A Review of NOx Reduction for Urea-SCR System

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Abstract

Exhaust after-treatment selective catalytic reduction (SCR) systems based on urea-water solution are state of the art technologies mitigating NOx emissions for diesel engine. Major challenges for implementing the systems are high NOx reduction performance. This study presents a detailed analysis of the urea-water spray wall impingement and influences on reducing agent distribution formation, thus system performance [13]. So in this review we have according to studies SCR by urea has been reported to be the most promising method for the control of NOx emissions from diesel engines. Catalytic decomposition of urea over a fixed flow reactor system has been examined for the selective catalytic reduction (SCR) of NOx from mobile sources. The conversion of urea into NH_3 the major product from the thermal decomposition of urea, increased with the reaction temperature [1].

Keyword: *Selective Catalytic Reduction (SCR), Urea, Nox, Emission treatment, pollution, Diesel Emission Fluid (DEF).*

Introduction

Selective catalytic reduction (SCR) is a means of converting nitrogen oxides, also referred to as NOx with the aid of a catalyst into diatomic nitrogen (N_2), and water (H_2O). A gaseous reduction, typically anhydrous ammonia, aqueous ammonia or urea, is added to a stream of flue or exhaust gas and is adsorbed onto a catalyst. Carbon dioxide, CO_2 is a reaction product when urea is used as the reduction. Selective catalytic reduction of NO*x* using ammonia as the reducing agent was patented in the United States. Development of SCR technology continued in Japan and the US in the early 1960s with research focusing on less expensive and more durable catalyst agents. The first large-scale SCR was installed by the IHI Corporation in 1978.

Commercial selective catalytic reduction systems are typically found on large utility boilers, industrial boilers, and municipal solid waste boilers and have been shown to reduce NO*x* by 70-95%. More recent applications include diesel engines, such as those found on large ships, diesel locomotives, gas turbines, and even automobiles.

Selective catalytic reduction (SCR) of NO by NH_3 is a well-developed technique and the most common technology for the control of nitrogen oxides emitted from stationary sources.
NH_3 might not be a suitable reducing agent for mobile sources mainly because of difficulties in its storage, handling, and transportation. As an alternative to overcome these problems associated with NH_3, urea is currently being considered as an NH_3 carrier for automotive emission control applications. It is generally accepted that urea decomposes into NH_3 as follows. When urea solution is atomized into a hot exhaust gas stream, the primary step for the decomposition is the evaporation of water from the droplets of urea solution [1].
Urea SCR method is suitable for heavy duty and low duty applications due to its higher NOx reduction potential. In spite of the challenging parameters such as urea dosing, mixing and proper decomposition to NH_3 and spray preparation, the SCR technology has been successfully introduced in the design passenger car market. In urea SCR, the chemical reactions take place at lower temperature of 200- 400ºC with the aid of a catalyst bed. Urea is injected in liquid form. DEF (Diesel emission fluid) is an aqueous solution with 32.5% urea content and

67.5% deionised water. 32.5% of urea is chosen to be optimum since it provides the lowest recrystallization temperature (-11°C). The commercial names for aqueous urea solution are DEF. The average DEF consumption is around 2% of diesel fuel consumption. The decomposition of urea into NH_3 takes place in 3 steps: evaporation, thermal decomposition and hydrolysis.

In equation (1) the water droplets evaporate from the urea water solution and results in molten urea.

$$NH_2\text{-}CO\text{-}NH_2\ (aqueous) \rightarrow NH_2\text{-}CO\text{-}NH_2\ (molten) + H_2O\ (gas) \qquad (1)$$

Equation (2) represents the thermal decomposition of molten urea to NH_3 and HNCO. This process starts around 152°C.

$$NH_2\text{-}CO\text{-}NH_2(molten) \rightarrow NH_3(gas) + HNCO(gas) \qquad (2)$$

The above two reactions do not require any catalyst and takes place in the decomposition tube. Equation (3) represents the hydrolysis of isocyanic acid to NH_3 and CO_2 in the presence of a catalyst.

$$HNCO(gas) + H_2O(gas) \rightarrow NH_3(gas) + CO_2(gas) \qquad (3)$$

In general, one mole of urea generates 2 moles of NH_3. Overdosing of urea is practiced to fully utilize the SCR catalyst. Also, the exhaust conditions of the engine vary with respect to flow rate, composition and temperature. Due to these factors, there is a risk of NH_3 slip especially at high temperature operating conditions. Euro VI norms regulates NH_3 emissions. Hence there is a need to oxidize NH_3 to N_2 by a downstream Ammonia Slip Catalyst (ASC). The major drawback of this method is handling of large quantities of NH_3 because NH_3 is toxic and corrosive. The SCR reactions are classified as standard, fast and slow reaction based on NH_3, NO and NO_2 availability.

