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Reduction of No_x emissions in Diesel engines by selective Catalytic reduction using Dual Layer Catalyst configurations

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ABSTRACT

NO_X denotes NO and NO_2, it is one of the primary emissions in diesel engines. NO_x is primarily formed due to the high in cylinder temperatures. It causes a variety of respiratory illness in humans. The future emission norms demand a strict reduction of the NO_x levels from the vehicle exhaust. Selective catalytic reduction (SCR) is the most effective technique adopted to reduce engine NO_X emissions. SCR employs the usage of a reducing agent, ammonia over a catalytic surface to reduce NO_x emissions. SCR has certain drawbacks; the light off temperatures for the catalyst to become active is not reached during cold start conditions, at such conditions the injected ammonia passes unreacted into the exhaust. Ammonia has to be stored in a separate tank. The catalysts also lack thermal durability and are prone to poisoning by the exhaust species. This work introduces a dual layer configuration of CuZ and FeZ catalysts which are known to have good NO_X conversion individually at low and high temperatures respectively. Using a dual layer configuration allows us to have the advantages of both the catalysts and improves the NO_x conversion of SCR over a wide temperature range. In the observed results there was a good NO_X conversion of over 84% at moderate temperatures. There was a 20% NO_X conversion efficiency in cold start conditions.

KEY WORDS: SCR, NO_X, Dual Catalyst, CuZ, FeZ, Catalyst.

1. INTRODUCTION

NO_x is the collective term for mono nitrogen oxides such as NO, NO_2, NO_3, etc. NO_X is one of the three primary emissions from automobile engines and is more prominent in case of CI engines. NO_X is primarily formed due to an endothermic reaction between nitrogen and oxygen in the fuel air mixture, with the presence of high temperature. The NO_X can be divided into three types based on the sources a) Thermal NO_x - formed due to high temperature oxidation of atmospheric nitrogen found in the combustion air. Thermal NO_X depends on the residence time of nitrogen in that specific temperature and is prominent over 1100°C. The primary reactions for thermal NO_x were given by Zeldovich. The Zelodvich reactions for NO_X formation are given below

$$O + N_2 \rightarrow NO + N$$
$$N + O_2 \rightarrow NO + O$$
$$N + OH \rightarrow NO + H$$

b) Fuel NO_x is formed due to the presence of nitrogen radicals in fuels. It is very common in coal fuelled power plants. Fuel NO_x from coal contributes to about 80% of total Fuel NO_x c) Prompt NO_X - It is not dependent on the flame temperature. Near the flame zone some O and OH radicals enhance the NO_x formation.

95% of the NO_X emitted from diesel engines is said to be NO. NO is said to be a colorless gas, while NO_2 is said to be a reddish brown gas. They are said to undergo photochemical reactions to produce smog. The emission standards for diesel engine are getting stricter with every passing year. The Euro 6 standards have set a limit of 0.170 g/Km for LCV's of NO_X in comparison to 0.230 of Euro 5b, which is a 26% reduction. Currently Lean NOx traps (LNT), EGR (Exhaust Gas Recirculation) and Selective Catalytic Reduction (SCR) are some of the NO_x control techniques used. LNT makes use of PGM group metals Platinum, Palladium, thus making it expensive. EGR at higher circulation rates causes a loss of power and mileage, SCR on the other hand is comparatively cheaper. NO_x is reduced in SCR by using a reducing agent over a catalytic surface .The conventional reducing agent used as an ammonia source is AdBlue, which is a solution of 32.5% of Urea mixed with water. About 90 % of NO_X is reduced using Urea SCR. During cold start conditions, the NO_x conversion is said to be very poor, the reason behind this being, insufficient temperature at the tailpipe for the reaction between NH_3 and NO_x to occur. During such conditions the usage of urea has certain drawbacks such as having a freezing point of -11°C and solid deposit formation in the exhaust pipe at temperatures below 200°C. Urea requires a separate tank for storage and it has to be refilled over a 1200 km range based on the storage capacity. Currently Platinum, Zeolite, Vanadium, Titanium based materials are being used as catalysts for the SCR process. Some of these materials are precious and are expensive and the others have thermal durability issues. The catalyst materials are prone to thermal ageing and poisoning by a variety of species in the exhaust gas, which reduces its effectiveness. Since the catalyst and the reducing agent are the two primary constituents of the SCR system, alternative and more effective means are being researched in them

Catalyst selection: Catalysts are a vital part of an SCR system. The reduction reaction between Ammonia and NO_X ,which takes place around 870°C- 1200°C in SNCR is made to occur in the temperature range of 165°C-

600°C in the presence of an catalyst. The temperature at which the reaction occurs is determined by the choice of catalyst used.

