

A Review on Selective Catalytic Reduction (SCR)-A Promising Technology to mitigate NO_x of Modern Automobiles

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Abstract:

Diesel engine exhaust emissions like nitrogen oxides (NO_x) should be effectively removed by the suitable De-NO_x techniques to meet the stringent emission norms. This can be accomplished by a technique called Selective Catalytic Reduction (SCR) effectively. In SCR, the reducing agent ammonia (NH₃) which is required for the reduction of NO_x is obtained by the addition of Urea Water Solution (UWS) (32.5% aqueous urea solution) into high temperature exhaust gases in the form of an atomized spray. Even though this technique is more promising, there are many drawbacks associated within it like NH₃ slip, incomplete conversion of NO_x, deposit formation, etc. To overcome these drawbacks and also to optimize NH₃ generation, research work is underway worldwide in different wings. The paper deals with the an overview of SCR, construction, advantages, drawbacks etc. The alternate solution for ammonia formation by solid reactants were also highlighted

1. Introduction

The highly efficient aftertreatment technology to tackle NO_x is SCR. In SCR, ammonia (NH₃) or urea (NH₂-CO-NH₂) is used as reducing agent if nitrogen oxides (NO_x) have to be eliminated from the exhaust gases of diesel engines. The method is most efficient for the NO_x removal from stationary power plants. SCR technology was initially implemented in Japan in the 1970s and employed in fossil fuel power plants all over the major Japanese cities [14]. Stationary engines and power plants have been using NH₃ and urea based SCR systems since many decades. In the last 10 years, automobile manufactures focused their attention towards the further improvement of the technique to make it suitable for automobiles having diesel engines.

The major challenge involved with SCR systems is the reduction of catalytic converter volume at low temperatures and the suitable dosing strategy for NH₃ at frequently varying load conditions of the diesel engines.

Additionally, the risk associated concerning storing and handling of gaseous NH_3 is significant and consequentially it is not commonly used as a reducing agent directly. For reasons of toxic nature of NH_3 and handling and storing problems, urea is the preferred substitute for NH_3 as a reducing agent in automotive applications. The best procedure is injecting Urea Water Solution (UWS) in the form of spray to hot exhaust stream before the entry to the SCR catalyst.

Urea is an environmentally benign chemical which makes it more suitable for application to the SCR process. Urea is a fertilizer used in agriculture and available in a number of quality grades at a lower cost. Development of Urea-SCR over NH_3 -SCR has gained momentum due to various problems involved with the use of NH_3 . NH_3 is corrosive, toxic in nature and also a secondary pollutant. Handling of NH_3 to be accurate and it is required store at high pressure. In order to introduce NH_3 into the exhaust gas stream, proper dosage control mechanism is required [2].

The main advantage with this SCR system is high De- NO_x efficiency (90% or higher). The disadvantages involve the space required for the catalyst, high capital- and operating costs, formation of other emissions (NH_3 slip) and formation of undesirable

species which may lead to catalyst poisoning and deactivation. The NH_3 slip can be controlled by installing an oxidation catalyst after the SCR system. Although the SCR system has some drawbacks the technology has been chosen by the majority of the diesel engine manufactures due to absence of better technology to meet the stringent emission standards.

2. Selective Catalytic Reduction (SCR)

2.1 Reducing agents

There are different possible ways to introduce the reducing agent to the system; anhydrous NH_3 , aqueous NH_3 or an aqueous urea solution that decomposes to NH_3 . In order to avoid direct handling of both anhydrous and aqueous NH_3 , urea is often used as NH_3 source [3]. It has been shown that best SCR performance is obtained by gaseous NH_3 , followed by injection of NH_3 solution. The performance with solid urea and urea solution is comparatively poor due to incomplete evaporation and decomposition of urea [4]. Injecting a UWS is more convenient than any other form of urea injection.

2.2. Components and Working of SCR System

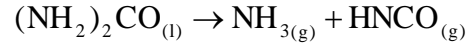
The major components of SCR system are 1) Catalyst where the conversion of NO_x into N₂ takes place 2) UWS injection system 3) UWS storage tank 4) Data acquisition system. Fig.1 gives the complete details of SCR system of modern automobile.

