnerable countries and communities are unexpected to withstand these impacts, potentially exacerbating poverty and economic disparities globally [5, 6].

To mitigate the GHGs emissions and reach well-below 2°C climate target, REmap team at IRENA has proposed a pathway which is based mainly on renewable energy and energy efficiency [7]. However, renewable energy resources can be inconsistent and far from where it is needed; for which energy storage technologies are required to transport energy in the temporal and spatial dimensions. Figure 1 shows the most established energy storage technologies e.g. batteries, pumped hydro, compressed air, supercapacitors, and flywheel storage, and they are all displayed. These technologies are well-established and widely used for storing energy. Other storage methods (chemical storage (e-fuel)), like synthetic methane, hydrogen, and ammonia are being tested for longer energy storage. Chemical storage (e-fuel) could store energy for a long time, and research is ongoing to make it more efficient and cost-effective [8, 9].

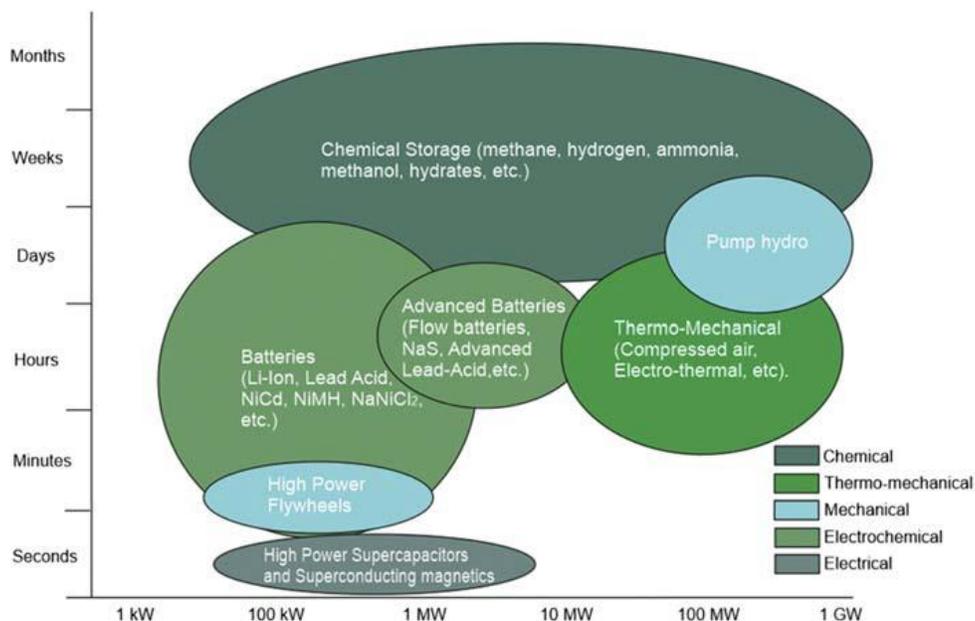


Figure 1 Comparison between different energy storage technologies in terms of power and storage time [8, 9].

One of the most promising carbon free e-fuel is ammonia, which can be a sustainable fuel for remote applications because of its high hydrogen content. It can be synthesized from fossil fuels or renewable sources as wind, biomass, solar, and marine energy. Ammonia is better than pure hydrogen because it is cheaper and more energy dense. It also has an existing infrastructure and contains more hydrogen per unit volume than liquid hydrogen itself. The International Energy Agency (IEA) recognizes ammonia as a prime energy vector for decarbonization.

Despite ammonia's potential as a carbon-free fuel, ammonia-based combustion systems face challenges related to its high igniting energy, low laminar velocity and higher nitrogen oxides (NO<sub>x</sub>) which lead to severe environmental [9-11]. To mitigate NO<sub>x</sub> emissions, further development and innovative solutions are required to achieve a comprehensive DeNO<sub>x</sub> solution. Interestingly, post-combustion DeNO<sub>x</sub>ing systems have been the subject of research, development, and utilization in both academia and industry [12-16]; these systems are mainly Selective non-catalytic reduction (SNCR) and Selective catalytic reduction (SCR) [17-37]. The technology readiness level of post-combustion DeNO<sub>x</sub>ing systems is at test launch and operations [38, 39]. The research question of the present work is focused on:

### ***How to reduce and prevent NOx emissions of the e-fuel NH<sub>3</sub> combustion?***

Single-stage DeNOx methods like SCR and SNCR work well for reducing NOx emissions. With stricter emission standards, there is a higher need for NOx reduction and flexible operation. The new standards require a reduction of NOx below 100 mg/Nm<sup>3</sup> for new power plants [8]. To overcome these challenges, multi-stage DeNOx processes incorporate several techniques in a specific order. Using different DeNOx technologies allows for better NOx reduction in different operating conditions.

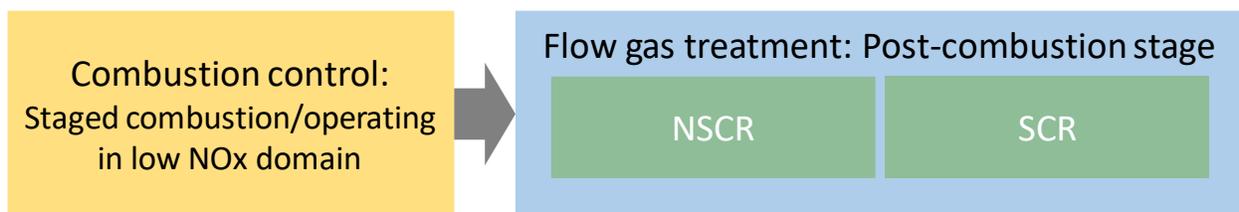


Figure 2 Flow diagram of the Multi-stages DeNOx process

In the deliverable report (D2.7), we delve into the principles and applications of multi-stages DeNOx processes. We investigate how techniques like during combustion and post-combustion stages e.g. narrow low NOx window, SCR, SNCR, and advanced oxidation work together to improve NOx removal. Through a comprehensive analysis of multi-stages DeNOx processes, this report aims to provide valuable insights into the cutting-edge strategies employed to control NOx emissions control. Integrating approaches can lead to better DeNOx solutions for a cleaner environment.

