Study of No_x Treatment with Selective Catalytic Reduction and Diesel Exhaust Fluid with Emphasis on Importance of Mixer in Flow

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Abstract This paper deals with chemical reactions of nitrogen oxide formation at higher temperatures, when the stable nitrogen disintegrates and forms unstable compounds. It discusses the effect of the unstable nitrogen compounds on human health and environment. To meet Bharat Stage VI norms, which will be implemented in the year 2020, NOx reduction techniques such as alteration in engine operation, changes in engine design, alteration in fuel, after treatment of exhaust have been discussed. Focus on after treatment of exhaust gas, by use of selective catalytic reduction, with problems of urea decomposition, and the effect of further higher temperature on urea was given. Properties of diesel exhaust fluid and factors affecting NO_X reduction such as droplet size, droplet behaviour, urea decomposition, urea deposits, injector positions, vaporization rate, and mixer designs are also discussed. Test method to obtain the best dynamic or static mixture increasing the urea exhaust mixing for better ammonia formation and NOx reduction was also carried out.

Keywords NOx · Emission · SCR · Urea · NH_3 · BS VI

1 Introduction

Engines in which combustion is initialized by compression of diesel fuel are diesel engines, and in these engines, fuel–air mixture is used which on compression absorbs necessary amount of energy so that the fuel can ignite. When surplus air is abounding via a turbocharged intercooled intake method, while the temperature in the combustion chamber is high, nitrogen in the intake air reacts according to the

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Table 1 Nitrogen oxides (NO_X)

Formula	Name	Nitrogen valence	Properties
N_2O	Nitrous oxide	1	Colourless gas, water soluble
NO, N_2O_2	Nitric oxide, dinitrogen dioxide	2	Colourless gas, slightly water soluble
N_2O_3	Dinitrogen trioxide	3	Black solid water soluble, decomposes in water
NO_2	Nitrogen dioxide, dinitrogen tetroxide	4	Red-brown gas very water soluble, decomposes in water
N_2O_5	Dinitrogen pentaoxide	5	White solid very water soluble, decomposes in water

extensive Zeldovich's mechanism [1], and the reactions are as follows.

$$\begin{aligned} O + N_2 &= NO + N \\ N + O_2 &= NO + O \\ N + OH &= NO + H \end{aligned} \tag{1}$$

Formation of NO_X: Continuation of nitrogen in the atmosphere is in the structure of N_2 (di-atomic modulus of nitrogen), a extremely stable state. For the duration of combustion, temperature reaches 800–1000 °C within the cylinder. At this elevated temperature, the di-atomic particle nitrogen N_2 into mono-atomic nitrogen which is extremely reactive. This mono-atomic nitrogen (N) reacts with the oxygen which is previously present in the cylinder and forms oxides of nitrogen. Oxides of nitrogen usually occur in the structure of NO and NO_2. These are normally created at high temperature. Elevated temperature and accessibility of free oxygen are the main two reasons for the development of NO and NO_2. Many other nitrogen oxides like N_2O_4, N_2O, N_2O_3, and N_2O_5 also created in low concentration, but they decompose impulsively at ambient circumstances of NO_2 [2] (Table 1).

When the combustion temperature is high nitrogen compound which is N_2 gas that disintegrates into free radical of nitrogen which is highly reactive, the present technology offers us to inject inferior quality of air in which the content of oxygen will be less. In simple terms, it is the exhaust gas recirculated into the intake manifold now this exhaust gas is first food so that the heat energy within the exhaust gas does not add up the combustion temperature. Generally, the set-up is called EGR which stands for exhaust gas recirculation, a simple working can be understood why as a part of the exhaust is taken back via exhaust gas recirculation set-up which calculates the amount of NO_X generated or the temperature in the combustion chamber. Its calculations of amount of EGR of the exhaust which has to be injected are free calculated while engine designs are fed into electronic control unit. Amount of exhaust is injected into the intake manifold, and as the fresh charge is blended with exhaust gases which are not rich in oxygen, the combustion temperature reduces and the possibility of NO_X formation also reduced. On the other hand, because of this interior combustion the amount generated will be high so basically is a trade-off NO_X formation and hydrocarbon.

