Effect of oxygenated liquid additives on the urea based SNCR process

M. Tayyeb Javed a,*, W. Nimmo b, Asif Mahmood a, Naseem Irfan a

a Department of Chemical and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences (PIEAS), P.O. Nilore Islamabad, Pakistan
b Energy and Resources Research Institute, The University of Leeds, Leeds LS2 9JT, UK

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ABSTRACT

An experimental investigation was performed to study the effect of oxygenated liquid additives, H2O2, C2H5OH, C2H4(OH)2 and C3H5(OH)3 on NOx removal from flue gases by the selective non-catalytic reduction (SNCR) process using urea as a reducing agent. Experiments were performed with a 150 kW pilot scale reactor in which a simulated flue gas was generated by the combustion of methane operating with 6% excess oxygen in flue gases. The desired levels of initial NOx (500 ppm) were achieved by doping the fuel gas with ammonia. Experiments were performed throughout the temperature range of interest, i.e. from 800 to 1200 °C for the investigation of the effects of the process additives on the performance of aqueous urea DeNOx. With H2O2 addition a downward shift of 150 °C in the peak reduction temperature from 1130 to 980 °C was observed during the experimentation, however, the peak reduction efficiency was reduced from 81 to 63% when no additive was used. The gradual addition of C2H5OH up to a molar ratio of 2.0 further impairs the peak NOx reduction efficiency by reducing it to 50% but this is accompanied by a downward shift of 180 °C in the peak reduction temperature. Further exploration using C2H4(OH)2 suggested that a 50% reduction could be attained for all the temperatures higher than 940 °C. The use of C3H5(OH)3 as a secondary additive has a significant effect on the peak reduction efficiency that decreased to 40% the reductions were achievable at a much lower temperature of 800 °C showing a downward shift of 330 °C.

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1. Introduction

Stringent emission regulation throughout the world has put pressure for development of NOx control technology. Selective non-catalytic reduction (SNCR) is a cost effective technology for post combustion flue gas treatment that could be retrofitted alone or in combination with other NOx control techniques to achieve the increasingly strict regulatory requirements. The SNCR process is based on the injection of an amine based reagent that is effective for flue gas NOx reduction within a specific reactor temperature range converting it to N2. A certain amount of oxygen is required in the process to initiate the formation of the active NH2 radicals. The technique can be employed in all types of stationary-fired equipment and have relatively low capital and running cost. It is attractive as the process is not affected by fly ash and can be coupled with other combustion modification techniques (Hampartsoumian et al., 2003; Tayyeb Javed et al., 2007).

Various N-based reducing agents including ammonia, urea, cyanuric acid and ammonium carbonate have been used in various investigations with the most popular being ammonia, which is patented as the thermal DeNOx process (Lyon, 1975). The reaction mechanism of SNCR using ammonia is based on the concept that ammonia is first converted to amidogen (–NH2), by reacting with a hydroxyl radical (–OH), amidogen then reduce the NO in the flue gas stream. Thus, molecular radical species such as NH2 and OH dominate the reduction chemistry. Urea could serve as an alternative source of NH2 radicals as proposed by Salimian and Hanson (1980) by rapid decomposition to produce amidogen radicals directly.

Arand et al. (1980) reported the first application of urea solution in a natural gas fired furnace. The background NOx was simulated by adding nitric oxide to the combustion air. Varying the flow of air and natural gas also controlled the excess oxygen. The results demonstrated that urea was capable of reacting with nitric oxide, giving about 67% reduction at a molar ratio of 0.5, an oxygen level of 2.5% and at a temperature in the range of 1015–1060 °C.

Very few studies have been reported in the open literature on the various parameters that affect the performance of urea DeNOx. However, the effect of process additives have been studied (Teixeira and Muzio, 1991; Lee and Kim, 1996; Rota and Zanoelo, 2003; Han and Lu, 2007; Tayyeb Javed et al., 2008) as well as the effect of very low initial NOx levels (Quartucy et al., 1990) and process residence...
time (Muzio et al., 1993). The process additives reported include glycerol, methyl acetate, phenol, succinic acid, propylaldehyde, diethyl ether, methanol, ethanol, carbon monoxide, propane, hydrogen and sodium carbonate.

