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Research on selective non-catalytic NOx reduction (SNCR) for diesel engine

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ABSTRACT

This paper proposes a selective non-catalytic reduction (NOx) system for diesel engine with 40% methylamine (CH_3NH_2) aqueous solution as the reducing agent, and carries out an engine bench test. According to the results, CH_3NH_2 began to separate NH_2 out at the exhaust temperature of 250~300℃, the NOx reduction rate of the SNCR system increased rapidly with the increase of the engine load and it reached 70% at the exhaust temperature of 470℃. On this basis, this paper establishes a database containing 13 kinds of physical parameters of methylamine, uses CHEMKIN to establish the reduction process of the gas phase chemical reaction mechanism and imports the file into the general CFD software FireV2011 to numerically simulate the reduction process of the SNCR system. The results indicate that NOx is fully reduced in one rreaction cycle starting from the injection of the reducing agent.

1. INTRODUCTION

The particulate matters (PM) and nitrogen oxides (NOx) in the exhaust gas emitted from diesel engines have become one of the main sources of air pollution in urban areas. With the application of the electronically controlled high-pressure common rail technology, the national III emission standard can be achieved just by optimizing the diesel engine combustion system; however, when it comes to the national IV and above emission standards, optimizing the combustion system and other in-engine purification methods can no longer work. Therefore, post-emission treatment has become the most effective means to reduce PM and NOx emissions. Currently, selective catalytic reduction (SCR) NOx systems is widely applied internationally to reduce NOx emissions from diesel engines [1], which uses 32.5% urea aqueous solution as the reducing agent. The urea aqueous solution is injected into the high-temperature diesel engine exhaust gas by the fuel supply device. In the presence of the catalyst, the NOx in the exhaust gas is reduced to N_2 and H_2O. The SCR system combined with a diesel oxidation catalyst (DOC)+ a particle trap (POC) or heated DPF can meet the requirements of the national V and even the European VI emission standards [2].

2. PHYSICAL AND CHEMICAL PROPERTIES OF THE METHYLAMINE AQUEOUS SOLUTION

The physical and chemical properties of the 40% methylamine (CH_3NH_2) aqueous solution and the 32.5% urea aqueous solution are shown in Table 1. As can be seen, the 40% methylamine aqueous solution has a melting point of -39°C, and the 32.5% urea aqueous solution -11°C. The former is significantly lower than the latter. This means, in low temperature conditions in winter, if there is no additional heating device, the 32.5% urea aqueous solution will be frozen below -11°C and cannot be used as a reducing agent. The 40% methylamine aqueous solution, on the other hand, can be used in low temperature weather without other insulation measures. In addition, the urea aqueous solution also has the problem of urea precipitation in the exhaust gas, while the reaction between the 40% methylamine aqueous solution and 40% methylamine aqueous solution can be transformed directly into a product in a high temperature waste atmosphere, so there is no concern that the reducing agent nozzle will be clogged with crystals.

Table 1. Physical and chemical properties of methylamine and urea [4]

Chinese name	甲胺	尿素
English name	Monomethylamine Aminomethane	Urea
Appearance	Colourless transparent liquid	Colourless transparent liquid
Molecular	CH_3NH_2	$CO(NH_2)_2$
Molecular	31.10	60.1
Solubility	Soluble in water, ethanol and	Soluble in water and liquid
Melting point	40% aqueous solution: -39°C	32.5% aqueous solution” -11 °C
Density	0.91 g/cm^3	1.335g/cm^3
Acidity	Weakly alkaline; PH8.8	Weakly alkaline; PH7.6
Viscosity	40℃1.5mPa.s	25℃1.4m Pa.s

2.1 Reaction mechanisms of SCR and SNCR reducing agents

The reaction mechanisms of SCR and SNCR are different. The chemical reaction equations of urea water with NOx are roughly as follows:

$$NH_2CONH_2+H_2O\rightarrow 2NH_3+CO_2 \quad (1)$$

$$NO+NO_2+2NH_3\rightarrow 2N_2+3H_2O \quad (2)$$

$$4NO+O_2+4NH_3\rightarrow 4N_2+6H_2O \quad (3)$$

$$2NO_2+O_2+4NH_3\rightarrow 3N_2+6H_2O \quad (4)$$

As can be seen from the above, the reducing agent in the urea aqueous solution that reacts with NOx is NH_3, but in the absence of catalyst, NH_3 and NO can react only at a temperature of above 700℃, while the maximum temperature of exhaust gas from a diesel engine is about 550℃. Therefore, the reducing agent in the 32.5% urea aqueous solution can only be used in catalytic reduction.

