



## Study on Catalytic Activity and Kinetics of Urea-SCR Processes for NO<sub>x</sub> Removal from a Marine Diesel Exhaust Flow†

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NO<sub>x</sub> removal efficiencies (DeNO<sub>x</sub> rate) of marine urea-SCR systems are strongly depended on the catalyst activity and urea solution consumption rate, leading to a high installation and operation cost. For enhancing the DeNO<sub>x</sub> rate and reducing the urea consumption rate, catalytic activity and kinetics of urea-selective catalytic reduction (SCR) processes in the marine diesel exhaust systems are studied by employing computational fluid dynamics coupled with chemical reaction kinetics. In the paper, a 3-dimensional transient reaction model for a marine urea-SCR system is proposed. Based on the model, the catalytic processes of the urea-SCR system is studied and DeNO<sub>x</sub> rates and NH<sub>3</sub>-slips under different urea consumption rates are discussed. It is found that the calculated value of DeNO<sub>x</sub> rate is in good agreement with the measured value *ca.* 92.2 % at 5.3 gallons per hour of urea consumption rate. It is also provided that catalytic processes of urea-SCR systems can be predicted well with the model in the paper.

**Key Words:** Urea-SCR system, Catalytic processes, Catalytic activity, DeNO<sub>x</sub>, Chemical reaction kinetics.

### INTRODUCTION

With increasingly stringent emission limits for diesel engines<sup>1</sup>, urea-selective catalytic reduction (SCR) technology would be built large-scale applications to the marine and automotive diesels. Due to the limitation of marine and automotive space, the scale of diesel exhaust system cannot be too large. As well as exhaust flow rates of marine and automotive diesels are very large, space velocities of these urea-SCR systems are much higher than power plants, leading to reducing the DeNO<sub>x</sub> rates of these systems. While changing diesel loads frequently, the problem is especially serious<sup>2</sup>.

Urea-selective catalytic reduction (urea-SCR) is a complex gas-solid heterogeneous catalysis, including urea thermolysis, HNCO hydrolysis, NH<sub>3</sub> adsorption on the catalyst, DeNO<sub>x</sub> reactions and resultants desorption from the catalyst, *etc.* Owing to lack of catalysis theories and experimental technologies, there is not a recognized mechanism for selective catalytic reduction reactions<sup>3</sup>. However, main macro-reactions (DeNO<sub>x</sub> reaction) in selective catalytic reduction catalytic processes are known. Study of urea-selective catalytic reduction catalytic processes by employing computer numerical simulation technology is based on the chemical reaction kinetics, plays an important role in the developments of selective catalytic

reduction technology. In this paper, main macro-reactions in urea-SCR catalytic processes are selected and numerical simulation of catalytic processes in a marine diesel. Urea-SCR system is carried out with the aid of computational fluid dynamics coupled with chemical reaction kinetics. The effects of different DeNO<sub>x</sub> reactions and urea consumption rates on the DeNO<sub>x</sub> rate are studied and also distributions of different species are discussed in the paper, in order to provide theoretical principles for the design of urea-SCR systems.

### EXPERIMENTAL

**Mathematical model:** Urea-SCR system, using urea as reducing agent, is a catalytic converter device, which can reduce NO<sub>x</sub> emissions to N<sub>2</sub> and H<sub>2</sub>O. A marine diesel urea-SCR system (Fig. 1), is studied in the paper, which has 1-layer catalyst for selective catalytic oxidation to reduce ammonia escaped from the system called NH<sub>3</sub>-slip and avoid secondary pollution. The reducing agent is introduced into the exhaust flow through nozzles. Key parameters of the urea-SCR system and catalyst are shown in the Table-1.

According to the characteristics of urea-SCR systems, the model is simplified and the meshing is completed. The computational mesh consists of 26, 7120 structured hexahedral grids.

