A REVIEW ON SOLID SELECTIVE CATALYTIC REDUCTION FOR POST COMBUSTION NOx REDUCTION IN CI ENGINES

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Abstract

The increasing rate of pollution is a matter of global concern nowadays. One of the major sources of pollution is found to be the combustion products of diesel engine containing hazardous gases like carbon mono oxide, carbon dioxide, unburnt hydrocarbons and oxides of nitrogen. NOx reduction from the exhaust of diesel engines is the topic of research for the automobile manufacturers nowadays. Lean NOx trap was used for a long time for this purpose but it was not successful. Then SCR technology came into existence which was found to be the very effective Technology for reduction of nitrogen oxides from diesel engine exhaust. This paper involves the study of a better NOx reduction technology called solid selective catalyst reduction (SSCR). After analysis the results of various experiments it is concluded that NOx reduction efficiency of about 95% can be easily achieved using the SSCR system. The problem of contamination and malfunctioning can be reduced to a great extent by using ammonia in gaseous form. In this review the decomposition of solid ammonia salt, the temperature range of catalyst and dosing of ammonia is discussed.

Keywords

Diesel Engines, Pollution, NOx reduction, SSCR, Conversion Efficiency, Ammonia dosing

Introduction

In this century the most important task for lifesavers is to save the earth from the effects of pollution. Almost all countries are struggling with this problem. Instead, people are working day and night to solve the problems created from pollution. Climate change due to global warming has given indications about the seriousness of the problem. Ozone along with NOx has Adversely affected the air quality of many countries including China, the United States and Europe. The impact of these components on Environment was found to be much critical in urban areas than in rural ones[1]. Investigations show that the transport industry has played a major role in disturbing the climate cycle due to the Pollution created by emission of serious gases from their exhaust. Major cities of the world including New Delhi, are facing the problem of increasing Pollutants in the air causing respiratory diseases. During the investigation, the demand for Automobiles in these areas were found extremely high compared to other cities not facing many environmental problems[1].Unburnt hydrocarbons, particulate matter and oxides of Nitrogen is the contents of the exhaust of Diesel engines which are highly responsible for Pollution. The percentage of composition of exhaust emission from diesel engines is shown in Fig. (1)

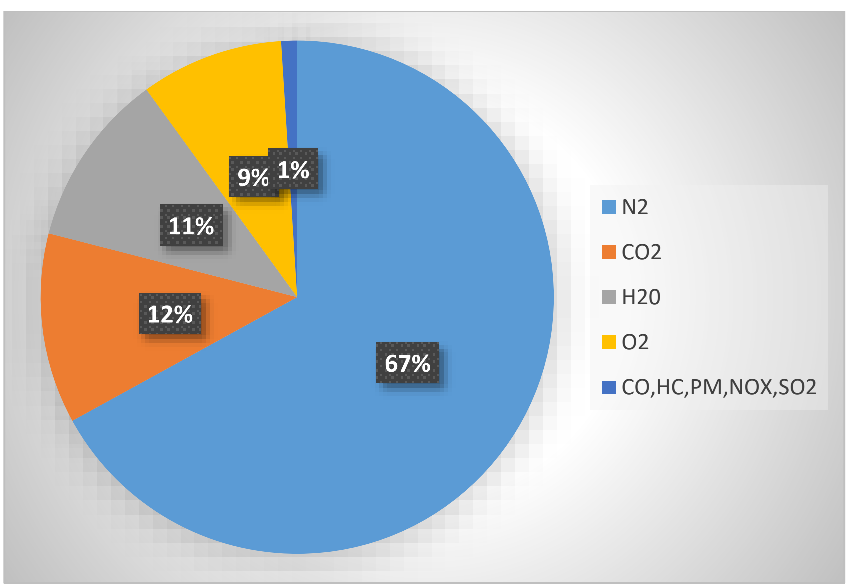


Fig. (1) composition of diesel engine exhaust[2]

