NO_x Emissions of N-butanol and Methane in Low-speed Two Stroke Diesel Engines

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Abstract: This article firstly structures a detailed combustion reaction mechanism including methane、N-butanol、nitrogen oxide. According to two-stroke low-speed diesel engine's parameter with the characteristics of engine firing, homogeneous charge compression ignition is selected as simulation model. At the same the output power and the excess air coefficient is 1.5, by means of the simulation calculation and analysis of reaction path and reaction mechanism, when N-butanol and methane are mixed in different proportions, the exhaust temperature in the reactor reduces with the increase of methane proportion in reactants. At the same time NO mole fraction increases with the proportion of CH_4 in the mixed fuel decreases, but the NO_2 mole fraction will increase with the proportion of CH_4 in the mixed fuel increases.

1. Introduction

The International Maritime Organization Research Report pointed out that the total emissions of global sea transport CO_2 in 2012 were 796 million tons, accounting for about 2.5% of the total global total. If no measures are taken, the discharge of the shipping greenhouse gas by 2050 will increase 50%-250% over 2012. [1] In 2020, my country proposed the development goal of "2030 carbon peaks and carbon neutrality in 2060", which provides a development direction for my country to respond to global warming and achieve green low-carbon emissions.[2] The shipping industry as an important part of the national economy has attracted more and more attention from various countries due to emissions. [3]In the face of energy and environmental crisis, and under the strict emission regulations of the International Maritime Organization, adopting clean energy instead of traditional fossil fuels as current research hotspots.[4-5]

Methane is the least carbon-containing fossil fuel, but its reserves are abundant and the heat value is high. [6] Its combustion does not contain harmful substances such as sulfide, which can effectively reduce the emissions of nitride and sulfides. [7] Positive n-butanol is a relatively ideal biofuel. Alcohol fuel can partially replace diesel and can effectively reduce the emissions of diesel engine nitrogen oxides and carbon smoke. [8] The chemical preparation of N-butanol by ethanol can reduce the dependence on non-renewable resources and also effectively reduce greenhouse gas emissions. [9] And n-butanol and diesel can be completely dissolved without solvents. Its cetane number is higher and can better ignite diesel. [10]

In order to reduce the emission of pollutants from internal combustion engines, dual fuel engines have developed rapidly. The type and proportion of fuel used in dual fuel diesel engine directly affect the emission of ship pollutants and the output performance of diesel engine. In this paper, starting from the mixing ratio of methane and n-butanol, the simulation method is used to study the changes of diesel engine combustion and pollutant content in different proportions of mixed fuels, which is widely used for dual fuel engines in ships and promotes the accelerated development of ' carbon neutralization ' in the shipping industry.

2.The technical parameters of the two-stroke internal combustion engine

The model of the diesel engine selected in this study is MAN 6S35ME-B9 medium and low speed two-stroke diesel engine. The main parameters of the diesel engine required for simulation are shown in table 1. The simulation software of this study is CHEMKIN-PRO, and the model of the reactor is a homogeneous charge compression ignition, HCCI. The compression ratio of HCCI engine is higher than that of ordinary gasoline engine, and the non-uniform diffusion combustion of diesel engine is not used, so the fuel efficiency is improved.

Tab 1. Basic technical parameter of 6S35 diesel engine[11]

Parameter name	Technical specification
Nominal power /KW	3570
Rated speed /$r\cdot min^{-1}$	142
Compression ratio	21

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Cylinder diameter /mm	350
Stroke /mm	1550
Sweep port timing /(°)CA	-38/38
Exhaust valve timing /(°)CA	-64/98

3.Calculation model and chemical reaction kinetics model

Excess air coefficient, also known as the excess air coefficient, refers to the ratio of the air volume actually supplied to the fuel combustion to the theoretical air volume. It is an important parameter reflecting the ratio of fuel to air. In the simulation calculation, the ratio of reactants is calculated according to the ratio of fuel to air reaction (excess air coefficient) of the two-stroke large engine of the overload medium and low speed ship. In order to make the fuel fully burn and reduce the formation of incomplete combustion products such as carbon deposition and CO and HC during ship operation, the mixing ratio of air and fuel is generally set to 1.5 : 1.0. In this study, the excess air coefficient is set to 1.5 to make the fuel of the two-stroke medium and low speed diesel engine fully burn during operation.
CHEMKIN-PRO software was used to simulate the combustion of n-butanol and methane in different proportions under 75 % operating conditions. The reaction mechanism required for simulation includes detailed kinetic and thermodynamic data of reactants, products and intermediates. The reaction mechanism of n-butanol and methane comes from the mechanism model of the software. The mechanism includes the kinetic and thermodynamic data of all reactions in the low temperature combustion and high temperature combustion stages. However, the reaction mechanism only contains C, H and O elements. In the high temperature combustion stage, N and O elements will undergo oxidation reaction to produce NOx. Therefore, adding Zeldovich 's NOx reaction mechanism to the mechanism simulates the production and conversion of NOx during the combustion reaction.
The chemical reaction equation of complete combustion of n-butanol and methane is :

$$C_4H_{10}O+6O_2 \rightarrow 4CO_2+5H_2O \quad (1)$$

$$CH_4+2O_2 \rightarrow CO_2+2H_2O \quad (2)$$

According to Formulas (1) and (2), the amount of oxygen and nitrogen required for complete combustion of n-butanol and methane with different mixing ratios can be obtained when the air excess coefficient is 1.5 and the total power is constant. As shown in Table 2, the mass of fuel and air required at different mixing ratios under 75 % load conditions.