The UWS decomposition is as given below

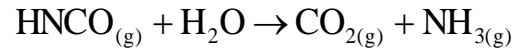
1) Evaporation of water from UWS



2) Urea decomposition (Thermolysis) urea into NH₃ and HNCO,



(3) Conversion of Isocyanic acid to NH₃(Hydrolysis of HNCO)



The SCR process makes use of various catalysts, mostly in the form of oxides of metals such as titanium, vanadium or molybdenum, impregnated onto a metallic or ceramic substrate. The present study is based on the SCR of NO_x with a commercially available vanadium based catalyst, V₂O₅-WO₃/TiO₂ commonly known as VWT. Typical operating temperatures for an SCR application ranges from 200-500^oC [5].

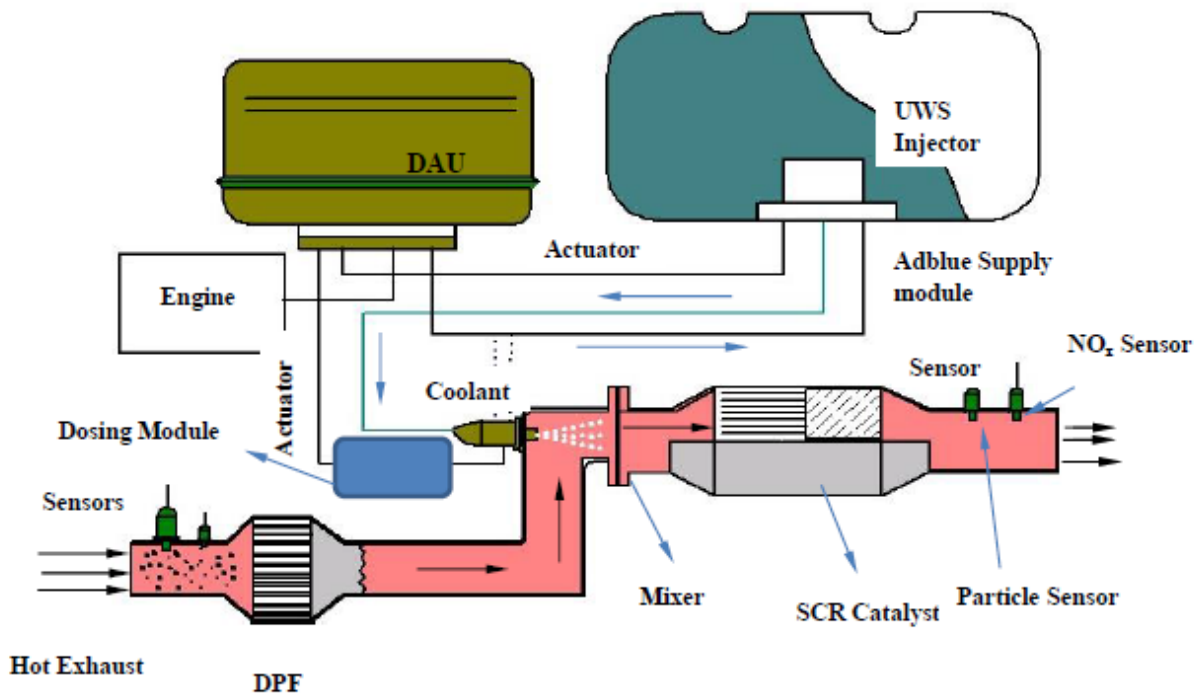
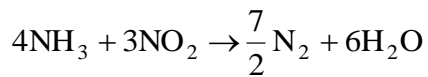
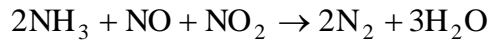
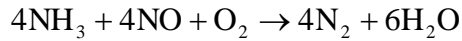


Fig.1. Components of SCR System of Automobiles [6].

