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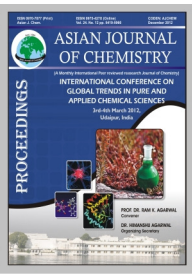

Study on Mechanisms of NO_x and SO_x Formation in a Marine Diesel Engine Based on Quantum Chemistry†

SONG ZHOU*, YUANQING ZHU and GUOJING HE

College of Power and Energy Engineering, Harbin Engineering University, Harbin, P.R. China

*Corresponding author: Fax: +86 451 82519852; Tel: +86 451 82568384; E-mail: songzhou@hrbeu.edu.cn

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This paper presents the study on mechanisms of NO_x and SO_x formation in a marine diesel engine and models about NO_x and SO_x formation were set up based on theory of quantum chemistry. The new NO_x model covers thermal NO, prompt NO, fuel NO and NO *via* N_2O, *etc*. SO_x formation model discovers the detailed composition changes of sulphur-contained materials during combustion process. The correction and availability of the models were proved by engine emission tests. In the last, simulations of NO_x and SO_x formation in a marine diesel engine were carried out and by that the laws of engine parameters on engine emissions were obtained. The models suggested in present work can do help to reduce engine emissions.

Key Words: NO_x, SO_x, Model, Mechanism, Marine diesel engine.

INTRODUCTION

Most of phenomenon in the processes of combustion, including fuel combustion, pollutants formation and piston knock for the internal combustion engine, can be described on the rid of chemical reaction kinetics. Since formation and decomposition of pollutants are depended strongly on the chemical reaction mechanisms and chemical reaction rates. It is necessary to study deeply reaction mechanisms for the combustion processes in the inter combustion engine. However, simulation studies for detailed reactions, especially in the turbulent combustion, waste lots of resources by the limitation of low time scale for chemical reaction. Especially, computational fluid dynamics should also be employed to predict the flow fields in the combustion chamber, in the simulation studies. Therefore, chemical kinetic models for hydrocarbons should be simplified to decrease the computing resources.

The pollutants from the inter combustion engine, which are harmful to the environment, are nitrogen oxides (NO_x) and sulfur oxides (SO_x). In the combustion processes, NO_x sources consist of thermal NO, prompt NO, fuel NO and nitrous oxide NO. And SO_x mainly depends on sulfur oxidation[1,2].

EXPERIMENTAL

Using the NO_x and SO_x model built in the paper, the model of KIVA is be modified and simulation studies for NO_x and SO_x formation in the diesel combustion are carried out in the paper.

NO_x formation model: After a systematic study on NO_x formation in the combustion of hydrocarbon fuel, Hewson and Bollig proposed a detailed chemical mechanism, called Hewson-Bollig model including semi-detailed mechanism and simplified mechanism in 1996, which can describe comprehensively the process of NO_x formation. The NO_x formation mechanism contains two parts-the oxidation mechanism of hydrocarbon fuel and a simplified mechanism for nitrogen chemistry[3]. In the Hewson-Bollig model, the oxidation mechanism of CH_4 is makes up of 61 elementary reactions about C1 and C2 and nitrogen chemistry contains 13 species of components and 52 elementary reactions. Therefore, both of them can be further simplified with their semi-detailed mechanism.

On the basis of Hewson-Bollig model, a new simplified mechanism for NO_x formation, which is an add-in model, is proposed in the paper, according to computational chemistry theory and chemical reaction kinetics[4-6]. And the new model has the following characteristics: (1) The new model should be compatible with Zeldovich model in the KIVA and the simplified reaction pathway should meet requirements of the simulation study. (2) The new model should contain the formations of prompt NO, fuel NO and nitrous oxide NO, in order to improve the accuracy of calculation results. (3) Kinetic parameters in the new model should be confirmed and effects of the model on other chemical reactions should be considered.

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The main reactions in the new model are as follows[3]:

Fuel combustion:

$$2C_{12}H_{23} + 37O_2 \rightarrow 24CO_2 + 26H_2O$$

Thermal NO:

$$O_2 + 2N_2 \leftrightarrow 2NO + 2N$$
$$N_2 + 2O_2 \leftrightarrow 2NO + 2O$$
$$N_2 + 2OH \leftrightarrow 2NO + 2H$$

Prompt NO:

$$CH + N_2 \leftrightarrow HCN + N$$
$$HCN + O \leftrightarrow NHCN + N$$
$$NCO + O \leftrightarrow NO + CO$$
$$NCO + H \leftrightarrow NH + CO$$
$$NH + H \leftrightarrow N + H_2$$
$$N + O_2 \leftrightarrow NO + O$$
$$N + OH \leftrightarrow NO + H$$

Nitrous oxide NO:

$$NH + NO \leftrightarrow N_2O + H$$
$$N_2O + O \leftrightarrow 2NO$$

HC formation:

$$C_{12}H_{26} \rightarrow 12CH + 14H$$

Several components, including HCN, CN, N_2O and NH, *et al.*, are added in the new model. And effects of HCN reaction, OH reaction, NH reaction, homogeneous oxidation of ammonia and Nitrous oxide NO on the NO_x formation are considered in the new model.