Latest studies showed that globally 7.6% out of 4.2 million people, died due to the emission of particulate matter in 2015[3].Various pretreatment and post-treatment technologies have been adopted to reduce exhaust emission. Pretreatment technologies include a change in the design of combustion chamber, recirculation of exhaust gases, retarding injection timing etc. [4] but they remain unable to reduce the oxides of nitrogen from exhaust emission which is the most challenging task in reducing pollutants. An increased amount of NO_x in the exhaust emission of Automobiles cause the diffusion of alveolar cells which in turn give rise to respiratory diseases, Lung infections and pneumonia etc. [5].An increasing amount of NO_x in the environment gives rise to acid rains and smog formation[2]. Oxides of Nitrogen may cause acid rain as well as the depletion of the Ozone layer. Beyond these negative effects on nature, these oxides also affect the Human health badly[5]. Because of the above facts, stringent EURO-VI emission norms have compelled the diesel engine manufacturers to think about this alarming situation. Limits decided for NOx emission in the latest norms of EURO-VI are 0.4Kg/KWh from 2Kg/KWh in the steady-state condition and 0.46Kg/KWh from 2Kg/KWh in transient state. [6].By adopting EURO-VI emission norms a human being can get rid of disease like asthma, stroke, heart attack and lung cancer[6]. In EURO-VI emission norms NO_x reduction efficiency must be greater than 95% and Ammonia slip is limited to 10ppm.In the US and Europe, SSCR technology is adopted in large diesel trucks which is feasible and cost-optimized.

Euro V	Euro VI
• High fuel injection pressure • Variable fuel injection timing and quantity • Redesigns to combustion chamber • NO_x controlled mainly by SCR-Vanadium based systems • EGR offered by few manufacturers and mainly for small trucks	• DPFs required for Euro VI compliance with PM and PN standards • SCR catalyst changes from Vanadium to Zeolite • EGR no longer offered

Figure:2[6] **Requirements of components for EURO –V and EURO –VI norms**

Reduction of nitrogen oxides is one of the most challenging issues for diesel engine manufacturers. Various after treatment technologies like selective catalytic reduction (SCR), lean NOx trap (LNT) and SCR filter are adopted for the reduction of NOx [7]but conversion efficiency of NOx could not be achieved more than 75%. Although SCR has shown good results in the reduction of Nitrogen oxides it has some limitations. During the use of aqueous urea as reduction agent, some amount of nitrogen oxides is left unreduced which is called urea slip. This problem occurs due to the reason that the conversion efficiency of the catalyst is decreased at low temperatures. Catalyst efficiency is found to be maximum when the exhaust temperature ranges from 200^0C to 400^0C[8]. The catalyst cylinder needs to be filled regularly when working at these temperatures usually before the fuel cylinder is empty[9]. The problem of contamination and malfunctioning also occur during the process of deNO_x. After the development of one state control-oriented SCR model and its validation under transient and steady-state conditions, it was found that it is best suited for exhaust analysis. Based on this SCR model MPC was established which showed better control over catalyst storage and ammonia slip[10].

Use of solid catalyst in place of aqueous urea may give much better results. This technology uses a catalyst in solid form is called solid selective catalytic reduction (SSCR). Use of SSCR technology for NO_x reduction may reduce the problem of contamination and malfunctioning.

Literature Review

Sr. No	Year	Author	Title	Journal	Parameters	findings
1	1990	Yoshiaki KINTAICHI, Hideaki HAMADA, Mitsunori TABATA, Motoi SASAKI and Takehiko ITO	selective reduction of nitrogen oxides with hydrocarbons over solid acid catalysts in oxygen-rich atmospheres	Catalysis Letters 6 (1990) 239-244	Effect of water vapour on catalytic reaction	In oxygen-rich atmosphere deNOx efficiency of SCR system increases.
2	1994	H. Hamada	Selective reduction of NO by hydrocarbons and oxygenated hydrocarbons over metal oxide catalysts	catalysis Today 22 (1994) 21-40	Formation of N2 was discussed using metal oxide catalysts, Catalytic effectivity	Alumina shows better conversion efficiency of NOx
3	1996	Paul Zelenka, Wolfgang Cartellieri, Peter Herzog	Worldwide diesel emission standards, current experiences and future needs	Applied Catalysis B: Environmental 10 (1996) 3-28	EGAS system developed for the reduction of tailpipe emission from diesel engines	Use of three-way catalyst reduces exhaust emission.
4	1999	David N Belton, and Kathleen C Taylor	Automobile exhaust emission control by catalysts	Current Opinion in Solid State & Materials Science 1999, 4:97-102	Comparison of catalysts suitable for emission control of diesel engines.	Three-way catalysts control the particulate matter and NOx reduction from diesel engine exhaust.
5	2000	M. Koebel, M. Elsener, M. Kleemann	Urea-SCR: a promising technique to reduce NOx emissions from automotive diesel engines	Catalysis Today 59 (2000) 335–345	Reduction of catalyst volume, urea dosing	catalyst volume is decreased with the use of coated catalysts having considerable cell density.
6	2001	Christine Lambert, John Vanderslice, Robert Hammerle and Rich Belaire	Application of Urea SCR to Light-Duty Diesel Vehicles	2001 SAE International	Use of catalysed DPF	High particulate material and NOx reduction is achieved