NO_x reacts with NH₃ over catalyst and reduces to N₂. NO_x can be successfully

removed from lean diesel exhaust gases by using selective and catalytically supported

reduction technique. Ammonia(NH₃) reacts selectively with NO_x, along with oxygen to generate harmless products like nitrogen and water vapor. The following three overall SCR reactions are considered [7, 8].



The first reaction is known as *standard- SCR reaction* involves reduction of NO in equi-molar ratio with NH₃. The second reaction includes both the reduction of NO and NO₂ and this reaction is called *fast SCR reaction* which shows increased reaction rates in the presence of NO₂. The third reaction is *slow-SCR reaction* i.e., at NO₂/NO_x ratios higher than 50%, the De-NO_x behavior is lowered because of stronger involvement of slow SCR reactions reducing NO₂ only.

Despite this technology which was implemented by the some of the automobile companies there are some problems still exist like wall deposition, lower urea conversion efficiency, lower NO_x conversion efficiency, NH₃ slip, poisoning of catalysts etc. The problems associated with SCR systems can be reduced substantially by optimizing some parameters related to i) exhaust pipe

dimensions at the upstream of the catalyst ii) UWS injection system iii) Dosage of UWS iv) mixer and iv) catalyst.

2.3. UWS Sprays and UWS Spray Techniques

The UWS spray is a major process in SCR system and it has to be generated to suit flow conditions, size and shape of mixing pipe, and dosage is based on NO_x content in exhaust gas. If any error occurs in the injection of UWS (trade name: Ad Blue) results errors in flow at the upstream of the catalyst. The main intention with atomization processes is to maximize the gas-liquid interface since all transport processes are directly dependent upon this surface area and the exchange between the phases will improve with an increased surface area. The exchange between the phases in a spray system increases by several times compared to the case where the liquid is not disintegrated through atomization process [9].

The sizes of the droplets in a spray are usually described by 1) A suitable droplet size distribution function 2) The (mean) size parameter 3) The relative width of the distribution [10].

The different types of spray produced: hollow cone, solid cone and flat sprays. The droplet sizes ranging from 20-

150 μ m with an injection velocity of 5-25m/sec with injection pressure of 10 bar. The exact design and principle of the spray nozzles used for the Euro 6 trucks is known by individual provider. The principles of two types of spray nozzles might be of interest to try to understand the atomization mechanisms in these types of nozzles. Varieties of spray nozzles are available for SCR UWS injection [11]. Among them pressure nozzles and two fluid nozzles are mostly used.

The important feature for the atomization is the dimension of the orifice. The finest disintegration is reached when the orifice is small. But the constraint is, it is more difficult to keep the opening free from foreign particles. So, the minimum size of the orifice is usually limited to approximately to 0.3 mm [12]. The drawback with the pressure atomizer is naturally the need of a pressurized

liquid but also that the droplets size produced is relatively uneven and practicable when mass flow rate is low [9].

2.4. Injector Mountings

Straight pipe with angular injection is preferred when mixing length is not sufficient. Here spray impaction takes place on wall, thereby the solid hot surface of the pipe enhances evaporation. On the other hand at lower temperature of exhaust gas the wall increases evaporation.

The S-pipe is intended to test the advantage of spraying co axially to enhance the distribution of droplets. In both cases the injector is targeting at the bottom of the mixer; in S-bent pipe, the injector is further shifted downward because of additional lifting effect from flow deflection of S-bent design. The both the designs are shown in Fig 2.

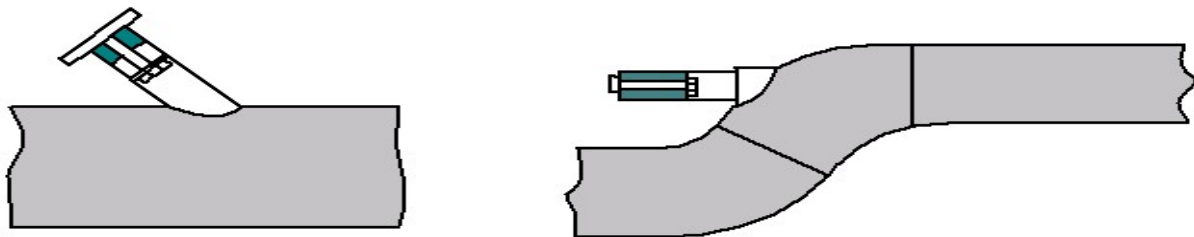


Fig.2. Angular injection mounting on a straight pipe (left) coaxial injection mounting on S- pipe (right)