## 2 DeNOX during Combustion stage

### 2.1 Low NOx/NH3 window in ammonia combustion

Ammonia oxidation chemistry has been researched for many years to clarify NOx formation pathways. Comprehensive reviews of this oxidation chemistry can be found in the literature [40, 41]. The major ammonia oxidation emissions are nitric oxide NO, Nitrous oxide N<sub>2</sub>O and Nitrogen dioxide NO<sub>2</sub> and NH<sub>3</sub>. NOx formation during ammonia combustion is affected by several parameters, e.g. temperature, equivalent ratio (ER), and pressure. These parameters affect NOx species formation in different manners.

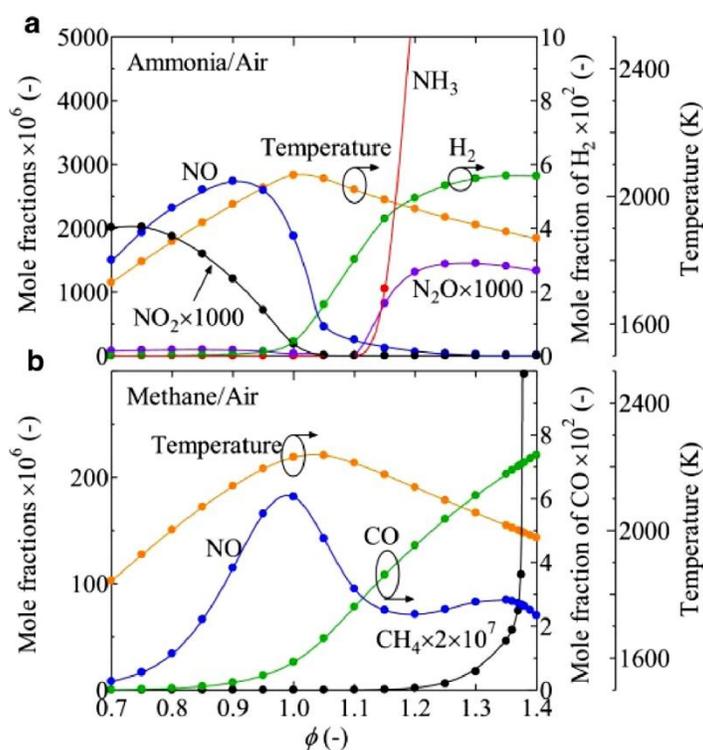


Figure 3 - Variation in emissions at 0.1 MPa and 40 mm downstream from the point of maximum heat release rate, for (a) NH<sub>3</sub>-air flame and (b) CH<sub>4</sub>-air flame, based on mixture equivalence ratio ( $\Phi$ ) [42]

Nitric oxide (NO) can be formed through several pathways [41-43] during ammonia combustion, where nitrogen and hydrogen in ammonia molecules react with oxygen. NO is mainly generated through the fuel pathway in ammonia flames. The concentration of NO increases in the reaction zone and gradually decreases away from this zone [44]. A study by Kobayashi et al. shows an increase of NO concentration



with increased ER to hit a peak at  $ER \sim 0.9$ , after that, the concentration of NO decreases drastically at  $ER > 1.0$  (Figure 3).

The NO emission concentration is likely higher in the  $NH_3$ /air combustion case than  $CH_4$ /air combustion case due to the  $NH_3$  content of nitrogen and fuel pathway generation of NO. Furthermore, nitric oxide (NO) itself is a precursor to other nitrogen oxides e.g. nitrogen dioxide ( $NO_2$ ) and dinitrogen pentoxide ( $N_2O_5$ ), which can further contribute to  $NO_x$  emissions.

Interestingly, in ER range from 0.75 to 1.80, the  $NO_2$  and  $N_2O$  concentrations are lower than the NO concentration (Figure 1).  $NO_2$  concentration decreases with the increased ER to reach an insignificant concentration at  $ER \sim 1.0$ . In contrast, the  $N_2O$  and  $NH_3$  concentrations start to increase significantly at  $ER \sim 1.0, 1.1$ . The total emissions concentration of NO,  $N_2O$ ,  $NO_2$  and  $NH_3$  exhibits U-shape behavior with minimal concentration in the ER range from 1.0 to 1.4 [42, 45-47]. At elevated pressure 0.5 MPa, Somarathn et al. found that at the equivalence ratio of 1.2, NO and unburnt  $NH_3$  emissions are minimal [48].

It is advised to operate burners at ER levels domain where the minimal  $NO_x/NH_3$  is achieved. However, this narrow window could be changed depending on the operating conditions such as pressure, temperature, mixing rate and operating conditions of each gas turbine. In the following, in WP2's tasks, namely T2.1, T2.2 and T2.4, the experimental works were carried out at Cardiff University.

### 2.1.1 Experimental Setup and procedure:

A tangential swirl burner of industrial-scale was utilized at a consistent thermal power of 8 kW, an equivalence ratio of  $\Phi = 1.2$ . The fuel and air flows were regulated using a set of Bronkhorst mass flow controllers (MFCs) with a precision of  $\pm 0.5\%$ .

Figure 4 and Figure 5 illustrate the schematic of the tangential burner. Ammonia/cracked ammonia were thoroughly mixed with the air flow, while hydrogen was introduced below the burner exit using 6 evenly spaced injection holes. The mixing was improved by using injection holes that were angled at  $45^\circ$ . For optical diagnostics, the researchers used a quartz tube made from GE214 material [49]. All the experiments were conducted at ambient inlet pressure and temperature. Chemiluminescence traces of different species of interest were obtained using a pair of LaVision CCD cameras equipped with UV and

visible ranges. The units were initiated concurrently, resulting in a 90% increase and a gate-time of 700,000 ns. Each species was subjected to distinct Edmund filters, namely OH\* (325 nm), CH\* (420 nm), NH\* (337 nm), NH<sub>2</sub>\* (632 nm). Data collection involved the utilization of the LaVision Davis v10 system, capturing 200 frames per experimental data point. A specially designed MATLAB script was then utilized to conduct Abel Inversion after averaging.