Commercially Vanadium based catalysts are used to achieve the Euro norms, these catalysts are said to be effective in a temperature ranges of 300-450°C and are resistant to sulfur poisoning. V_2O_5 a toxic compound is formed from these catalysts at temperature range of 600ºC. They also have a high catalyzing potential to oxidize SO_2 into SO_3. In DPF and SCR configurations, the active regeneration of DPF involving high temperatures will deactivate this catalyst. Barium, Cerium, Terbium, Zirconium and erbium can be added to Vanadium to stabilize the catalyst, Guan.

Castagnola (2011), did extensive research on Cu and Fe SCR and gave the below findings. Copper Zeolite based catalysts are proved to have very good low temperature NO_X conversion efficiency (around 95%) especially below 350°C. It demonstrates excellent $DeNO_X$ efficiency with low NO_2/NO_X ratios. NSC (Nitrogen Storage capacity) for CuZ catalyst is said to be high, which is the reason for its superior activity at lower temperatures. However high surface oxidation ability of CuZ, SCR can lead to unwanted oxidation of NH_3 at higher temperatures and thus reduce the $DeNO_X$ efficiency over 400°C. Effect of SO_2 poisoning on CuZ was more prominent in lower temperatures than those at higher temperatures

Iron Zeolite based catalysts show better NO_X conversion over 400°C. It is more resistant to sulfur poisoning than CuZ, presence of NO_2 accelerates the NO_X conversion on FeZ catalyst especially at lower temperatures. FeZ also is effective in decomposition and reduction of N_2O into N_2. FeZ is susceptible to HC poisoning but can be regenerated at elevated temperatures.

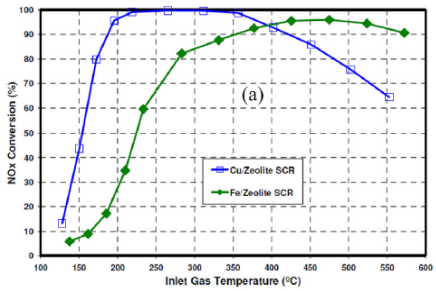

Figure.1. DeNox characteristics of CuZ and FeZ

Research work carried out by Pranit (2011), investigated the effect of various configurations of CuZ and FeZ catalysts on the NO_X conversion efficiency .Three different types of configurations namely

- "Sequential brick" catalyst comprising Fe-zeolite and Cu-zeolite monolith.
- "Mixed wash coat" catalyst comprising a wash coat layer having equal mass fractions of Fe- and Cu zeolites.
- "Dual layer" catalyst comprising monolith coated with individual layers of Fe- and Cu-zeolites of different thicknesses and mass fractions.

It was found that out of the three configurations, the sequential brick design with Fe-zeolite brick followed by a Cu-zeolite brick gave a higher conversion than the Cu/Fe sequence of equal loadings. Fe (33%)/Cu (67%) achieved the highest NOx conversion over a wide range of temperatures. The mixed wash coat catalyst achieved NO_x conversion that was nearly an average of the individual Fe-only and Cu-only catalysts. The dual layer catalyst with a thin Fe-zeolite (33% of the total wash coat loading) layer on top of a thicker Cu-zeolite layer (67%) resulted in very high NOx removal efficiencies over a wide temperature range for both the standard and fast SCR reactions. The performance of this dual-layer system was comparable to the series arrangement of Fe and Cu-bricks. An assessment of the extent of wash coat diffusion limitations shows that the dual layer configuration is superior to the sequential brick configuration. So this dual layer configuration with (33% of FeZ over 67% of CuZ) has been selected and implemented in this work.