1.1 Effect on Health

Unstable compounds of nitrogen are very toxic to human. Because of the high temperature of the combustion chamber and uncontrolled combustion please free radicals even after the implementation of BS VI there is a huge lot of improvement required to reduce the NO_X emission. Compounds of nitrogen are an NO_2 decrease in human immunity. Compounds of nitrogen can cause acid rain acidification of soil and other undesired chemical reactions even formation of HNO_3 [3].

Acidification of water will reduce availability of water for drinking, and also, it will affect the marine life the possibility of acid rain as these are unstable compounds and will react with oxygen and hydrogen at a higher extent. Because the uncontrolled NO_X formation certain results have been seen in the past some of them have been seen in Delhi see and around cities where there is formation of smog and there have been reports of acid rain in Agra [4]. There are also reports of landlocked lakes being converted into acid ponds because of acid of rain. With the introduction of BS VI, there are norms which state for the reduction in rock formation per kilometre, complete combustion is highly desired for a better fuel economy higher temperatures are needed, but on the other hand, they will be NO_X formation if the compression temperature goes high for this there is a introduction of after treatment setup which is SCR + D e f, which stands for selective catalytic reactor + diesel exhaust fluid this has to be implemented by all the Companies selling vehicles in India by April 2020 further details are discussed below.

1.2 Emission Regulation for Bharat Stage VI

BS VI emission standard adds for MNN class vehicle which has gross vehicle weight GVW you not more than 3.5 turn for 1 April 2020, as per GSR 889 dated 16 September 2016 [5] (Tables 2, 3 and 4).

There are many techniques which are tried to organize NO_x emission from diesel engine. The subsequent methods may be employed whichever as a single technique or as a grouping.

1. Alteration of engine operations
2. Changes in the engine design
3. Alteration of fuels
4. After treatment of exhaust gases.

Table 2 Bharat stage VI emission standards

		Reference mass (kg)	Mass of carbon monoxide (CO)	Mass of total hydrocarbons (THC)	Mass of non-methane hydrocarbons (NMHC)	Mass of oxides of nitrogen (NO_x)	Combined mass of hydrocarbons an oxides of nitrogen (THC = NO_x)
			mg/km	mg/km	mg/km	mg/km	mg/km
Category	Class		CI	CI	CI	CI	CI
M_1 and M_2	–	All	500	–	–	80	170
N_1	II	1305 < RM ≤ 1760	630	–	–	105	195
	III	1760 < RM	740	–	–	125	215
N_2	–	All	740	–	–	125	215

CI Compression ignition

Table 3 OBD 1 BS6 [9]

		Reference mass (kg)	Mass of carbon monoxide (CO)	Mass of non-methane hydrocarbons (NMHC)	Mass of oxides of nitrogen (NOx)
			mg/km	mg/km	mg/km
Category	Class		CI	CI	CI
M_1 and M_2	–	All	1750	290	180
N_1	II	1305 < RM ≤ 1760	2200	320	220
	III	1760 < RM	2500	350	280
N_2	–	All	2500	350	280

CI Compression ignition

Table 4 OBD 2 BS6

		Reference mass (Kg)	Mass of carbon monoxide (CO)	Mass of non-methane hydrocarbons (NMHC)	Mass of oxides of nitrogen (NOx)
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	III	1760 < RM	2500	350	220
N_2	–	All	2500	350	220

CI Compression ignition

2 After Treatment of Exhaust Gases

A. **Selective catalytic reduction SCR**:

It is the after treatment attachment which is generally placed doc. In this set-up, urea is injected which because of high-temperature exhaust converts into ammonia gas; this ammonia gas mixes with exhaust gases which have NO_X in it, and then, these mixtures of ammonia and exhaust move to SCR where uh generally of vanadium catalyst with the largest surface area is placed the nitrogen within the ammonia gas that reacts with unstable NO_X compounds and forms nitrogen. The quantity exhaust fluid varies with the formation of NO_X. It is well understood that the ammonia which is already present in it on the SCR which reacts with NO_X, and not the current ammonia which is injected. The injector injects the aqueous urea which is water + urea at a higher pressure in small droplet form with the flow of the exhaust. The temperature of the exhaust helps the urea to get convert into ammonia gas [6].