7	2009	Daniela Schonauer,Kerstin Wiesner, Maximilinan Fleischer,Ralf Moos	Selective mixed potential ammonia exhaust gas sensor	Sensors and Actuators B 140 (2009)585-590	Effect of electrical conductivity, catalyst activity on sensor performance.	In sensor-based SCR high deNOx efficiency is achieved and Ammonia slip is also reduced.
8	2009	M.Weibel, N.Waldbußer, R.Wunsch, D. Chatterjee, B. Bandl-Konrad, B. Krutzsch	A Novel Approach to Catalysis for NOx Reduction in Diesel Exhaust Gas	Springer Top catal (2009)52:1702-1708	Development of a system combining NOx storage catalyst (NSC) and selective catalytic reduction (SCR)	NSC & SCR, when combined together, shows better NOx conversion efficiency
9	2009	J.Rodriguez-Fernandez,A.Tsolakis,R.F.Cranckne l,R.H.Clark	Combining GTL fuel,reformed EGR &HC-SCR after treatment system to reduce NOx emissions.Astatistical approach	International journal of hydrogen energy34 (2009)2789-2799	Engine speed, engine load, EGR/REGR ratio	89-95% NOx emission is reduced using an optimal combination of fuel type, REGR type and REGR ration
10	2011	Junhua Li, Huazhen Chang, Lei Ma,Jiming Hao,Ralph T.Yang	Low temperature selective catalytic reduction of NOx with NH3 over metal oxide and Zeolite catalysts-A review	Catalysis Today 175 (2011) 147-156	The affectivity of various catalysts is discussed for NOx reduction	Iron and copper zeolites with higher stability are found to be the best catalysts for NOx reduction.
11	2011	Jorn Dinh Herner, Shaohua Hu, William H. Robertson, Tao Huai, M.-C. Oliver Chang, Paul Rieger and Alberto Ayala	Effect of Advanced After-treatment for PM and NOx Reduction on Heavy-Duty Diesel Engine Ultrafine Particle Emissions	|Environ. Sci. Technol. 2011, 45, 2413–2419	Thr occurrence of nucleation was discussed	Soot particles are removed efficiently with less NOx generation.
12	2011	Ming-Feng Hsieh, Junmin Wang	NO&NO2 concentration modelling and observer-based estimation across a	Journal of Dynamic Systems, Measurement, and	Observation of NO/NO2 concentration in diesel exhaust	Control oriented models easily identify the NO/NO2 ratio and thus provides a