SO_x formation model: Sulfur oxides including SO_2 and SO_3 is one of the main pollutants in the combustion processes and SO_3 is only 1-5 % of the total SO_x. At a lower temperature, sulfur in the fuel can be oxidized easily to SO_x. Owing to numbers of sulfur-containing components in coal, inorganic components containing sulfur can be decomposed in a lower temperature, but the decomposition of organic components containing sulfur is very complex, in which -SH and -S- would be separated out and other components would be decomposed above 1000 ºC. It is found that 90 % of dry decomposition products in the coal combustion above 1000 are H_2S and then H_2S would be oxidized finally to SO_2. The reaction pathway is as follow[7]:

$$S \rightarrow H_2S \rightarrow HS \rightarrow SO \rightarrow SO_2$$

According to the SO_x formation mechanism for coal combustion, SO_x formation process mainly contains inter-conversion between H_2S and HS and oxidization of HS. Although the inter-conversion process of H_2S and HS is very complex, the control step is the decomposition of H_2S to HS and the core reaction of HS oxidization is HS + O → H + SO. Basing on the SO_x mechanism for coal combustion and analyzing the working processes of marine diesel engine, a new simplified mechanism for SO_x formation is proposed in the paper. And the reactions of the new model are as follows:

$$Diesel \rightarrow S + diesel$$
$$OH + SO \rightarrow SO_2 + H$$
$$O_2 + SO \rightarrow SO_2 + O$$
$$O + SO + M \rightarrow SO_2 + M$$
$$S + O_2 \rightarrow SO + O$$

It is found that reaction **1** is the control step among the reactions above. Therefore, simulation studies should be based on the mass fraction of sulfur in the fuel. Because the process of SO_x formation is carried out before the fuel combustion, the reaction rate is very large. And most of the reactions in the process are forward reactions. On the basis of the quantum chemical calculation, the back reactions in the process can be ignored, comparing with the forward reactions.

RESULTS AND DISCUSSION

A 8 cylinders, 4 strokes middling-speed supercharged diesel engine is selected to study in the paper. According to the test methods made by the international maritime organization, the experimental values of NO_x, which is reported in the Table-1, is received by the Horiba pollution analyzer.

TABLE-1
EXPERIMENTAL DATA OF NO FOR THE MARINE DIESEL (ppm)

Test	Load			
	100 %	75 %	50 %	25 %
1st	949	947	946	859
2nd	959	950	925	855
3rd	931	943	933	860
Average value	953.3	946.3	935	858

Effects of new model on NO_x emission: Comparing Figs. 1 and 2, the quantity of NO_x is increased by 5 % after prompt NO model added in the Zeldovich model (thermal NO model). It is proved that effects of prompt NO on the NO_x formation are slight. And nitrous oxide NO model is contained in the new model. It is found that an increasing NO formation is received as the result of prompt NO model, but the reduction of N_2O would lead to the decrease of total NO_x formation. However, the conclusion value of NO_x formation is agreement well by the new model.

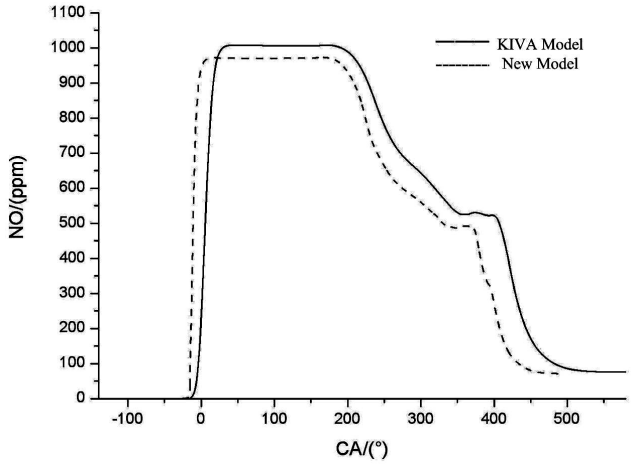

Fig. 1. Effects of KIVA model and new model on the NO in the cylinder

Effects of new model on SO_x emission: From Figs. 3 and 4, sulfur in the fuel is almost oxidized to SO_2 and volatile sulfur is absent in the exhaust gas. Therefore, by the new model, the formation regularity of SO_x and volatile sulfur in the fuel are predicted well with the working characteristics of diesel engines.

