Nox Reduction by Using Urea Injection and Marine Ferromanganese Nodule as Scr of a Diesel Engine Fulled With Soybean Oil Methyl Ester (Some)

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Abstract: Across the globe, researchers are concentrating on to reduce the tail pipe emissions, which have high environmental impact either by adapting to new technologies or alternate fuels or both. Soybean oil methyl ester (SOME) is chosen as alternative fuel for diesel engines. It is renewable, non-toxic and offer potential reduction in CO; HC and smoke emissions due to higher O2 contents in it compared to diesel fuel but higher nitrogen oxides (NOx) emission. Nitrogen oxides (NOx) in the atmosphere cause serious environmental problems, such as photochemical oxidant, acid rain, and global warming. The removal of nitrogen oxides (NOx) from the exhaust of diesel engines is still a very challenging problem even though there have been many studies. Technologies available for NOx reductions either enhance other polluting gas emissions or increase fuel consumption

The objective of this work is to investigate the possibility of decreasing the NOx emissions in the tail pipe of a diesel engine. Injection of aqueous solutions of urea in the tail pipe of a diesel engine for the reduction of oxides of nitrogen (NOx) was carried out in a four stroke, single cylinder, water cooled, constant speed diesel engine fuelled with Soybean oil methyl ester (SOME). Four observations were made for the exhaust emission NOx analysis of concentration of urea solution 0%, 10%, 20%, and 30% by weight with different flow rates of urea solution as reductant by fitting Marine Ferromanganese nodule as SCR catalyst. It was observed that 60.56% of NOx reduction achieved.

Keywords: Soybean oil methyl ester, Diesel engine, NOx, SCR, Marine Ferromanganese nodule.

INTRODUCTION

The energy requirement has increased exponentially over the past decades due to industrialization and the change of subsequent lifestyle. Most of this energy is generated from fossil fuels such as coal, natural gas, gasoline and diesel. Almost 90% of the present energy source is based on the combustion of fossil fuels and biomass [1]. In last few decades, the environmental effects of pollutant emission from combustion sources have become increasingly serious.

The ongoing emission of NOx is a serious persistent environmental problem due to; it plays an important role in the atmospheric ozone destruction and global warming [2]. NOx is one of the most important precursors to the photochemical smog. Component of smog irritate eyes and throat, stir up asthmatic attacks, decrease visibility and damages plants and materials as well. By dissolving with water vapor NOx form acid rain which has direct and indirect effects both on human and plants.

The idea of using urea SCR systems for the reduction of NOx emissions in diesel engines is two decades old. Since then, many applications have been developed, some of which have reached commercialization [5]. But, it is still a challenge for researchers.

There are several techniques for NOx removal. Selective catalytic reduction (SCR) of NOx with Urea is considered as promising technology for NOx reduction in diesel engine tail pipe emission. The main requirements for an SCR catalyst of automotive applications are high volumetric activity, stability over a wide temperature range (180-650°C), and high selectivity with respect to the SCR reaction. In the last years, a main challenge was the development of catalysts with higher volumetric activity and this has been achieved by increasing the intrinsic activity of the catalyst formulation and by increasing the cell density of the monoliths

An SCR (Selective Catalytic Reduction) exhaust gas after treatment system which uses a urea solution as a reducing agent has a high NOx reduction potential and is a well-known technique for stationary applications [4].

Ammonia has been ruled out as a reducing agent, due to toxicity and handling issues, and urea appears to be the reductant of choice for most applications, stored on board in an aqueous solution. To overcome the difficulties associated with pure ammonia, urea can be hydrolyzed and decomposed to generate ammonia.

 $CO(NH_2)_2 \Rightarrow NH_3 + HNCO$

$$HNCO + H_2O \Rightarrow NH_3 + CO_2$$

It seems that urea, as ammonia source, is the best choice for such applications because urea is not toxic and also can be easily transported as a high-concentration aqueous solution. As a result, NOx can be reduced with not only ammonia but also the urea itself and its decomposition by product, HNCO, as shown in reactions [6].

$$2\text{CO (NH2)}2 + 6\text{NO} \Rightarrow 5\text{N}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}$$

 $4\text{HNCO} + 6\text{NO} \Rightarrow 5\text{N}_2 + 4\text{CO}_2 + 2\text{H}_2\text{O}$
 $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \Rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$

Even though the use of urea in the reduction of NOx from the flue gas streams of power plants is a well-established method [6], there have not been many studies on the use of urea as a reductant in treatment of the exhaust of lean-burn engines.

