Study on Dynamic Response Characteristics of Cu-Zeolite SCR Catalyst based on Kinetic Model

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Abstract. Traditional SCR control methods can't fit the high efficiency SCR and keep the coherence of production. Model-based SCR control methods is developed to compensate the defect. A simulation model for a Cu-zeolite SCR catalyst has been developed. The model is capable of predicting the conversion of NO_X, NH_3 slip and calculate the amount of urea on real time. It also can be used to study the impact of temperature, space velocity on NO_X conversion and NH_3 storage. Testing validations were taken based on WHTC test cycle. The results show that the average error between calculated and measured NO_X conversion efficiency is about 3.4% during the test cycle. In general, good agreement between model prediction and the experimental data was achieved.

Introduction

Diesel Particulate Filters (DPFs) and Selective Catalytic Reduction (SCR)which is widely used to remove harmful particulate matter(PM) and NO_X have become an indispensable feature of the modern diesel engines due to strict emissions[1-3]. SCR systems work by chemically reducing NO_X to N_2. In a lean gas stream, it is necessary to add a reductant, which is typically ammonia- NH_3, to the system to enable this reaction to take place. The PM, however, can clog the DPF after long-term use and affect the operation of the engine. As too much PM accumulates in the DPF, the back pressure increases resulting in low fuel economy or other problems. This has necessitated a technology for removing the PM to ensure the efficiency during long term operation of the engine. The trapped PM can be removed by regeneration either periodically or continuously. DPF regeneration is divided into active regeneration and passive regeneration. Typically, active regeneration depends on oxidation of the soot by O_2 at higher exhaust temperature, which operates by injecting fuel into exhaust pipe and using Diesel Oxidation Catalysts (DOC) to oxidize it to raise the temperature to approximately 600℃ [4], and passive regeneration depends on continuous oxidation of the soot by NO_2 in the temperature range 200-500 ℃, which operates by DOC to oxidize NO from exhaust to NO_2 and engine exhaust NO_X/PM ratio. Numerous studies have been conducted which discuss both active and passive regeneration characteristics [5-10]. Active regeneration need much fuel and is likely to lead to DPF damage. Prolonging the interval of it or realizing pure passive regeneration is requisite for modern after treatment systems. Therefore, we need lower PM and higher NO_X emission.

Urea-based SCR catalysts use aqueous urea that is injected into the exhaust stream to produce NH_3 as the active NO_X reducing agent. The NO_X contained in the engine exhaust gas then reacts with the stored NH_3, which produces nitrogen and water. The amount of urea injected is controlled to provide a high NO_X conversion whilst keeping the emissions of excess NH_3 (slip) to low values. Both demands are conflicting targets, because higher concentrations of NH_3 lead to better conversion, but also increased slip. It presents an interesting control challenge, especially at high conversion, because both reagents (NO_X and ammonia) are toxic, and therefore an excess of either is highly undesirable.

In this study, a one-dimensional numerical model for a Cu-zeolite SCR catalyst has been developed. The model is based on kinetics developed from laboratory micro reactor data for the various NH_3-NO_X reactions, as well as for NH_3 oxidation. The kinetic scheme used is discussed and evidence for it presented. The model is capable of predicting the conversion of NO and NO_2, NH_3 slip and the formation of N_2O, as well as effects associated with NH_3 storage and desorption. It can improve SCR management on minimum calibrated labels, real time feedback, potential to minimize sensors and adaptable controls.

Experimental setup

The engine used in these experiments is equipped with common rail system of BOSCH. Table 1 and Fig. 1 show relating specification and detailed information about test bench, respectively. The experiments were carried out by using AVL INDYS66JD, AVL 483, HORIBA MEXA-7100D, METTLER TOLEDO KA32s to focus on torque and speed, soot emission, concentration of NO_X and O_2, soot weight in DPF, respectively.

Tab.1 Test engine specifications

project	specification
Engine type	6 cylinder in-line/intercooling
Bore stroke[mm ×mm]	108×130
Swept volume[L]	7.14
Compression ratio	18
Rated power[kW]	200
Rated speed[r/min]	2100
Max torque[N·m]	1100

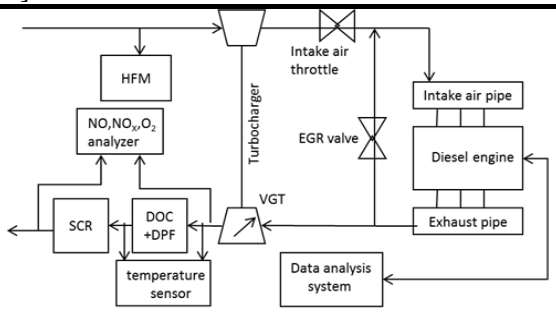

Fig.1 Schematic of experimental setup

Exhaust after-treatment system consists of DOC, DPF and SCR. Table 2 shows the detailed specification.