From the Fig. 5, temperatures of the gas in the cylinder are reduced slightly, because sulfur volatilization in the fuel is

endothermic. And the maximum of the temperature is appeared earlier in the new model, as a result of the higher reaction rate of sulfur oxidization. It is also found that the SO_x formation is predicted well by the new model and the effects of the decreased temperature on the NO_x formation is also found in the paper.

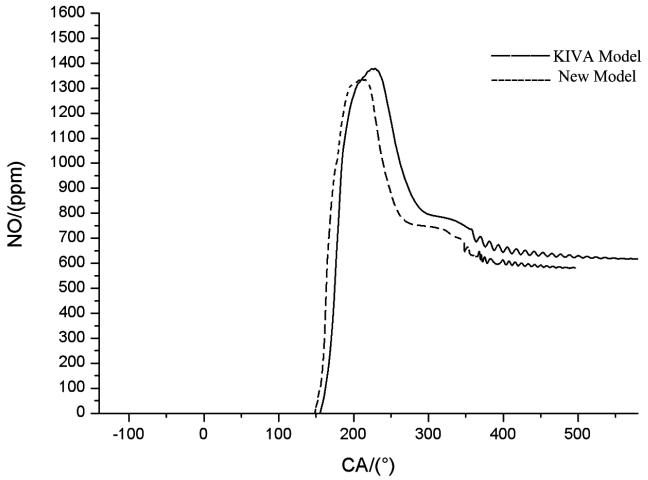

Fig. 2. Effects of KIVA model and new model on the NO in the exhaust pipe

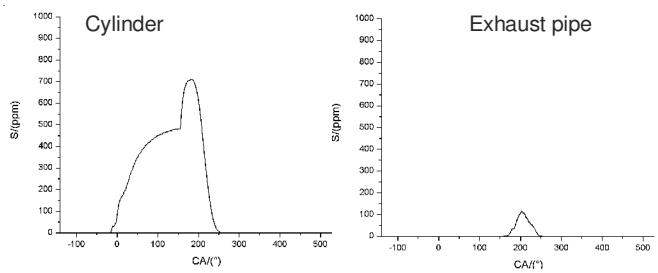

Fig. 3. Formation of volatile sulfur at different crank angles

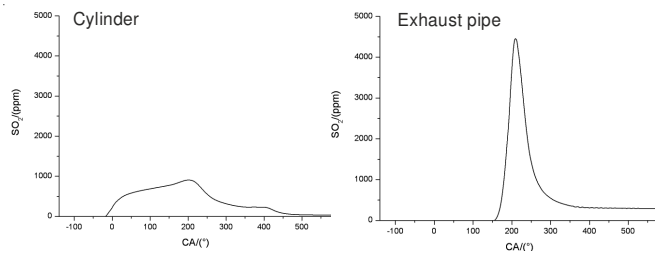

Fig. 4. Formation of SO_2 at different crank angles

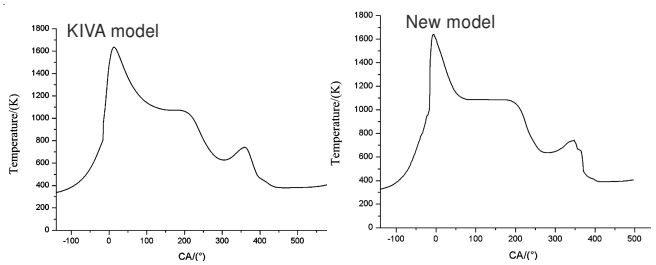

Fig. 5. Temperatures in the cylinder at different CAs

Conclusion

In the paper, a new simplified model for NO_x and SO_x formation is proposed and 3D simulation studies on the combustion process of a marine diesel engine is carried out by the new model. The results are as follows:

(1) The NO_x and SO_x formations in the marine diesel are predicted well by the new model and the calculation results is agreement well with the measurement results.

(2) The NO_x formation is reduce by 5 % of the thermal NO by the new model, as a result of the reduction of N_2O on NO_x.

(3) The formation regularity of sulfur, SO and SO_2 in the diesel are received by the SO_x formation model and the gas temperature in the cylinder is reduced slightly, owing to the endothermic volatilization of sulfur in the fuel.

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