The chemical reaction equations of the methylamine aqueous solution with NOx are as follows [5]:

$$CH_3NH_2+O_2\rightarrow CH2NH_2+HO_2 \quad (5)$$

$$CH_2NH_2+O_2\rightarrow CH_2NH_2OO \quad (6)$$

$$CH_2NH_2OO+CH_3NH_2\rightarrow NH_2CH_2OOH+CH_2NH_2 \quad (7)$$

$$NH_2CH_2OOH\rightarrow NH_2+CH_2O+OH \quad (8)$$

$$NH_2+NO\rightarrow N_2+H_2O \quad (9)$$

Methylamine at 250℃~300℃ will decompose and produce NH_2. The energy required to activate the reaction is relatively low, so the reaction can proceed at a relatively low temperature. The reaction causes NH_2 to be rapidly consumed, while NO is converted to N_2. Since the reaction rate of NH_2 is much greater than that of NH_3, the methylamine aqueous solution as the reducing agent has a better NO reduction rate.

2.2 Theoretical injection quantity of the methylamine aqueous solution

More than 90% of the NOx exhausted from diesel engines is NO. It is believed that methylamine reacts mainly with NO. In the chemical reaction of methylamine with NOx, the molar ratio of CH_3NH_2 to NO is 1:1. Assuming that the gas mass exhausted per unit time is Akg, and that the molar mass of the exhaust gas is 29kg/kmol, when the NOx emission is Bppm, the NOx mass in the exhaust gas per unit time can be expressed as:

DeNOx=AB*10-6/29 kmol

The mass of NO and NO_2 in the exhaust gas is 0.9DeNOx kmol and 0.1DeNOx kmol, respectively,The molecular weight of methylamine is 31.1,So the mass of methylamine required for the reaction is m=0.9DeNOx*31.1 kg.

If the 40% CH_3NH_2 aqueous solution is used, the mass of the methylamine aqueous solution consumed will be M=2.41AB*10-6 kg.

Based on this, the electronic control unit (ECU) for controlling the amount of methylamine aqueous solution is calibrated.

2.3 Physical and chemical parameter database of the methylamine aqueous solution

Most general-purpose CFD software (e.g. Fire V2011 and Fluent, etc.) does not have a database that describes the physical and chemical properties of the methylamine aqueous solution [7]. In order to analyze the flow field within SNCR and the NOx reduction reaction process, this paper calculates 13 parameters describing the physical and chemical properties of the 40% methylamine aqueous solution, namely liquid density, liquid viscosity, liquid specific heat, surface tension, liquid thermal conductivity, number of liquid surface layers, liquid diffusion coefficient, latent heat of vaporization, vapour pressure, thermal conductivity of gas, kinetic gas viscosity, gas specific heat (including integral specific heat and differential specific heat). From 1 to 5000K, the critical temperature of the 40% methylamine aqueous solution is 560.30K [8]. At a calculation interval of 10K (liquid) or 100K (gaseous), 13 kinds of physical and chemical parameters are calculated, and then thousands of physical and chemical parameters are input into the Fire V2011 methylamine aqueous solution database. For details, please see reference [8].

3. COMPUTATIONAL MODEL AND ANALYTICAL METHOD

3.1 Calculation model

Figure.1 CHEMKIN reaction model diagram

In the above reaction model diagram, Inlet1 indicates the inlet of the engine exhaust gas and Inlet2 the inlet of methylamine injection. The reactor chooses PSR.Product as the exhaust gas outlet. Assuming that the tail gas and methylamine enter the reactor at a steady flow rate, in an instant, the tail gas and methylamine are dispersed evenly throughout the reactor and are mixed completely, and that is why the reactor PSR (perfectly stirred reactor) is selected, where the rate at which the reactant is converted into a product is controlled by the rate of the chemical reaction rather than by the mixing process.