			diesel engine after treatment system	Control JULY 2011, Vol. 133 / 041005-13		better design for their reduction.
13	2011	S.Liu, H.Li, C.Liew,T.Gatts,S. Wayne,B.Shade,N .Clark	An experimental investigation of NO2 emission characteristics of a heavy -duty H2-diesel dual fuel engine	International journal of hydrogen energy36 (2011)12015-12024	Effect of unburnt H2 on NO2 formation.	Maximum temperature and engine load are not much responsible for NO2 formation than unburnt H2.
14	2011	Figen Lacin, Adam Kotrba, Granville Marek tatur, Jason Jacques, dean tomazic and hoon cho	SOLID SCR: Demonstrating an improved approach to NOx reduction via a solid reductant	2011 SAE International	Temperature, Nox reduction efficieny, Dosing rates	SSCR is found more efficient in heavy vehicles with more conversion efficieny and less frequency of filling reductant tank.
15	2012	C. L. MYUNG and S. PARK	Exhaust Nanoparticle Emissions From Internal Combustion Engines: A Review	International Journal of Automotive Technology, Vol. 13, No. 1, pp. 9−22 (2012)	Particulate emission	introduction of direct fuel injection, an increase in system pressure and advances in engine management systems can reduce particulate emission
16	2013	R.Vallinayagam,S. Vedharaj,W.M.Ya ng,C.G.Saravanan ,P.S.Lee, K.J.E.Chua, S.K.Chou	Emission reduction from a diesel engine fuelled by pipeline biofuel using SCR and catalytic converter	Elsevier	Front peak heat release rate and maximum in-cylinder pressure	Emission of CO, hydrocarbons and particulate matter is decreased using biofuel.
17	2014	Kai zhang,Luyan Fan,Dawei Qu	Research on SSCR Technologyto reduce NOx emission for diesel engines	(2014) Trans tech publications, Switzerland	The conversion efficiency of NOx	Compared to the SCR system the conversion efficiency of SSCR is more.
18	2014	Dawei Qu, Shaohua Liu, Luyan Fan and Junyan Ma	Nozzle opening time's impact on flow characteristics of SSCR	(2014)Trans tech publications, Switzerland	Nozzle opening and nozzle flow rate	Due to very less response time of Ideal jet valve opening and

						closing happens in a flash. electromagnetic induction in the inductance of the coil is the reason for the jet valve not to open and close instantly after receiving the pulse signal. Instead, it must be a period of time for the opening and closing.
19	2014	Dawei Qu, Kai Zhang, Luyan Fan and Haibo Gao	Simulation study for mixing characteristics of NH3 and automobile exhaust in the SSCR system	(2014)Trans tech publications, Switzerland	engine condition, NH3 temperature, nozzle installation angle and nozzle position.	engine condition highly Influence NH3 and automobile exhaust mixing. mixing is better, exhaust flow is larger, exhaust temperature is high, increase in nozzle angle is good for better gas mixing
20	2015	Xinmei Yuan,Hongqi Liu,Ying Gao	Diesel engine SCR control: Current development and future challenges	Springer SIP,AG2015	Control system in SCR using system configuration, modelling & control strategy	Computer control of SCR system is much effective and high performace algoriythms needed for better control of parameters.
21	2015	Ibrahim Aslan Resitoglu, Kemal Altinis¸ik,Ali Keskin	The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems	Clean Techn Environ Policy (2015) 17:15–27	Characteristics of main pollutants from exhaust of diesel engines	Increased exhaust temperature is provided by DOC for DPF regeneration and thus increasing NOx conversion efficiency. DPFs

						reduce particulate emissions and SCR systems decrease the NOx emissions
22	2015	Jan Czerwinski , Yan Zimmerli , Andreas Mayer , Giovani D'Urbano & Daniel Zürcher	Emission Reduction with Diesel Particle Filter with SCR Coating (SDPF)	Springer SIP, AG 2015	Emission components along with NH3,NO,NO2 generation analysed using FTIR	Use of SDPF in comparison to SCR has fluctuating NOx conversion with fluctuating ammonia generation.
23	2015	Pingen Chen, Junmin Wang	Nonlinear Model Predictive Control of Integrated Diesel Engine and Selective Catalytic Reduction System for Simultaneous Fuel Economy Improvement and Emissions Reduction	Journal of Dynamic Systems, Measurement, and Control AUGUST 2015, Vol. 137 / 081008-1	Conversion efficiency and ammonia slip With start of injection timing and urea solution injection rate	Proposed controllers were found to be capable of reducing high percentage of NOX with less ammonia slip
24	2017	V.Praveena,M.L.J. Martin	A review on various after treatment techniques to reduce Nox emission in a CI Engine	Journal of the energy institute (2017)	operating parameters such as nature of catalyst, temperature range of catalyst, flow of DEF to injector and mixing of NH3 and NOx are discussed.	Gas hourly space velocity, quantity of reducing agents and exhaust gas temperature are the factors affecting the de-NOx performance of a HC SCR.Solid SCR is effective in NOx reduction but requires warm liquid HTF to be sprayed on solid salt making the system costly.
25	2018	GM Hasan Shahariar, Hyun Jo, Ocktaeck Lim	Analysis of the spray wall impingement of urea water solution for automotive SCR DeNOx systems	Energy procedea	Conditions of impingement and spray droplets distribution over walls	High wall temperature causes bounce and swirl thus better mixing of sprayed droplets and

