

## ASSESSMENT AND IDENTIFICATION OF SOME NOVEL NO<sub>x</sub> REDUCING REAGENTS FOR SNCR PROCESS

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Nitrogen oxides (NO<sub>x</sub>) are one of the most hazardous air pollutants arising from the combustion processes. Because of the implementation of strict emission limits many NO<sub>x</sub> removal technologies have been developed. In the present work post combustion NO<sub>x</sub> removal technique that is Selective Non-Catalytic Reduction (SNCR) has been investigated in a pilot scale 150 kW combustion rig facility. Investigation has been performed using some novel NO<sub>x</sub> reducing reagents like urea, ammonium carbonate and mixture of their 50%-50% aqueous solution within the temperature range of 700 to 1200 °C, at 1.1% excess oxygen and background NO<sub>x</sub> level of 500 ppm. The effects of these reagents were determined in term of their temperature characteristics and molar ratio. Among the reducing reagents used urea solution gave the highest NO<sub>x</sub> removal efficiency (81%) and was attractive due to its superior high temperature (1000 to 1150 °C) performance, ammonium carbonate was more effective at lower temperature range (850 to 950 °C) though its efficiency (32%) was lower than urea, while 50-50% solution of urea and ammonium carbonate gave higher efficiency than ammonium carbonate but slightly lesser than urea within a wide temperature range (875 to 1125 °C). It was also observed that the NO<sub>x</sub> removal efficiency was increased with increasing the molar ratio.

**Keywords:** Nitrogen oxides (NO<sub>x</sub>), SNCR, Urea, Ammonium carbonate, Molar ratio

### 1. Introduction

The rapid industrialization brought severe air pollution problems caused by combustion processes in industries and transportation sector. Nitrogen oxides (NO<sub>x</sub>) are one of the most hazardous pollutants arising from these processes. Generally the term NO<sub>x</sub> is used to mean the total concentration of NO plus NO<sub>2</sub> and it exclude other oxides of nitrogen. Nitrogen oxides are formed during high temperature combustion processes from the oxidation of nitrogen in the air or fuel and are released into the atmosphere mainly in the form of NO, which is then readily oxidized to NO<sub>2</sub> by reaction with ozone. Elevated levels of NO<sub>x</sub> occur in urban environments under stable meteorological conditions, when the air mass is unable to disperse. Emissions of NO<sub>x</sub> play an important role in many environmental issues, including acidification, eutrophication, ozone formation and hence the greenhouse effect. Because of these air pollution problems, air quality has become worse and worse so that the air pollution control regulations became stringent accordingly. Therefore, new technologies should

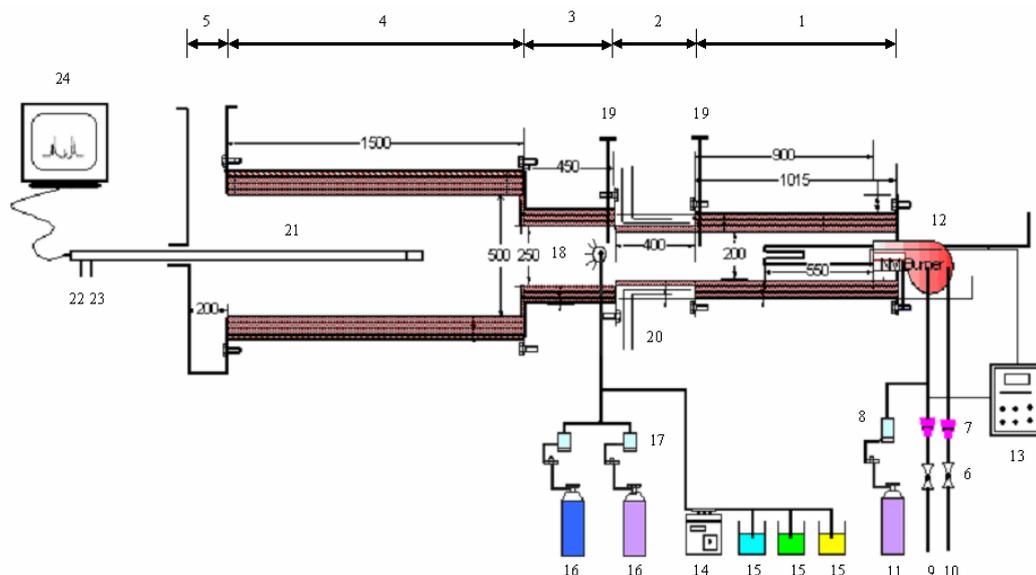
be developed to reduce the pollutants within the regulation limit from combustion processes. Numerous studies have been reported for cost-effective NO<sub>x</sub> reduction from stationary combustion sources. These technologies include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). The SNCR process is a useful method for NO<sub>x</sub> reduction by injecting amines (-NH-) or cyanides (-CN-) containing selective reducing agents such as NH<sub>3</sub>, urea and cyanuric acid into the flue gases [1,2]. The SNCR process could reduce nitric oxides to nitrogen and water rapidly and effectively at rather higher (1073–1373 K) temperatures as compared to SCR [3]. It has been reported that injection of some additives together with the reducing agents in SNCR processes can lower and widen the optimum reaction temperature window for NO<sub>x</sub> reduction [4, 5].

