Prediction of Optimum Parameters for NO_x Reduction Utilizing Selective Non-Catalytic Reduction (SNCR) Technique(Thermal DeNO_x Process)

M. Mansha[1], A.H Qureshi[1] and E.M. Shahid[1]

[1]*Department of Mechanical Engineering. University of Engineering and Technology, Lahore.*

Abstract

In this paper thermal DeNO_x process for Selective Non-Catalytic removal (SNCR) of nitric oxide from engine exhaust gases has been discussed and optimum parameters i.e optimum temperature, optimum residence time, and optimum molar ratio has been calculated by using CHEMKIN-II software. To run the code exhaust emission data has been obtained from reciprocating engine power plant operating on duel fuel system (40% Natural gas & 60% HFO). Finally it is concluded that if the conditions prescribed as predicted results are met in the exhaust stream, then with ammonia injection a substantial decrease in NO_x. (about 96%) can be achieved.
Sources of NO_x formation and different NO_x control techniques are also discussed in the paper.

Key Words: SNCR; Thermal DeNOx Process ; HFO; Natural Gas

1. Introduction

Combustion of natural gas and other hydrocarbon fuels in an engine produces different species along with normal combustion products, CO_2 and water vapors. The major pollutants from combustion include carbon monoxide (CO), non- methane organic gases (NMOG), oxides of nitrogen (NO_x) and particulate matters.

NO_x covers various oxides of nitrogen but among them nitric oxide (NO) and nitrogen dioxide (NO_2); are currently regulated.

NO is by far the most dominant nitrogen oxide formed during combustion. However, subsequent further oxidation leads to NO_2 in the environment and it is the nitrogen dioxide that reacts with the NMOG in the presence of sunlight to form photochemical smog including ozone and some form of acid precipitation.

NO_x has many harmful effects on human health and the environment as a primary as well as secondary pollutant NO_2 is irritating and upon inhalation can cause damage to the lung tissues. Furthermore ground level ozone can make breathing difficult in some people at concentration as low as .01 ppm. It also increases the calcification of bones resulting in premature aging and depletes body fats. [1]

A study based upon prediction and modeling reveals that in Pakistan in the year 1990 total NO_x emissions inventory was 271Gg, which may increase to 2056 Gg by the year 2020. This forecasted increase would be the result of the growing energy demand due to anticipated population and economic growth [2]. Another study conducted jointly by JICA (Japan International Cooperation Agency) and PAK-EPA (In 2006) showed the concentration level of NO_2 in five major cities of Pakistan i.e. Islamabad, Lahore, Peshawer, Quetta and Karachi. The concentration level is found to be more than threshold value. The highest concentration of NO2 (399.65 $\mu g/mm^2$) was found at Karimabad Karachi followed by Lahore, Quetta, Peshawer and Islamabad in descending order, the average value being 76$\mu g/mm^2$ at Karachi and Lahore. [3]

1.1 Sources of NO_x Formation

The major sources of formation of NO_x during combustion processes are

- Thermal NO_x
- Fuel NO_x
- Prompt NO_x

Thermal NO_x is produced when nitrogen reacts with excess oxygen at higher temperature (greater than 1800 K) in the combustion

Corresponding Author: M Mansha (engg_mansha@yahoo.com)

process. The quantity of NO_x formation depends on reaction temperature, residence time, the local stoichiometric condition and turbulence. Two of the main reactions for the formation of thermal NO_x are described by the Zeldovich mechanisms [4].

$$O + N_2 \Leftrightarrow N + NO \quad (1)$$

$$N + O_2 \Leftrightarrow O + NO \quad (2)$$

An additional reaction has been shown necessary at near stoichiometric and fuel rich mixture is

$$N + OH \Leftrightarrow H + NO \quad (3)$$

Thermal NO_x contributes the largest portion to the total NOx produced.

Fuel NO_x is formed in the combustion system due to reaction from chemically bound nitrogen in fuel; before entering the combustion zone, the nitrogen compounds in fuel decompose to low molecular weight nitrogen containing compounds or radicals such as NH_3, NH_2, NH, CN etc. this will further facilitate oxidation of fuel bound nitrogen compound to form nitric oxide rapidly [5]. In spark ignition engines there is normally negligible fuel bond nitrogen.

It was also revealed in JICA-PAK EPA report [3] that at Qadirpur purification plant the observed level of fuel bound nitrogen in the natural gas is 11percent, which is too high nitrogen ratio in natural gas.