This paper presents the experimental results concerned with an investigation of oxygenated liquid additives such as hydrogen peroxide (H$_2$O$_2$), ethanol (C$_2$H$_5$OH), ethylene glycol (C$_2$H$_4$(OH)$_2$) and glycerol (C$_3$H$_5$(OH)$_3$) on selective non-catalytic reduction of nitrogen oxides with urea in a pilot reactor over a temperature range of 800–1200 °C. The influence of using C-containing additives on carbon monoxide emission was also verified. The experimental study includes a systematic investigation of the effect of these process additives on the performance of aqueous urea DeNOx with application in power plants. Process parameters such as shift in temperature window, peak reduction efficiency and residence time have been studied.

2. Experimental setup

A schematic diagram of the experimental system used in this investigation is shown in Fig. 1. The flow reactor assembly, for gas phase reaction, was fabricated from five mild steel sections flanged together: the combustion section, the temperature control section, the injection and mixing section, the reactor section and the exhaust section. In the combustion section a 150 kW burner was used so that a flue gas mixture could be generated by the combustion of methane with some addition of ammonia for production of NOx. The temperature control section was equipped with two wall mounted cooling coils to control the temperature of the flue gas stream, which has a square cross section of 25 cm. The third section incorporates a water-cooled injector and a thermocouple to measure the temperature of the flue gases at the injection point. The fourth section was the reactor section, which was coupled to the flue gas exhaust section. The width of these sections was 50 cm square with internal length of 200 cm. These dimensions were chosen such that it is a representative of a section of the much larger cross sections present in full scale power plants. In the full scale power plants multiple injectors could be fitted so that mixing would be as good as possible and would behave as multiple volumes of the facility described here.

The stainless steel injector was water-cooled and the reducing agent solution, aqueous urea with or without additives, was pumped with a variable speed peristaltic pump (model LEAD-1 by Longer Pump Co. Ltd., China). The liquid flow rates were controlled...
by adjusting the RPM of the pump in accordance to the calibration curve for the pump. Nitrogen and compressed air was used as a carrier for liquid reducing agents to increase the momentum, thereby improving the penetration and mixing with the flue gas.

The temperature of the flue gases in the reactor section was controlled by two water-cooling coils installed upstream in a temperature control section of the rig. The water-cooling coils were fixed alongside the walls such that if they could be withdrawn or inserted into the flue gas flow for temperature control. The temperature was measured by Platinum–Rhodium thermocouple installed in front of the injector and a chromel–alumel thermocouple installed at the end of reaction section. Also a 2.5 m suction pyrometer was used to measure the centerline temperature of the reaction section at various locations to track the true flue gas temperatures during the reaction progress.

A portable flue gas analyzer by LAND instruments international model LANCOM III was used to measure the flue gas composition. The analyzer measure O$_2$ in the range of 0–25% volume (accuracy ±1%), CO in the range of 0–2000 ppm (accuracy ±2%), SO$_2$ in the range of 0–2000 ppm (accuracy ±2%), NO in the range of 0–1000 ppm (accuracy ±2%) and NO$_2$ in the range of 0–100 ppm (accuracy ±2%). The analyzer was calibrated using standard gases with nominal concentration accuracy of ±5%. The gas filler then certifies it to the actual concentration accuracy of ±2%.

In the experimental investigation, 2.5 and 1.25 m water-cooled stainless steel probes (~4 mm ID) were used to collect and quench the samples from the combustor. In addition water-cooling also maintained the structural strength at high temperatures encountered in the combustor. Literature indicates observations associated with the sampling of NO$_x$ that are specifically related to catalytic affect of stainless steel probes particularly at high temperature. NO to NO$_2$ conversion in the presence of excess oxygen and solubility of NO$_x$ in the condensed water vapours in flue gas (Hampartsoumian and Gibbs, 1982). Earlier studies reveal that due to the fragile nature of quartz, stainless steel probes may be used if sample temperature within the probe is reduced to 200 °C (Pershing and Wendt, 1977). To avoid NO$_2$ and NH$_3$ losses in condensed water vapour within the sample line, water traps were incorporated into the system and were designed to prevent the sample gas from being bubbled through the collected liquid.