Tab.2 DOC and DPF specification

parameter/unit	DOC	DPF	SCR
PGM[g/L]	1.06	0.18	0
material	cordierite	cordierite	cordierite
Pore[cell/cm2]	62	31	62
Wall thick[mm]	0.10	0.32	0.10
Diameter[mm]	267	267	267
Length[mm]	102	305	305
Volume[L]	5.7	17.0	17.0

Model

Reaction Kinetics. Following the Eley-Rideal mechanism and other studies [11-15], there are 7 main chemical reactions representing the relevant dynamics in the catalytic converter as shown:

$$S + NH_3 \rightarrow (NH_3)_S \quad (1)$$

$$(NH_3)_S \rightarrow S + NH_3 \quad (2)$$

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

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

$2(NH_3)_S + 3NO_2 \rightarrow 3.5N_2 + 6H_2O$ (5)

$2(NH_3)_S + 3NO_2 \rightarrow N_2 + N_2O + 3H_2O$ (6)

$2(NH_3)_S + 1.5O_2 \rightarrow N_2 + 3H_2O$ (7)

Where S is an unoccupied active catalytic site. (NH_3) is NH_3 molecule adsorbed at S.

In these reactions, the reaction Eq.1 and Eq.2 is adsorption and desorption of NH_3 on the catalyst. NH_3 must be adsorbed on the active catalyst site can react with other reactants (NO_X, O_2) [16-20]. Eq. (3-5) is the reaction of removing NO_X and is the fast-reaction, standard-reaction and slow-reaction, respectively. Other reactions, despite of Eq. (6-7), can be neglected.

Rates of the above reactions are listed respectively as followed:

$$r_1 = k_1 e^{\frac{-E_1}{RT}} C_{NH3}(1-\theta) \quad (8)$$

$$r_2 = k_2 e^{\frac{-E_2(1-\alpha\theta)}{RT}} \theta \quad (9)$$

$$r_3 = k_3 e^{\frac{-E_3}{RT}} C_{NO} C_{NO2} \theta \quad (10)$$

$$r_4 = k_4 e^{\frac{-E_4}{RT}} C_{NO} C_{O2} \theta \quad (11)$$

$$r_5 = k_5 e^{\frac{-E_5}{RT}} C_{NO2} \theta \quad (12)$$

$$r_6 = k_6 e^{\frac{-E_6}{RT}} C_{NO2} \theta \quad (13)$$

$$r_7 = k_7 e^{\frac{-E_7}{RT}} C_{O2} \theta \quad (14)$$

Where k and E are the preexponential factor and the apparent activation energy, respectively. R is the molar gas constant, 8.314 J/ (mol·K). T is the temperature in DPF, K. C is the concentration of reactant. θ Is the ratio of the existing amount of NH_3 storage and max amount of NH_3 (Q_{max}) storage on the catalyst.

The key to calculate reaction rate isθ. Summarized from above:

$$d\theta/dt = Q_{max}(r_1 - r_2 - 2*r_3 - 4*r_4 - 2*r_5 - 2*r_6 - 2*r_7) \quad (15)$$

Generally, NO and NO_2 is about 95% and 5% ratio of NO_x from exhaust gas. In order to improve the reaction rate of Eq.3, SCR catalysts are typically used downstream of DOC. It can converts NO to NO_2 and approximately optimize the NO_2: NO ratio to 1:1. On this condition, the NO_X reduction activity can be improve.

Fig. 2 shows the NO conversion efficiency of DOC under the space velocity of 50000 h^{-1}. As can be observed in the figure, at low temperature, NO conversion efficiency is lower and at high temperature, chemical balance limits the production of NO_2. Hence, the optimal efficiency can be obtained at temperature about 300 ℃.

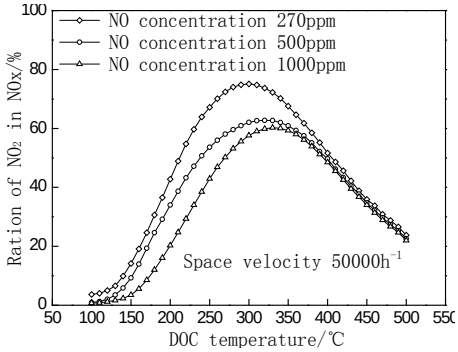

Fig.2 The conversion efficiency of NO by DOC oxidation

NO_2 concentration upstream DPF can be calculated:

$$C_{NO_2} = C_{NO_X} \times \eta \quad (16)$$

Where C_{NO_X} is the NO concentration upstream DOC, ppm. η Is the NO conversion efficiency by DOC?