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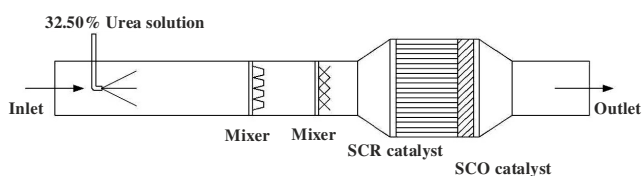


Fig. 1. Schematic diagram of urea-SCR system for a marine diesel

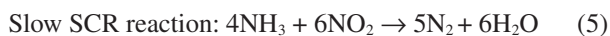
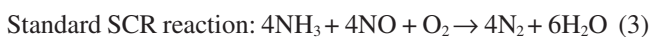
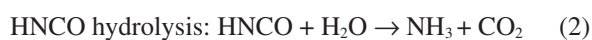
TABLE-1  
KEY PARAMETERS OF THE MARINE UREA-SCR SYSTEM

Diesel	Rated output	1,640 kW
	Rated speed	1800 rpm
Urea-SCR system @100 % load	Catalyst cell density	87 cpsi
	Reducing agent	32.5 %-wt urea solution

**Basic equations:** Since urea-SCR catalytic process is a complex gas-solid heterogeneous catalysis, the mathematical model for urea-SCR systems should be able to describe convective, diffusive and conductive transport in the gas phase, mass and energy transfer through the boundary layer, diffusion and catalytic conversion in the wash-coat and conduction in the solid phase. The mathematical model for urea-SCR catalytic converter built in the paper is a 3-dimensional transient model including continuity equation, momentum equation, energy equation and state relations for the gas phase, energy equation for the solid phase and  $k-\zeta-f$  turbulence equation. The turbulence equation originally proposed by Durbin, has become increasingly popular in the last decade. Its accuracy and stability are very well, but the computing time is more than  $k-\epsilon$  model by 15 %<sup>4</sup>.

**Chemical reaction model:** Urea-SCR catalytic process contains lots of chemical reactions and its detailed reaction mechanism has not yet been confirmed. To a certain extent, the initial and final states of a chemical reaction process can be described with a macro-chemical reaction. Therefore, urea-SCR process can be studied with the main macro-reactions known. For building the chemical reaction model of urea-SCR processes easily, the assumptions are as follows<sup>5,6</sup>:

(1) The adsorption and desorption of  $\text{NH}_3$  are in a quasi-equilibrium state, ignoring the effects of them on the DeNOx reaction; (2) The urea-SCR process consists urea thermolysis, HNCO hydrolysis, standard selective catalytic reduction reaction, fast selective catalytic reduction reaction, slow selective catalytic reduction reaction and  $\text{NH}_3$  oxidation reaction, of which reaction equations are as follows:



## RESULTS AND DISCUSSION

**Calibration and verification of the mathematical model:** Many phenomena are difficult to be described adequately, owing to limitations of measuring techniques and equipment. To some extent, most of them could be predicted

well by the computer simulation technology, only taking a few resources. However, the accuracy of calculation results must be calibrated with some parameters, which must be most effective and accessible. In the paper, the concentrations of  $\text{NO}_x$  in the inlet and outlet are selected as calibration parameters, in order to predict the DeNOx rates and selective catalytic reduction reaction processes.

The operating and calculating data for the marine urea-SCR system are shown (Table-2). At the testing load, the experimental value of DeNOx for the urea-SCR system is 92.2 % at 5.3 gallons per hour of urea consumption rate and the calculation value predicted by the model is 88.2 %. The result shows that the calculated value of DeNOx rate is in good agreement with the measured value. It is also proved that the catalytic progresses for urea-SCR systems can be predicted well with the model in the paper.

TABLE-2  
CALCULATED AND MEASURED VALUES OF CALIBRATION PARAMETERS FOR THE UREA-SCR SYSTEM

Parameter	Load	$\text{NO}_x$ conc. (inlet)	$\text{NO}_x$ conc. (outlet)	DeNO <sub>x</sub> rate
Calculated value	1,640 kW	724 ppm	62 ppm	92.2 %
Measured value	1,640 kW	724 ppm	94 ppm	88.2 %

