Analysis of Pollutant Emission Characteristics of Marine Diesel Engine Using Chemical Kinetics under the Background of Energy Shortage

Changfei Sun a, Jie Hui b
School of Jiangsu Maritime Institute, Nanjing 211122, China

a scfeijsmi@126.com, b hjjsmi@126.com

Abstract. The study aims to reduce the environmental pollutants produced in the ship transportation in the environment of energy shortage, and realize the comprehensive development of energy saving and emission reduction. Based on the theoretical basis of chemical kinetics, a new type of NOx emission generation model of marine diesel engine was proposed according to the traditional HB model. Second, the combustion chemical kinetics of sulfide was described, on which the sulfide generation and emission model of marine diesel engine was proposed. Third, the characteristics of NO, N2O and SO2 were analyzed according to the emission model of NOx and sulfide generation in marine diesel engine. The results showed that when the crankshaft angle was 230° and 250°CA, the content of NO and N2O in the exhaust pipe of diesel engine had an obvious peak. The content of NO and N2O in the cylinder and exhaust pipe of diesel engine increased at the beginning. As the crankshaft angle increased, the content of both decreased gradually, and the trend of change in the cylinder was slower than that in the exhaust pipe. The SO2 content in the diesel cylinder kept stable after a small increase until it disappeared. The SO2 content in the exhaust pipe first increased and then decreased. When the crankshaft angle was 230°CA, the SO2 content in the exhaust pipe of the diesel engine had an obvious peak. The emission characteristics of nitrogen oxide and sulfide were consistent with the correct change trend, which conformed to the theoretical mechanism. In a word, the study provides a practical basis for energy conservation and emission reduction, development of low-carbon economy, and efficient use of energy.

1. Introduction
As China's economic growth level improves fast, China's comprehensive national strength has also been greatly improved. However, in the rapid development of economy, the imbalance between supply and demand of resources has become increasingly prominent, and the limited amount of resources has been out of proportion to the rapid development of economy [1]. Thus, in the case of energy shortage, the trend of developing low-carbon economy is becoming more urgent, and it is essential to implement energy conservation and emission reduction in the whole society.

The effective way to develop low-carbon economy in the marine area is to reduce the discharge of ship wastes [2]. The pollution of marine environment by the pollutants discharged from the diesel engine has become a major concern in China and even in the world. The International Maritime Organization...
and many countries have taken many effective measures to control and prevent the emission of pollutants from the diesel engine of ships [3]. There are strict requirements for the emissions of pollutants such as nitrogen oxides and sulfides from diesel engines of ships. Reducing the emissions of nitrogen oxides and sulfides requires an effective analysis of the characteristics of these compounds, thereby reducing the investment in the development of low-carbon economy and improving the implementation efficiency of energy conservation and emission reduction.

Based on the theory of chemical kinetics, the emission model of NOx and sulfide in marine diesel engine are put forward. The emission characteristics of NOx and sulfide in the model are analyzed by computer software, and the calculated results are consistent with the theoretical basis. It can be used for the analysis of pollutant emission characteristics of marine diesel engine, thus reducing the energy utilization and improve the utilization efficiency of energy.

2. Method

2.1. Model of NOx emission based on chemical kinetics

Nitrogen and oxygen combine to form nitrogen oxides under high temperature. As the temperature becomes higher, the chemical reaction rate will increase significantly. When the temperature is less than 1500 °C, the amount of NO will be very small. If the temperature is more than 1500 °C, the chemical reaction rate will increase more than 10 times when the temperature is 100 °C [4]. The chemical reaction of nitrogen at high temperature is shown in equation (1).

\[ N_2 + O_2 \rightarrow 2NO \]

According to chemical kinetics, equation (2) is obtained from the above reactions.

\[ \frac{d[NO]}{dT} = M_1[N_2][O] - M_2[NO][N] + M_3[N][O_2] - M_4[NO][O] \]  

N is an intermediate. If the reaction time is relatively short, it can be assumed that the growth and reduction rate of nitrogen are the same.

\[ \frac{d[NO]}{dT} = 0 \]  

The simplified HB model [5] is used to establish a model for the emission of nitrogen oxides. Assuming that the states of the active groups such as NH, NH2, N2H, HNO, CN and N are all stable, the formation process of NO is shown in equation (4).

\[ N_2 + O_2 \rightarrow NO \]  
\[ HCN + H + 2H_2O \rightarrow NO + CO + 3H_2 \]  
\[ HNCO + O_2 + H_2 \rightarrow NO + CO + H_2O \]  
\[ NH_3 + H + H_2O \rightarrow NO + 3H_2 \]  
\[ N_2 + H_2O \rightarrow N_2O + H_2 \]  
\[ NO + H_2O \rightarrow NO_2 + H_2 \]  