						reducing soot accumulation.
26	2018	Wang, G., Ali, H.L., Zhang, J., Qi, J. et al	Development of Model Predictive Control Strategy of SCR System for Heavy-Duty Diesel Engines with a One-State Control-Oriented SCR Model	SAE international	NOx emission, NH3 slip, and NH3 storage of the SCR catalyst.	NOx conversion efficiency was found to be 96% and average slip in the cycle was 10ppm
27	2019	Qihua Ma, Dongjian ZhangID, Xuehui Gan	Simulation of the flow field and the chemical reaction coupling of selective catalytic reduction (SCR) system using an orthogonal experiment	PLoS ONE 14(7): e021613	exhaust temperature, the mass flow, and the exhaust pressure using simulation of flow field and chemical reaction.	For constant injection parameters, the NOx conversion efficiency is highest when the exhaust temperature is 200˚C— 400˚C.
28	2019	Caneon Kurian, Ajay Kumar Srivastava, Niranjan Gandigudi, Karan Anand	Soot deposition effects & microware regeneration modelling of diesel particulate filtration system	Journal of the energy institute	Conversion efficiency and filtration behaviour on regeneration of particulate matter, electric field distribution and temperature in DPF substrate	Soot deposition rate decreased at higher rate at higher load due to rise in temperature of exhaust giving rise to passive regeneration
29	2020	YounminKim, HasanRaza, SanghoLee, HongsukKim	Study on the thermal decomposition rate of ammonium carbamate for a diesel NOx reducing agent-generating system		Thermal decomposition rate of Ammonium carbamate and NOx conversion of SSCR system	High conversion efficiency was achieved with a reduction in soot formation and nozzle blockage problem was successfully solved.

Urea SCR

Urea SCR is one of the most promising techniques of NOx reduction which can convert about 95% of the oxides of nitrogen. It can efficiently work with exhaust temperature of200^{0}C. Basic components used in the system are Diesel oxidation catalyst (DOC), Diesel particulate filter (DPF), Diesel exhaust fluid (DEF) and Selective catalytic reduction (SCR).

Particulate matter consists of elemental carbon, total carbon, organic carbon, ions and water-soluble organic carbon. One of the effective methods of reducing particulate matter is the introduction of retrofits like Diesel oxidation catalyst (DOC), Diesel particulate filter(DPF) and Selective catalytic reduction (SCR). Use of these retrofits results in 90-95% reduction of particulate matter from the exhaust emission of diesel engines. [11]

Use of DPF reduces elemental carbon by easily capturing the soot particles. Presence of organic carbon can be reduced by the use of catalysts as they oxidize hydrocarbons and reduce the condensable organic carbon. Reduction of soot particles accumulation leads to the increased content of sulphate nanoparticles in DPF equipped vehicles.[11]

Vehicles equipped with catalyzed DPF and urea SCR reduced the particulate matter with efficiencies of 99.9% and 90% respectively. The plasma-assisted burner type DPF effectively reduces the particle number over the entire size range.[12]

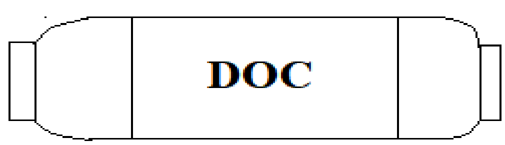


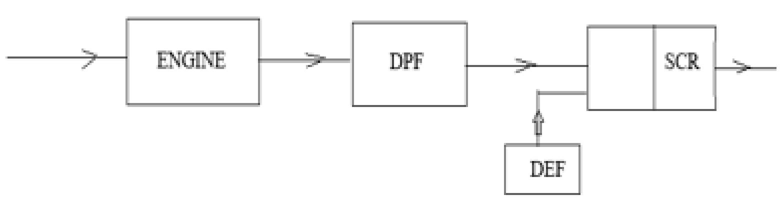
Fig:6(DOC with inlet & outlet loft)