Prompt NO_x forms in the flame zone, the breakdown of hydrocarbon fragments (C, CH, CH_2) may react with atmospheric nitrogen and their subsequent combination to produce other nitrogen species such as (CN, HCN, H_2CN and NH) under fuel rich condition. In prompt NO_x formation, the focus area is flame front and the regions near it.

1.1.1 NO_x Control Techniques

Pre and post combustion NO_x control techniques are most promising in the engine with premixed and non premixed combustion. Combustion modification methods are also effective in abating NO_x in engines, but these methods lower the maximum temperature of the combustion thereby reducing efficiency. In general these methods include lowering of compression ratio, retarding the spark timing, using the exhaust gas recirculation (EGR) and enriching the fuel mixture. EGR lowers both flame temperature and flame speed and gives significant reduction in NO_x. Between 5 and 10% EGR is likely to halve NO_x emissions. However EGR can lower the efficiency at full load and reduces the lean combustion limit.

Pre-combustion NO_x techniques include treating the fuel and effective control on air-fuel mixture preparation and distributions. With respect to fuel treatment, the concept is to minimize any fuel bound nitrogen.

In the category of post combustion exhaust gas treatment for NO_x reduction, the techniques are:

1. Selective non catalytic reduction (SNCR)
2. Selective catalytic reduction (SCR)
3. Non-selective catalytic reduction (NSCR), other possibilities includes combining SNCR and SCR techniques. Also the use of Plasmas combined with a version of SNCR using ammonia has been found in literature [6].

It may be mentioned here that combustion modification and pre combustion NO_x control techniques although provide significant NO_x removal but often are not enough to meet regulations. To get substantial reduction in emissions, post combustion control is more feasible and better option.

In SNCR technique nitrogen containing additives like ammonia, urea or cyanuric acid is injected and mixed with the exhaust gases to effect chemical reduction of NO to N_2 without the aid of the catalyst. Depending on which agent is used, the SNCR is classified in to the three main processes

- Thermal $DeNO_x$ (using ammonia)
- RAPRE NO_x (using Cyanuric acid)
- NO_x Out (using urea)

For most cases SNCR is effective over a narrow temperature range.

2. Thermal $DeNO_x$ Process

In this process, ammonia is injected in to the hot exhaust gas stream emitting from combustion devices. The ammonia may be in the form of aqueous solution or as anhydrous ammonia. Certain precautionary methods are required in storage, handling and delivery of ammonia. Another concern with ammonia process is the “ammonia slip”, that is the ammonia that is not consumed during the process and escapes out with the exhaust stream.

In general a number of factors affect the overall performance of SNCR process. These factors include the detail chemistry, the mixing of the agent with the exhaust gases and the non-uniformity of the gas temperature. The chemistry is affected by the specific agent, temperature, pressure, concentration of species and residence time. Specific features that are important include the ratio of the agent to the nitric oxide concentration, and the oxygen, carbon monoxide and water concentration [8].

For a number of reasons the internal combustion engines , boilers and furnaces operated with combustion at different stoichiometric conditions and their exhaust may contain oxygen ranging from less than 1 % to over 15 % (by Volume) depending upon the overall equivalence ratio (or air fuel ratio). For example a successful design for medium speed diesel engine employs mixture with an equivalence ratio of about 0.5 and smaller automotive engine may be designed to operate closer to stoichiometric mixtures, as exhaust catalytic system requirements are best achieved (maximum performance) if the engine is operated at equivalence ratio ≈1.

Some original studies of SNCR processes focused on cases with oxygen concentration of about 1 or 2 % which would be typical of furnaces and boilers [9]. But other studies are available in which cases for higher concentration are also discussed. For example Caton etal [10, 11] have reported on cases for the use of ammonia with oxygen concentration up to 15 %. Also Kasuya etal [12] have reported on results for ammonia for oxygen concentration up to 50 %. Srivasta and Caton have reported the results by using urea concentration up to 15 %.

3. Prediction of Optimum Parameters using Chemical Kinetic Code

3.1 Engine Specification and Exhaust Gas Data

For the present study 5.6 MW 4 Stroke V-60, 18 cylinders, Nigata Reciprocating Type Engine has been selected. The engine employs dual fuel system for operation i-e Natural gas and HFO (40% CH_4, 60% HFO). The cylinder pressure is 150 kg /cm^2 , bore = 320 mm, stroke = 420mm, compression ratio = 14.1, r.p.m = 600.