The setup was found to have non-uniformity of the temperature profile just like present in the practical fullscale installations. The fuel gas and air input was set to give a flue gas residence time of 3 s, while the flue gas O$_2$ maintained at 6% and a background NO$_x$ concentration was kept typically at 500 ppm. The temperature range studied was 700–1200 °C.

3. Characterization of PIEAS experimental setup

The characterization of PIEAS experimental setup is discussed in relation to temperature distribution patterns within the reactor section and reproducibility of the results.

3.1. Temperature characteristics of PIEAS setup

The temperature at various locations inside the reaction section was measured in axial and radial direction. Fig. 2 shows the temperature profiles at different mean temperatures varying from the temperature of 850–1125 °C. It was observed that a non-isothermal condition exists in the reactor and the axial gradient of temperature is increased with the increase of the inlet reactor temperature. The reason for the existence of axial gradients of temperature is the heat transfer in the radial direction.

Fig. 2. Temperature profiling for different mean temperatures. [■] mean temperature = 1125 °C; [●] mean temperature = 1050 °C; [▲] mean temperature = 970 °C; [▼] mean temperature = 900 °C; [●] mean temperature = 850 °C.

3.2. Reproducibility of collected data

Verification of reproducibility was necessary to ensure that consistent results can be achieved for experiments under similar operating conditions. For this purpose several experiments were performed with ammonia as reducing agent. Two different molar ratios, i.e. NH$_3$/NO$_x$ of 1.0 and 1.5 were used at a temperature of 970 °C keeping all other parameters same.

Figs. 3a,b show the results from two different runs for ammonia SNCR where the background NO concentration was 500 ppm and ammonia injected at a molar ratio of 1.0 and 1.5, whereas the mean temperature was kept at 970 °C. The methane flow rate was kept constant at 10 m$^3$/h and the air supply was maintained at 135 m$^3$/h at STP. The profile shown in the figure indicates the progress of reaction as ammonia reacts with the NO in the flue gas along the reaction section while it flows towards the exhaust section. The NO concentration is the average of the two tests conducted at a particular NH$_3$/NO molar ratio. It is observed that in the first run in which the NH$_3$/NO molar ratio was set at 1.0 the concentration of NO is reduced from 475 ppm at a residence time of 0.25 s to 189 ppm in about 2 s near the exhaust thus giving an overall NO reduction of about 61%. In the second run a similar trend was observed along the reaction and the concentration of NO is reduced from 485 to 187 ppm giving a similar overall NO reduction efficiency as previously found with a slight variation of ±15 ppm. For the molar ratio of 1.5, the concentration of NO reduced from 485 to 145 ppm with higher efficiency and thus demonstrated the effect of increased molar ratio of the SNCR process performance. When this run was repeated the final concentration came out to be the same at 145 ppm. Thus, at a molar ratio of 1.0 and 1.5, the trends were quite similar, overall efficiency is comparable and hence the experimental setup demonstrated good reproducibility.

4. Results and discussion

4.1. Effect of H$_2$O$_2$

Azuhata et al. (1982) had found that H$_2$O$_2$ could accelerate the NO reduction if introduced at a temperature above 500 °C. Miller and Bowman (1989) also performed calculations for addition of H$_2$O$_2$ with SNCR reducing agent and showed that for the H$_2$O$_2$ + NH$_3$ reaction, the effective temperature window would be broadened and the peak reduction shifted to a lower temperature compared to pure NH$_3$ addition. Keeping these studies in mind H$_2$O$_2$ was blended with aqueous urea solution in three molar ratios...
(H₂O₂/NO₃) of 0.5, 1.0 and 2.0 and injected with constant urea to NO₃ molar ratio of 3.0. The results are presented in Fig. 4. It was observed that in the presence of H₂O₂ the effective temperature window was broadened and shifted to a lower temperature compared to pure urea. Moreover, the optimum temperature was shifted from 1130 °C (without the presence of H₂O₂) to 1050, 1020 and 980 °C for the three blends. The peak reduction efficiencies were decreased from 81 to 71, 68 and 63% at M(H₂O₂/NOᵢ) of 0.5, 1 and 2, respectively.