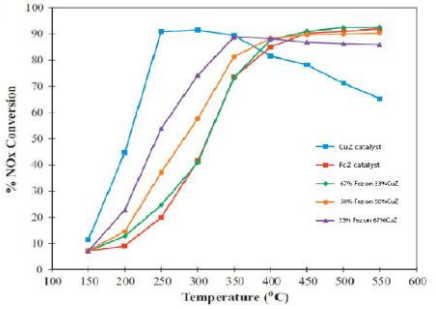

Figure.2. Comparison of NO_X conversion of various CuZ and FeZ configurations

Table.1. Catalyst Details

Substrate	Catalyst	Cell density	Dimension
Cordierite	67% Cuz on 33% FeZ	400cspi	5.67'' x 9''

Experimental Setup:

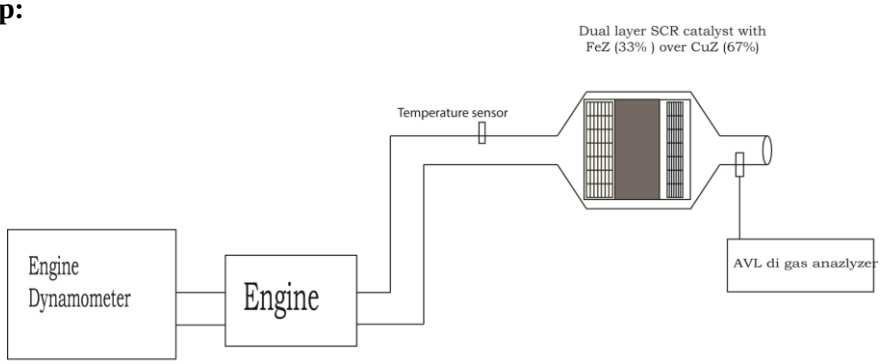

Figure.3. Schematic diagram of Experimental set up

Table.2. Details of engine used to carry out the tests

Manufacturer	Kirloskar oil engines ltd
Cylinder bore	80 mm
Stroke	110 mm
Rated Speed	1500 rpm
Compression ratio	17:1
Number of cylinders	1
Cubic Capacity	552 cc
Injection system type	Direct injection
Injection pressure	200 bars
Injection angle	23^{O} BTDC
Rated Power	3.7Kw
Cooling fluid	Water

2. EXPERIMENTAL TEST PROCEDURE

A single cylinder naturally aspirated diesel engine was used to carry out the experiment. An eddy current dynamometer has been connected to the engine, through which a range of loads can be applied. The exhaust temperature was measured by a K type thermocouple. Initially the engine was made to run without load for duration of 15 minutes so that, steady state conditions were obtained. The eddy current dynamometer was calibrated before starting the experiment, so that loading errors are avoided. The temperature of lubricating oil and cooling water were held constant in order to avoid any interference with the results. The various sensors and emission measurement devices were calibrated to ensure the repeatability and are attached to the exhaust tail pipe after the engine attains steady state conditions.

The engine was run and the base engine readings were taken for increasing loads. The amount of NO_X for each specific load was found out. The other readings recorded were exhaust gas temperature, exhaust oxygen concentration, HC, CO and etc. A gas analyzer was used to measure the amount of NO_X in the exhaust stream. Two to three readings were taken for the same load conditions and are averaged in order to get more accurate results. A look up table was created which relates the amount of NO_X released with respect to various engine loads. Based on the base NO_X, the amount of Urea to be injected into the exhaust stream is said to be calculated.

A second set of readings were then taken by implementing a SCR system which uses AdBlue. The tailpipe was replaced with one coated with the dual layer FeZ on CuZ catalyst. The dosing system was controlled by a microcontroller and urea was injected only when the exhaust valve is open and the amount injected depends on the quantity of NO_X per load in the exhaust, determined from the base NO_x values. Engine was made to run with similar load conditions and the values were tabulated.