The flow rate of fuel (CH_4 + HFO) is 550.662 m^3 / hr. It may be mentioned here that the engine has been recently converted in to dual fuel system. Originally it was being operated on HFO type fuel. The observed exhaust gas data of the engine is as follows:

NO_x= 1470 ppm, CO = 1808 ppm [13] and
Excess air = 160%

3.1.1 Application of the chemical Code (CHEMKIN- II)

CHEMKIN-II is a FORTRAN based chemical kinetics package for the analysis of gas-phase chemical kinetics. The package can be used to model gas phase reactions such as those occurring in combustion. For this present study the exhaust gas data of NO_x and CO of the above mentioned engine is used to run the code; after going through different chemical reactions,CHEMKIN-II is used to predict the optimum temperature, residence time and molar ratio, for which the reduction is maximum

4. Predicted Results

The predicted results at optimum temperature, optimum residence time and optimum molar ratio is as follows

4.1 Optimum Temperature

Table 1 shows the percent removal of NO at different temperatures as predicted by CHEMKIN-II code.

This data plotted as temperature versus NO_x removal indicate that the optimum temperature at which considerable NO_x removal may be achieved is a window from 700 °C to900 °C with peak efficiency of 96.55% at about 800 °C [Figure 1]

4.2 Optimum Residence Time

Keeping the optimum temperature as predicted by the code, the optimum residence time was investigated through kinetic modeling at which the reaction was complete. This is necessary to estimate the required length of the exhaust pipe in which reaction may be completed.

Table 1: % removal of NO at different temperatures

Temp °C	% reduction in NO
700	18.36
750	44.625
800	96.55
850	92.51
900	86.8

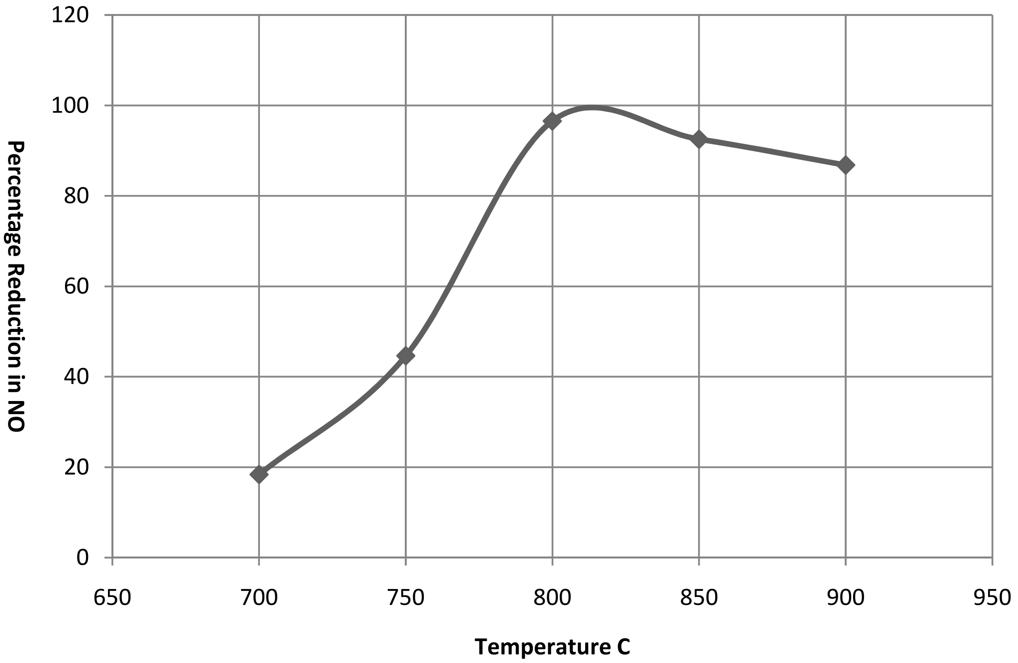


Figure 1: Determination of Optimum Temperature.

Code runs were performed for residence times from 0.25 seconds to about 3.0 seconds. The corresponding NO removal was tabulated in Table 2 and plotted as a function of residence in Figure 2.

