The Selective Non Catalytic Reduction And
Selective Catalytic Reduction Of
$\text{NO}_x$: A Critical Review And Experimental Investigations

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ABSTRACT

In this paper, the applicability of selective non catalytic reduction and
selective catalytic reduction processes has been compared. The effect of
oxidation catalyst i.e. catalytic converter on emissions like HC, CO, NO$_x$
on a single cylinder diesel engine has been investigated. Three major
SNCR processes for removal of oxides of nitrogen from engine exhaust
gases are compared with SCR process. The three SNCR processes are
similar each uses a different chemical agent ammonia, urea and cyanuric
acid and were found to be most effective at low, intermediate and high
concentrations of oxygen respectively. The implications of these results
for a single cylinder 500cc diesel engine are discussed.

INTRODUCTION

Global air pollution is a serious problem. Much
of this pollution is caused by the use of fossil fuels
used for transportation. There is an urgent need for
suitable alternative fuels for use in diesel engines. In
view of this, biodiesel is a promising alternative be-
cause it is renewable, environmental friendly and pro-
duced easily in rural areas. The main driving forces
behind implementation of these bio-fuels in the coun-
try are rural economy, energy self-sufficiency and en-
vironmental concern. It is evident that there are vari-
ous problems associated with biodiesel oil being used
as CI engine fuel compared with conventional diesel
diesel. Biodiesel blends show lower carbon monoxide
but higher oxides of nitrogen emission. Various tech-
Techniques are available at this end to reduce the oxides of nitrogen emission from conventional diesel fuelled vehicles. These methods of reducing the emission of oxides of nitrogen are termed as post combustion gas treatment. In general SNCR processes involve injecting one or more chemical agents downstream of primary combustion zone\(^3\). SNCR is effective over a narrow temperature range. Reduction at higher temperatures is poor because the reducing agent itself oxidizes to NO\(_x\).

**The three main SNCR (selective non catalytic reduction) processes are**

**The ammonia process**

This was the original SNCR process and has been named thermal DeNO\(_x\). In this, ammonia is injected into hot exhaust gas. The form of ammonia may be aqueous solution or anhydrous ammonia. The specific concerns with ammonia process include storage, handling and delivery of the ammonia. For these reasons alternative agents have been proposed over the years\(^3\).

**The urea process**

NO\(_x\) out is the name of the process, which uses urea. Typically either solid urea or a urea solution with water is injected into the hot exhaust gases. Urea may decompose into HNCO and NH\(_3\) under certain conditions.

**The cyanuric acid process**

In this process, solid cyanuric acid is injected into hot exhaust gases. The solid cyanuric acid sublimes at about 377\(^\circ\)C to gaseous isocyanic acid initiates a series of reactions, which result in the removal of oxides of nitrogen.

**The SCR process**

An oxidation catalyst enables and accelerates the chemical conversion of HC, CO and NO\(_x\) to CO\(_2\), H\(_2\)O and N\(_2\) at temperatures well below that at which it would occur spontaneously. The oxidation of HC, CO is facilitated by completing the combustion process, nitrogen oxides are catalytically reduced. The catalysts consist of ceramic/metallc Materials coated with precious metals. For better conversion efficiency, it is necessary to have a very careful control of concentrations of all the gases on catalytic surface. Therefore these systems require a fuel injection system capable of maintaining precise control of fuel to air ratios under all driving conditions. The objectives of this work are:

1. To compare the emission reduction performance of SNCR and SCR processes by using single cylinder diesel engine\(^10\).
2. To review the possibilities of using these techniques for biodiesel fuelled diesel engines\(^6\).

**EXPERIMENTAL**

The data discussed below has been obtained from similar experimental systems\(^3\). The overall experimental facility consists of four distinct systems.

1) The input gas mixture metering and delivering system.
2) The chemical agent metering and delivering system.
3) Reactor assembly
4) The output gas mixture analysis

**Input gas mixture**

In these experiments, the exhaust gas was simulated by using bottle gases. Comparisons with the use of actual exhaust have demonstrated that the use of simulated exhaust gas is an effective technique. The advantages of simulated exhaust include that the input gas stream is well characterized, is not subject to transient variations, and is not limited to a relatively narrow range of compositions.

Mass flow controllers are used to insure accurate metering of individual gases. The individual gas streams are combined and the mixture enters the reactor.

**Metering and delivery of chemical agent**

The mode of delivery of chemical agent to the simulated exhaust stream is mainly dependent on the phase of agent. For ammonia gas, the delivery is straightforward and same as delivery of other gases. For urea as a solution with water, the solution is fed into the exhaust stream by the use of syringe, which is advanced at a controlled rate using precision stepper motor. Urea solution vaporizes before it enters to the reactor. Cyanuric acid is not soluble in water to any appreciable degree. It must be utilized as a
Figure 1: Schematic of experimental system.

Figure 2: The ratio of outlet NO\textsubscript{x} to inlet NO\textsubscript{x} as function of reactor temperature for 15% using urea.
Solid powder. The cyanuric acid is carefully packed into a syringe, which is advanced at a controlled rate using a precision stepper motor. The cyanuric acid powder sublimes to vapor before it enters the reactor.

The reactor is constructed with quartz tube to minimize any catalytic reactions that might occur with steel or other metal reactors.