### 2. Experimental Setup and Procedure

#### 2.1. Experimental Setup

The experimental work was performed on the

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- |                       |                          |                       |                                       |
|-----------------------|--------------------------|-----------------------|---------------------------------------|
| 1. Combustion Section | 2. Temp. Control Section | 3. Injection Section  | 4. Reaction Section                   |
| 5. Flue Gas Exhaust   | 6. Control Valve         | 7. Rota Meters        | 8. Mass Flow Controller               |
| 9. Methane Gas        | 10. Air                  | 11. Ammonia (For B.G) | 12. Burner                            |
| 13. Control Panel     | 14. Peristaltic Pump     | 15. Liquid Reagents   | 16. Carrier Gas (Air/N <sub>2</sub> ) |
| 17. Pressure Gauge    | 18. Injector             | 19. Thermocouples     | 20. Cooling Coils                     |
| 21. Sampling Probe    | 22. Water Inlet          | 23. Water Outlet      | 24. Flue Gas Analyzer                 |

Figure 1. Schematic representation of experimental setup.

“Combustion Rig” which we have developed in PIEAS and is a simulation of the modern fossil fuel fired power plant. The furnace was made of stainless steel and contains five sections as combustion section, temperature control section, injection and mixing section, reaction section and exhaust section (Figure 1). The other necessary equipments and the supply systems which were required to complete the setup include natural gas supply system, air supply system, ammonia supply system, thermocouples and suction pyrometer and flue gas analyzer. The detail of each section is given below:

### 2.1.1. Combustion section

Combustion section is the section where we are producing the flue gases according to our requirement. Combustion section is made of mild steel with the insulation of fire bricks, gas kits used to join combustion section with the other sections is made of asbestos.

### 2.1.2 Temperature control section

Next to the combustion section is temperature control section. The main purpose of this section is to control the temperature of the flue gases being

generated in result of combustion. For SNCR process the main limitation is that we have to inject the chemical for the reduction of the NO<sub>x</sub> at specific temperature, the temperature is controlled by extracting the heat duty from the flue gases. This heat duty is extracted with the help of cooling coil provide inside the temperature control section. The material of construction for this section is again Mild Steel, and that for the cooling coils is copper with the covering of Kao wool. Cooling coil is moveable from the side wall of the section to the center of the section. The thickness of insulation in this section is 275mm. The flow area of this section is 250mm x 250mm (Figure 1).

### 2.1.3. Injection and mixing section

The purpose of this section is to inject chemical that will reduce the NO<sub>x</sub>. For this purpose an entrance is given for the injector from the side of the section. Injector is properly designed so that it can bear the intense environmental condition inside the furnace. Since the temperature inside the furnace can go high to 1300-1400 °C. At such a high temperature the metals alloys like stainless steel can deform and can bent so to avoid such circumstances we have provided a water jacket to

the injector. The flow area of the flue gases in this section is 250mm x 250mm (Figure 1).

