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Nox REDUCTION BY USING UREA INJECTION AND MARINE FERROMANGANESE NODULE AS SCR OF A DIESEL ENGINE FULLED WITH PONGAMIA PINNATA METHYL ESTER

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Abstract: *Pongamia pinata methyl ester (PPME) is chosen as alternative fuel for diesel engines. It is renewable and offer potential reduction in CO; HC and smoke emissions due to higher O_2 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.*

Injection of aqueous solutions of urea in the tail pipe of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) for the reduction of oxides of nitrogen (NOx) was carried out in a four stroke, single cylinder, water cooled, constant speed diesel engine. Four observations were made for various 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 which improves the chemical reactions. 64% NOx reduction achieved with the urea flow rate 0.60 lit/hr, 30% concentration of urea solution and marine ferromanganese nodule as SCR.

Keywords: *Pongamia pinata methyl ester, Diesel engine, NOx, SCR, Marine Ferromanganese nodule.*

I. Introduction

The minimization of fuel consumption and the reduction of emissions have been two driving forces for engine development throughout the last decades. The first objective is in the financial interest of the vehicle owners. The second is imposed by legislation, sometimes also supported by excise reductions or customers' demands for clean engines.

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 [1]. 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. An SCR (Selective Catalytic Reduction) exhaust gas after treatment system which uses urea solution as a reducing agent has a high NOx reduction potential and is a well-known technique for stationary applications [2]. 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 [3]. But, it is still a challenge for researchers.

There are numerous techniques for NOx removal. Selective catalytic reduction (SCR) of NOx with Urea is considered as potential 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 extensive temperature range (180°C–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 concentration of the monoliths [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 connected 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 as 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 [5].

$$2CO(NH_2)_2 + 6NO \rightarrow 5N_2 + 2CO_2 + 4H_2O$$
$$4HNCO + 6NO \rightarrow 5N_2 + 4CO_2 + 2H_2O$$
$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

Even though the use of urea in the reduction of NOx from the flue gas streams of power plants is a well-established method, 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) [6] suggested 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. [7] have 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 NH_3, and may have a broader temperature window for selectivity of SCR towards N_2. Secondly the optimization of the urea injection strategy under transient engine operating conditions, in order to provide the necessary amounts of NH_3 for NOx removal and at the same time minimize the amount of excess NH_3 slipping to the environment. Koebel et al. (2003) [8] presented that atomization of urea-water-solution in hot exhaust stream yields to solid or molten urea.

Birkhold et al. [9] have claimed for automotive applications, that the urea-water-solution based SCR was a promising method for control of NOx emissions. Urea-water-solution containing 32.5 wt% urea was sprayed into the hot exhaust stream, for the subsequent generation of NH_3 in the hot exhaust gas. As the evaporation and spatial distribution of the reducing agent upstream the catalyst were vital 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 included 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 [$(NH_2)2CO$] [10]. Koebel et al. (2000) [11] suggested the basic problems and challenges of the use of urea-SCR in mobile applications. Though urea-SCR is very effective method for removing NOx at temperatures above 250° C there was 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. [12] suggested that molten urea evaporates to gaseous urea at temperatures above 413 K, but mainly decompose directly to NH_3 and HNCO above 425 K.Fang et al. (2003) [13] presented 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^oC). The DRIFTS measurements showed that the final brown colour product formed at 450^oC 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^oC). Wolfgana Held et al. (1990) [14] 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 Pongamia pinata methyl ester (PPME) for the reduction of oxides of nitrogen (NOx) was carried out in a four stroke, single cylinder, water cooled, constant speed diesel engine.

- **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 [15]. The physical and chemical properties revels that the nodules in general has high porosity, large specific surface area [16]. It has high structural stability [17]. It has also acidic and basic sites as it is chemically an assembly of oxide [18, 15]. The nodule is easily reduced at 200°C to form Fe_3O_4, MnO, Ni, Cu, Co and is oxidized by oxygen to Fe_2O_3, MnO_2, NiO, CoO [19]. The nodule catalyses the oxidation of CO, CH_4 [17], and the CO oxidation activity is better than $Pt.Al_2O_3$ catalyst [20].

- **SELECTIVE CATALYTIC REDUCTION (SCR)**

Selective catalytic reduction (SCR) is an after treatment process. A SCR system attempts to reduce oxides of nitrogen (NOx) back to harmless nitrogen and elemental oxygen that are constituents of air. It permits the NOx reduction reaction to take place in an oxidizing atmosphere. It is called "selective" because the catalytic reduction of NOx with ammonia (NH3) or urea as a reductant occurs preferentially to the oxidation of NH3 or urea with oxygen.

