Numerical calculation and analysis of diesel Urea-SCR system

Yunjing Jiao 1,*, Yashuang Bai 1, Qingping Zheng 2

1 Department of Mechanical and Electrical Engineering, North China Institute of Aerospace Engineering, Langfang, 065000, China
2 School of Energy and Environmental Engineering, Hebei University of Technology, Tianjin, 300030, China

Corresponding author: jiaoyj1234567@163.com

Abstract. The urea selective catalytic reduction (Urea-SCR) system is a after-treatment device to control diesel engine emissions. On the basis of the experiment, a one-dimensional calculation model for the catalytic reduction of the engine is established. Through the one-dimensional simulation, the effect factors such as urea injection, exhaust temperature and length of catalysis converter in the diesel engine Urea-SCR system on NOx conversion efficiency are studied. This study provides a theoretical basis for the selection and matching of catalytic converters.

1. Introduction

With the increasing stricter of emission regulations, it is difficult to use the internal purification technology such as optimized combustion and cooling EGR technical route to meet the emission standards. Therefore, the technology of external purification has been developed rapidly. At present, more research is on the use of catalytic technology to reduce NOx emissions, mainly including NOx storage reduction (NSR) and selective catalytic reduction (SCR) [1-2]. NSR technology is suitable for lean burn gasoline engine and light diesel engine. While NH3-SCR technology is considered as the main technical route of future and heavy diesel engine to meet future emission regulations because of its advantages of high efficiency, high selectivity, high economy and sulfur tolerance [3-6]. It will also be the main technical direction of domestic diesel engine emission upgrading in the future [3].

NH3-SCR removal of NOx in diesel engine exhaust reaction is a kind of gas-solid heterogeneous catalytic reaction. The reaction mechanism of the research and the establishment of the mathematical model is to improve the SCR catalytic conversion efficiency and optimize the design of converter. Urea-SCR system is a post-treatment device for controlling diesel engine emission. Its working principle is shown in figure 1. Concentration of 32.5% urea solution is injected into the exhaust pipe, then the urea solution is decomposed into ammonia and carbon dioxide at the high temperature of the

Figure 1. Principle diagram of SCR system
exhaust. Under the action of catalyst, ammonia can react with NOx and reduce NOx to harmless nitrogen and water.

2. Methodology

2.1. Basic chemical reaction

2.1.1. Generation of ammonia gas.
After the urea solution was injected into the exhaust pipe, the urea solution was first evaporated to precipitate the urea particles. The isomoles of ammonia and ISO-isocyanic acid were generated by the urea pyrolysis reaction.
\[ \text{CO(NH}_2\text{)}_2 \rightarrow \text{NH}_3 + \text{HNCO} \] (1)

Further hydrolysis of isocyanic acid:
\[ \text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2 \] (2)

2.1.2. Catalytic reduction of NOx
NOx reduction with ammonia is mainly controlled by the three SCR reactions expressed in Equation (3-5), which are usually referred as standard, fast and slow SCR[9].

Standard SCR reaction:
\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \] (3)

Rapid SCR reduction:
\[ 4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \] (4)

Slow SCR reduction:
\[ 4\text{NH}_3 + 3\text{NO}_2 \rightarrow 3.5\text{N}_2 + 6\text{H}_2\text{O} \] (5)

Equation (3) and (4) are the main reactions in the catalytic reduction of NOx. When NH3 selectively restores NOx, the following side effects will also occur.
\[ 4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \] (6)
\[ 8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \] (7)
\[ 4\text{NH}_3 + 7\text{O}_2 \rightarrow 4\text{NO}_2 + 6\text{H}_2\text{O} \] (8)
\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \] (9)
\[ 4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} \] (10)
\[ 2\text{NH}_3 + 2\text{O}_2 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O} \] (11)

In the exhaust emission of diesel engines, the content of NOx is mainly NO, which usually accounts for 85%–95% of NOx content. So in catalytic reduction of NOx equation (3) is the main reaction. The SCR reaction kinetic highly depends on temperature and NO2/NOx ratio[10-11]. So the equation (4) has the higher priority than equation (3), and the NO2 and a part of NO in the exhaust gas can be quickly eliminated through the reaction formula (4). Through the reaction of equations (3) and (4), most NOx is transformed into harmless N2 and H2O.

2.2. Establishment of calculation model and model verification

2.2.1. Calculation model
The flow part of the cellular catalytic converter consists of hundreds of independent channels surrounded by the wall of the matrix. The following physical / chemical effects are mainly included in a single channel, including the convection, diffusion and conduction of gas, wall heat transfer, pore diffusion, surface coverage and active site catalytic conversion.
One-dimensional calculation method is used in this study. The single channel model is used to calculate the inlet flow and component concentration. The radial wall heat transfer is not considered.