As can be seen from Figure 2 that at predicted optimum temperature, the residence time in which the reaction is almost complete is 2.5 sec after which there is no appreciable change in the NO removal. The NOx reduction at optimum residence time (at 2.5 sec) is 96.21%

4.3 Optimum Molar Ratio

Code runs for prediction of optimum molar ratio of ammonia to background nitric oxide [NH_3/NO] was required in order to estimate the quantity of SNCR reducing agent to be injected in the flue gas steam coming from the engine exhaust. It would not be feasible to inject more than optimum amount of ammonia, which would, simply comes out as it is and would form another source of pollutant. A range of molar ratio is investigated from 0.25 to 2.0 and corresponding NO percent removal was investigated

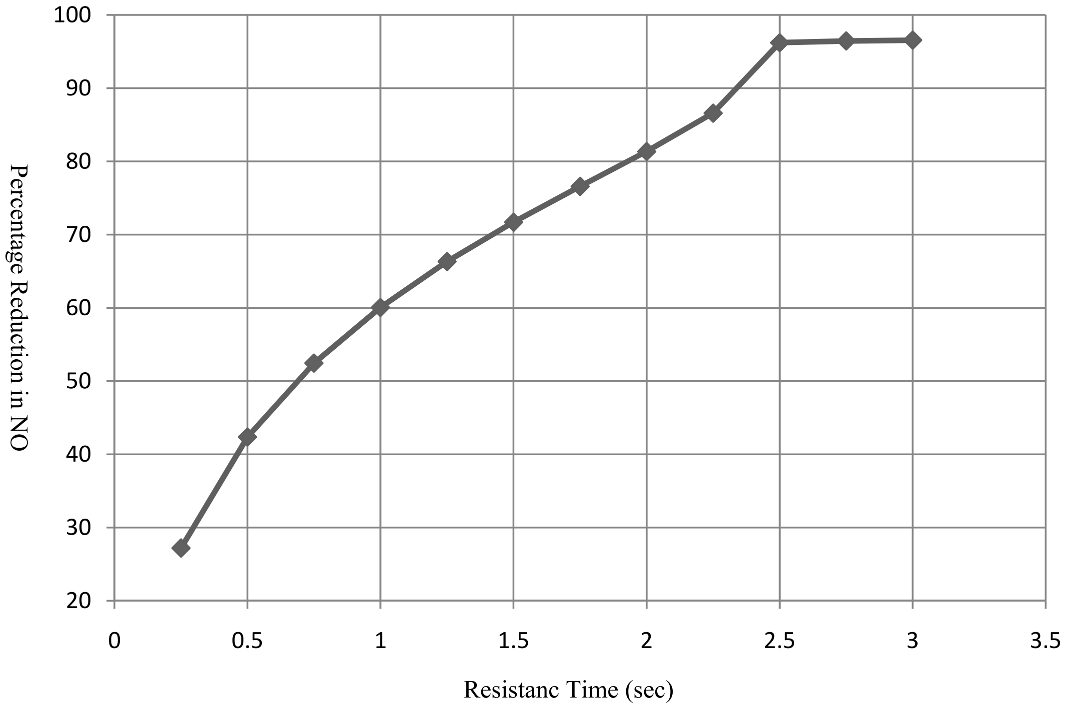
The chemical kinetic modeling results are tabulated in Table 3 and Figure 3. As can be seen from the plot of percent NO removal as a function of molar ratio, optimum molar ratio was found to be 1.0. The NO_x reduction at optimum molar ratio is 96.21%

Table 2: Data for finding optimum residence time

Residence Time	Percentage Reduction in NO
0.25	27.21
0.5	42.38
0.75	52.45
1	60.06
1.25	66.32
1.5	71.7
1.75	76.59
2	81.36
2.25	86.59
2.5	96.21
2.75	96.44
3	96.55

Table 3: Data for finding optimum molar ratio

Molar ratio (NH_3 / NO)	%age Reduction in NO	Molar ratio (NH_3 / NO)	%age Reduction in NO
0.25	26.53	1.25	80.61
0.5	52.45	1.5	77.61
0.75	77.41	1.75	76.26
1	96.21	2	75.51