**Injection rates and DeNOx rates at different times:** It is very important for selective catalytic reduction systems to calibrate the injections of urea solution under different conditions, which are not only effective on DeNOx rates of selective catalytic reduction systems, but also be effective on  $\text{NH}_3$ -slips. At the testing load of the marine diesel engine, injection rates and DeNOx rates of the urea-SCR system at different times are studied in the paper. Figs. 2-4 report injection rates of urea solution and concentrations of HNCO,  $\text{NH}_3$  and  $\text{NO}_x$  at different times. It can be seen that the concentration of urea becomes to grow suddenly after injecting urea solution into the exhaust system and concentrations of HNCO and  $\text{NH}_3$  increase subsequently as a result of reaction (1) and reaction (2). While stopping the injection of urea solution, both of them would decrease either. During optimizing urea injection strategies of urea-SCR systems, it is very difficult to balance DeNOx rates and  $\text{NH}_3$ -slips for achieving higher DeNOx rates and lower  $\text{NH}_3$ -slips with the minimum consumption of reducing agent. To some extent, the problem can be solved by simulating reducing agent consumption rates under different loads with computer numerical simulation technology. From the Fig. 4, calculated value of DeNOx rate is in good agreement with the measured value-92.2 % at 5.3 gallons per hour of urea consumption rate.

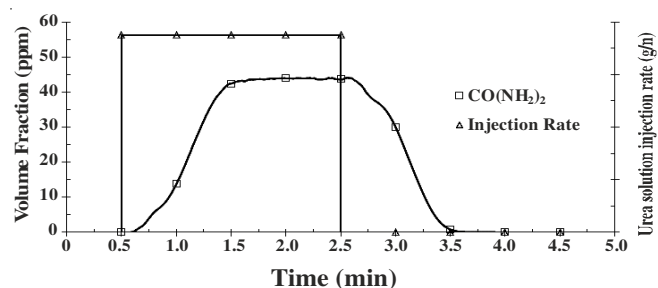
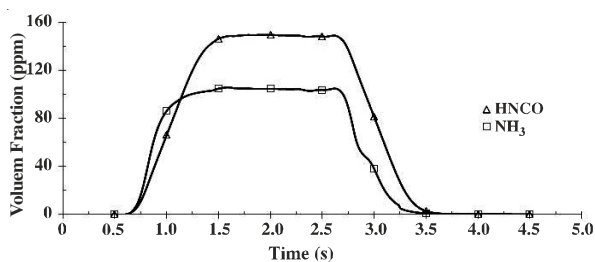
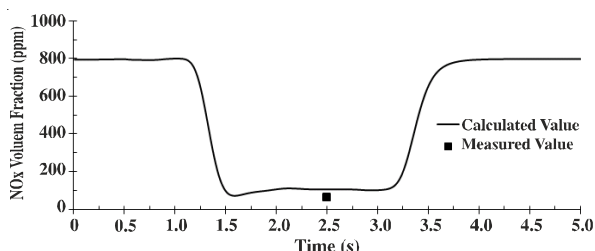
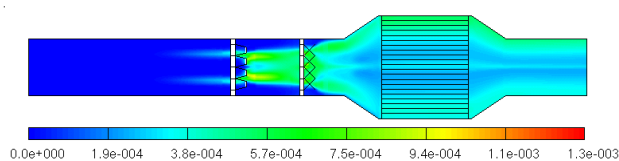
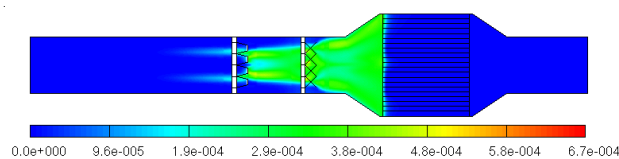


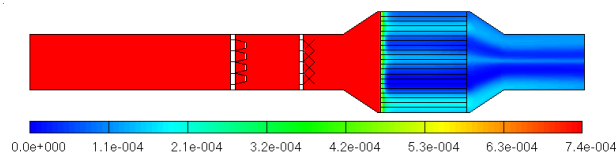
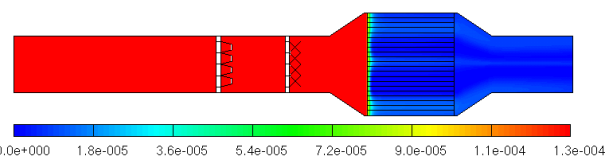
Fig. 2. Concentrations of urea and injection rates of urea solution at different times