The mass conservation equation in a single channel can be expressed as following equation (12).

\[
\frac{\partial \rho_g}{\partial t} + \frac{\partial \rho_g \cdot v_g}{\partial z} = 0
\]  

(12)  

\(\rho_g\): gas density, t: time, \(v_g\): gas velocity in the channel, z: the axial space coordinate.

Considering the gas component and its chemical reaction, the equation of gas component balance in a single channel can be expressed as equation (13) \[8\].

\[
\varepsilon_g \frac{\partial}{\partial z} (\rho_g \cdot D_{eff} \cdot \frac{\partial w_{k,g}}{\partial z}) + MG_{k,g} \sum_{i=1}^{l} v_{i,k} \cdot \dot{r}_i (c_i^L, T_i)
\]

(13)

\(\varepsilon_g\): porosity, \(w_{k,g}\): mass fraction of components of \(k\), \(D_{eff}\): effective diffusion coefficient, \(v_{i,k}\): measurement coefficient of \(k\) components in the chemical reaction \(I\), \(MG_{k,g}\): molar mass of component \(k\), \(\dot{r}_i (c_i^L, T_i)\): the molar reaction rate of ith reaction.

Assuming that the viscous dissipation can be ignored, the energy equation of gas phase is as following equation (14).

\[
\varepsilon_g \frac{\partial}{\partial z} (\rho_g \cdot \sum_{k=1}^{K} w_{k,g} \cdot h_k) = -\varepsilon_g \frac{\partial}{\partial z} (\rho_g \cdot \sum_{k=1}^{K} w_{k,g} \cdot v_g) + \varepsilon_g \frac{\partial}{\partial z} (\lambda_g \cdot \frac{\partial T_g}{\partial z})
\]

(14)

\(T_g\): gas temperature; \(h_k\): enthalpy value of components; \(\lambda_g\): Coefficient of thermal conductivity; \(k_h\): heat transfer coefficient between gas phase and wall; \(a_{trans}\): total channel surface area per unit volume; \(\Delta h_i\): the molar heat of reaction.

Assuming that the heat of chemical reaction is first transmitted to the solid phase and then to the gas phase by convection, the equation of energy conservation of the solid phase is as following equation (15).

\[
(1-\varepsilon_g) \rho_s \cdot \frac{\partial (c_{p,s} \cdot T_s)}{\partial z} = (1-\varepsilon_g) \rho_s \cdot \frac{\partial (\lambda_s \cdot \frac{\partial T_s}{\partial z})}{\partial z} - a_{trans} \cdot k_h (T_s - T_g) + \sum_{i=1}^{l} \Delta h_i \cdot \dot{r}_i (c_i^L, T_i) + \dot{q}_{Rad}
\]

(15)

\(T_s\): temperature of the inner wall of the catalytic converter channel; \(\lambda_s\): the thermal conductivity; \(\dot{q}_{Rad}\): represents the radial heat radiation quantity of the wall surface, and represents the environmental heat loss in the one-dimensional model.

2.2.2. Verification of model

Figure 2 is SCR catalysts model, which mainly includes three parts. The first part is the entrance boundary conditions, which need to define the inlet temperature, inlet flow, as well as the concentration of the gas composition and so on. In the entrance to the gas composition, the concentrations of the urea decomposition HCNO and NH3 are input under the corresponding conditions. In the calculation, urea evaporation and pyrolysis reaction are complete, so in theory the urea component all transformed into HCNO and NH3. The second part defines the physical properties and chemical reaction rate parameters. Physical properties include catalysts size, density, and the holes.
of the porous carrier density, specific heat and thermal conductivity, and chemical reaction rate parameters include activation energy and frequency factor, etc. The third part of the model is the exit condition, and the pressure, temperature and exhaust components of the outlet are defined. Before numerical calculation, the model should be verified at first. In this study, the calculated value of catalytic conversion efficiency under 13 working conditions was compared with the experimental value, as shown in figure 3.

### Table 1. Main structural parameters of catalyst

| parameter types     | Value            |
|---------------------|------------------|
| Catalyst type       | V-SCR            |
| Matrix diameter     | 266.7mm          |
| Matrix length       | 152.4mm          |
| Hole density        | 400mesh          |
| Substrate thickness | 6/1000 inch      |

Figure 3 is simulation value and experimental value. Under the working condition of steady state (ESC), test value and the calculated value of the overall trend is consistent. The operation condition of the maximum relative error for the working condition is the condition of 5, 7 and 11 and the three condition are the partial load condition at different speed. Under partial load conditions, the working condition of operating point of 5 and 7, respectively is under 50% load condition and 25% load conditions at A speed. Operating mode 11 is under 25% load at C speed. The maximum error is less than 10%. It shows that the model boundary setting and parameter selection are reasonable.