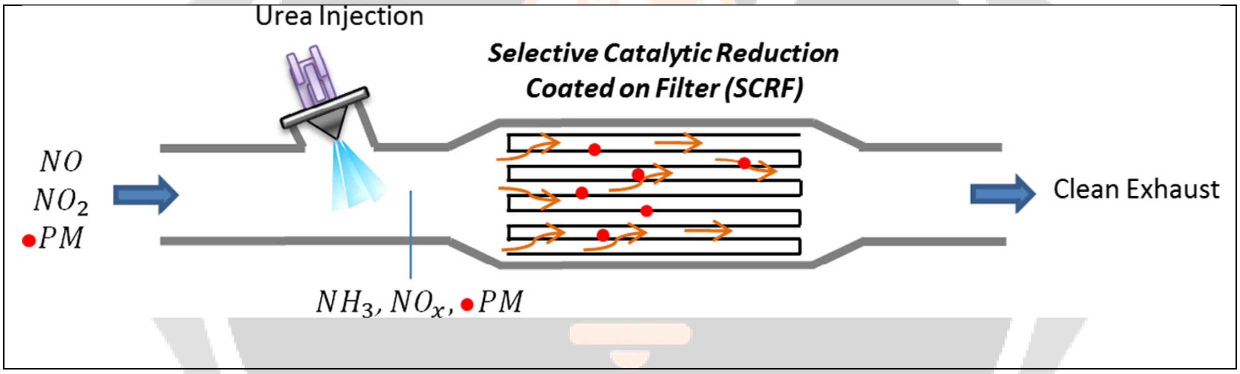

Fig. Urea-SCR operational principle

$$NH_3 + 4\ NO + O_2 \rightarrow 4N_2 + 6\ H_2O \qquad \textbf{(4)}$$

$$8NH_3 + 6\ NO_2 \rightarrow 7N_2 + 12\ H_2O \qquad \textbf{(5)}$$

4

$$NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6\ H_2O \qquad \textbf{(6)}$$

2

$$NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \qquad \textbf{(7)}$$

Equation (4) represents standard SCR reaction in which the ratio of NH_3 and NO is 1:1 and some moles of O_2 are consumed. Equation (5) represents slow SCR reaction where pure NO_2 takes place in the reaction. Equation (6) represents fast SCR reaction with NO and NO_2 ratio of 1:1. Besides these reactions, certain undesirable reactions also occurs which limits the NOx conversion. At lower temperatures below 200º C, NO_2 in the exhaust gas forms Ammonium Nitrate according to the reaction in equation (7).

The commonly used SCR catalysts are vanadium based. They demonstrate good NOx reduction at 300-450ºC, high temperature tolerance and superior resistance to sulphur poisoning. Improve the performance at high temperature. Vanadium demonstrates high temperature durability, good performance at low temperature conditions and high efficiencies and high space velocities. NO_2/NOx ratio improves the low temperature performance of SCR. Ammonia storage capacity is more for these catalysts at low temperature and less at higher temperature. The oxidation of NH_3 in the absence of NOx leads to formation of NO and N_2O (undesirable side reaction).

Thermal aging especially in the presence of moisture leads to degradation of SCR catalyst. Sintering, deillumination and thermal collapse are the mechanisms through which degradation occur. Effect of Sulphur poisoning is noted below 300ºC. Vanadium based SCR catalyst shows a little impact. The impact of Sulphur varies with thermal ageing for some catalysts, whereas for other catalysts it is the same. Due to this, NH reacts with oxygen rather than reacting with NOx, thus reducing the conversion efficiency [14].

Urea SCR System advantages

- Permits more optimized combustion
- Can enable better fuel efficiency/power
- No concerns about engine durability/oil degradation
- End product is nitrogen, water and carbon dioxide
- Urea not classified as hazardous to health
- Law sensitivity to fuel sulphur content its high conversion efficiency

Urea SCR System SCR trade-offs

- System adds weight
- Adequate urea supply infrastructure not yet in place
- Purchasing urea is additional cost
- System, including sensors and other compliance-related devices, must be maintained
- Urea freezes at 12 deg. F., so may require heated storage
- Most effective at constant speeds and high loads; least in stop/start
- Urea (also in some fertilizers) is a water pollutant/harmful to fish
- Not least is the particulate matter (PM) emission from the DI engine.

Literature Survey

Sung Dae Yim et al. (2004) the major products from the thermal decomposition of urea are NH_3. The disappearance of urea and the formation of NH_3 strongly depend on the reaction conditions, including the reaction temperature and the residence time of the feed gas stream. At a reaction temperature of 350 °C and a residence time of 0.113 s, urea was completely decomposed into NH_3. As the reaction temperature increased, complete decomposition of urea was achieved at shorter residence times. When the reaction temperature was sufficiently high (above 400 °C), the kinetic model for the thermal decomposition of urea described well the experimentally observed concentration variations of urea, isocyanic acid, and ammonia.