Fig. 3. Concentrations of HNCO and NH<sub>3</sub> at different timesFig. 4. Concentrations of NO<sub>x</sub> (NO+NO<sub>2</sub>) at different times

**Distributions of different species in the selective catalytic reduction system:** Figs. 5 and 6 report distributions of HNCO and NH<sub>3</sub> concentrations in the selective catalytic reduction system at  $t = 2.5$  s. Due to pipe expansion and HNCO hydrolysis, HNCO concentration before the selective catalytic reduction catalyst is reduced gradually. While HNCO concentration in the front end of the selective catalytic reduction catalyst is reduced rapidly for reaction (3) being occurred on the catalyst. According to the literature<sup>3</sup>, HNCO hydrolysis is promoted on the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and HNCO hydrolysis is carried out mainly on the catalyst. Therefore, activation energy of HNCO hydrolysis on the catalyst is significantly lower than that before the catalyst and also reaction rate of HNCO hydrolysis on the catalyst is much higher. Owing to HNCO hydrolysis, NH<sub>3</sub> concentration before the catalyst is increased gradually, while NH<sub>3</sub> concentration on the catalyst is increased initially and then decreased rapidly. Reaction rate of HNCO hydrolysis on the catalyst is about 2 times higher than that of DeNO<sub>x</sub> reaction<sup>3</sup>. Therefore, NH<sub>3</sub> concentration on the catalyst is increased initially. However, as decreasing HNCO concentration, reaction rate of HNCO hydrolysis is decreased gradually on the catalyst. Then, DeNO<sub>x</sub> reaction rate is higher than reaction rate of HNCO hydrolysis and also NH<sub>3</sub> consumption rate is higher than NH<sub>3</sub> formation rate. Consequently, NH<sub>3</sub> concentration is reduced in the system.

Fig. 5. Distribution of HNCO mass fraction with a stable injection at  $t = 2.5$ sFig. 6. Distribution of NH<sub>3</sub> mass fraction with a stable injection at  $t = 2.5$ s

Figs. 7 and 8 report distributions of NO and NO<sub>2</sub> concentrations in the selective catalytic reduction system at  $t = 1.5$  s. Most of DeNO<sub>x</sub> reactions are carried out on the front end of selective catalytic reduction catalyst and selective catalytic oxidation catalyst is used to prevent the secondary pollution of NH<sub>3</sub> escaped from the system at lower loads. Since space velocity of marine urea-SCR systems is higher than that of power plant selective catalytic reduction systems, it is necessary to use multi-layer catalysts in the urea-SCR converters. Comparing Figs. 7 with 8, the reducing speed of NO<sub>2</sub> concentration is significantly larger than that of NO concentration for the high reaction rate of fast selective catalytic reduction reaction. In the existence of NO and NO<sub>2</sub>, the reaction rate of fast selective catalytic reduction reaction is higher than that of standard selective catalytic reduction reaction by 1 to 2 orders of magnitude at lower temperature. However, DeNO<sub>x</sub> rate in the catalytic process mainly depends on the standard selective catalytic reduction reaction, since NO mole concentration is much more than that of NO<sub>2</sub>. And also slow selective catalytic reduction reaction and NH<sub>3</sub> oxidation reaction only have very small effects on the DeNO<sub>x</sub> rate in the catalytic process.

Fig. 7. Distribution of NO mass fraction with a stable injection at  $t = 2.5$ sFig. 8. Distribution of NO<sub>2</sub> mass fraction with a stable injection at  $t = 2.5$ s

In conclusion, a 3D model of a marine diesel urea-SCR system containing 2-layer catalyst is presented and catalytic processes of the system are studied with the model. The results show that physical and chemical processes, DeNO<sub>x</sub> rate and distributions of species for selective catalytic reduction systems can be predicted well with employing computational fluid dynamics coupled with chemical reaction kinetics.

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