Use of DOC, DPF and SCR highly affects the emission of particle number, particle mass and nitrogen compounds. Fuel consumption and engine power are not affected by the use of these retrofits.[13].These filters can reduce more than 90% of the particulate matter. At the same time, particulate size is also reduced.[14]

The exhaust of diesel engine contains about 17% unused oxygen by volume which is used for the oxidation of hydrocarbons. DOC converts hydrocarbons and carbon mono oxides into carbon dioxide and water. DOC is generally placed before DPF to utilize the oxidation of nitrates for regenerating the soot [4]. It is investigated that due to oxidation high heat is released which increases the temperature of exhaust line supporting DPF. For every 1% oxidation of CO, the exhaust gas temperature is supposed to increase by 90^0C[2]. Diesel particulate filter (DPF) is used to remove the particulate matter from the exhaust stream. DPF is so designed that it removes the collected particles by thermal regeneration process.

Use of DOC in upstream reduces the efficiency of CDPF.NO_2 proportion is increased with the use of DOC and a higher rate of particulate emission is observed which reduces the lower side temperature. Using the combination of DOC & DPF can reduce 90% of soot,80% hydrocarbons and 45% of carbon mono oxide (CO).[13]

DEF is an aqueous solution with 32.5% urea and 67.5% deionized water which is sprayed in exhaust stream for the reduction of NOx. The consumption of DEF was found to be 2% of fuel consumption. The spray of urea water solution on the walls of a constant volume combustion chamber plays an important role in avoiding the deposition risks. Development of the spray front increase the distribution area for spray which leads to better mixing and evaporation leading to low deposit risks.[15] Swirl and bouncing produced due to high wall temperature increases the mixing length which helps in reducing the deposits of urea from the exhaust pipe.[16]



Fig(3) schematic diagram of urea SCR

when DEF is injected into the exhaust stream urea decomposes into ammonia and isocyanic acid due to exhaust temperature.

$(NH_2)CO(NH_2)$ (molten)→ NH_3 + HNCO (1)

Due to hydrolysis of this isocyanic acid ammonia and carbon dioxide gases are produced.

HNCO +H_2O → CO2 + NH_3 (2)

Now ammonia in the presence of oxygen and a catalyst present in SCR reduces the oxides of Nitrogen

$4NH_3+4NO+O_2 \rightarrow 4N_2+H_2O$ (3)

$8\ NH_3+6NO_2 \rightarrow 7N_2+12\ H_2O$ (4)

$4\ NH_3+2NO+2NO_2 \rightarrow 4N_2+6\ H_2O$ (5)

$2\ NH_3+2NO_2 \rightarrow NH_4NO_3+N_2+\ H_2O$ (6)

Equation (1) shows how urea in molten form is decomposed into ammonia and hydrocyanic acid when it comes in contact with the high temperature of the exhaust. Equation (2) represents the hydrolysis of isocyanic acid in which ammonia and carbon dioxide are the main product. These two reactions occur without the requirement of any catalyst. Equation (3) can be considered as the standard reaction where the same amount of ammonia and NO react with oxygen. Equation (4) represents the slow and fast SCR reactions. Some undesirable reactions also take place as a result of which ammonium nitrate is produced at low temperatures below 200^0C. These undesirable reactions reduce the conversion of NOx and result in urea slip[17].

The efficiency of conversion of NOx is one of the major parameters in performance analysis of SCR

$$\text{NOx conversion} = (1 - (\text{NOx out}/\ \text{NOx in})) \times 100\% \qquad [18]$$

Catalysts used in SCR

Copper zeolite and iron zeolite are widely used catalysts in SCR. The reason being their high-temperature stability and good performance when working at low temperature. Copper zeolite-based SCR were found comparatively better than Fe zeolite due to their higher ammonia storage capacity and oxidation which results in reduced ammonia slip[19]

In addition to copper and iron zeolite, Vanadium based SCR catalysts, SiO_2 and TiO_2 are also used as the catalysts. Monolith catalysts are also used. Manganese based catalysts show good performance characteristics while using low-temperature SCR systems as efficiency is not much affected.[20]

Challenges in SCR

Various urea SCR systems have been used in trucks and in passenger cars[9]. Solution of Urea is injected into the catalytic tank of SCR with help the of a nozzle but it shows the low ammonia carrying capacity [21]. The major problem in SCR is freezing of DEF at temperatures below -11^{0}C which necessitates an integrated electric heater in the tank of DEF. It was investigated the regeneration of soot particles in the filter is difficult and microwave technology was supposed to get rid of the problem[17]. With SCR systems the cylinder of DEF needs to be filled frequently usually before the fuel tank gets empty.