In the presence of O2 in the feed gas stream, the NH_3 produced by the urea decomposition was rapidly oxidized to N_2 over catalyst at the reaction temperatures above 250 °C. The model based on two main reactions including the thermal decomposition of urea and the catalytic oxidation of ammonia during the course of the decomposition of urea adequately describes the experimental data for the concentrations of urea, NH_3, for all the reactor operating conditions considered. The results suggest that the decomposition of urea into NH_3 occurs via the thermal decomposition route, whereas the subsequent the oxidation of ammonia is mainly caused by catalytic reaction.

Xiaobo Song et al. (2015) in summary, an engine experimental setup and test procedures were developed and conducted to determine the SCR inlet NH_3. Additionally, model was developed and studies of data the effects of NH_3 distribution on the SCR performance. Furthermore, the conclusions of the study are as follows:

1. The SCR outlet NOx distribution without the upstream urea injection is uniform. Based on this, the NH_3 distribution was determined to be present at the SCR inlet during urea injection through downstream NOx measurements.

2. The changes in exhaust mass flow rate, temperature and urea injection rate have a minor effect on the uniformity of the SCR inlet NH_3 and ANR with changes in the UI of less than 0.03.

3. The NH_3 distribution reduces the SCR NOx reduction efficiency by up to 7% and increases the NH_3 slip by 10–20 ppm with the inlet average ANR of 0.8 and higher. The NH_3 distribution does not affect the SCR performance at low ANR (0.6). Improving the UI of the SCR inlet NH_3 distribution reduces the urea usage by up to 15% to achieve the NOx reduction efficiency of 90%.

Jibing Jiang et al. (2015) a novel design of exhaust temperature control is proposed for assisting SCR systems in eliminating NOx emissions in diesel vehicles. The dynamic behaviour of exhaust temperature control is demonstrated by a theoretical and numerical approach. The following conclusions were drawn from this work. Firstly, the warm up condition will largely save the preheating time for the temperature control system and the working condition required in ETC testing significantly affects the start point of the novel design Finally, the NOx emissions reduction after the temperature control are evaluated by the simulated SCR model validated by specific experimental factors. The improved NOx emissions reduction efficiency can exceed 90% with more steady working performance, which satisfies the severe emissions regulations with more environmentally friendly and sustainable practical application.

Andreas Åberg et al. (2016) validation was done by simulating the output from a full-scale SCR monolith that was treating real engine gases from the European Transient Cycle (ETC). The methodology was successful in estimating the parameters. The predictive capabilities of the single-channel models were analysed, and it was found that the model with simplifications related to mass transfer, gave the lowest information of emission loss.

Azael Capetillo et al. (2017) an analysis of urea–water injection for an automotive SCR system using multiphase simulation by CFD commercial code was presented. For the operation point under analysis, only injection velocity and spray angle had significant impact on performance in relation to UI NH_3 and wall film formation. Second order interaction showed minimal impact. Results showed good agreement between the regressions predicted performances and the CFD calculated performances. DoE techniques can be used as a design improvement tool. In order to improve the performance of the system, the results here presented apply only for the specific engine design and operation point under study. Simulations still need to be validated against experimental data. Moreover, a quadratic regression model is necessary in order to carry design optimization.

V. Praveena et al. (2017) this article provides particularized information on after treatment methods in recent decades. Technology such as SCR reduces NOx in the exhaust gas to harmless N_2. Among these, SCR is a sustained technology in which the chemical reaction takes place at low temperature range of 200-400ºC. NH3 is used as a reduction in Urea SCR. The low temperature performance of this catalyst is improved by NO2/NOx ratio. The catalytic volume and type of injector influences the NOx conversion efficiency. Distance of injection from the SCR unit is another factor to be optimized. SCR control methods are used to control the excess of NOx and NH_3. In cold conditions, a mixer is used which favours the vaporization of the spray by impaction on its walls. The wall temperature is an important factor which decides whether the droplet after impingement will deposit or splash or rebound. A common issue in Urea SCR is the NH_3 slip. Pre-saturation of the system with NH_3, thermal management and urea dosing helps the system to achieve 98% NOx conversion. Presence of moisture in the catalyst is an obstacle in the application of SCR at cold start conditions. Electrical heaters are used to raise the exhaust temperature**.**

Conclusion

The urea reaction in a SCR system was investigated catalyst. The spray behaviour of Urea Water System analyzed. NH_3 was compared between the experimental method for temperature gradient at the outlet of the catalyst and NH_3 gradient at the inlet of the catalyst.

The standard deviation of NH_3 concentration decrease Nox emission in experimental results. The injection of urea can be divided into this stage. In the steady stage, droplets remain at the inlet of the mixer. Increase residual time of urea droplets in mixing evaporation and thermolysis reaction. The conversion rate of NOx reduction in this case is higher than that of the experimental case. Further, Results are in good with the experimental results. Thus, it is possible to effectively predict the actual NOx reduction rate of the Urea SCR system. The improved NOx emissions reduction efficiency can exceed 95% with more steady working performance, which the severe emissions with more environmentally friendly and sustainable practical application.

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