B. **Urea decomposition**:

DEF is a solution of water and urea generally with 32.5% of urea and 67.5 water buy weight. The formula of urea is the formula of urea is CO (NH_2). This is used because of its ability to disintegrate into ammonia. This solution is injected via injector with the flow of the exhaust in the exhaust pipe before the SCR. First because of the heat the urea and water solution evaporates and ammonia and isocyanic acid are formed further, and because of vapours of water, this isocyanic acid converts into ammonia and carbon dioxide.

$$CO(NH_2)_2 + \text{Heat} \rightarrow NH_3 + HNCO \tag{2}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{3}$$

C. **NO_X Reaction with NH_3**:

Now, we will see NO_X reaction with ammonia, and these reactions happen on the surface of catalyst which is in the SCR. Ammonia reacts with nitrogen oxide and nitrogen dioxide to form nitrogen gas and water for the ammonia reacts with nitrogen oxide + oxygen which will give again nitrogen and water, this reaction keeps on happening till there is no more nitrogen oxide available, and still, there is ammonia are also available in which the reactions are stated below; these reactions are all endothermic which means they need heat energy to react because a wedge, a catalyst, is required [7].

$$\begin{aligned} &2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \\ &4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \\ &8NH_3 + 6NO_2 + O_2 \rightarrow 7N_2 + 12H_2O \\ &4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \end{aligned} \tag{4}$$

At higher temperatures, these unwanted reactions occur.

$$\begin{aligned} &4NH_3 + 4NO + 3O_2 = 4N_2O + 6H_2O \\ &4NH_3 + 5O_2 = 4NO + 6H_2O \end{aligned} \tag{5}$$

3 DEF/Ad Blue Specification

See Table 5.

- **Factors Affecting NO*x* Reduction**:

Table 5 Diesel exhaust fluid data [10]

Urea % by weight	31.8–33.2
Alkalinity as NH_3% by weight maximum	0.2
Biuret % by weight maximum	0.3
Insoluble, ppm maximum	20
Aldehyde, ppm maximum	5
Phosphate PO_4, ppm maximum	0.5
Aluminium, ppm maximum	0.5
Calcium, ppm maximum	0.5
Iron, ppm maximum	0.5
Copper, ppm maximum	0.2
Zinc, ppm maximum	0.2
Chromium, ppm maximum	0.2
Nickel, ppm maximum	0.2
Magnesium, ppm maximum	0.5
Sodium, ppm maximum	0.5
Potassium, ppm maximum	0.5
Density at 68 °F (20 °C), lbs/gal	9.07–9.12
Refractive index at 68 °F (20 °C)	1.3814–1.3843
Salt-out temperature, °F (°C)	12(−11)
Recommended storage temperature, °F(°C)	40–80 (4.5–26.6)

1. Droplet behaviour—In gas phase disintegrate of a dewdrop is by shear stress and vaporization. On the surface, break-up is by impingement, liquid film vaporization, sometimes deposits are formed.

- Urea deposit, decomposition of DEF, a common problem, has been seen in urea injection, which is the position of urea as white matter inside the exhaust pipe [8]. This position of urea clogs the pipe an increase back pressure this happens when there is improper injection hydrolysis evaporation of urea, sometimes it also happens because of very high temperatures in which isocyanic acid does not form any further ammonia but forms amides torrent melamine and other deposits.

$$\begin{aligned}
&CO(NH_2)_2 + HNCO \rightarrow NH(CONH_2)_2 \\
&NH(CONH_2)_2 + HNCO \rightarrow \text{Triuret} \\
&3HNCO \rightarrow C_3N_3(OH)_3 \\
&NH(CONH_2)_2 + C_3N_3(OH)_3 \rightarrow \text{Ammeline} + 2H_2O \\
&NH(CONH_2)_2 + C_3N_3(OH)_3 \rightarrow \text{Ammelide} + H_2O
\end{aligned} \tag{6}$$