#### 2.1.4. Reaction section

The purpose of this section is to provide the space and the residence time to flue gases and the chemical being inserted in the flue gases to reduce the NO<sub>x</sub>. For this reason this reaction section is provided. In the reaction section there are provided holes for the injection of the thermocouple so that we can find the temperature inside the reaction section. Also from these holes we can insert the suction pyrometer to check the exact flue gas temperature. This all is done for the purpose of temperature profiling. We can check the temperature in the reaction section and these are used for the verification of the fluent NO<sub>x</sub> module. Due to the reason of the high temperature thick insulation is also provided here. The thickness of the insulation in this section is 300mm and the flow area in this section is increased to 500mm x 500mm (Figure 1).

#### 2.1.5 Exhaust section

The purpose of the exhaust section is to provide the space to flue gases to exit from the furnace. There is also thick insulation provided to maintain the surface temperature to the bearable limits. The flow area here is also 500mm x 500mm which is then reduced in the chimney. There is provided a sight glass to see the flame inside the furnace and a hole for the insertion of suction pyrometer. With the help of suction pyrometer we can check the temperature of the flue gases at the center line of the flue gas flow. In the reaction section we check the temperature in transverse direction only.

#### 2.2. Operating conditions

The operating conditions for general experimentation are listed in Table 1.

#### 2.2. Experimental procedure

Switch on the power socket, blower and exhaust fan then check the water level in the water tank and open all the valves are used to control the supply of water to all the probes (like reducing reagent injection probes and the flue gas analyzing probes) and switch on the circulating water pump because all of the experiments were to be performed at high temperature so cooling was necessary. Check the connection of sparking plug

and open the main gas valve. Then switch on the air blower and check the air supply, and purged the rig by passing air through it for one to two minutes, this was done to remove the flue gases which would be present in the rig. Slightly open the pilot natural gas valve, switch on the burner from the control panel and adjust the flow rate of natural gas at nearly 3 m<sup>3</sup>/hr. then checked the main indicator light from control panel, if it was on then it means that rig had been started otherwise, switch off the burner and reset it and repeat the previous steps starting from the started of burner until the control panel show the green signal which means that the rig had been start. At the end adjust the Fuel to Air Ratio as 1/10 by keeping the flow rate of air at 100 m<sup>3</sup>/h and of natural gas at 10 m<sup>3</sup>/h then opened the main NH<sub>3</sub> valve and its flow rate was adjusted by using the digital fine controller. It was allowed to reach the temperature of the injection section at 700 °C in case of using additives or blending solution and 800 °C in case of using urea alone. If temperature was higher or lower than 700 or 800 °C then it was controlled by inserting or withdrawing the cooling coils.

Table 1. Operating conditions.

Parameter	Value
Air flow rate	80-100 m <sup>3</sup> /h
CH <sub>4</sub> flow rate	8-10 m <sup>3</sup> /h
Carrier gas (N <sub>2</sub> ) flow rate	150-200 Ft <sup>3</sup> /hr
Urea flow rate	2.67 * 10 <sup>-7</sup> m <sup>3</sup> /sec
Pressure of CH <sub>4</sub>	0.2 bar
Pressure of N <sub>2</sub>	3-4 bar
Pressure of NH <sub>3</sub>	2-5 bar
RPM of Urea pump	75 rpm
Injection point temperature	700-1200 °C
Temperature drop in Reaction Section	300-500 °C
Background NO <sub>x</sub> level	450-500 ppm

The background NO<sub>x</sub> was produced by the introduction of ammonia and was measured by using the fuel gas analyzer. After measuring the background NO<sub>x</sub> level, the reducing reagent solution of specific concentration was injected in the injection section by using the peristaltic pump and air as carrier gas. The reduction of NO<sub>x</sub> occurred in the reaction section and the NO<sub>x</sub> were converted into the nitrogen molecules and the water. This reduction in the NO<sub>x</sub> was observed on the digital flue gas analyzer. Each time of the analysis the temperature was also measured at the injection as well as at the measuring point in order

to know the effect of temperature on the reduction. The samplings were done at same point in case of finding the effect of temperature and molar ratio on the reduction efficiency of a specific reagent and were done at various point of the reaction section of the rig by inserting and withdrawing the flue gas analyzing probe (connected to analyzer) in case of determining the effect of residence time. Each position corresponds to different residence or reaction times. So the rig serves as a flow reactor through which flue gases were flowing. At the end the injection temperature, molar ratio and residence times were plotted versus amount of  $\text{NO}_x$  reduced.