Spray wall impingement phenomena of ad blue were analyzed with help of high-speed imaging technique and it was observed that pray front development differs at high temperatures and low temperatures. Low wall temperature leads to much wetting of walls and thus increasing the solid deposit risk. At high-temperature wall wetting reduces thus reducing the accumulation of solid deposits and the blockage of the pipe.[16]

Solid SCR

SSCR technology utilizes a solid reducing agent with higher ammonia density. In these systems ammonia is directly injected in the downstream side with help of nozzle. Due to less mixing time and low decomposition temperature of ammonia salt, the problems like blockage of urea carrying nozzle, low catalyst efficiency and low NOx efficiency are eliminated[22]**.**

Solid SCR needs a set up in which the use of DOC is required. Diesel particulate filter (DPF) maintains the pressure drop.DOC reduces various oxides except the oxides of nitrogen. Diesel particulate filter (DPF) reduces the carbon monoxide and carbon dioxides to carbon particles. Since exhaust temperature is high these carbon particles are burnt in this filter and are easily exhausted to the environment. The most typical work is to reduce the oxides of nitrogen. For this purpose, a solid catalyst is used in SSCR systems.

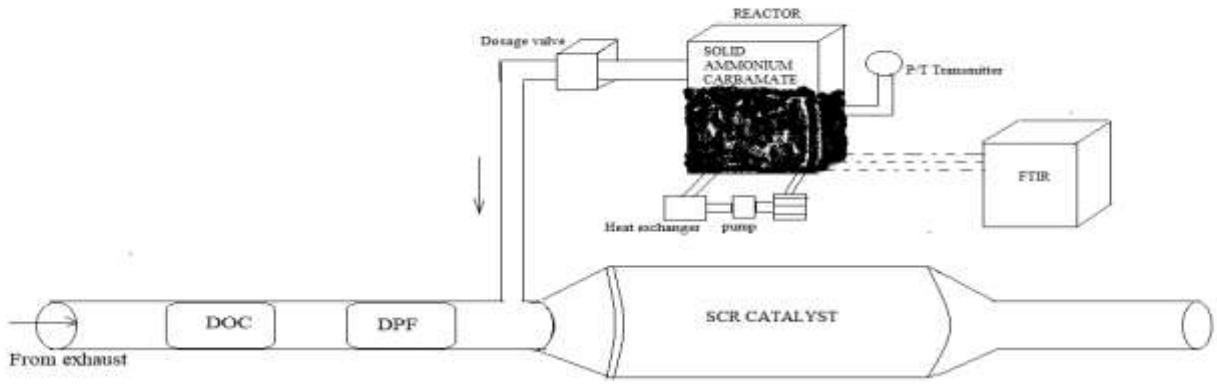


Fig:3 Line diagram of proposed emission system

Fig.(4) Solid SSCR system

Urea in aqueous form is not able to produce a higher amount of ammonia. In SCR systems using DEF produces Cyanuric acid and some other acids which gives rise to blockage of urea nozzle, decreases the catalyst activities thus reducing the NOx efficiency[23]. Injection of urea at a specific temperature is required in these systems. The above-mentioned problems can be reduced from SCR systems if ammonia is directly injected into the exhaust. This is the basic concept of SSCR where ammonia is generated with the help of a solid reductant. In SSCR systems the mass of reductant is reduced reason being the higher ammonia densities of solid salts. Emission reduction is also increased at lower temperatures which eliminate the problem of deposition risks. Compared to SCR system, in SSCR decomposition occurs at lower temperature and also reduces the mixing time. Generally used ammonia salts for production of ammonia gas are ammonium carbamate, ammonium carbonate, amino strontium chloride, amino calcium chloride etc.[23]. Among various available salts, ammonium carbamate is found to be the best option to use in the SSCR system in India as it has a minimum decomposing temperature. Ammonium carbamate decomposes fully at about 60^0C[22]. Metal salts of amino having decompose temperature of 30^0C to 50^0C are not opted in India due to their preservation complexities. In Europe countries, metal amino salts are preferred.