Among them, ① represents the net formation of nitrogen oxides, including the reaction between nitrogen active group and NO, which eventually makes NO be reduced to N2 again. ②③④ indicates the transformation of nitrogen in harmful components, which occurs on the side where the flame is burning vigorously. ⑤ belongs to the re-combustion reaction, ⑥ refers to the decomposition process of nitrogen oxides, ⑦ suggests the formation process of N2O, and ⑧ is in a balanced state in the diffusion flame, indicating that the emission process of N2O and NO is controlled by the freezing effect of pollutant consumption reaction. ⑥ generally occurs in the low temperature region, and the stability
of the active group in this region is difficult to guarantee, so the conversion of NO and N₂O cannot be estimated, but the process only affects the measurement results, and has no substantial impact on the final emissions of nitrogen oxides, so ⑥ can be ignored in the actual calculation process.

2.2. Model of sulfide emission based on chemical kinetics

In the combustion process, sulfide emission is an important pollutant emission process. The pollutants generated include sulfur dioxide and sulfur trioxides. However, sulfur trioxides emissions are very small, accounting for only 1% of sulfur dioxide emissions [6]. The sulfide produced by marine diesel engine during its operation is 5% of the total emission of sulfide in the environment, so the establishment and research of sulfide generation and emission model is an effective measure to control its emission. Sulfur can take part in chemical reaction at relatively low temperature and form sulfide quickly. Its chemical kinetic reaction is shown in equation (5).

\[
\begin{align*}
H_2S + CO &\rightarrow COS + H_2 \\
H_2S + CO_2 &\rightarrow COS + H_2O \\
COS + O_2 &\rightarrow SO_2
\end{align*}
\] (5)

The mutual conversion between H₂S and HS is divided into two stages. Even though the conversion of sulfhydryls is relatively complex, the main process is that H₂S produces HS under the action of catalyst. The reaction process is shown in equation (6).

\[
HS + O \rightarrow H + SO
\] (6)

The above reaction process is very fast, especially at high temperature, it can finish the reaction quickly. The related reaction process of FeS₂ and the decomposition principle of three sulfur compounds are usually the core control factors of the whole emission generation model of sulfur dioxide. The conversion process of sulfur oxide to sulfur dioxide is also an important reaction process in the model, which also includes the steps of forming sulfur oxide in the direct form of volatile sulfur, and the mutual transformation process between sulfur dioxide and sulfur trioxide.

However, the sulfur generation and emission of marine diesel engine is different from that of combustion. The content of sulfur in diesel is very low, including active sulfur, such as sulfur elemental and hydrogen sulfide, which can directly react with metals, and inactive sulfur, such as SO₂ and thioether, which cannot directly react with metal [7]. During the operation of marine diesel engine, there are few intermediate products of sulfide, and the reaction is very fast in high temperature environment, which can be solved by dynamic reaction equation. In the generation steps of sulfide in marine diesel engine, only the total amount of sulfide is considered, so some transformation relations in the intermediate process can be simplified. The sulfur generation and emission model of marine diesel engine is shown in equation (7).

\[
\begin{align*}
OH + SO &\rightarrow SO_2 + H \\
O_2 + SO &\rightarrow SO_2 + O \\
O + SO + N &\rightarrow SO_2 + N \\
S + O_2 &\rightarrow SO + O \\
\text{Diesel oil} &\rightarrow \text{S+diesel oil}
\end{align*}
\] (7)

Among them, ⑤ is the control factor of the whole chemical reaction. In the actual calculation process, the mass fraction of sulfur should be used as the starting point for distribution. The reaction takes place before diesel combustion, and the chemical reaction kinetics is very fast. ④ the reaction formula can only be determined after the conversion of sulfur hydrogen compounds and the kinetic calculation, and after the calculation, all the reactions in (7) are positive and fast, so the reverse reaction can be ignored.
Due to the estimation of sulfur-related chemical reactions, the sulfur chemical reactions will affect the numerical calculation results in the model, and the sulfur precipitation reaction belongs to endothermic reaction [8], which also certainly impacts the simulation of model temperature, which is a problem that needs attention in the settlement process of the model.

3. Results and discussion

3.1. Emission of NOx in diesel engine

The generation rule and amount of NOx in diesel engine are analyzed by computer software program. The generation mechanism of N₂O and NO in the model should also be considered, as shown in Figure 1.