### 3. Results and Discussion

On the basis of the fact the compounds containing the  $\text{NH}_2$  group are able to reduce  $\text{NO}_x$  from flue gas the aqueous solution of urea, ammonium carbonate and their 50%-50% mixture were employed to investigate their performances. Their temperature characteristics, effect of molar ratio, residence time and  $\text{CO}$  emission were determined and are discussed below.

#### 3.1. Urea as $\text{NO}_x$ reducing agent

Keeping in mind the advantages of urea like it is a solid, inert, non-corrosive material which is easily handled, safely stored and can be readily introduced into a combustion gas stream either as a solid or in solution, most of the experiments were performed by using the aqueous urea solution in the temperature range of 800-1200 °C and for a range of normalized stoichiometric ratio NSR, i.e.  $(\text{NH}_2/\text{NO}_i) = 1, 2, 4$  and 6 at constant residence time (~3.5 sec). It was in case of finding the effective temperature window. But in case of finding the effect of residence time on the  $\text{NO}_x$  removal efficiency temperature was kept constant at the optimum value found in the previous experiments and residence time was varied.

The effect of temperature on the  $\text{NO}_x$  reduction efficiency for the normalized stoichiometric molar ratio (NSR) i.e.  $M(\text{NH}_2/\text{NO}_i)$  of 1, 2, 4 and 6 is summarized in Figure 2. Background  $\text{NO}_x$  level and excess  $\text{O}_2$  were within range of 400 to 500 ppm and up to 1.1% respectively. It can be seen that at NSR of 6, performance is characterized by a plateau of maximum reduction of about 80% covering a temperature range of 1050–1150 °C. At temperature above 1170 °C, reduction efficiency

falls with increase in temperature for all values of NSR investigated. Except of the higher value of NSR which may due to the use of commercial grade urea all other observations were comparable to those of other studies such as that by *Chen et al. (1988)*, *Irfan, N. (1995)* and *Irfan, et al. (1997)* [6-8].

It was investigated that the effective temperature window was slightly shifted toward the high temperature with increasing NSR. The peak efficiencies were found to be at ~1075 °C and at NSR of 6 it lies at 1130 °C. The shift of temperature window was agreement with the results reported by Nylander et al. (1989). The  $\text{NO}_x$  removal efficiency remains greater than 40% within the temperature range of 1025-1150 °C at normalized stoichiometric ratio (NSR) of 3 and above. A maximum efficiency of 80% was achieved with a NSR of 6 at 1130 °C and greater than 60% efficiency can be achieved within the temperature range of 1050-1170 °C at NSR 6. These results are similar to results available in literature (except high value of NSR) the slight difference in the optimum temperature, maximum efficiency and NSR values may be attributed to the difference in system parameters like geometry, flue gas constituents and the most important is the purity of urea used because in this case.

At the optimum temperature the  $\text{NO}_x$  reduction was found to be increases along the length of the rig and at below the optimum temperature the curve obtained has the similar shape as obtained at optimum temperature but efficiency is less and it may be due to the reason that at temperature below than optimum temperature the  $\text{NO}_x$  reduction reaction was too slow, whereas at above than optimum temperature the maximum reduction takes place at about 0.25 sec and then it decreases with increase in residence time.

Figure 2 shows the effect of increasing the amount of urea injected (as NSR) into the flue gas and demonstrate the behavior of  $\text{NO}_x$  reduction versus temperature profile with increasing NSR at constant residence time, It was observed that the increasing the amount of urea injected into the flue gas, the maximum  $\text{NO}_x$  removal efficiency was 19%, 41%, 53% and 81% at NSR 1, 2, 4 and 6 respectively. At 1190 °C the  $\text{NO}_x$  removal dropped from 19% to 3% at a NSR of 1, 41% to 8% at a

NSR of 2, 53% to 20% at a NSR of 4 and 81% to 35% at a NSR of 6.