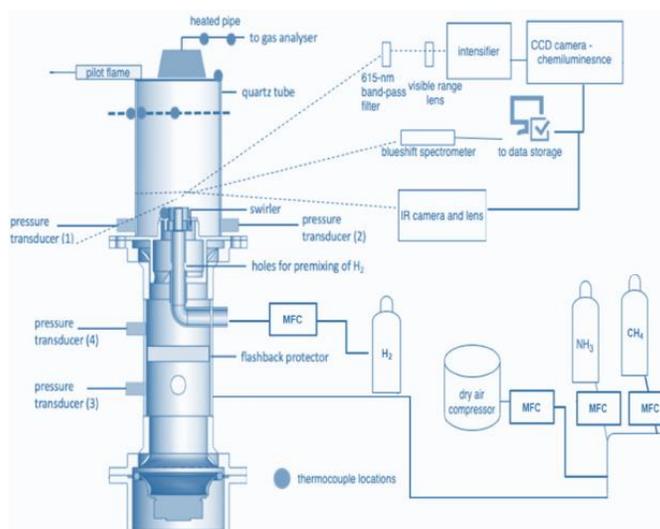


Figure 4 illustrates a tangential combustor featuring measuring techniques and control systems [50].

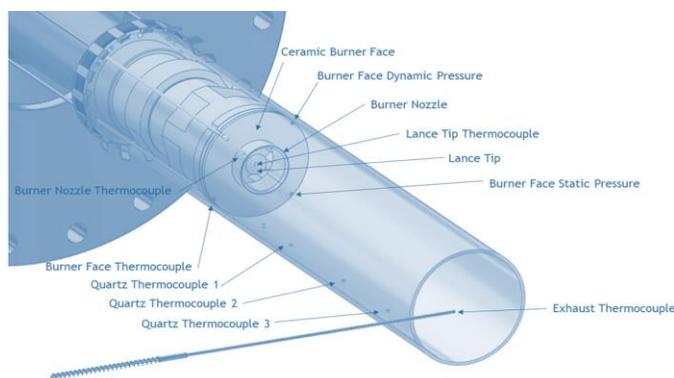


Figure 5 Tangential combustor with measuring techniques and control systems.

The measurement of exhaust emissions was conducted using the Emerson CT5100 Continuous Quantum Cascade Laser analyzer at a frequency of 1 Hz, exhibiting a repeatability of  $\pm 1\%$  and a linearity of 0.999.

The temperature of the samples was maintained at 433K to prevent condensation. More details on the experimental setup can be found in the previous work by Mashruk et al. [50].

### 2.1.2 Results and discussions

Figure 6 and Figure 7 show the sampled NO and NO<sub>2</sub> emissions with 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends and changing equivalence ratios from 0.6 to 1.4, respectively.

Both NO and NO<sub>2</sub> peak at  $\Phi = 0.8 \pm 0.1$ , which coincided with maximum OH\* production. This observation is in line with the findings from previous studies [51-53]. The reaction of OH with NH yields HNO via the reaction  $\text{OH} + \text{NH} \leftrightarrow \text{HNO} + \text{H}$ , and later interacts with OH, O, and H radicals to produce NO. NO<sub>2</sub> is directly related to NO through the reactions  $\text{NO} + \text{HO}_2 \leftrightarrow \text{NO}_2 + \text{OH}$  and  $\text{NO} + \text{O} + \text{M} \leftrightarrow \text{NO}_2 + \text{M}$  and revert to NO by reacting with H radical [54].

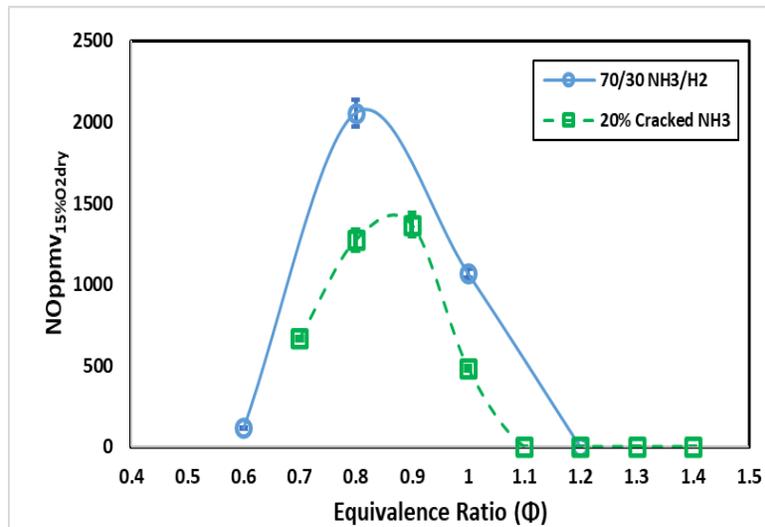


Figure 6 Sampled NO emissions with 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends and  $\Phi$ .

NO emissions increase to reach a peak at  $\Phi=0.8$  in the 70/30 NH<sub>3</sub>/H<sub>2</sub> mixture case. Meanwhile, the peak is reached at  $\Phi=0.9$  with 20% cracked NH<sub>3</sub>. At  $\Phi=1.15 \pm 0.05$ , NO emissions decrease to as low as zero.

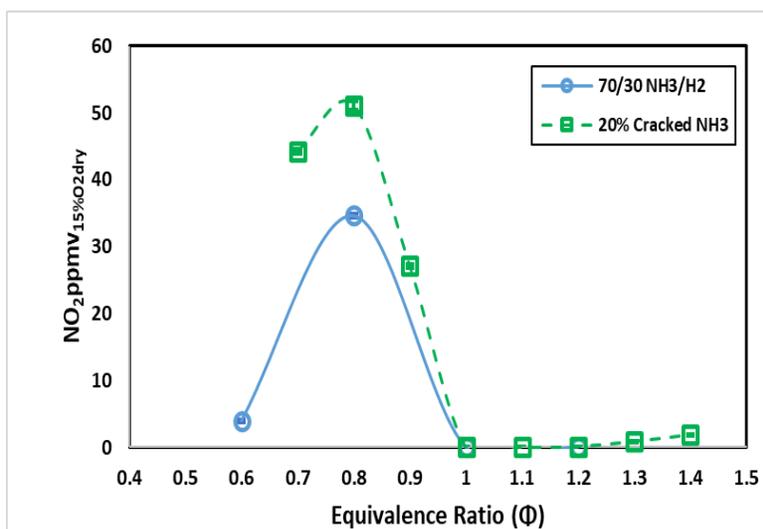


Figure 7 Sampled NO<sub>2</sub> emissions with 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends and  $\Phi$ .