Schar et al.(2003) [7] presented an advanced controller for a urea SCR catalytic converter system for a mobile heavy-duty diesel engine. The after treatment system consists of injecting device for urea solution and a single SCR catalytic converter.

Chakravarthy et al. [8] done a comprehensive literature review on the performance of zeolite catalysts compared to vanadia catalysts, and found that zeolite catalysts generally have a higher NOx reduction efficiency of SCR with NH3, and may have a broader temperature window for selectivity of SCR towards N2. The second is the optimization of the urea injection strategy under transient engine operating conditions, in order to provide the necessary amounts of NH3 for NOx removal and at the same time minimize the amount of excess NH3 slipping to the environment.

Koebel et al. (2003) [9] revealed that atomization of urea-water-solution in hot exhaust stream yields to solid or molten urea.

Birkhold et al. [10] for automotive applications, claim that the urea-water-solution based SCR is a promising method for control of NOx emissions. Urea-water-solution containing 32.5 wt.% urea is sprayed into the hot exhaust stream, for the subsequent generation of NH3 in the hot exhaust gas. As the evaporation and spatial distribution of the reducing agent upstream the catalyst are crucial factors for the conversion of NOx, the urea dosing system has to ensure the proper preparation of the reducing agent at all operating conditions. Specific concerns with the ammonia process include the storage, handling, and delivery of the ammonia. Also, any ammonia not consumed in the process may be emitted ("ammonia slip") as a result of this process. For these and other reasons, alternative agents have been proposed over the years. Two of these that have received significant interest include cyanuric acid [(HNCO)₃] and urea [(NH₂)2CO] [11].

Koebel et al. (2000) [12] suggested the basic problems and challenges of the use of urea-SCR in mobile applications. Though urea-SCR is very powerful method for removing NOx at temperatures above 250° C there is a need for removing NOx in a wide range of temperatures because of a large temperature variation of exhaust gas according to the operation condition of the engine and because of further reduction of NOx emission limits

Schaber et al. [13] reported that molten urea evaporates to gaseous urea at temperatures above 413~K, but mainly decompose directly to NH3 and HNCO above 425~K.

Fang et al. (2003) [14] also investigated the effect of moisture on urea decomposition process and found that the moisture could assist the hydrolysis of HNCO only in the temperature region below the first decomposition stage (below 250°C). The DRIFTS measurements showed that the final brown colour product formed at 450°C could be a chemical complex of polymeric melamines with high molecular weights which might actually block the active sites on the catalyst surface. Their study showed that urea thermo-lysis exhibits two decomposition stages, involving ammonia generation and consumption respectively. Decomposition occurring after the second stage leads to the production of melamine complexes that hinder the overall performance of the catalyst. They asserted that polymeric melamine complexes can be formed both with and without the catalyst and they do not undergo further decomposition (at least up to 320°C).

Wolfgana Held et al. (1990) [15] have suggested that, the use of urea is usually regarded as safe, it is easy to transport in the vehicle in an aqueous solution, which make it also easy to dose as necessary. Copper-exchange zeolite catalysts can selectively convert nitrogen oxides over a much wider range of fuel-air ratios than nobel-metal catalysts and they achieved only 65% of NOx reduction, the urea dosage was not analyzed, also they have not given the required construction la out of engine arrangement. Also they have not explained the secondary reaction.

In this study injection of aqueous solutions of urea and Marine Ferromanganese Nodule as SCR in the tail pipe of a diesel engine fuelled with Soybean oil methyl ester (SOME) for the reduction of oxides of nitrogen (NOx) was carried out in a four stroke, single cylinder, water cooled, constant speed diesel engine.

II. MARINE FERROMANGANISE NODULE

Ferromanganese Nodule which, is easily available from sea bed, is considered an economically important source of Ni, Co, Cu, Si and rare earth elements [16]. The physical and chemical properties revels that

the nodules in general has high porosity, large specific surface area [17]. It has high structural stability [18]. It has also acidic and basic sites as it is chemically an assembly of oxide [19, 16]. The nodule is easily reduced at 200°C to form Fe₃O₄, MnO, Ni, Cu, Co and is oxidized by oxygen to Fe₂O₃, MnO₂, NiO, CoO [20]. The nodule catalyses the oxidation of CO, CH₄ [18], and the CO oxidation activity is better than Pt.Al₂O₃ catalyst [21].

III. SELECTIVE CATALYTIC REDUCTION (SCR)

Selective catalytic reduction (SCR) is an after treatment process. SCR technology permits the NOx reduction reaction to take place in an oxidizing atmosphere. It is called "selective" because the catalytic reduction of NOx with ammonia (NH_3) or urea as a reductant occurs preferentially to the oxidation of NH_3 or urea with oxygen.