In the calculation of CHEMKIN, four subsequent examples are set up, where only the temperature parameter setting is changed. The initial temperature of the reactor is set to 550K, 600K, 650K, 700K and 750K, respectively, and then operation calculation is carried out. After post-processing, the graph of the nitrogen oxides reaction curve is obtained (Figure.2). This figure shows the temperature characteristics of the methylamine-NO_X reaction system, where the higher the temperature, the more nitrogen oxides are reduced, and the higher the conversion rate is. The maximum value can be as high as 70, which is consistent with the experimental result of

SNCR, proving the effectiveness of the calculation model of the NH_2-NO system.

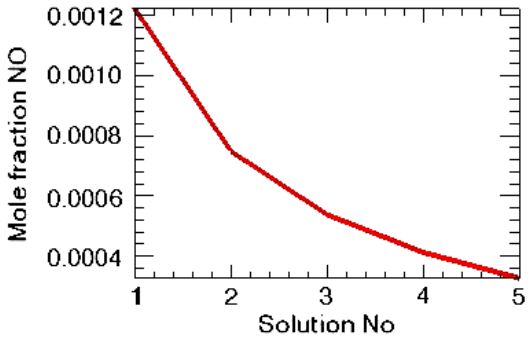

Figure 2. Nitrogen oxide reaction curve

The governing equation used to describe the spray, droplet evaporation and decomposition of aqueous solution of methylamine in SNCR system, mixing with high temperature exhaust gas and reduction reaction process is not only include the basic governing equations such as mass conservation equations, momentum conservation equations, energy conservation equations but also standard k-ε model and standard wall function.The concrete calculation also includes the material transport model, the droplet breakage model, the evaporation model and the turbulence diffusion model. Due to the presence of N_2, O_2, H_2O, CO_2, NO_X and other gas components in the exhaust gas, the multi-phase component transport model in Fire V2011 is selected, and according to the physical and chemical properties of the methylamine aqueous solution, the Huh-Gosman model, the thermolysis model and the Enable model in Fire V2011 are selected for the droplet breakage model, the evaporation model and the turbulence diffusion model [7].

Since there is no model setting for the reaction mechanism of methylamine-NOX in FireV2011 software,before calculation,a gas phase chemical reaction mechanism file describing the reduction process based on the NH2-NO reaction mechanism model and kinetic parameters shown in Table 2.1 was established by the gas phase chemical reaction kinetics software package CHEMKIN.Then,the gas phase chemical reaction mechanism file (chem.inp), thermodynamic database file (therm.dat), transport property file (trans.dat), etc. will be coupled to FireV2011 via the CHEMKIN interface in the FIRE software.Finally, the calculation model of the SNCR system was established.

Table 2. Detailed reaction mechanism model of the NH_2-NO system [7]

Serial number	Base reaction	Pre-exponential factor	Temperature Coefficient	Reaction activation energy
1	NH2 + NO =>	2.610E+19	-2.369	3623.0
2	NH2 + NO =>	4.290E+10	0.294	-3640.0
3	NNH + NO =>	1.200E+06	2.00	-4987.0
4	NNH => N_2 + H	1.00E+04	0.00	0

According to the chemical reaction mechanism in Table 2, the gas kinetics file is prepared as follows (Figure.3):

```
ELEMENTS H C N O
END
SPECIES N2 H2O NH2 NO CH3 CH3NH2 NNH HNO OH H
END
REACTIONS
  NH2 + NO => N2 + H2O        2.610E+19   -2.369   3623.0
  NH2 + NO => NNH + OH        4.290E+10    0.294   -3640.0
  NNH + NO => HNO + N2        1.200E+06    2.00    -4987.0
  NNH => N2 + H               1.00E+04     0.00    0
END
```

Figure 3. Gas kinetics file

4. FEASIBILITY VERIFICATION OF THE CALCULATION METHOD

The bench test of the SNCR system was carried out using a 6-cylinder direct injection diesel engine, as shown in Table 3. The system diagram is shown in Figure.4.