Interestingly, at the same range of  $\Phi=1.15\pm 0.05$ , NO<sub>2</sub> emissions are minimal (Figure 7).

Sampled N<sub>2</sub>O and NH<sub>3</sub> emissions for 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends with changing  $\Phi$  from 0.6 to 1.4 are shown in Figure 8 and Figure 9, respectively. N<sub>2</sub>O is a greenhouse gas with global warming potential (GWP) 280 times of CO<sub>2</sub> [50]. The reaction between NH and NO in the flame results in the production of N<sub>2</sub>O. However, the majority of N<sub>2</sub>O is subsequently reduced to N<sub>2</sub> through the reactions  $N_2O + H \leftrightarrow N_2 + OH$  and  $N_2O + M \leftrightarrow N_2 + O + M$ . The recent studies have confirmed that the blends investigated in this study show a low production of H radicals and a low flame temperature at  $\Phi = 0.6$ , thus underscoring the issue of N<sub>2</sub>O emissions [54-58].

Unburnt ammonia emissions are drastically higher in highly rich conditions but can be mitigated by operating the system in the correct equivalence ratio domain and implementing two-stage rich-quench-lean (RQL) burner systems [59-61].

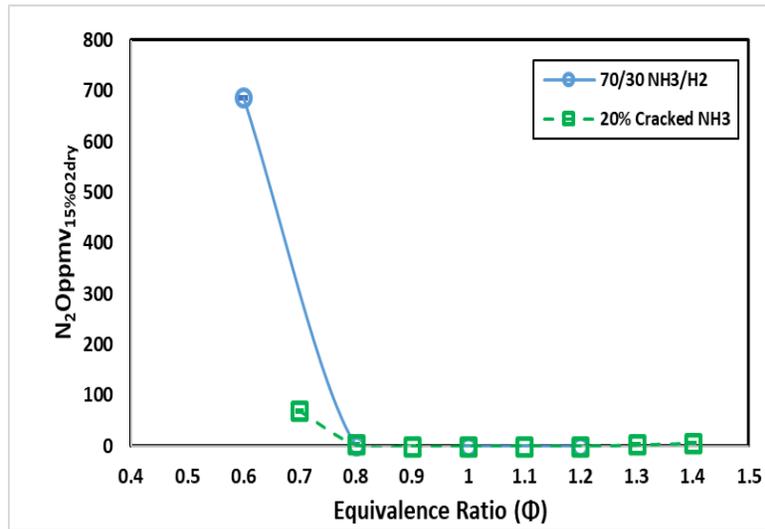


Figure 8 Sampled NO<sub>2</sub> emissions with 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends and Φ.

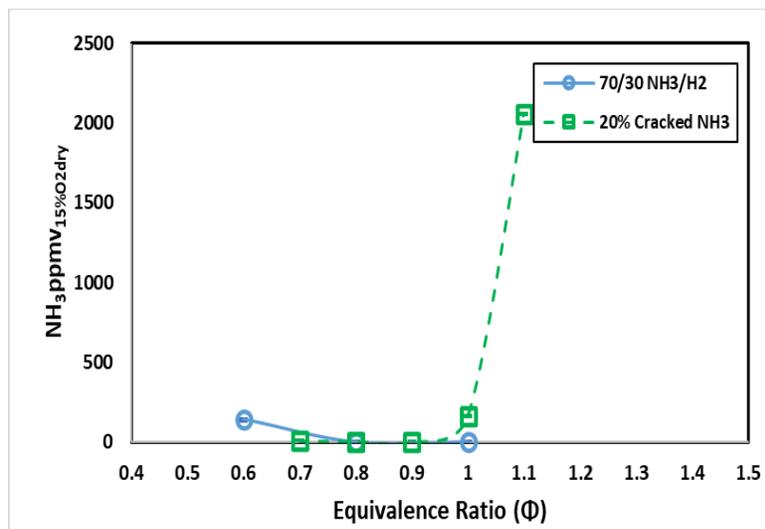


Figure 9 Sampled NH<sub>3</sub> emissions with 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends and Φ.

Overlapping the emission profiles of NO, NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> shows a narrow window of low NO<sub>x</sub> emissions at Φ = 1.0 ± 0.1 (Figure 10).

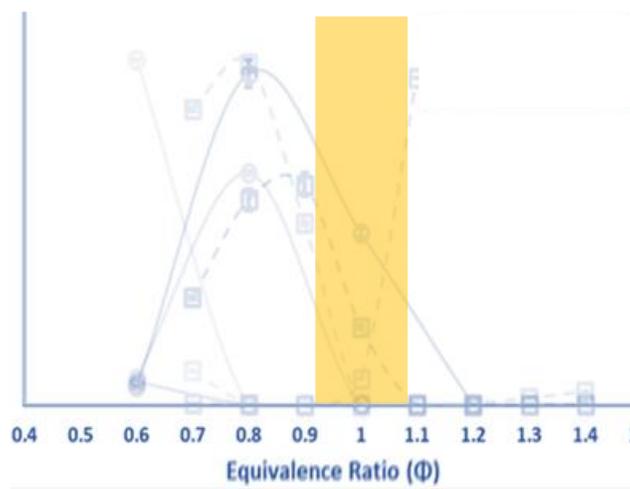


Figure 10 Overlapped emissions (NO,NO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub>) profiles with 70/30 NH<sub>3</sub>/H<sub>2</sub> and 20% cracked NH<sub>3</sub> blends and  $\Phi$ .

This narrow window is an ideal spot at which NO<sub>x</sub> and unburned ammonia are at their minimum. However, the remaining NO<sub>x</sub> emissions would require Selective non-catalytic reduction (SNCR) and Selective catalytic reduction (SCR) stages.