The efficiency of SCR for NOx reduction also offers without a fuel penalty. It allows diesel engine developers to take advantage of the trade-off between NOx, PM and fuel consumption and calibrate the engine in a lower area of fuel consumption than if they had to reduce NOx by engine measures alone. Particulate emissions (PM) are also decreased and SCR catalytic converters can be used alone or in combination with a particulate filter.

For mobile source applications ammonia is used as a selective reductant, in the presence of excess oxygen, to convert over 70% (up to 95%) of NO and NO_2 to nitrogen over a specified catalyst system. Different precursors of ammonia can be used; but for vehicles the most common option is a solution of urea in water carefully metered from a separate tank and injected into the exhaust system where it hydrolyses into ammonia ahead of the SCR catalyst. Urea solution is a stable, non-flammable, colorless fluid containing 32.5% urea which is not classified as hazardous to health and does not require any special handling precautions.

Several types of catalysts are used, the choice of which is determined by the temperature of the exhaust gases. In many countries, SCR catalysts were mainly based on vanadia. However, if DPFs are used in combination with SCR systems, zeolites are preferred due to the better high temperature durability needed when exotherms associated with DPF regeneration can expose SCR catalysts to temperatures up to 800° C. Currently copperzeolites have the best low temperature performance and iron-zeolites have the best high temperature performance. Optimized operation of SCR catalysts depends on control of adsorbed urea and use of oxidation catalysts to deliver the appropriate NO_2/NOx ratio.

To determine the type of catalyst to be used that depend on exhaust gas temperature, reduction of nitrogen oxides required, oxidation of SO_2 and the concentration of other exhaust gas constituents.

IV. EXPERIMENTAL SETUP

Injection of aqueous solutions of urea from a separate urea tank in the tail pipe of test the diesel engine for the reduction of oxides of nitrogen (nox) was carried out in a four stroke, single cylinder, water cooled, constant speed diesel engine with eddy current dynamometer. Four observations were made for the exhaust gas analysis of various concentration of urea solution 0%, 10%, 20%, and 30% by weight with different flow rates of urea solution by fitting Marine Ferromanganese nodule as oxidant catalyst. The technical specifications of the engine are given in Table I, and the schematic of the experimental setup is shown in Fig. 1. The power output of the engine was measured by an electrical dynamometer. AVL gas analyzer was used for the measurement of amounts of exhaust emissions. Digital control panel was used to collect data such as torque, water flow of engine etc. A three way control valve and needle are used to maintain the urea flow rate. Urea solution for different concentration is made before the experiment. The measurements were taken after steady state of the engine for each set of readings.

| Type of engine | Four stroke single cylinder Diesel engine |
|---------------------|---|
| Type of engine | Four stroke single cyllider Dieser engine |
| Bore | 87.6mm |
| Stroke | 110mm |
| Compression ratio | 17.5:1 |
| Rated speed | 1500 |
| Rated power | 7HP (5.2 kW)@1500rpm |
| Displacement volume | 661.5cm ³ |

Table 1. Specification of engine

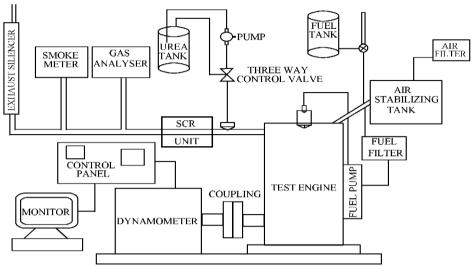


Figure 1. Schematic of Experimental Setup

V. RESULTS AND DISCUSSIONS

The output obtained from the experiment is plotted to determine the effect of the injection of urea solution at various concentration and flow rate as reductant and marine ferromanganese nodule as SCR on the NOx emission analysis of the test engine.

1. NOx v/s Brake power without urea and SCR

Fig. 2 shows the variations of NOx emissions with brake power of SOME fuel without urea solution and SCR at constant speed of the engine. From the graph it is observed that the NOx emission increases in the tail pipe of the test engine with the increase of brake power due to more oxygen content of fuel chemistry and better combustion resulting high combustion temperature in the combustion chamber. Higher combustion temperatures in CI engines results in higher NOx emission. Nitrogen oxide (NO) is rapidly converted to nitrogen dioxide (NO₂) in the presence of oxygen. NO and NO2 are customarily treated together and referred to as oxides of nitrogen (NOx).