3. RESULTS AND DISCUSSION

From the results for the base engine readings, it can be seen that there was an increase in NO_X with an increase in load. The increase was almost linear in nature. There was also an increase in the NO_x with an increase in exhaust temperature. This can be explained as a higher in cylinder temperature, that will help the reaction between nitrogen and oxygen consequently increasing the NO_x concentration, the increase in the NO_X with the

exhaust oxygen content can be due to lean air fuel ratio leading to greater quantity of oxygen available during combustion, subsequently a greater amount of oxygen leads to a rise in the NO_X concentration.
When AdBlue was injected over the dual layer catalyst there was seen to be increase in the NO_x concentration until a temperature of 220°C. The NO_X conversion was below 60 % at 250°C. It reaches a value of about 80 % around 300°C and continues to rise. The low temperature activity can be explained as insufficient amount of heat energy in the exhaust for the decomposition of urea to NH_3 to occur. The NO_X conversion efficiency was about 12 % near 150°C and it rises to about 82% near 320°C.

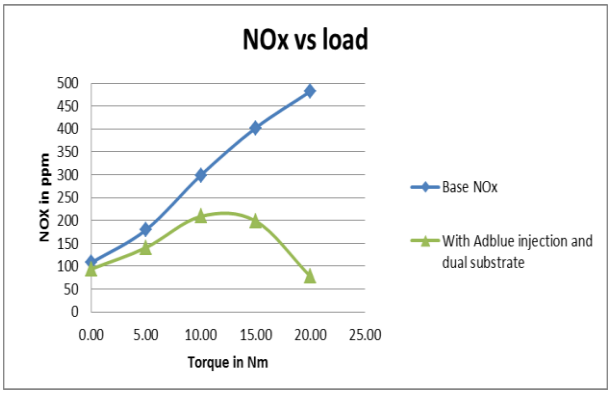

Figure.4.Variation of NO_X against load

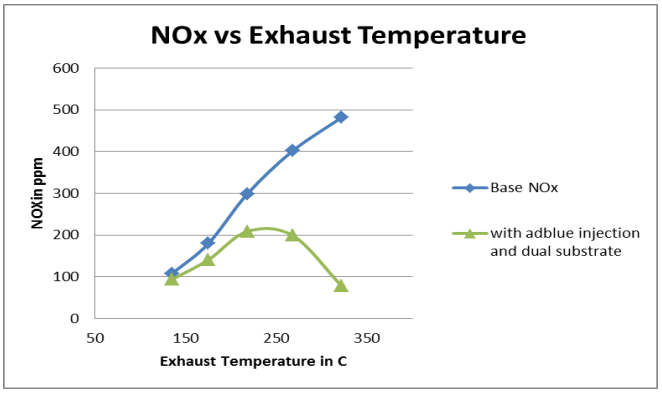

Figure.5.Variation of NO_X against Exhaust Temperature

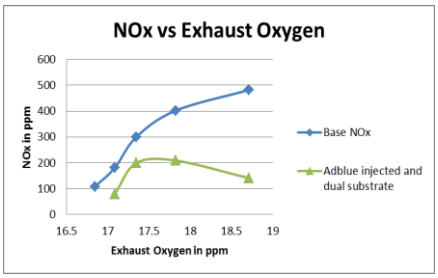

Figure .6.Variation of NO_X against Exhaust Oxygen

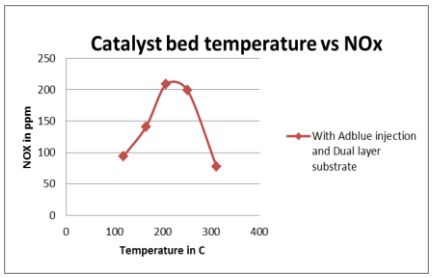

Figure .7. Variation of NO_X conversion efficiency against temperature

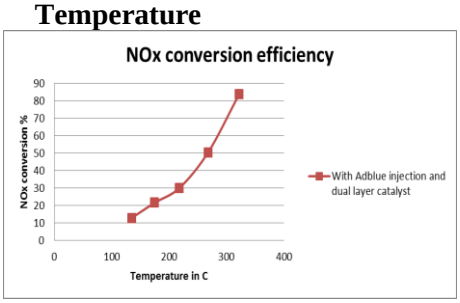

Figure .8. Variation of NO_X conversion efficiency against temperature

The variation of NO_X with catalyst bed temperature was also studied .It was seen that there was an initial increase in NO_X with temperature. It initially increases up to 209 ppm upto 200°C then the amount of NO_x decreases, to about 80 ppm in 310°C.