2.5. Spray-wall Interaction

Based on the flow conditions of exhaust gas, spray condition of UWS, type of fluid and wall temperature, the different

phenomena may result when droplets impinge on wall. Chen et al. [13] have shown impinging droplets of UWS in six types of flow regimes. i) Adhesion-the droplet retains at the wall in a spherical form, ii) Rebound-the droplet bounces and hits back to the wall, iii) Spread- the droplet spreads out and forms a liquid film with increased fluidity, iv) Splash- some of the droplets break up and come out as smaller droplets while the rest remains in the wall, v) Rebound with break-up- the droplet bounces back and breaks up into multiple droplets and vi) Break-up-the droplet bounces back and breaks up into a number of small droplets.

2.6. Deposit Formation

The gaseous products of urea and their compounds at low temperature operation may result in health problems by inhaling exhaust gas of engines. The major drawback of the SCR system is incomplete evaporation and thermolysis where the injection parameters play a major role. The impingement of droplets over the walls of SCR mixing pipe and catalyst setup because of slow evaporation and thermolysis as well as the inertia of the droplets. However, if the evaporation and conversion do not take place fast enough, non-decomposed urea and other

byproducts may form crystals and become deposit inside the exhaust system. In addition to this, many factors affect the formation of urea deposits. If conversion does not happen quickly and efficiently, it can form liquid pool resulting in solid urea and other solid byproducts that attach to the inner pipe wall or mixers. The worst case scenario is the deposit formation for lower exhaust gas temperature and high NO_x levels. In this situation, there is low heat to decompose the large flow rate of urea.

The factors affecting deposit formation are categorized as 1) Geometrical factors: i) Injector mounting geometry ii) Pre injector exhaust pipe design iii) Pipe design after injector iv) Mixer type v) Mixer orientation and location vi) Insulation 2) Engine exhaust temperature and weather conditions outside the exhaust pipe 3) Dosing conditions: type of injection system, injector pulse width, frequency, etc.

Back pressure is another problem created due to deposit formation over SCR components such as UWS injector, mixing pipe and mixer. This back pressure reduces engine performance. The deposit formation on the SCR catalyst can reduce NO_x conversion efficiency. Decomposition of urea by heating in an open vessel at different temperatures showed that a variety of

byproducts by undesirable ways can form at different decomposition temperatures [41].

2.7. Urea and alternative NH₃ generation from the solid reductants

However, the UWS which is used has a number of drawbacks. It is a corrosive liquid with that freezes below -11 °C, decomposes slowly in the tank at temperatures above 50-60°C, crystallizes easily and has to be made from rather pure urea and distilled water to avoid a buildup of impurities on the SCR catalyst and DEF injection system. Another drawback is spray of UWS into the exhaust line, decreases the temperature of exhaust gas 10-15°C[1]. Moreover, there is solid deposit formation in the exhaust, and difficulties in dosing at exhaust temperatures below 200°C[15]. Additionally, creating a uniform NH₃ by UWS spray most challenging. Gaseous NH₃ can be generated from various solid reductants, each associated with various decomposition characteristics. The ammonium salts such as ammonium carbamate and ammonium carbonate are generally liberate ammonia. Similarly Magnesium ammine chloride, Calcium ammine chloride Strontium ammine chloride can also liberate ammonia by multiple reaction steps.

Conclusion

Selective Catalytic Reduction (SCR) technique of reduction of NO_x is most suitable for automobile diesel engines to meet the upcoming stringent emission norms. Although the technology is more efficient, there are several drawbacks like ammonia slip, deposit formation, etc. that are associated with it. It requires up gradation of technology. In order to avoid these problems mixers are most commonly used in SCR systems. Alternately, some of the reducing agents find their suitability as substitute for urea to generate NH₃.

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