### 2.1.1 Two-stage rich-lean combustion

Two-stage rich-lean combustion effectively controls NO<sub>x</sub> emissions in combustors that use NH<sub>3</sub>-air mixtures, as shown in studies [42, 62, 63]. Ammonia oxidation is employed under fuel-rich conditions to effectively decrease NO<sub>x</sub> production in this method. In the second stage, the technique employs air to eliminate any residual unburned NH<sub>3</sub> and H<sub>2</sub> in the secondary zone, thereby averting the generation of NO<sub>x</sub>. Okafor et al. [63] found that NO<sub>x</sub> emissions from two-stage combustors fueled with NH<sub>3</sub>-air mixtures decreased until a minimum value was reached at an equivalence ratio  $\Phi = 1.10$ . By using premixed NH<sub>3</sub>-air combustion at optimal conditions, they achieved 42 ppmv NO<sub>x</sub> emissions with 99.5% combustion efficiency. The achieved NO<sub>x</sub> level, namely 42 ppmv meets the regulatory limit imposed by the Japanese government for NO<sub>x</sub> emission from gas turbine which is 70 ppm.

Kurata and co-workers [64] have achieved significantly lower NO<sub>x</sub> emission and wider turbine operating power range by partially closure of the swirler area, avoiding any sort of air dilution in the primary combustion zone that might lead to high NO production and enhancing fuel-air mixing through inclined fuel injection. The modifications made to the combustor extended the lower operating power limit of the



micro gas turbine, and an increase in the fuel injection angle significantly achieved NO<sub>x</sub> emission of 337 ppm (16% O<sub>2</sub>) from the micro gas turbine. With a 95% NO<sub>x</sub> reduction efficiency, ordinary SCR systems aim for an emission level of approximately 200 ppm from ammonia gas turbine combustors.

In the following sections, a review of Selective non-catalytic reduction (SNCR) and Selective catalytic reduction (SCR) is presented to give a comprehensive solution for eliminating the NO<sub>x</sub> emissions.

## 2.2 Flow gas treatment: Post-combustion stage

The flow gas treatment for reducing NO<sub>x</sub> emissions has reached a significant level of maturity, and it is being implemented at the industrial scales. Both of Selective non-catalytic reduction (SNCR) and Selective catalytic reduction (SCR) are being used in conventional industrial power plants. These technologies can be integrated to minimize the NO<sub>x</sub> emission in ammonia/hydrogen combustion-based power plants. In the following sub-chapters, a brief review on the SCR and SNCR is presented.

### 2.2.1 Selective Non-Catalytic Reduction (SNCR) stage

In 1975, the introduction of NH<sub>3</sub> injection for SNCR was pioneered by Exxon Research and Engineering [65]. The process has undergone investigation in laboratory, pilot-scale, and full-scale commercial facilities. The literature provides a summary of the general performance of NH<sub>3</sub>. Selective non-catalytic reduction (SNCR) is used to diminish NO<sub>x</sub> (nitrogen oxides) to N<sub>2</sub> (nitrogen) in the presence of oxygen. This reaction is facilitated by amine-based agents, namely ammonia (NH<sub>3</sub>) or urea (CO(NH<sub>2</sub>)<sub>2</sub>), and occurs within a temperature range of 800–1100 °C. The higher end of this temperature spectrum is essential for urea-based reactions. The process doesn't require a catalyst due to its high temperature operation. The reagent reacts best with NO<sub>x</sub> within a certain temperature range and when there is a lot of oxygen in the gas. Consequently, it is classified as a selective chemical process.

SNCR systems exhibit the capability to decrease NO<sub>x</sub> emissions by approximately 30–70% [64]. However, the degree of reduction varies significantly across different applications. The optimal NO<sub>x</sub> removal occurs around 870 °C when using ammonia, or approximately 1000 °C when urea is employed [65]. When the temperature surpasses 1000 °C, the NO<sub>x</sub> removal rate diminishes due to the thermal decomposition of ammonia or urea. At lower temperatures, NO<sub>x</sub> and ammonia/urea reactions are slowed, which could cause more ammonia to mix with other combustion byproducts and create ammonium salt.



Ammonia or urea reagents can be directly introduced into the combustion chamber. Urea-based SNCR is safer and easier to handle than ammonia-based systems because urea is less toxic and less volatile. Droplets of urea solution penetrate better and mix with flue gas. This characteristic is particularly valuable for larger units. It is important to note that urea is costlier than ammonia and the reduction process involving urea generates more  $N_2O$  (nitrous oxide) compared to ammonia-based systems [66].

Ammonia combustion, also known as ammonia DeNO<sub>x</sub>, is a widely adopted technique for mitigating NO<sub>x</sub> emissions, which are a significant environmental concern due to their harmful effects on air quality and public health. Ammonia combustion offers an efficient and reliable solution to meet stringent emission standards with no costly catalysts.

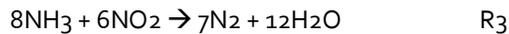
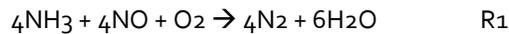
In the multi-level De-NO<sub>x</sub> approaches, staged burning comes as a first step for De-NO<sub>x</sub>ing that can reduce ~35% of NO<sub>x</sub> emissions to reach as low as 170 ppm level. And followed by Selective Non-Catalytic Reduction (SNCR) stage which is less expensive compared to Selective Catalytic Reduction (SCR). SNCR can reduce ~54% of the NO<sub>x</sub> and reach a level of NO<sub>x</sub> of ~80 ppm. Finally, SCR minimizes the remaining NO<sub>x</sub> below regulatory restrictions of 45 ppm and it can minimize NO<sub>x</sub> to less than 20 ppm level. This promising solution of multi-level approaches for De-NO<sub>x</sub> was successfully implemented [67].

### **Industrial scales:**

The SNCR has already been scaled up and used for industrial power plants, e.g. ANDRITZ has enhanced the SNCR system, drawing from numerous references, to ensure its cost-effectiveness and applicability to different fuel types, as well as industrial and power generation sectors. Because of the significant impact of process parameters (including temperature, residence time, reagent injection rate, and mixing of reagent and flue gas), NO<sub>x</sub> removal is contingent upon the particular installation, making each SNCR solution unique. The essential elements of the ANDRITZ SNCR system can be succinctly described as follows: streamlined design, low capital expenditure, efficiencies of up to 60%, quick installation process, and zero generation of solid or liquid waste [68].