4. CONCLUSIONS

With the introduction of a dual layer catalyst of 33% FeZ on 67% CuZ, there was almost a 25% reduction near 200°C in NO_X and almost a 85% NO_X reduction near 325°C. Thus there was a improvement in the low temperature performance of the SCR system and further tuning of this would prove as an amicable solution to the cold start issues faced. This method can be implemented suitably in SCR systems to meet future standards

The future work would involve a better study of the high temperature characteristics of the catalyst and an investigation of the Ammonia slip and the effect of thermal ageing of the catalyst in the NO_X conversion of the catalysts, investigation of the life time of the ammonia generation system.

REFERENCES

Balland J, Parmentier M, and Schmitt J, Control of a Combined SCR on Filter and Under-Floor SCR System for Low Emission Passenger Cars, SAE, 7 (3), 2014, 1252-1261.

Castagnola M, Caserta J, Chatterjee S, Chen H.Y, Conway R, Fedeyko J, Engine Performance of Cu- and Fe-Based SCR Emission Control Systems for Heavy Duty Diesel Applications, SAE, 2011, 01-1329.

Cavataio G, Jen H.W, Warner J.R, Girard J.W, Kim J.Y, and Lambert C.K, Enhanced Durability of a Cu/Zeolite Based SCR Catalyst, SAE, 2008.

Cavatio G, Jen H.W, Warner J.R, Girard J.W, Kim J.Y, and Lambert C.K, Enhanced durability of Cu/Zeolite Based SCR Catalyst, SAE, 2008.

Culbertson D, Khair M, Zhang S, Tan J, The Study of Exhaust Heating to Improve SCR Cold Start Performance, SAE, 8 (3), 2015.

Fulks G, Fisher G.B, Rahmoeller K, Wu M.C, D'Herce E, A Review of Solid Materials as Alternative Ammonia Sources for Lean NO_x reduction with SCR, SAE, 2009.

Guan B, Zhan R, Lin H, Huang Z, Review of state of the art technologies of selective catalytic reduction of NOx from diesel engine exhaust, Applied Thermal Engineering, 2014.

Johannessen T, 3rd Generations SCR System Using Solid Ammonia Storage and Direct Gas Dosing-Expanding the SCR Window for RDE (Real Driving Emissions), U.S. Department of Energy DEER Conference, Dearborn, Michigan, 2012.

Johannessen T, Schmidt H, Svagin J, Johansen J, Oechsle J, and Bradley R, Ammonia Storage and Delivery Systems for Automotive Nox after treatment, SAE, 2008.

Joseph R, Theis, SCR catalyst Systems Optimized for Light off and Steady-State Perfomance, SAE, 2009.

Kim H, Yoon C, Lee J, and Lee H, A Study on the Solid Ammonium SCR system for control of Diesel NO_X emissions, SAE, 2014.

Koebel M, and Strutz E.O, Thermal and hydrolytic decomposition of urea of automotive selective catalytic reduction systems: Thermochemical and practical aspects, Ind.Eng.Chem.Res., 42 (10), 2003, 2093-2100.

Lacin F, Kotrba A, Hayworh G, Sullivan H, Solid SCR: Demonstrating an improved approach to NO_X reduction via a solid reductant, SAE, 2011.

Pranit S, Michael P, Selective Catalytic reduction of NO_X on combined Fe- and Cu-zeolite monolithic catalysts, Sequential and dual layer configurations, 2011.

Theis J, Dearth M, and Mc Cabe R, LNT+SCR Catalyst Systems Optimized for NOx Conversion on Diesel Applications, SAE, 2011.

Xu L, Mc Cabe R, Ruona W, and Cavataio G, Impact of a Cu-zeolite SCR Catalyst on the Performance of a Diesel LNT +SCR System, SAE, 2009.