2 Enhance mixing of spray and exhaust gases and evenly distributing the mixture on the SCR catalyst.

- The conventional approach results in having one fixed mixer orientation angle for the entire operating range of engine and can be valid for smaller engines operating with limited exhaust mass flow and temperatures. However, for bigger engines with wider range of mass flow and temperature, there is a compromise for the mixer orientation angle. This can result in higher or lower spray load on the mixer over the entire operating range, thereby leading to issues like deposition, incomplete utilization of urea solution, etc. Proposed idea is to use the exhaust brake flap as a mixing enhancer of NH_3 + exhaust gas, the system is to be tested with different projection on the plate via CFD analysis.

3 Orientation of injector—the urea injector can be oriented with the flow or against the flow we can also use a static mixer or a dynamic mixer, usually we are using a static mixture, and in this case, we can also use a dynamic mixture. A dynamic mixture can be explained in a better way with the help of the last diagram. Here in the diagram, we can see that exhaust brake flap is welded with fins over it when the exhaust brake is switched off, the flap is in open condition and there is a very less back pressure created in this situation, and the friends over the flap help in better mixture of urea and exhaust gas.

Now, we will see what will happen if the injector is placed against the flow when the injector is placed against the flow, the urea is injected against the flow of the exhaust gas. Now in this case, there is a possibility of reducing the length of the mixture which is required to form ammonia exhaust mixture. The working can be understood why the following steps are. Step 1—a constant flow exhaust will be flowing. Step 2—urea will be injected against the floor after detecting the NO_X formation, and in this case, the urea will evaporate and will convert into ammonia gas which will then move to SCR. Problem in this case is that DEF contains urea and water.

- **Analysis Result** (Fig. 1):

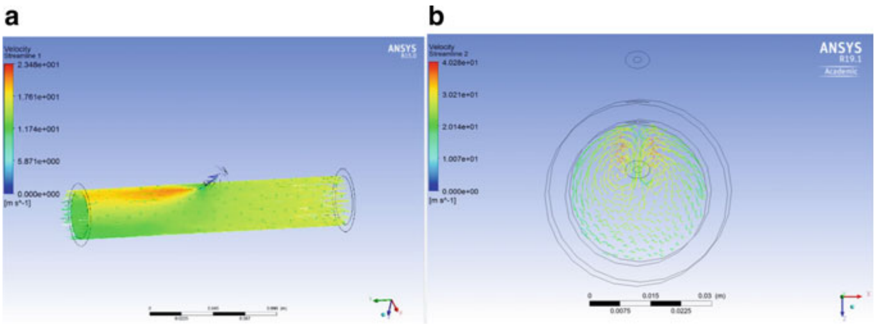

Fig. 1 **a** Injection of urea and which flows without mixing with exhaust. **b** Cross-sectional view of exhaust pipe after injection of urea into exhaust flow, and figure shows the minimal turbulence created. Low turbulence reduces the uniformity index (which defines the quality of mixture)

4 Conclusion

From the group study of the paper, a conclusion can be drawn that NO_X is a harmful by-product of exhaust, as we need complete combustion of a fuel, the temperature increases because of which stable nitrogen reacts. This unstable state of nitrogen compound reacts in the form of acid rain and also affects the human immunity system. Emission regulations in Bharat Stage IV were stringent, but with the introduction of Bharat Stage VI norms, the production of NO_X per kilometre should further be reduced. This will come in action from 1 April 2020. There are many after treatment methods such as exhaust gas recirculation, but it is a trade-off between carbon and nitrogen unstable compounds. With the introduction of selective catalytic reduction + diesel exhaust fluid which is also known as Ad blue NO_X can be reduced. Further, it is discussed the orientation of the injector, and the use of static and dynamic mixer is also discussed. Closing the conclusion can be made in a way that dynamic mixture which is the exhaust brake flap mounted fins, this future ahead as the orientation of the flap can be changed with the changing velocity of the exhaust and a better exhaust urea mixture can be obtained which will completely eliminate reduces the NO*x* coming out of the exhaust.

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