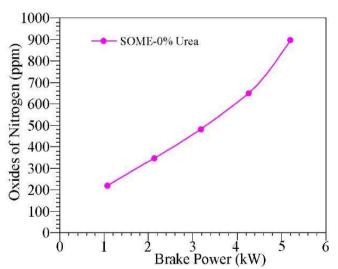


Figure 2. NOx v/s Brake power without urea and SCR

2. NOx v/s Brake power with 10% urea solution without SCR

Fig. 3 shows the variations of NOx emissions with brake power of SOME fuel 10% urea solution without SCR at constant speed of the engine. From the graph it is observed that the NOx emission decreases with the injection of 10% urea solution. It is also observed that as the urea flow rate increases NOx reduction increases due to better mixing of the exhaust gases in the tail pipe. With the 10% urea concentration and 0.60 lit/hr 24.77% NOx reduction was achieved.

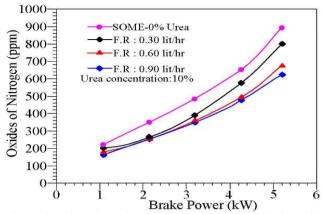


Figure 3. NOx v/s Brake power with 10% urea solution without SCR

3. NOx v/s Brake power with 20% urea solution without SCR

Fig. 4 shows the variations of NOx emissions with brake power of SOME fuel with 20% urea solution without SCR at constant speed of the engine. From the graph it is observed that the NOx emission decreases with the increase of the concentration of the urea solution and urea injection flow rate. With 20% urea concentration and 0.60 lit/hr urea flow rate 32.66% NOx reduction is achieved.

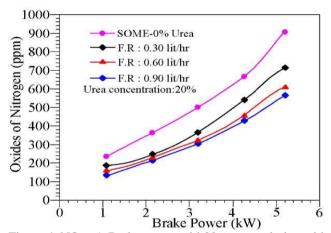


Figure 4. NOx v/s Brake power with 20% urea solution without SCR

4. NOx v/s Brake power with30% urea solution without SCR

Figure.5 shows the variations of NOx emissions with brake power of SOME fuel with 30% urea solution without SCR at constant speed of the engine. From the graph it is observed that the NOx emission further decreases with the increase of the concentration of the urea solution and urea injection flow rate due to better surface contact. NOx reduction was approximately same for 0.6 lit/hr and 0.9 lit/hr flow rate with 30% urea concentration.

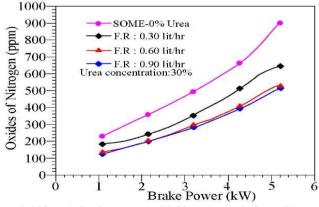


Figure 5. NOx v/s Brake power with30% urea solution without SCR

5. NOx v/s Brake power with varying urea solution concentration without SCR at constant injection flow rate

Figure.6 shows the variations of NOx emissions with brake power of SOME fuel with various concentrations of urea and constant flow rate 0.60 lit/hr without SCR at constant speed of the engine. From the graph it is observed that the NOx emission decreases with the increase of the concentration of the urea solution at constant urea injection flow rate 0.6 lit/hr.

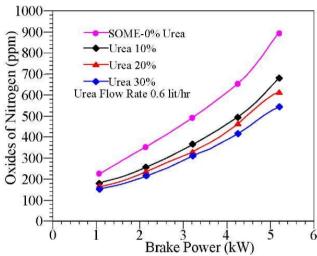


Figure 6. NOx v/s Brake power with varying urea solution concentration without SCR at constant injection flow rate

6. NOx v/s Brake power with varying concentration of urea solution at constant injection flow rate with Marine Ferromanganese Nodule as SCR.

Figure.7 shows the variations of NOx emissions with brake power of SOME fuel with various concentrations of urea and constant injection flow rate 0.60 lit/hr with SCR at constant speed of the engine. From the graph it is observed that the NOx emission decreases remarkably with the introduction of the Marine Ferromanganese Nodule as SCR in tail pipe of the engine. With the introduction of urea solution of constant flow rate 0.60 lit/hr and using marine ferromanganese nodule as SCR 60.56% NOx reduction is achieved.

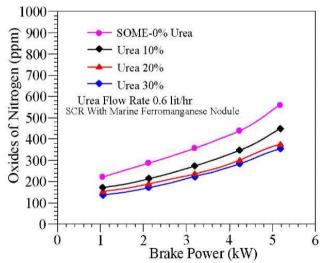


Figure 7. NOx v/s Brake power with varying concentration of urea solution at constant injection flow rate with Marine Ferromanganese Nodule as SCR.