It was observed that the  $\text{NO}_x$  removal efficiency was increased with increase in the residence time or in other words efficiency was increased along the length of the rig and significantly increase was observed in the first half of the reaction section of the rig where the residence time was 1.5 sec and then it was increased slowly until in the last quarter part of reaction section where the residence time was nearly 2.5 sec it became constant. This may be attributed to the fact that urea decomposition was occurred more at high temperature thus near the injector amidogen radicals ( $\text{NH}_2$ ) were produced so near the injector lesser time was available for them to react with  $\text{NO}_x$  while along the length of the reactor more time was available for them to complete the reaction so that's why  $\text{NO}_x$  removal efficiency was increased along the length of the rig or residence time and in the last quarter part of the reaction section constant efficiency was observed due to presence no or a small number of amidogen radical that was in consistent with the results of kinetic modeling performed by the *Miller and Bowman (1989)* [9].

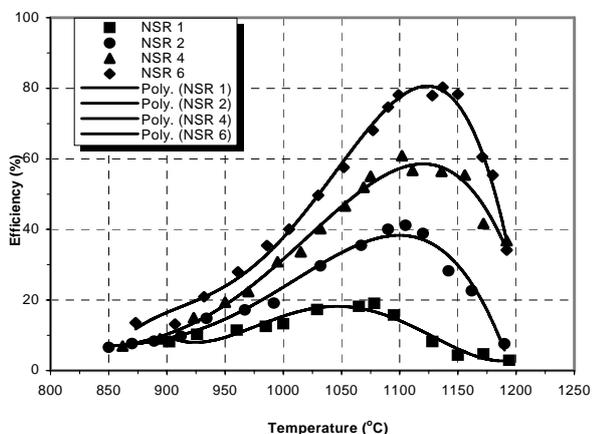


Figure 2. Effect of Temperature and Normalized Stoichiometric Ratio on Efficiency [urea].

It investigated that for a particular NSR the CO concentration was first increased with increase in temperature, reached to a maximum value and then was decreased with increase in temperature.

### 3.2. Ammonium carbonate as $\text{NO}_x$ reducing agent

Ammonium carbonate contains amidogen radical which could also be tested as potential reducing agent for SNCR process. Thus in order to investigate its performance characteristics test were performed by using the molar ratio 1, 2 and 3 in a temperature range of 700 to 1100 °C.

Figure 3 shows the  $\text{NO}_x$  reduction efficiency profiles as a function of temperature at molar ratios i.e.  $M(\text{NH}_2/\text{NO}_i)$  of 1 and 1 to 3 respectively for ammonium carbonate. The figures reveal that ammonium carbonate behaves in a similar fashion as urea and it also has a temperature window in which  $\text{NO}_x$  reduction takes place. But as compared to urea its temperature window laid from 850 to 950 °C, which was lower than what was found in case of urea and also its efficiency was lower than that of urea solution.

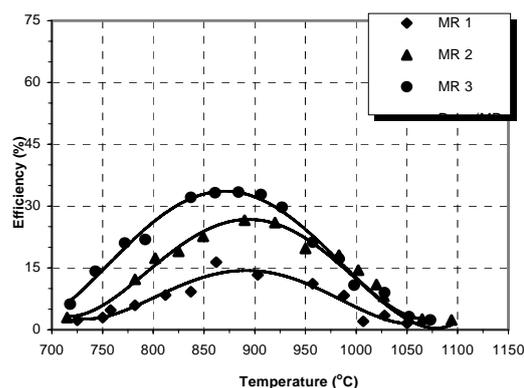


Figure 3. Effect of Temperature and Molar ratio on Efficiency [ammonium carbonate].