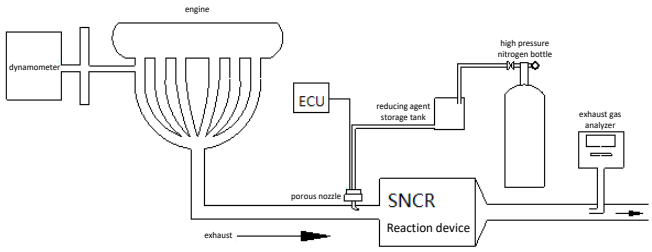

Figure 4. SNCR system experimental diagram

Table 3. Main technical parameters of the test engine

Specification	Parameter
Engine type	Four-stroke, water-cooled, inline engine
Displacement	6.94 (L)
Number of cylinders	6
Bore × travel	105×125 (mm)
Compression ratio	17:1
Rated speed	2800r/min
Maximum torque	400Nm
Rated power	103kw

In order to increase the reaction time of CH_3NH_2 with NOx, the NO reduction rate was increased in one reaction cycle after the injection of the reducing agent. The SNCR reaction device shown in Figure.1 is designed with a labyrinth structure, as shown in Figure.5. The test load conditions are respectively 1400r/min, 1800r/min and 2200r/min.

Take the load of 1800r/min for example. The concentrations of NO before and after the 40% methylamine (CH_3NH_2) aqueous solution is sprayed are measured by the AVL DIGAS4000LIGHT five gas analyzer, as shown in Figure.6. It can be seen that CH_3NH_2 initially decomposed and produced a large amount of NH_2 at an exhaust temperature of 250 to 300°C, resulting in the significant reduction of NO emission. With the increase of the engine load, the NO conversion rate increased rapidly. When the exhaust gas temperature reached

470℃, the NO conversion rate in the SNCR systems was up to 70% [10]. The decomposition temperature for NH_2 was between 300 and 550°C, which is also consistent with the exhaust temperature range for diesel engines (Figure.6).

The results of the numerical analysis using the same initial and boundary conditions as in the 1800r/min case are shown in Figure.7. It can be seen that the calculation results of the NO conversion rate are quite consistent with the experimental results, thus verifying the feasibility of the calculation method.

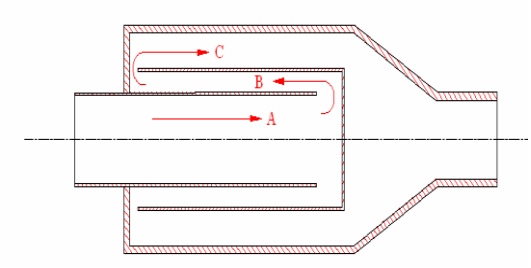

Figure 5. Schematic diagram of the reaction device

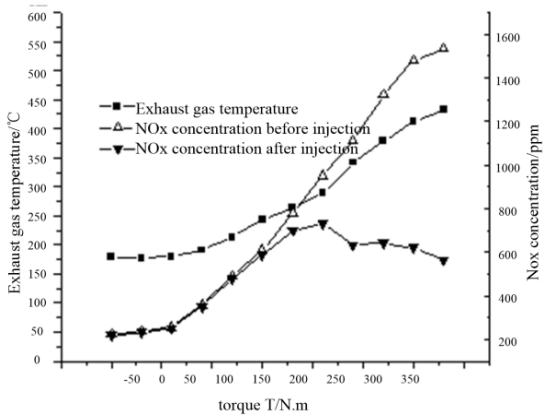

Figure 6. NOx concentration and exhaust gas temperature curves under the 1800r/min load measured in the SNCR test

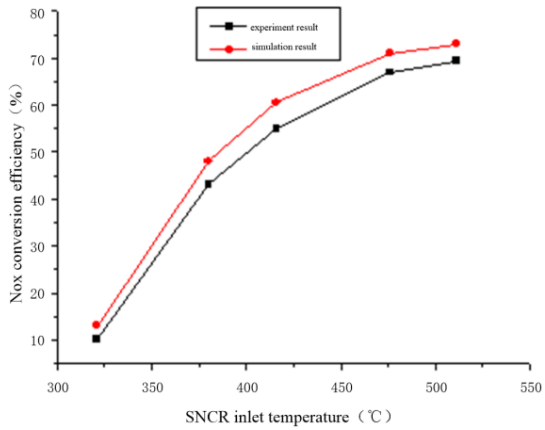

Figure 7. Simulation results vs. experimental results of the NO conversion rate in the SNCR system