It is well established that the OH radical concentration is a critical factor influencing the overall NOₓ reduction (Miller and Bowman, 1989; Miller and Glarborg, 1999). Normally these OH radicals are supplied by H₂O₂ decomposition. Urea is thought to be decomposed into NH₃ and HNCO. For ammonia, OH radicals can readily abstract H from NH₃ by the reaction [NH₃ + OH ↔ NH₂ + H₂O] and the resulting NH₂ radicals then take part in the key NO removing reactions [NH₂ + NO ↔ N₂ + H₂O] as well as by reaction [NH₂ + NO ↔ NNH + OH] which subsequently reacts with NO to form N₂ via reaction [NNH + NO ↔ N₂ + HNO]. HNCO reacts primarily with OH to form N₂O₃ and hence the NO reduction is initiated earlier, that is the window of NO reduction is shifted to a lower temperature range. The reactions involving NH₂ and NCO radicals and the sequence that converts NO to N₂ have higher reaction rates at higher temperature. Hence, there is some reduction even at lower temperature. However, though there is some reduction as can be seen by Fig. 4, the efficiencies are lower and the window is shifted towards lower temperatures.

4.2. Effect of C₂H₅OH

Robin et al. (1991) reported studies carried out on the efficiency of methanol in modifying the behavior of the SNCR process. Results showed that, at low methanol/NOᵢ ratio, methanol does yield some enhancement of the SNCR process. Lee and Kim (1996) had also reported the influence of liquid additives (methanol and ethanol) into urea solution. It was observed that an addition of 0.5 molar ratio of ethanol to NO along with urea to NO molar ratio of 2.0 has lowered the temperature window such that the peak reduction efficiency of 85% at 1015 °C was decreased to 62% at 855 °C.

Due to the current use of ethanol as a substitute fuel some traces of the ethanol could also be present in the flue gas stream thus it is inevitable to study its effect on SNCR process. A blended solution of aqueous urea and ethanol was injected into the flue gas stream over a temperature range of 700–1200 °C to investigate its performance. Three molar ratios (C₂H₅OH/NOᵢ) of ethanol were applied (0.5, 1.0 and 2.0) by keeping the urea/NOᵢ molar ratio 3.0. The results obtained are shown in Fig. 5. It was observed that the presence of C₂H₅OH has broadened the effective temperature window such that 50% reduction was achieved in a window extending from 1040 to 1175 °C in absence of additive to 910–1085 °C for molar ratio of 0.5 and 870–1040 °C for that of 1.0. The peak reduction efficiency of 81% at 1130 °C (without the presence of C₂H₅OH) was reduced to
operating at 50 MW. A solution of urea containing 35% by weight ethylene glycol, with the molar ratio of urea to baseline NOx being 1.0, was sprayed into the boiler by means of seven nozzles positioned 14.63 m above the top row of burners where the temperature was about 900 °C. Teixeira and Muzzio (1991) also presented the data of laboratory tests showing the effect of a number of additives on NOx removal efficiency and by-product emission as a function of temperature. These additives include ethylene glycol.

A blended solution of aqueous urea and ethylene glycol was injected into the flue gas stream in temperature range of 700–1200 °C to investigate its performance. Two molar ratios (C2H4(OH)2/NOi) were employed, i.e. 1.0 and 2.0 while keeping the urea/NOi molar ratio at 3.0. The results obtained are shown in Fig. 7. It was observed that the presence of C2H4(OH)2 has a significant effect on the temperature window for NOx reduction such that 50% reduction was achieved in a window extending from 875 to 1100 °C for a molar ratio of 1.0 and 930–1200 °C for that of 2.0 but the peak reduction efficiency was reduced to 65% at 975 °C for C2H4(OH)2 to NOi molar ratio of 1.0 and 55% at 975 °C for that of 2.0. It was also observed that at a lower temperature of about 725 °C, about 6% of NO was converted to NO2 which shows a competitive oxidation reaction of ethanol in the flue gas assisting the SNCR process by lowering and broadening the effective temperature window. It was observed that injecting C2H4(OH)2 at molar ratio of 2.0 shows higher efficiencies than those of 1.0 at temperatures below about 870 °C while it (i.e. the case of molar ratio of 2.0) showed lower efficiencies at temperatures from about 870 to 1100 °C. The presence of OH radical due to higher concentration of additives had potential for better efficiencies at lower temperature while at higher temperature oxidation rate has more significant then reduction (cf. Section 4.1).