**Experimental Conditions**

The typical temperature range examined is between 378°C and 1077°C. The typical range of inlet oxygen concentration is 0% to 15%.[3]

**Experimental results and discussions**

The oxides of nitrogen removal is often defined as $\text{NO}_x\text{ removal} = 1 - \frac{\text{NO}_x\text{Out}}{\text{NO}_x\text{In}}$.

Figure 2 shows that the removal of oxides of nitrogen is not significant for temperature below 680°C. For oxygen concentration 5-15% it becomes significant for temperatures above 780°C. As the gas temperature increases above 875°C the removal of oxides of nitrogen decreases. Maximum removal is achieved up to 75% when oxygen concentration is about 15%. Then as the oxygen concentrations increase above this value i.e. 2%; the removal is different at different temperatures.

For further increases in the oxygen concentration, the removal decreases somewhat, but is still typically above about 75%. Clearly, the effect of oxygen concentrations is important.

Figure 3 shows the effect of oxygen concentration on removal of oxides of nitrogen for the three processes. For urea process the removal level decreases from 0% to 90% as oxygen concentration increases from 0 to 5%.

For ammonia process the removal level decreases from 0 to over 95% as oxygen concentration increases from 0 to 1%. Cyanuric acid process removal of oxides of nitrogen increases rapidly as oxygen concentration increases from 0 to 2%. The maximum overall removal of oxides of nitrogen using cyanuric acid is obtained for 12% oxygen.

The catalytic converter used is having metallic base and coated with 5 grams per cubic feet of precious metals[10]. The emission test with 5 gm/cuft of noble metals like platinum and palladium used as oxidation catalyst gives us 82% reduction in CO emission, 37% reduction in HC emission, & 1% reduction in NOx emission, 46% reduction in PM emission.

**Discussion of the key reactions**

A common characteristic of these SNCR processes is the production of radicals, which is necessary so that the overall reaction mechanism is self-sustaining[6]. Reaction steps responsible for generation of radicals are

$$\text{H} + \text{O}_2 = \text{OH} + \text{O}$$

$$\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$$

**Ammonia process**

The ammonia process begins with the breakdown of ammonia to NH$_2$ by O and OH radicals. The process continues with the following reactions to remove oxides of nitrogen.

$$\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$$
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NH₂ + NO = NNH +OH

Cyanuric acid process

The HNCO converts into NCO and NH₂ by the following reactions.

H + HNCO = NH₂ + CO
H + HNCO = NCO + H₂O
OH + HNCO = NCO + H₂O
OH + HNCO = NH₂ + CO₂

The formation of NCO and NH₂ then results in the following,

NCO + NO = N₂O + CO
NH₂ + NO = NNH +OH
NH₂ + NO = N₂ +H₂O

These three reactions are the key oxides of nitrogen removal steps.

Urea process

Depending on the products of urea decomposition, the urea process may be divided into the above cases on proportion to the specific concentrations of the products of decomposition.

SCR process

There are five reactions that are important:

CO+1/2O₂=CO₂
HC+O₂=H₂O+CO₂
H₂O+ 1/2 O₂= H₂O + O
NO+CO= 1/2N₂+ CO₂
NO+H₂= 1/2N₂+H₂O

The desired products are N₂, CO₂, H₂O. The overall conversion is determined not only by activity of the catalysts but also by availability of oxidation and reducing agents.

Implications to engine exhaust

The composition of engine exhaust will be different for different applications. For engine designs based on rich air-fuel ratio such that the exhaust has more than 10% oxygen, the use of cyanuric acid may be more effective. For other engines, which operate at or near stoichiometric operation, the use of ammonia may be more effective. And for engines operating on lean air fuel ratio, urea process may be the most effective of the four possible candidates.

CONCLUSION

This paper has compared three SNCR processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Temperature (°C)</th>
<th>Oxygen %</th>
<th>NOₓ reduction %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia process</td>
<td>877</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>Cyanuric acid process</td>
<td>927</td>
<td>15</td>
<td>95</td>
</tr>
<tr>
<td>Urea process</td>
<td>877</td>
<td>15</td>
<td>85</td>
</tr>
<tr>
<td>Oxidation catalyst</td>
<td>452</td>
<td>15</td>
<td>01</td>
</tr>
</tbody>
</table>
for removal of oxides of nitrogen using ammonia, urea and cyanuric acid and SCR (oxidation catalyst). The three SNCR processes share a common characteristic such as the processes require some minimum amount of oxygen. The processes are optimal for a narrow temperature range (878°C to 930°C). The processes do not require additional fuel or other substances to proceed. Each process has unique features and each of these processes is most effective for specific conditions. In particular the processes are most effective for different oxygen concentrations.

The ammonia process is most effective for low oxygen concentrations and the cyanuric acid process is most effective for high oxygen concentrations. The urea process is most effective for intermediate values of oxygen concentrations. SCR process is more effective for removal of HC and CO and negligible NOX removal is achieved.

From above discussions it is clear that the cyanuric acid process would be expected to be more effective for applications with higher air-fuel ratio operation such as diesel engines. By combining SCR with cyanuric acid process better removal of HC, CO and NOX is possible. EGR is also helpful in reducing harmful emissions from exhaust along with SCR and cyanuric acid process. From emission point of view biodiesel fuelled diesel engines produces more NOX as compared with conventional diesel fuelled engines. This combination can be effectively used for reducing NOX emission from biodiesel-fuelled diesel engines.

REFERENCES