5. GRID MODEL AND INITIAL BOUNDARY CONDITIONS

The physical geometry model was drawn using the 3D modelling software Pro/E according to the structure size of the actual SNCR reaction device and then imported into FireV2011 to generate the grid model, as shown in Figure.8. In order to improve the calculation accuracy, the grid boundary and the reduction reaction zone are properly programmed. In the figure, Horeac is defined as the mounting position for nozzle, that is, the reaction zone where the 40% methylamine aqueous solution is mixed with the high-temperature exhaust gas. INI-SNCR is used for the reduction reaction zone. Inlet, outlet, WALL and SNCR-inlet and SNCR-outlet respectively indicate inlet, outlet and wall, and the inlet and outlet boundaries of the reduction reaction zone.

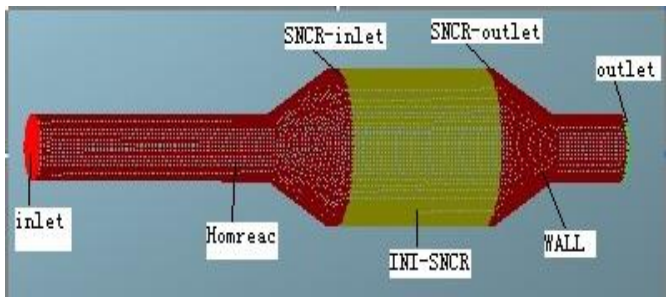

Figure 8. SNCR calculation model

In the SNCR experiment, the exhaust parameters and the inlet boundary of the model and the initial conditions are shown in Table 4 and Table 5 when the rotational speed is 1800r/min and the torque is 300Nm.

Table 4. Inlet boundary conditions

Component name	Volume concentration	Quality score
NO	1479×10^{-6}	1.5282×10^{-3}
H_2O	8.09%	5.0199×10^{-2}
O_2	8.02%	8.8495×10^{-2}
CO_2	9.31%	1.4121×10^{-1}
N_2	74.46%	7.1882×10^{-1}
NH_2	0	1×10^{-10}

Table 5. Initial conditions for inlet

Parameter	Parameter value
Initial temperature	436.7℃
Initial pressure	0.113MPa
Gas density	$0.501kg/m^3$
Turbulent energy	$0.001m^2/s^2$
Turbulence length scale	0.001m

6. ANALYTICAL RESULTS AND ANALYSIS

A 4-hole nozzle was used to make the reducing agent distributed as evenly as possible in the exhaust pipe section, and the CH_3NH_2/NO molar ratio was set to 1.2 to appropriately increase the injection amount of the reducing agent and reduce the reaction time of NH_2-NO. The analytical results are as follows.

6.1 Flow field distribution

Figure.9 shows the velocity distribution along the longitudinal profile of the SNCR model 0.1s, 0.4s and 0.6s after the reducing agent was injected.

Since the amount of reducing agent injected was very small

compared with the exhaust flow, the effects of the spray and its chemical reaction on the flow field were ignored; in other words, the velocity field within the SNCR system was almost constant during one injection cycle.

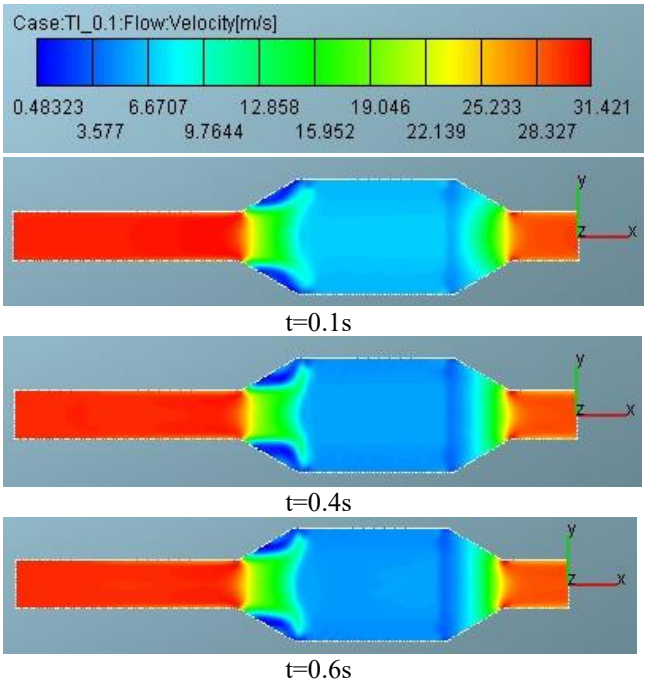

Figure 9. Velocity distribution along the longitudinal profile of the SNCR model at different time after injection