Fig. 8 presents the characteristics of CO emission during the addition of C2H4(OH)2 along with urea. It was observed that a high concentration of CO, i.e. 600 ppm was present at the temperature range of 770–850 °C. The observation suggest the potential of this composition where it could be used to give a wide range of operating temperatures from 950 to 1200 °C with a modest efficiency of 50% and nominal CO emission of less than 200 ppm. These high concentrations were observed near the injector but gradually reduced to lower levels, depending upon mean reaction temperature.

4.4. Effect of C3H5(OH)3

Rota and Zanoelo (2003) investigated the influence of oxygenated additives that include glycerol on NOxOUT process efficiency.
They found that the additives investigated are able to enlarge the width of the temperature window without compromising significantly on maximum reduction efficiency. However, the temperature window enlargement has been found only towards low temperature values, while in the high temperature region the additives made no significant effect. In other words, the window was shifted but not broadened. They argued that the main effect of these additives is to provide a larger pool of radical species required by the initiation reactions. At higher temperature, not only are the initiation reactions very fast regardless the presence of additives, but also the urea oxidation patterns prevail over the NO reduction ones, thus making the presence of any additive ineffective. The changing behavior of the SNCR process with the addition of OH has suggested the use of glycerol as an additive to urea.

In the present studies an aqueous solution of glycerol (16% w/v) and urea solution (31.8% w/v) was employed within the temperature range of 700–1200 °C, to investigate its performance characteristics. Three concentrations of glycerol were injected at molar ratios of M(C3H5(OH)3/NOx) = 0.5, 1 and 2 where as urea was maintained at a molar ratio of 3.

The results are shown in Fig. 9 where it is observed that 50% reduction could be achieved in a temperature range from 885 to 1120 °C when C3H5(OH)3/NOx was 0.5. Further increasing this molar ratio to 1.0 it was observed that more then 50% reduction could be achieved beyond 930 °C. Increasing the molar ratio to 2.0 the efficiency was hampered but it was observed that a reduction of greater than 40% could be achieved for temperatures of 800 °C and upward. The results suggested its potential use in power plants where loads and temperatures are varying.

The CO emission has similar trends as observed in the case of ethylene glycol where as high as 600 ppm is observed in lower temperatures but its concentration diminishes as the temperature increases (Fig. 10). Similarly, it was observed that NO oxidation to NO2 of 4% was measured at lower temperature.

5. Conclusions

The effect of secondary, oxygenated additives on the urea SNCR process for NOx control has been investigated in a 150 kW test reactor. Blending hydrogen peroxide with urea solution has slightly shifted the temperature window toward lower temperatures but to the detriment of peak reduction efficiency. Blending ethanol with urea solution shifted the temperature window toward low temperatures but a more prominent effect was a substantial decrease in peak efficiency with an increase in the molar ratio to levels of 50% at M(C2H5OH/OH) = 2. In addition CO emission was higher than that of urea solution alone. Similarly blending ethylene glycol with urea solution shifted the temperature window toward low temperature but efficiency decreased with increase in the molar ratio. However, at a molar ratio of 2, efficiencies greater than 50% can be achieved with a temperature window of 900–1200 °C. CO emission was found to be higher than that for ethanol. Blending glycerol with urea solution shows results similar to ethylene glycol but the CO emission is greater than in the case of a blended solution of glycerol as compared to ethanol and ethylene glycol. However, at a molar ratio of 2, reduction efficiencies greater than 40% can be achieved with a temperature range of 800–1200 °C.

The results obtained with the PIEAS SNCR reactor under simulated power plant conditions suggests that the reduction of NOx in power plants can be achieved even under adverse operating conditions involving variation of flue gas temperature. Mixtures of urea with ammonium carbonate or ethanol can shift the temperature window toward lower temperatures. By blending urea solution with glycerol or ethylene glycol, the temperature window may be broadened from as low as 800 °C to as high as 1200 °C with NOx a removal efficiency of greater than 45%.

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