NOx reduction by SCR process takes place without a fuel penalty. It also allows diesel engine developers to take advantage of the trade-off between NOx and PM without fuel penalty. 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 hydrolyzes into ammonia ahead of the SCR catalyst. Urea solution is a stable, colorless, non-flammable fluid containing 32.5% urea which is not considered as hazardous to health and does not require any special safety measures.

To determine the kind of catalyst to be used that depend on exhaust gas temperature, reduction of nitrogen oxides necessary, oxidation of SO2 and the concentration of other exhaust gas constituents.

II. EXPERIMENTAL SETUP

Injection of aqueous solutions of urea from a separate urea tank in the tail pipe of test the diesel engine fuelled with Pongamia pinata methyl ester (PPME) 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.

Table -1: Specification of engine

Type of engine	Four stroke single cylinder Diesel 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

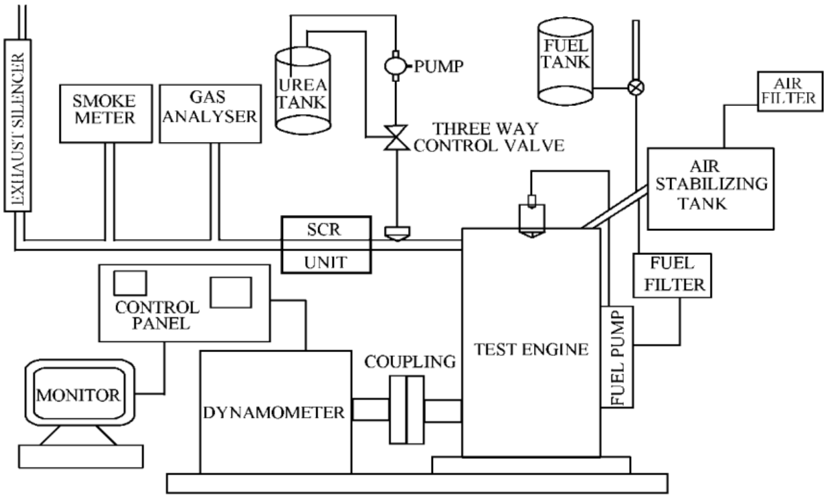

Figure 1. Schematic of Experimental Setup

III. 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. (NO_x) Emission v/s Brake power without urea and SCR

Fig. 2 shows the variations of NOx emissions with brake power of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) without urea solution and SCR at constant speed of the engine. From the graph it is observed that the NOx emission increases with the increase of brake power due to high combustion temperature in the combustion chamber. This indicates that the emission of NOx is very much influenced by the cylinder gas temperature and the availability of oxygen during combustion.

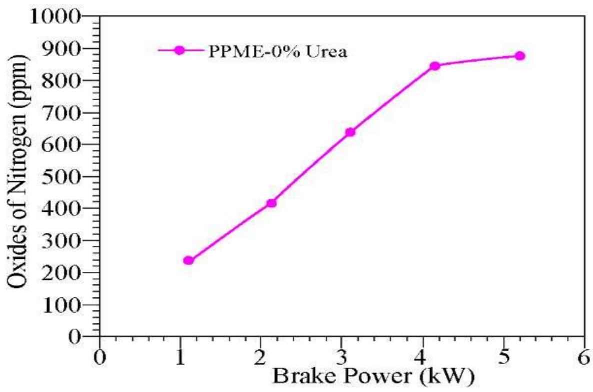

Figure 2. (NO_x) Emission v/s Brake power without urea and SCR

2. (NO_x) Emission v/s Brake power with10% urea solution without SCR

Fig. 3 shows the variations of NOx emissions with brake power of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) with 10% urea solution and 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.

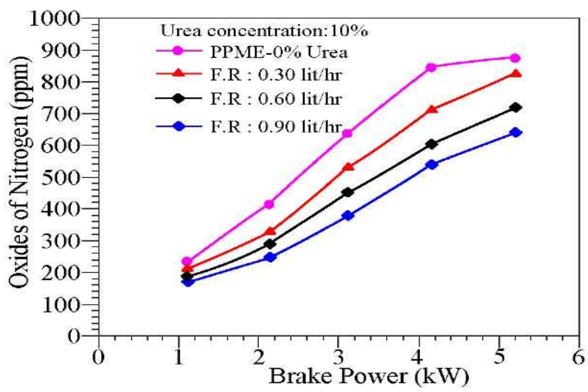

Figure 3. (NO_x) Emission v/s Brake power with10% urea solution without SCR

3. (NO_x) Emission v/s Brake power with20% urea solution without SCR

Fig. 4 shows the variations of NOx emissions with brake power of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) with20% urea solution and 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 due to further better mixing of the exhaust gases in the tail pipe.

