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

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Abstract

In this paper thermal DeNOx 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 NOx (about 96%) can be achieved.

Sources of NOx formation and different NOx 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, CO2 and water vapors. The major pollutants from combustion include carbon monoxide (CO), non-methane organic gases (NMOG), oxides of nitrogen (NOx) and particulate matters.

NOx covers various oxides of nitrogen but among them nitric oxide (NO) and nitrogen dioxide (NO2) are currently regulated.

NO is by far the most dominant nitrogen oxide formed during combustion. However, subsequent further oxidation leads to NO2 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.

NOx has many harmful effects on human health and the environment as a primary as well as secondary pollutant NO2 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 NOx 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 NO2 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 µg/mm²) was found at Karimabad Karachi followed by Lahore, Quetta, Peshawer and Islamabad in descending order, the average value being 76µg/mm² at Karachi and Lahore. [3]

1.1 Sources of NOx Formation

The major sources of formation of NOx during combustion processes are

- Thermal NOx
- Fuel NOx
- Prompt NOx

Thermal NOx is produced when nitrogen reacts with excess oxygen at higher temperature (greater than 1800 K) in the combustion
process. The quantity of NO\textsubscript{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\textsubscript{x} are described by the Zeldovich mechanisms \cite{4}.

\begin{align*}
O + N_2 &\leftrightarrow N + NO \\
N + O_2 &\leftrightarrow O + NO
\end{align*}

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

\[ N + OH \leftrightarrow H + NO \]

Thermal NO\textsubscript{x} contributes the largest portion to the total NO\textsubscript{x} produced.

Fuel NO\textsubscript{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\textsubscript{3}, NH\textsubscript{2}, NH, CN etc. this will further facilitate oxidation of fuel bound nitrogen compound to form nitric oxide rapidly \cite{5}. In spark ignition engines there is normally negligible fuel bond nitrogen.

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

Prompt NO\textsubscript{x} forms in the flame zone, the breakdown of hydrocarbon fragments (C, CH, CH\textsubscript{2}) may react with atmospheric nitrogen and their subsequent combination to produce other nitrogen species such as (CN, HCN, H\textsubscript{2}CN and NH) under fuel rich condition. In prompt NO\textsubscript{x} formation, the focus area is flame front and the regions near it.

1.1.1 NO\textsubscript{x} Control Techniques

Pre and post combustion NO\textsubscript{x} control techniques are most promising in the engine with premixed and non premixed combustion. Combustion modification methods are also effective in abating NO\textsubscript{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\textsubscript{x}. Between 5 and 10% EGR is likely to halve NO\textsubscript{x} emissions. However EGR can lower the efficiency at full load and reduces the lean combustion limit.

Pre-combustion NO\textsubscript{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\textsubscript{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 \cite{6}.

It may be mentioned here that combustion modification and pre combustion NO\textsubscript{x} control techniques although provide significant NO\textsubscript{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\textsubscript{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\textsubscript{x} (using ammonia)
- RAPRE NO\textsubscript{x} (using Cyanuric acid)
- NO\textsubscript{x} Out (using urea)

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

2. Thermal DeNO\textsubscript{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 %.


3.1 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% CH₄, 60% HFO). The cylinder pressure is 150 kg/cm², bore = 320 mm, stroke = 420mm, compression ratio = 14.1, r.p.m = 600.

The flow rate of fuel (CH₄ + HFO) is 550.662 m³/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:

\[ \text{NO}_x = 1470 \text{ ppm, CO} = 1808 \text{ ppm} \] and
\[ \text{Excess air} = 160\% \]

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 NOₓ 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 NOₓ removal indicate that the optimum temperature at which considerable NOₓ removal may be achieved is a window from 700 °C to 900 °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>
<thead>
<tr>
<th>Temp °C</th>
<th>% reduction in NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>18.36</td>
</tr>
<tr>
<td>750</td>
<td>44.625</td>
</tr>
<tr>
<td>800</td>
<td>96.55</td>
</tr>
<tr>
<td>850</td>
<td>92.51</td>
</tr>
<tr>
<td>900</td>
<td>86.8</td>
</tr>
</tbody>
</table>

Table 1: % removal of NO at different temperatures
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 \([\text{NH}_3/\text{NO}]\) 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 NOx reduction at optimum molar ratio is 96.21%

Table 2: Data for finding optimum residence time

<table>
<thead>
<tr>
<th>Residence Time</th>
<th>Percentage Reduction in NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>27.21</td>
</tr>
<tr>
<td>0.5</td>
<td>42.38</td>
</tr>
<tr>
<td>0.75</td>
<td>52.45</td>
</tr>
<tr>
<td>1</td>
<td>60.06</td>
</tr>
<tr>
<td>1.25</td>
<td>66.32</td>
</tr>
<tr>
<td>1.5</td>
<td>71.7</td>
</tr>
<tr>
<td>1.75</td>
<td>76.59</td>
</tr>
<tr>
<td>2</td>
<td>81.36</td>
</tr>
<tr>
<td>2.25</td>
<td>86.59</td>
</tr>
<tr>
<td>2.5</td>
<td>96.21</td>
</tr>
<tr>
<td>2.75</td>
<td>96.44</td>
</tr>
<tr>
<td>3</td>
<td>96.55</td>
</tr>
</tbody>
</table>

Table 3: Data for finding optimum molar ratio

<table>
<thead>
<tr>
<th>Molar ratio ((\text{NH}_3/\text{NO}))</th>
<th>%age Reduction in NO</th>
<th>Molar ratio ((\text{NH}_3/\text{NO}))</th>
<th>%age Reduction in NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>26.53</td>
<td>1.25</td>
<td>80.61</td>
</tr>
<tr>
<td>0.5</td>
<td>52.45</td>
<td>1.5</td>
<td>77.61</td>
</tr>
<tr>
<td>0.75</td>
<td>77.41</td>
<td>1.75</td>
<td>76.26</td>
</tr>
<tr>
<td>1</td>
<td>96.21</td>
<td>2</td>
<td>75.51</td>
</tr>
</tbody>
</table>
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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\textsubscript{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 into which the engine out exhaust gases are fed and the gases are uniformly heated there by some heating mechanism to 800°C and Ammonia is injected at a molar ratio (NH\textsubscript{3} /NO) of about 1.0 and the gases remain in reactor for 2.5 seconds to complete the reaction.

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3- Dr. Lodhi Chief Chemist JICA Islamabad.

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