![Figure 1. Change of NO in marine diesel engine model](image1)

Figure 1 suggests that after considering the transient mechanism in the model, when the crankshaft angle is 230°CA, there is an obvious peak of NO content in the exhaust pipe of the diesel engine. The NO content in both the diesel cylinder and the exhaust pipe increases at the beginning. As the crankshaft angle increases, the NO content gradually decreases, and the change trend in the cylinder is slower than that in the exhaust pipe. In addition, the amount of NO in the part with less oil and more oxygen will increase, which shows that the model has accuracy and stability.

Figure 2 shows the change of N₂O in the model.

![Figure 2. Change of N₂O in marine diesel engine model](image2)
Figure 2 shows that N\textsubscript{2}O in diesel cylinder and exhaust pipe increases at the beginning. As the crankshaft angle becomes larger, the content of N\textsubscript{2}O decreases gradually. The trend of change in cylinder is slower than that in exhaust pipe. When the crankshaft angle is 250°CA, the content of N\textsubscript{2}O in exhaust pipe of diesel engine has an obvious peak. The change rule of N\textsubscript{2}O in diesel cylinder and exhaust pipe conforms to the correct trend. Moreover, the emissions are not very large, which is in line with the theoretical mechanism.

3.2. Emission of sulfide in diesel engine
The generation rule and amount of NOx in diesel engine are analyzed by computer software program, as shown in Figure 3.

Figure 3 shows that the SO\textsubscript{2} content in the diesel cylinder keeps stable after rising a little until it disappears. The SO\textsubscript{2} content in the exhaust pipe increases at the beginning. As the crankshaft angle increases, the SO\textsubscript{2} content decreases gradually. The trend of change in the cylinder is much slower than that in the exhaust pipe. When the crankshaft angle is 230°CA, the SO\textsubscript{2} content in the exhaust pipe of the diesel engine has an obvious peak. The change rule of SO\textsubscript{2} conforms to the correct trend in both the cylinder and the exhaust pipe, and the emission is not very large, which conforms to the theoretical mechanism.

4. Conclusion
Based on chemical kinetics, a model of nitrogen oxide and sulfide generation and emission of marine diesel engine is established, and the simulation calculation is carried out by computer software. By analyzing the content of nitrogen oxide and sulfide in diesel engine, it is found that the reaction process of nitrogen oxide calculated by instantaneous mechanism has little relationship with temperature, but N\textsubscript{2}O is greatly related to nitrogen oxide generation in the model. Based on the transient analysis of sulfide generation in the working process of diesel engine, the emission rule of sulfur and sulfide in the working process of diesel engine is clarified. There is not great difference between the emission and the theoretical calculation value, but the accuracy needs to be further improved, which provides a practical basis for the subsequent study of pollutant emission of marine diesel engine.
References

[1] C.Q. Mei, T.P. Yuan, W. Ni, Energy-Efficient Two-Way Relaying under Non-Ideal Power Amplifiers. IEEE Transactions on Vehicular Technology, 66(2) (2016) 1-1.

[2] Y.O. Kim, H. Yonekawa, Y. Chu, Development and Experimental Evaluation of a Prototype of the TF Secondary Quench Detection System for KSTAR Device. IEEE Transactions on Plasma Science, 44(9) (2016) 1-5.

[3] P. Malaspina, M. Casale, C. Malegori, Combining spectroscopic techniques and chemometrics for the interpretation of lichen biomonitoring of air pollution. Chemosphere, 198 (2018) 417.

[4] A.F. Barker, D. Hart, A.N. Hayhurst, Kinetics of production of nitric oxide during the pyrolysis of small particles of coal in a hot (electrically heated) bed of sand fluidised by pure nitrogen, 81(3) (2016) 125-130.

[5] D.F. Carlos, P.N. Carles, S.P. Morten, Heterotrophs are key contributors to nitrous oxide production in mixed liquor under low C-to-N ratios during nitrification - batch experiments and modelling. Biotechnology & Bioengineering, 114(1) (2016) 132.

[6] O. Auguet, M. Pijuan, G.B. Helena, Implications of Downstream Nitrate Dosage in anaerobic sewers to control sulfide and methane emissions. Water Research, 68 (2015) 522-532.

[7] L. Pirjola, M. Karl, T. Rönkkö, Model studies of volatile diesel exhaust particle formation: Are organic vapours involved in nucleation and growth?. Atmospheric Chemistry and Physics, 15(18) (2015) 10435-10452.

[8] N. A. Timothy, L.B. Stacey, Macroscopic Observations of Dissolving, Insolubility, and Precipitation: General Chemistry and Physical Chemistry Students’ Ideas about Entropy Changes and Spontaneity. Journal of chemical education, 96 (2019) 469-478.