Figure (4) shows a composite type of SSCR system in which two systems are used for producing heat to decompose the solid salt. When the engine starts, the temperature of water in the water tank remains insufficient to produce heat for the decomposition of solid salt. At this time electronic unit produces the heat and thus providing ammonia gas. When the engine is in running condition and is warmed up, the electronic unit stops working automatically and heat of water tank is used for decomposing the solid salt thus providing ammonia gas.[22]

In 2014 a set up was established by Kim et al for the comparison of NOx reduction using solid urea and ammonium carbonate as salts for producing the reducing agent ammonia. It was investigated that solid urea requires high decomposition temperature and formation of undesirable substances like cyanuric acid was also observed during its decomposition. The system using ammonium carbonate was found to be much compatible as it bears low decomposition temperature. But the system needs extra care while designing due to the removal of water produced during the process. It was only a comparison of two salts for the production of reducing agent. The experiment did not consider the effect of various parameters like temperature, pressure, the mass of salt etc. on the decomposition reaction.[24]

In 2011 a system containing ammonium carbamate for the production of ammonia was developed by Lacin et al. This system could not explain the effect of various parameters which affect the thermal decomposition of ammonium carbamate.[9]

In 2013 an experiment using thermogravimetric analysis and a calorimeter was conducted by Lee et al for calculating the energy required for thermal decomposition of ammonium salts. Sufficient data to was provided to understand the chemical reaction but they failed to develop any mathematical model for the production of ammonia using ammonia salts.[25]

Kim et al 2020 experimentally provided the information regarding optimum production of ammonia for reduction of NOx using ammonium carbamate as the salt for the production of reducing agent. They also investigated the effect of temperature, pressure and mass of ammonium carbamate on the decomposition rate of the salt.[26]

Rate of decomposition of ammonium carbamate varies linearly with temperature. At high temperature, the rate of thermal decomposition is high thus requiring a robust reactor design which can bear high pressure. Size of the reactor must be large enough to reduce the frequency of refilling the reactor with ammonium carbamate. Mass of salt present in the reactor influences the reaction rate of decomposition. The optimized reaction rate of decomposition of salt is obtained only when the mass of salt present in the reactor is high. The reactor should be refilled as soon as the pressure in the reactor is observed less than injection pressure.[26]

Chemical kinetics of decomposition

Ammonium carbamate thermally decomposes into ammonia and carbon dioxide. Ramachandran et at 1998 investigated that thermal decomposition of ammonium carbamate occurs in two stages thus producing the intermediate products. Fulks et al 2009 observed during their TGA test that decomposition of salt is a single-stage phenomenon.

$$NH_4COONH_2 \rightleftharpoons 2NH_3+CO_2 \qquad (1)$$

$$NH_4COONH_2 \rightleftharpoons NH_3+HCOONH_2 \qquad (2a)$$

$$HCOONH_2 \rightleftharpoons NH_3+CO_2 \qquad (2b)$$

Equation (1) was given by Fulks et al 2009 and shows that solid ammonium carbamate can remain in equilibrium with the products obtained after decomposition. Equations (2a) and (2b) were predicted by Ramachandran et al 1998 which explains that decomposition of ammonium carbamate occurs in two stages.

Conclusions and Recommendations

Use of ammonia as a reducing agent increases the conversion efficiency of NOx to a large extent as per the requirements of BS-VI regulations. Problems of ammonia slip and reduced conversion efficiency are much reduced when using gaseous ammonia as a reducing agent. For this purpose use of ammonium carbamate is found to be the best solution due to its large ammonia containing capacity and reduced decomposition temperature. Since SSCR systems can work efficiently below a temperature of 200^0C, they are highly desirable in heavy diesel engines.

Use of ammonia as a reducing agent enables the system to work at temperatures below 200^0C which results in greater efficiency of conversion of NOx thus providing better control over malfunctioning. Results show that an efficient SSCR system may result in reduced size of the reductant tank and also reduced frequencies of filling the tank.

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