### Figure 2. Catalytic converter model

### Figure 3. Comparision of catalytic conversion rate under steady state conditions

#### 3. Calculation results and analysis

3.1. **influence of ammonia nitrogen ratio and temperature on conversion efficiency**

The ratio of ammonia to nitrogen (n(NH3)/n(NOx)) is a very important index in the SCR operation. For one thing, the ammonia nitrogen n(NH3)/n(NOx) ratio will have a great influence on the NOx conversion rate. For another thing, the n(NH3)/n(NOx) ratio of ammonia nitrogen directly determines the dosage of reducing agent NH3. This calculation can provide theoretical support for the control of the amount of urea injection by studying the effect of ammonia nitrogen ratio on the conversion efficiency of catalytic converters under the condition of a certain discharge flow and temperature. Figure 4 shows the effect of different ammonia nitrogen ratios and exhaust temperature on catalytic converter efficiency. The overall trend is that the catalytic conversion efficiency of NOx increases with the increase of ammonia nitrogen ratio (n(NH3)/n(NOx)). At low temperature, the conversion rate of NOx tends to be constant value as the ratio of ammonia to nitrogen increases. When the exhaust temperature is 300°C, as the ratio of ammonia to nitrogen increases, the conversion efficiency increases and when the ratio of ammonia to nitrogen reaches 0.8, the conversion efficiency reaches the maximum value of 67.6%. When the NH3 supply exceeds this critical point, it will make NH3 too late to react and cause leakage. When the temperature is 370°C and 430°C, the conversion
efficiency reaches the maximum while ammonia nitrogen ratio is close to 1. When the temperature reaches 500 °C and the ratio of ammonia to nitrogen is 1, the conversion rate of NOx is obviously lower than that at 370°C and 430°C. But it can be seen from the Figure 4 that with the increase of the ratio of ammonia to nitrogen, the conversion rate of NOx has been in a slow rising state. Through one dimensional numerical calculation, the maximum conversion rate of diesel engine under specified working conditions can be quickly determined, and the leakage of ammonia can be controlled in the lowest range.

Figure 4.Effect of ammonia - nitrogen ratio and temperature on conversion efficiency

3.2. Influence of axial position of catalytic converter on NOx catalytic conversion rate

In figure 5, a, b, c, d, e and f correspond to the position of 0.15, 0.3, 0.45, 0.6, 0.75, 0.9 of the total length. Figure 6 shows the NOx conversion rate of different positions in the axial direction of catalytic converter at n(NH3)/n(NOx)=1 at different exhaust temperatures. Figure 6 shows that when the reaction temperature is low, the NOx conversion rate increases approximately linearly along the axial position of the catalytic converter due to slow SCR reaction. At 300 °C catalysts axial position 0.6 meet the light-off characteristics requirements, and at 370 °C to 500 °C the ignition characteristic is reached at the position of length ratio 0.2-0.3. Then the conversion efficiency rises slowly. When the temperature reaches 500 °C, NOx conversion rate is lower than 370°C to 430°C in the axial position. This is mainly due to the high temperature, which not only causes the overheating damage of the catalyst, but also makes the reductant NH3 directly oxidize the loss and produce a new NOx.

Figure 5. Schematic diagram of SCR system

Figure 6. Influence of axial position of catalytic converter on conversion efficiency
4. conclusion
On the basis of the experiment, a one-dimensional calculation model for the catalytic reduction of the engine is established. And the boundary conditions are determined by combining the structure parameters and the performance parameters of the catalyst. The feasibility of the one-dimensional model is verified by comparing with the test results. The effects of different ammonia nitrogen ratio, exhaust temperature and catalyst length on catalytic conversion efficiency are calculated and analyzed.

(1) With the improvement of ammonia nitrogen ratio n(NH3)/n(NOx), the catalytic conversion efficiency of NOx is increased. At low temperature, the NOx conversion rate tends to be fixed with the increase of ammonia to nitrogen ratio. When NH3 supply exceeds this critical value, NH3 leakage will increase rapidly. Through one-dimensional numerical calculation, the maximum conversion rate of diesel engine can be determined quickly and the ammonia leakage can be controlled within the minimum range.

(2) While the temperature is higher, the initial reaction speed of SCR is faster and the time required to complete reaction is shorter. But too high exhaust temperature caused NH3 to undergo oxidation reaction and generate NOx compound again, so that the catalytic conversion rate decreased with the continuous increase of exhaust temperature. Therefore, with the increase of exhaust temperature, the conversion of NOx increases first and then decreases.

(3) According to the influence of the axial position of the catalytic converter on the catalytic conversion rate of NOx, it can be concluded that the NOx conversion rate of different axial directions of the catalytic converter is also different at different exhaust temperatures. High and low temperature conditions have different requirements on the length of the carrier. In the design of SCR catalytic converter, the size of the carrier should be determined according to the exhaust temperature of diesel engine.

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