### 2.2.2 SCR catalysts

Selective catalytic reduction (SCR) is an effective way to reduce NO<sub>x</sub> emission. The process of deNO<sub>x</sub> SCR is based on the following reactions [69, 70]:



At temperatures [250–450] °C, R<sub>1</sub> proceeds quickly on the catalyst in excess oxygen and accounts for the overall stoichiometry of the process (NH<sub>3</sub> /NO = 1/1), since 90% of NO<sub>x</sub> is typically NO. Several factors such as temperature, residence time, space velocity and uniformity of the NH<sub>3</sub> concentration and flue gas velocity affect the efficiency of SCR deNO<sub>x</sub>.

Consequently, to enhance deNO<sub>x</sub> efficiency and attain low NH<sub>3</sub> slip, optimal design of the flow field and non-uniformed NH<sub>3</sub> injection strategy should be obtained for the SCR deNO<sub>x</sub> facilities [69, 70]. The vast majority of SCR deNO<sub>x</sub> facilities are π type which is studied and the flow field is optimized for this type. Typically, a SCR-deNO<sub>x</sub> facility with a tower design has fewer bends and a significantly larger expansion duct, resulting in a larger cross-sectional area and decreased turbulence. In the current scenario, owing to the surging number of tower type SCR deNO<sub>x</sub> facilities, it is indispensable to execute flow regulation and ensure optimal design. The compact configuration often leads to spatial limitations. As a result, the search for an effective means to optimize SCR deNO<sub>x</sub> facilities with tower configuration is more challenging.

CFD simulation has become a widespread method for regulating flow fields in SCR-deNO<sub>x</sub> facilities in recent times. This document outlines the optimal design of a tower-type SCR-deNO<sub>x</sub> facility for a 1000 MW power plant. To manage space and flow field, we use crossed and arc-shaped baffles. The evaluation of flow regulation at the AIG (ammonia injection grid) is being undertaken. After leaving the economizer, the flue gas passes through the AIG (ammonia injection grid) and gets mixed with NH<sub>3</sub>.

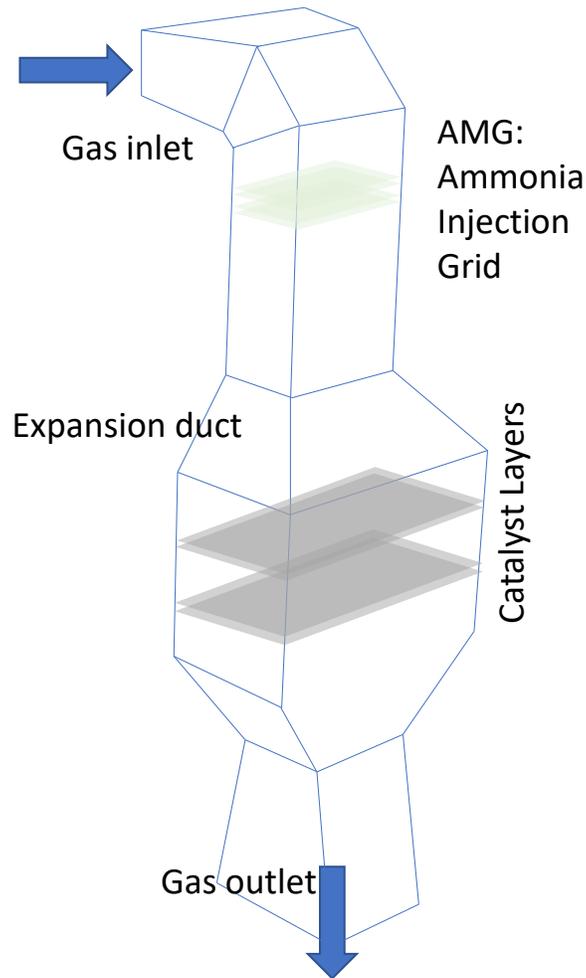


Figure 11 The schematic geometry of a tower type SCR-deNO<sub>x</sub> facility for a 1000 MW power plant. AMG: Ammonia Injection Grid.

Optimal design is necessary for this tower type SCR-deNO<sub>x</sub> facility because of spatial constraints. The first turning cannot have baffles since it is close to the economizer. During the design stage of the SCR-deNO<sub>x</sub> facility, various regulatory measures must be implemented. Using small arc-shaped baffles is better for regulating flow and lowering pressure loss.

Additionally, efforts are being made to control the flow field at the AMG as a remedy for spatial limitations. The difficulty in regulating downstream flow would be reduced by placing baffles upstream, especially in the expansion duct, which helps in getting uniformed NH<sub>3</sub> concentration distribution. However, insufficient turbulence and a large sectional area required a non-uniform NH<sub>3</sub> injection strategy to

improve mixing. Here, the AIG had 21 separate  $\text{NH}_3$  injection areas, each with a velocity proportional to the gas velocity distribution before the AIG. The regulated flow field at the AIG made it easier to determine injection velocities. The optimization process was conducted using CFD simulation and FMT validation as suggested in by Zeng et al. [70]. The first step involved conducting a CFD simulation of the tower type SCR-de $\text{NO}_x$  facility without baffles geometry to indicate the flow field. The geometry of the baffles was designed based on the initial simulation. The relative standard deviation (RSD) for gas velocity,  $\text{NH}_3$  concentration and pressure loss were determined. The baffles were modified until the RSDs and total pressure loss were minimized.

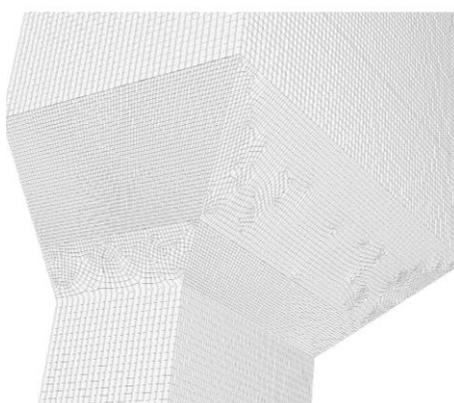


Figure 12 Meshing geometry of the SCR/SNCR-de $\text{NO}_x$  facility.