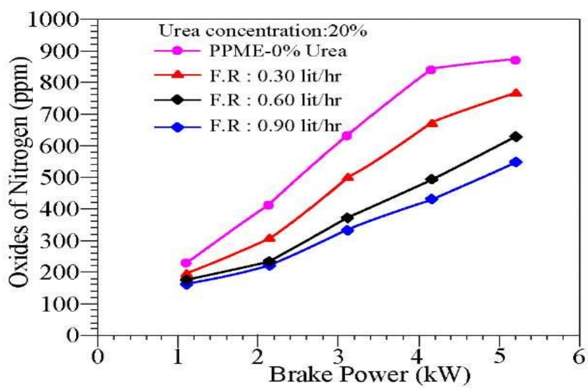

Figure 4. (NO_x) Emission v/s Brake power with20% urea solution without SCR

4. (NO_x) Emission v/s Brake power with30% urea solution without SCR

Fig. 5 shows the variations of NOx emissions with brake power of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) with30% urea solution and 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 of the exhaust gases.

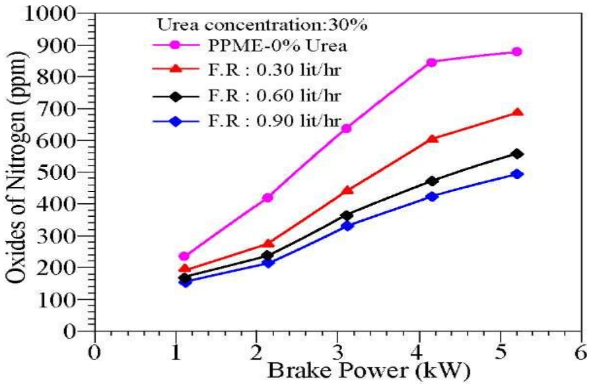

Figure 5. (NO_x) Emission v/s Brake power with30% urea solution without SCR

5. (NO_x) Emission v/s Brake power with varying urea solution concentration without SCR at constant injection flow rate

Fig. 6 shows the variations of NOx emissions with brake power of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) with various concentrations of urea solution 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.

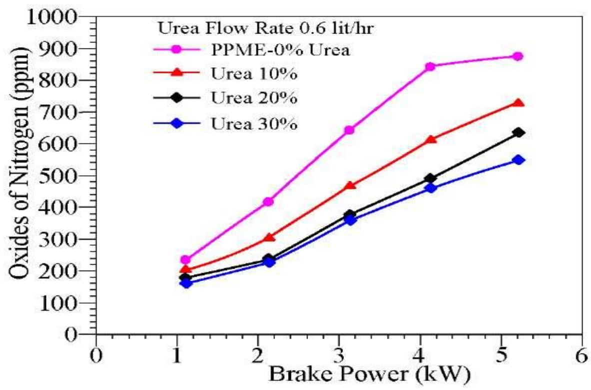

Figure 6. Oxides of Nitrogen emission (NO_x) v/s Brake power with varying urea solution concentration without SCR at constant injection flow rate

***6.* (NO_x) Emission v/s Brake power with varying concentration of urea solution at constant injection flow rate with Marine Ferromanganese Nodule as SCR.**

Fig. 7 shows the variations of NOx emissions with brake power of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) with various concentrations of urea solution and constant flow rate 0.60 lit/hr with Marine Ferromanganese Nodule as 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.

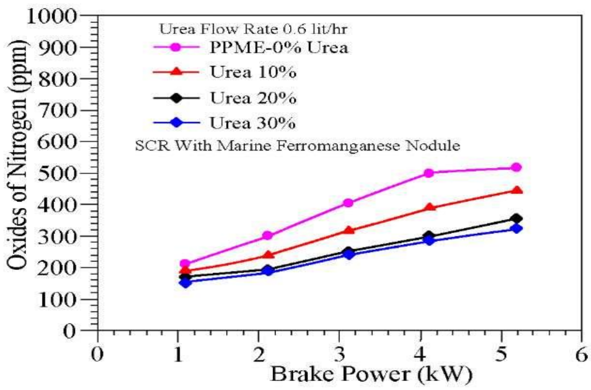

Fig. 7. (NO_x) Emission v/s Brake power with varying concentration of urea solution at constant injection flow rate (0.60 lit/hr) with Marine Ferromanganese Nodule as SCR.

IV. CONCLUSION

From the study it can be concluded that urea injection with Marine Ferromanganese Nodule as SCR in the tail pipe 64% NOx reduction achieved. Moreover, it also indicates that the catalyst used in the test engine commercially attractive as compared to noble metal catalyst.

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