Optimum residence time = 2.5 sec

Figure 2: Determination of Optimum Residence time

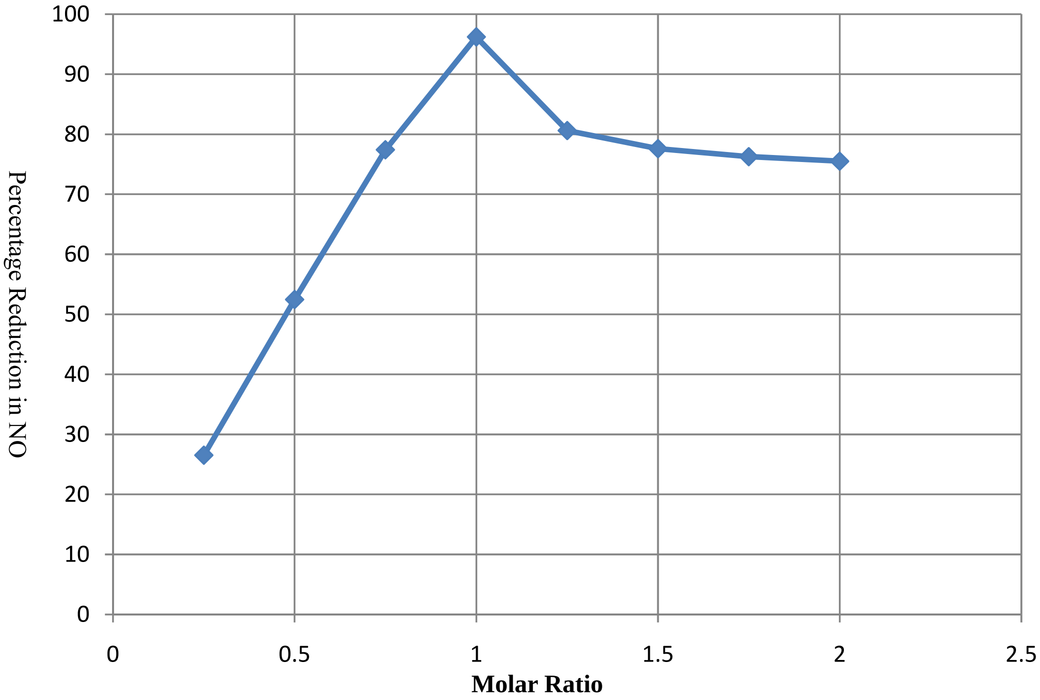


Figure 3: Determination of Optimum Molar ratio

5. Final Predicted Results And Conclusions

The optimum reduction of NO_x would be achieved when the following conditions are met in exhaust stream i.e If the temperature of the exhaust gases is.800 C, the residence time is 2.5 sec and the molar ratio is 1, then the reduction is 96 %, which amounts to reduction of 51 ppm from 1470 ppm.

Thus the exhaust pipe may contain a reactor in to which the engine out exhaust gases are fed and the gases are uniformly heated there by some heating mechanism to 800C and Ammonia is injected at a molar ratio (NH_3 /NO) of about 1.0 and the gases remain in reactor for 2.5 seconds to complete the reaction.

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References

[1]. U.S. Environmental Protection Agency; *Air Quality Criteria for Nitrogen oxides*, U.S.EPA, Washington D.C (1971).

[2]. John. A. Van Ardennes et al; *Atmospheric Environmental*, 33 (1999)

[3]. JICA, PAK EPA; *Measurement of Ambient Concentration of NO2 in Different Cities of Pakistan Using Diffusion Samplers*, April 2006.

[4]. Yong Hun Park; *An investigation of urea Decomposition and selective non-catalytic non-catalytic removal of Nitric Oxide with urea,* M.Sc Thesis submitted to Texas A & M university USA (2003)

[5]. Taraneh, Nowroozi and Isfahani'; *Theoretical study on the mechanisms of removing nitrogen oxide using Isocyanic acid*, M.Sc Thesis Submitted to, East Tennessee State University. (2001).

[6]. M. B. Chang; and C. F. Cheng; *Environment Engg. Science*, 14 (1997).

[7]. Y. ITaya, S. Deguehi, M. Takei. Yoshino; H. Matsuda; *4th International conference on Technologies and Combustion for a clean environment,* (1997)

[8]. A. Jerald, Caton and Zhiyong Xia; *Journal of Engg for Gas Turbines and power*. (2003)

[9]. R. K. Lyon; *Environmental science and technology*, 21 (3) (1987).

[10]. J. A. Caton, J. K. Narney, and W. R. laster; proceedings of the 1994 central states section/combustion institute spring technical meeting, Madison, W.I paper no. 15, (June 1994).

[11]. Kasuya, F; Glarborg, P., Johnsson, J.E, Dam- Johansen K; *Chemical Engineering Science*, 50(9).(1995).

[12]. Srivasta, S; *The selective Non catalytic reduction of nitric oxides using urea as the chemical agent*, *An Experimental Approach*, M.S. Thesis submitted to Department of Mechanical Engg; Texas A & M University (December 1997).

[13]. UNITEC; *Fuel Gas Analyzing Report*, Karachi, Pakistan (May 2006)