$\text{NH}_3$  concentration is suggested to be diluted to 5% and injected at 20 m/s and 1:1  $\text{NH}_3$ : $\text{NO}_x$  ratio. The outlet pressure is set at atmospheric pressure and the total pressure drop of the catalyst layers is set to 400 Pa.

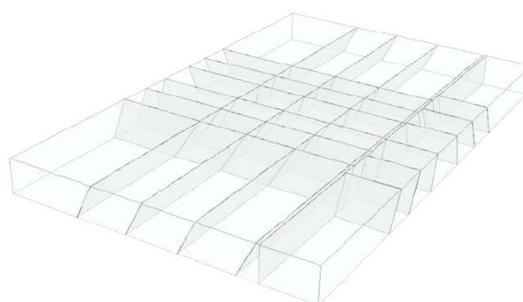


Figure 13 The crossed baffles installation at the upstream side of the ammonia injection grid (AIG) of SNCR-de $\text{NO}_x$  facility.



To optimize, the baffles' shape and ammonia injection, different methodologies are adjusted using computational fluid dynamics analysis. Gas velocity and ammonia concentration meet design requirements with standard deviations of 11.90% and 3.37% respectively.

The design's effectiveness is confirmed through a flow model test. During this test, air and CO<sub>2</sub> are used as substitutes for flue gas and ammonia. The resulting relative standard deviations are determined to be 11.24% and 4.98%, respectively. The flow is more uniform with the optimal design according to simulation and test.

For tower-type SCR-deNO<sub>x</sub> facilities, it is recommended to install smaller-sized baffles at the facility's upstream side. This approach has advantages like better flow uniformity, controlled pressure loss, and less steel plate used. Regulating the flow field at the ammonia injection grid is showed to be an effective strategy for addressing spatial limitations. The optimal design insights could help future research on flow field regulation in space-limited tower-type SCR-deNO<sub>x</sub> facilities.

Choosing the right catalyst is important for the SCR system to work well. The catalyst itself can take the form of a single component, a multi-component system, or an active phase combined with a supporting structure. This structure provides stability and can increase the surface area. The majority of SCR catalysts are constructed using active metals or ceramics, which possess a high degree of porosity. Within the pores of the catalyst, the reduction reaction occurs at specific sites known as activated sites. After the reduction reaction, these sites can be reactivated by rehydration or oxidation. Over time, the catalyst's activity diminishes, necessitating its replacement [71].

NH<sub>3</sub>-SCR catalysts vary in type and depend on factors like temperature, NO<sub>x</sub> removal, and regeneration. The catalysts consist of materials such as noble metals, metal oxides, activated carbon, and zeolites. The materials can be made into a honeycomb shape by extrusion or coated on a support made of metal or ceramic.

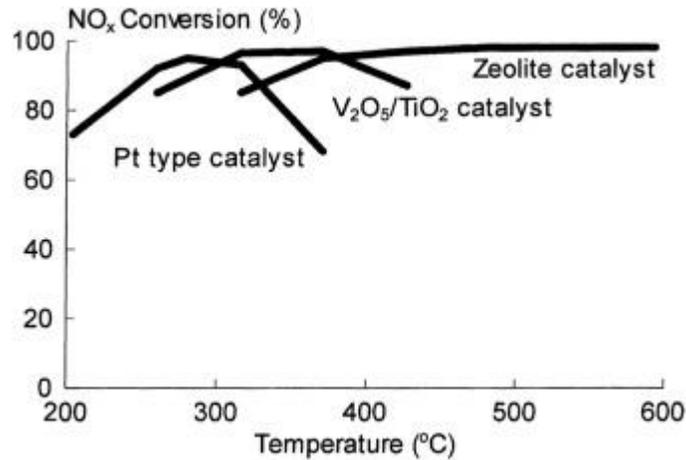


Figure 14 Three major families of SCR catalyst [72]

The catalyst V<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub>, with the addition of WO<sub>3</sub> or MoO<sub>3</sub>, is the most widely used industrial catalyst for reducing NO<sub>x</sub>. TiO<sub>2</sub> is the optimal support for SCR catalysts because it has strong SCR activity and can withstand SO<sub>2</sub>-induced deactivation, which prolongs the catalyst's operational lifespan. Titania in anatase form has a bigger surface area (50-120 m<sup>2</sup>/g) than the rutile phase (<10 m<sup>2</sup>/g) in SCR catalysts. A common commercial vanadia catalyst formulation comprises 1–5 wt% V<sub>2</sub>O<sub>5</sub> and 10 wt% WO<sub>3</sub> (or alternatively 6 wt% MoO<sub>3</sub>), supported on high-surface-area TiO<sub>2</sub> (anatase). WO<sub>3</sub> and MoO<sub>3</sub> are incorporated to prevent anatase-to-rutile transformation and inhibit SO<sub>3</sub> adsorption, thereby safeguarding against support sulfation [72].

Titanium/vanadium catalysts work best at 260-425°C, while zeolites work better at a higher temperature range of 345-590°C. To save money on reheating flue gas, the SCR reactors should be placed before the desulfurization and particulate control units.

This positioning has challenges, like catalyst deactivation and installation complexities. To reduce issues, place the SCR unit at the end of the flue gas control units, but this requires low-temperature SCR catalysts or an extra heat source for classic vanadium catalysts. We can heat more with flue gas reheating or economizer bypass, but it will cost more to operate the SCR.

Pt-based catalysts had limitations like N<sub>2</sub>O production and a narrow temperature range for low-temperature operation. Scientists used materials like activated carbon and transition metal oxides to study low-temperature catalysts. Among these, Mn-based catalysts demonstrate superior low-

temperature SCR activity. The addition of Ce and Mn, and the use of V<sub>2</sub>O<sub>5</sub> on a TiO<sub>2</sub>-SiO<sub>2</sub>-MoO<sub>3</sub> support were attempted to enhance the SO<sub>2</sub> resistance and activity of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts in high SO<sub>2</sub> conditions.

### 2.3 Industrial multi-stage DeNO<sub>x</sub> system for ammonia combustion based processes

In the current document, multi-stages DeNO<sub>x</sub>ing process has been proposed that starts with mitigating NO<sub>x</sub> emission at the combustion stage by operating the combustor at optimized equivalent ratio, applying rich-quench-lean (RQL) strategy, and followed by Selective non-catalytic reduction (SNCR) and Selective catalytic reduction (SCR) stages.