It was observed that like urea with ammonium carbonate the peak efficiency increases with increase in the molar ratio i.e.  $M(\text{NH}_2/\text{NO}_i)$ . The  $\text{NO}_x$  reduction was less than 15% at a molar ratio of 1 and reached to 34% at molar ratio of 3 (Figure 3). It was apparent that the width of the temperature window was increased with increase in the molar ratio and the peak of maximum efficiency was not shifted towards high temperature as observed in case of urea. So the optimum temperature at which maximum peak efficiency was observed was about 875 °C at all molar ratios.

### 3.3. Urea and ammonium carbonate mixture

Keeping in mind that ammonium carbonate behaves in a similar fashion as urea and reduction occurs over a temperature window of about 150 to 200 °C lower than urea, experiments were performed to assess the ability of 50-50% urea and ammonium carbonate as a NO<sub>x</sub> reducing agent at a molar ratio of 4. The results obtained are shown in figures 4.

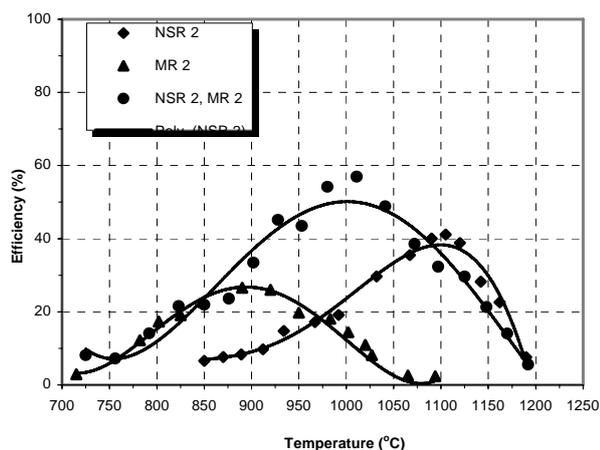


Figure 4. Comparison of Temperature window of Urea, Ammonium Carbonate and their 50%-50% mixture.

It was observed that the temperature window becomes broader and a maximum efficiency of 58% was achieved at 1000 °C. Thus the optimum temperature found in this experiment was nearly the average of the optimum temperatures 900 °C and 1100 °C found with ammonium carbonate and urea respectively. Figure 4 is showing the comparison of the performance characteristics investigated in case of urea at NSR of 2, ammonium carbonate at molar ratio of 2 and 50-50% mixture of urea and ammonium carbonate having overall molar ratio of 4. It can be seen that a maximum efficiency of 28% was achieved at an optimum temperature of 900 °C by using ammonium carbonate alone and after 900 °C. There was a fall of efficiency until no more reduction was observed after 1100 °C. A maximum reduction of 40% was achieved at optimum temperature of 1100 °C with urea and then it was dropped with temperature upto 1200 °C. Before 900 °C and after 1180 °C not more than 10% reduction was observed with urea alone.

Thus from 950 °C to 1050 °C none of the above single reagent performed efficiently but the 50-50%

mixture of urea and ammonium carbonate performed well not only in this temperature range but also in the temperature ranges covered by ammonium carbonate and urea alone. This can be explained on the basis of the fact that at low temperature ammonium carbonate contributed to the removal of NO<sub>x</sub> while at high temperature urea may here played its roles respectively but within their optimum temperature ranges there was an overlapping region in which both the reagents present were contributed toward the NO<sub>x</sub> reduction, so the overall effect was that the NO<sub>x</sub> reduction increased and hence a wide temperature range was observed in case of using 50-50% mixture of ammonium carbonate and urea.

It was investigated in case of urea and ammonium carbonate that the NO<sub>x</sub> reduction was maximum near to the injector or at low residence time, reached to 60% at a residence time of 2.5 sec and then a drop was observed in such away that at 3 sec the reduction was 40%. These results are in consistent with data observed in case of urea.

It was observed that CO concentration was maximum (20 ppm) at optimum temperature of 1000°C. The CO time profile may be explained on the basis of the fact that at high temperature (1000°C) its concentration is more near the injector because of greater decomposition of urea and ammonium carbonate and along the length of the reaction section its concentration decreases at 1000°C than at 900 °C because of oxidation of CO to CO<sub>2</sub> at high temperature.

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