VI. CONCLUSION

From the study it can be concluded that urea injection with Marine Ferromanganese Nodule as SCR in the tail pipe 60.56% NOx reduction achieved. Moreover, it also indicates that the catalyst used in the test engine commercially attractive as compared to noble metal catalyst.

REFERENCES

- [1] World Energy Council and International Institute for Applied System Analysis, Global energy perspectives and beyond, *World Energy Council*, London (1995).
- [2] Busca G., Lietti L., Ramis G., and Berti F., Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: A review, *Applied catalysts B: environmental*, 18(1-2), 1998, 1-36
- [3] Kleemann, M., Dissertation Nr. 13401, ETH Zurich, 1999.
- [4] H. Bosch, F. J. J. G. Janssen: Catalytic Reduction of Nitrogen Oxides: A Review on the Fundamentals and Technology, *Catalysis Today*, *2*(369), 1988.
- [5] Perry, R. A. and Siebers, D. L. Rapid reduction of nitrogen oxides in exhaust gas streams. *Nature*, 324, 1986, 657–658.
- [6] Hug, H. T., Mayer, A., and Hartenstein, A., SAE Technical Paper Series, 930363, Detriot, March 1–5, (1993).
- [7] C.M.SCHAR, C.H. Onder and H.P. Geering, M Elsener, Control of a Urea SCR catalytic Converter System for a Mobile Heavy Duty Diesel Engine, *SAE Transactions* 2003010776 (2003).
- [8] Chakravarthy, K., Choi, J.-S., and Daw, S. Modeling SCR on zeolite catalysts A summary of observations on SCR kinetics based on the open literature. *In Eighth DOE-CLEERS Workshop*, Dearborn, Michigan, 17–19 May 2005.
- [9] M. Koebel and E. O. Strutz, Thermal and Hydrolytic Decomposition of Urea for Automotive Selective Catalytic Reduction Systems: Thermo chemical and Practical Aspects, *Journal of Industrial and Engineering Chemistry Research*, 42, 2003, 2093-2100,
- [10] F. Birkhold, U. Meingast, P. Wassermann, and O. Deutschmann, Modeling and simulation of the injection of urea-water-solution for automotive SCR DeNOx-systems, *Applied Catalysis B: Environmental*, 70, 2007, 119-127
- [11] J. A. Caton and Z. Xia, The Selective Non-Catalytic Removal (SNCR) of Nitric Oxides From Engine Exhaust Streams: Comparison of Three Processes, *Journal of Engineering for Gas Turbines and Power, Transactions of the ASME*, 126, 2004, 234-240
- [12] M. Koebel, M. Elsener, and M. Kleemann, Urea-SCR: a promising technique to reduce NOx emissions from automotive diesel engines, *Catalysis Today*, *59*, 2000, 335–345
- [13] P. M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach, and J. Brauer, Thermal decomposition (pyrolysis) of urea in an open reaction vessel, *Thermochimica Acta*, 424, 2004, 131–142
- [14] H. L. Fang and H. F. M. DaCosta, Urea thermolysis and NOx reduction with and without SCR catalysts, *Applied Catalysis B: Environmental*, 46, 2003, 17-34,
- [15] Wolfgang Held, Axel Konig and Thomas Richter, Lothar Puppe, Catalytic NOx Reduction in Net Oxidizing Exhaust Gas, *SAE Transsactions* 900496, 1990
- [16] Mohapatra .B. K.,S. K. Mishra & R. K. Sahoo, Characteristics of marine ferromanganese concentrations at elevated temperature, *Thermochimica Acta*, *145*, 1989, 33-49
- [17] Bobonich F.M., Lazarenko V.I., Oriovskii G.N. and Solomakha V.S., Geol.Khim. Biol. Nauke, 6, 1987
- [18] Weisz P.B., Deep sea manganese nodules as oxidation catalysts, J. Catal, 10, 1968, 407
- [19] Cronan, D.S., and J.S. Tooms, The geochemistry of manganese nodules and associated pelagic doposits from the Pacific and Indian Oceans, *Deep-Sea Research*, 1969, 335-359
- [20] Dobet C., Noville F., Crine M. and Pirard J.P., Texture of manganese nodules used as a catalyst for demetallizing and desulphurizing petroleum residua, *Colloids and Surfaces*, 11 (1-2), 1984, 187-197
- [21] Nitta M., Characteristics of manganese nodules as adsorbent and catalysts, a review, *Appl. Catal.*, *9*, 1984, 151-176