Even though limited budget and time prevented applying proposed multi-stages DeNO<sub>x</sub>ing process, a similar process was recently applied but in ammonia combustion for industrial fabrication of ceramic at Foshan Xianhu laboratory. Cheng applied multi-steps to mitigate and control NO<sub>x</sub> emissions.

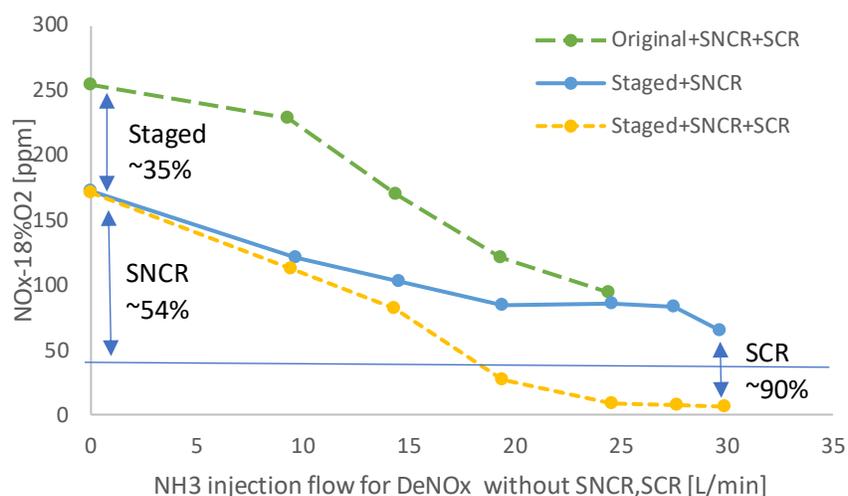


Figure 15 Industrial multi-stage DeNO<sub>x</sub> system for ammonia combustion based processes

It has been found that, in case of non-staged combustion with SNCR and SCR, the NO<sub>x</sub> emissions drop from 250 to 60 ppm with increases NH<sub>3</sub> injection from 0 to 25 L/min. Combining staged combustion with SNCR reduces ~35% of the NO<sub>x</sub> emissions with low NH<sub>3</sub> injection. Implementing three steps namely staged combustion, SNCR and SCR with high NH<sub>3</sub> injection up to 30 L/min leads to ~90% reduction of NO<sub>x</sub> compared with the non-staged combustion without SNCR and SCR. These interesting findings could be implemented in a similar manner for CCGT power plants.

### 3 Conclusions

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Strict emission regulations require advanced DeNO<sub>x</sub> techniques to reduce NO<sub>x</sub> emissions in industrial processes. As emission standards become stricter, the demand for robust NO<sub>x</sub> reduction strategies and operational flexibility intensifies. Established technologies like SCR and SNCR have been effective, but stricter emission limits require more comprehensive NO<sub>x</sub> reduction methods.

This deliverable report (D2.7) proposes integrated NO<sub>x</sub> emission control during the combustion stage and post-combustion. The combustion control stage improves NO<sub>x</sub> reduction by integrating different DeNO<sub>x</sub> technologies effectively, such as multi-stage and/or operating in a favorable low NO<sub>x</sub> domain. The report aims to provide valuable insights into cutting-edge strategies, emphasizing the synergy of different methods for creating cleaner and more sustainable DeNO<sub>x</sub> solutions.

The findings from the study highlight a pivotal operating domain at an equivalence ratio ( $\Phi$ ) of  $1.0 \pm 0.1$ , where NO<sub>x</sub> and unburned ammonia concentrations are minimized. Achieving the ideal window involves considering factors like pressure, temperature, and mixing rate. Techniques like chemiluminescence traces and quantum cascade laser analysis give a deeper understanding of forming and controlling of NO<sub>x</sub> emissions.

The report highlights the significance of two important stages in multi-stage DeNO<sub>x</sub> processes: Combustion and Selective Catalytic Reduction (SCR). Adjusting ER, temperature, and pressure during combustion is key to reducing NO<sub>x</sub> emissions. Two-stage rich-lean combustion techniques, leveraging fuel-rich conditions and precise air introduction, are pivotal.

SNCR is crucial for reducing NO<sub>x</sub> in multi-stage DeNO<sub>x</sub> processes with high-temperature reactions involving ammonia or urea. While effective, challenges such as high-temperature operation, ammonia slip, and N<sub>2</sub>O formation must be addressed. The multi-stage approach provides the versatility required to optimize NO<sub>x</sub> reduction under varying conditions.

Multi-stage DeNO<sub>x</sub> processes show promise for industries facing NO<sub>x</sub> emissions. By strategically combining techniques, these processes can significantly decrease NO<sub>x</sub> emissions and overcome



challenges of space, catalyst usage, and cost. The multi-stage DeNOx approach has the potential to make the industry eco-friendlier by reducing NOx emissions and improving air quality.

#### **Retrofitting power plants: recommended steps for DeNOxing.**

1. To reduce the NOx emissions of the conventional power plants that are repurposed to use NH<sub>3</sub>/H<sub>2</sub> as a fuel instead of natural gas, controlling the combustion is the first step to be followed. For instance, operating the gas turbine at a preferable operating condition where the NOx emissions are minimal is recommended (2.1.2). Operating at optimal equivalent ratios lead to NOx mitigation at lower cost with minimal capital and operating expenditures.
2. In the case that NOx emissions control via combustion control is not sufficient, the SNCR can be implemented if it has lower capital and operating expenditure compared to the SCR.
3. In the second flow gas treatment (post-combustion DeNOxing stage), SCR can be implemented to remove the remaining NOx emissions in the flow gases.
4. Two-stage combustion can be implemented in case the gas turbine of the conventional power plant is already designed to operate with two-stage rich-lean combustion technique. However, gas turbine of single stage combustion requires deep modification to adapt the two-stage rich-lean combustion. For which, further techno-economic assessment will be required to study the feasibility of retrofitting gas turbine.
5. The combination of SNCR, SCR and operating conditions of minimal NOx emissions are recommended for retrofitting CCGT to run on NH<sub>3</sub>/H<sub>2</sub>.

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