6.2 Concentration distribution

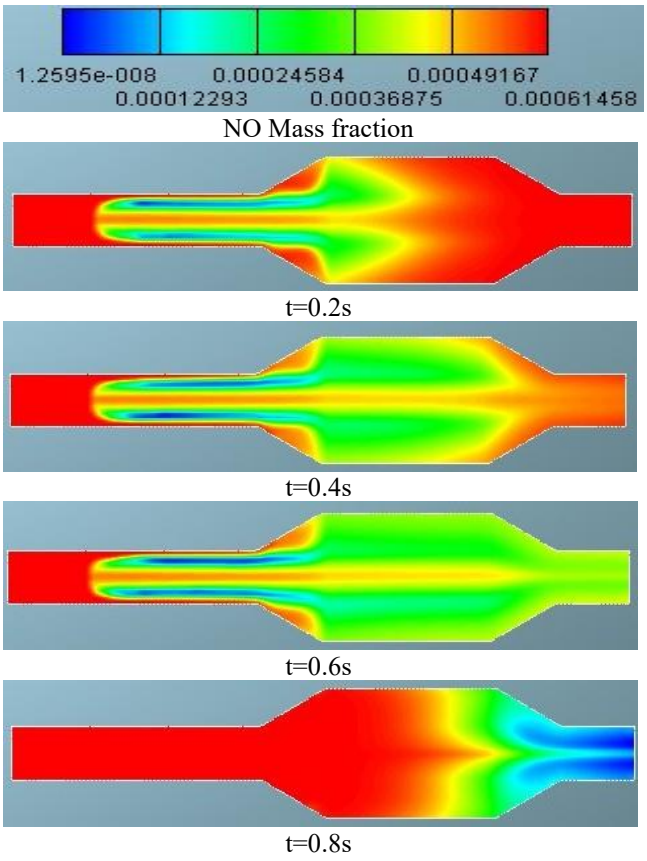

Figure 10. NO concentration distribution in a reaction cycle after the spraying of the reducing agent

Figure.10 shows the NO concentration distribution changes in a reaction cycle starting from the injection of the reducing agent. It can be seen that the methylamine aqueous solution rapidly evapourated and diffused into NH2 and began to reduce the high-temperature exhaust gas before and 0.2s after spraying, but the degree of reaction was not high. During the subsequent 0.4s~0.6s, the reduction reaction was carried out sufficiently within the SNCR system. The concentration field approached the outlet of the SNCR system at 0.8s, so it can be seen that the reduction reaction of NO was sufficient at the end of a reaction cycle.

7. CONCLUDING REMARKS

This paper proposes a selective non-catalytic reduction (NOx) system for diesel engine [11]. With 40% the methylamine aqueous solution as the reducing agent, this system can have good performance at low temperature, and what is more, it does not require any expensive catalyst, which provides an important technical route for solving the purification of diesel engine exhaust gas.

Then this paper compares and analyzes the physical and chemical properties of the 40% methylamine (CH_3NH_2) aqueous solution, establishes a diesel engine SNCR test system and carries out an engine bench test. The results show that when the exhaust temperature is 250~300℃, CH_3NH_2 begins to decompose and produce a large amount of NH2, and with the engine exhaust temperature rises, the NO conversion rate increases rapidly. The maximum NO conversion rate can reach 70%.

This paper establishes a database containing 13 kinds of physical parameters of the methylamine aqueous solution. After the gas phase mechanism and kinetic parameter file given by CHEMKIN are input into FireV2011, this paper carries out coupling calculation and numerical analysis of the SNCR system reduction process. The results indicate that the reduction reaction of NO is sufficiently carried out in one reaction cycle starting from the injection of the reducing agent [12].

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