Simulation model. SCR simulation model is established with Simulink based on the reaction kinetics equations. The NO_X sensor is upstream of the DOC. The valve of NO_2: NO ratio will change after passing through DPF. Because NO_2 will react with soot in the DPF. Therefore, calculating the NO_2 and NO concentration is required. The paper [21] shows the details. The sampling period is 100

ms, which is the test interval of the test-bench. Fig. 3 shows the main structure of the model and it's used to calculate the NO_X conversion efficiency, NH_3 storage and slip.

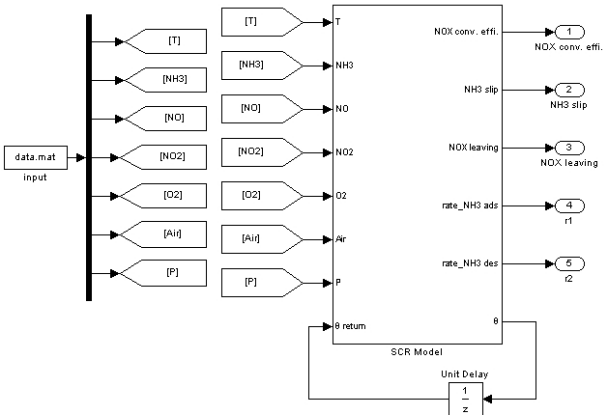

Fig.3 Simulation model of SCR

Results and Discussion. WHTC is applied to validate the transient accuracy of the model. During the experiment, NO_X concentration at downstream SCR is obtained from test-bench while NH_3 concentration is obtained from sensor. Fig.4 shows NO_X concentration at downstream SCR, which illustrates that the model gives a good prediction of the NO_X conversion efficiency during the whole WHTC cycle. Error between calculated and measured results is controlled at 3.4%. Boundary conditions of the inputs are vital to the model, including the vaporization, hydrogenation and distribution equality of ammonia during the design of after-treatment system. Temperature inside SCR is different from the sensor value sometimes because the thermal capacity of the catalyst. While temperature means a lot to the chemical reaction rate, some researchers adopt model to simulate the temperature inside SCR, which produces a more accurate result.

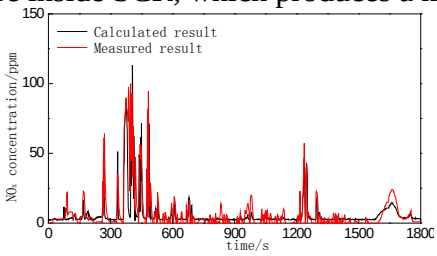

Fig.4 Comparison of calculated and measured NOx concentration

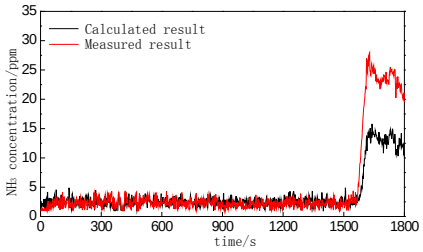

Fig.5 Comparison of calculated and measured NH3 slip

Amount of NH_3 slip is illustrated in Fig.5. Some study[13] shows that the NH_3 slip prediction is much more sensitive to the inlet NH_3 supplied to the model than the NO_X prediction. Thus a small error in the inlet NH_3 concentration could lead to a relatively large error in the NH_3 slip prediction but still give an acceptable NO_X prediction. Temperature error between measured and actual value can affect the accuracy of model results. But as we can see from Fig.5, calculated and measured results show the same trend. Concerning about the high load of the latter part of WHTC cycle, which results in larger error of the temperature, makes a greater difference between the calculated result and measured result.

Conclusion

This article describes a model-based approach for the control of urea injection amount based on reaction kinetics. Below is a summary of our study and the findings:

The NO_X conversion efficiency in the SCR can be predicted by the proposed model. During the WHTC test cycle, the average error between calculated and measured results is about 3.4%.

The model not only enables after treatment systems to be designed quickly with the minimal of testing, but also aids in the detailed understanding of the chemistry characteristics of the system. This model can be further used to explore a wide range of catalyst and system scenarios, which allow us to efficiently optimize systems for varied applications and rapidly investigate many parameters with the

after treatment system (e.g. catalyst position, size, aspect ratio, urea injection strategy, etc.) and the effect on the systems of varying engine calibration (e.g. inlet temperature, inlet NO_X levels, etc.).

Acknowledgements

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