Tab 2. Quality of mixtures with the air

serial number	n-butanol / methane	n-butyl (g)	methane (g)	oxygen (g)	nitrogen (g)
1	1：0	161.03	0.00	626.70	2357.58
2	7：3	93.60	40.13	605.05	2276.13
3	3：7	32.71	76.33	585.29	2201.79
4	0：1	0.00	95.79	574.72	2162.05

4.Results and discussion

HCCI is a new combustion mode between gasoline engine and diesel engine. It injects a very uniform proportion of air and fuel mixture into the cylinder like traditional gasoline engine, but its ignition process is similar to that of diesel engine. It burns itself when the temperature of the mixture is increased to a certain extent by piston compression. Fig 1 shows the combustion temperature distribution of n-butanol and methane in two-stroke low-speed HCCI. The combustion mode of HCCI can be well explained from the diagram. It can be seen from the diagram that the temperature in the HCCI reactor increases slowly with the increase of the crankshaft angle. When the piston moves near the top dead center, the temperature in the reactor rises abruptly to the maximum value, and then decreases until the exhaust port is opened. The main reason for the slow increase of temperature from the closing of the exhaust port to the occurrence of the reaction is that the piston is upward, the mixture is compressed, the pressure in the reactor is increased, and the temperature is increased. When the piston moves to the top dead center, the pressure and temperature rise to a certain value. The mixed fuel in the reactor burns and releases a lot of heat. The pressure in the reactor rises sharply and produces a large amount of gas. Due to the short combustion reaction time, the piston began to go down, and the temperature in the reactor decreased. From the simulation results, it can be seen that as the proportion of CH4 in the fuel continues to increase, the exhaust temperature decreases. When the sequence number 1, that is, the methane ratio is 0 %, the temperature when the exhaust port is opened is 1207.178 K. When the sequence number 2, that is, the methane ratio is 30 %, the temperature when the exhaust port is opened is 1196.53 K. When the sequence number 3, that is, the methane ratio is 70%, the temperature when the exhaust port is opened is 1190.81 K. When the sequence number 4, that is, the methane ratio is 100%, the temperature when the exhaust port is opened is 1184.36 K. In the case of the same output power, increasing the proportion of CH4 in the fuel can effectively reduce the exhaust temperature.

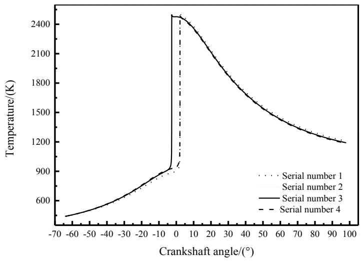


Fig 1 Cylinder temperature of different proportion of CH_4 fuel combustion

Fig 2 shows the relationship between the mole fraction of NO in the reactor and the crankshaft angle in the two-stroke low-speed HCCI. It can be seen from the diagram that the molar fraction of NO in the reactor does not change significantly with the increase of the crankshaft angle at 75 %. When the piston moves to the top dead center and the temperature in the HCCI reactor reaches more than 2000 K, the N_2 and O_2 in the reactor can undergo a large-scale oxidation reaction. The molar fraction of NO in the reactor rises abruptly, and then decreases rapidly with the increase of the crankshaft angle. When the crankshaft angle is about 20 °, the molar fraction of NO decreases slowly until the exhaust port is opened. It can also be seen from the figure that as the proportion of CH_4 in the reactants increases, the mole fraction of NO decreases when the exhaust port is opened. This is because in the reactor, the higher the proportion of methane in the mixed fuel, the lower the temperature in the reactor during the reaction, the shorter the time of high temperature oxidation reaction of N_2, and the less the amount of NO produced. Explain the phenomenon that the mole fraction of NO begins to decrease from the top dead center : The reaction equation involved in NO is analyzed. Fig 3 shows the reaction path, intermediate product and yield required for the reactant N_2 to the product NO, and the thickness of the line segment represents the yield. It can be seen from the figure that the intermediate products directly involved in the reaction are : NNH, HONO, O_2, HCO, CO_2, CO, HOCHO, H_2O. These intermediates will further react with other substances to form the final product. It can be seen from the figure that N_2 can directly generate NO, and can also generate NO through one or more intermediates. As shown in Fig 4, the main reaction equations involved in NO and the yield of the corresponding reaction equations when the crankshaft angle is 2.42 ° under the conditions of serial number 3 and 75 %. It can be seen from the listed reaction equations that NO acts as both a reactant and a product in the reaction.NO is a reactant in the chemical reaction $NNH+NO \Leftrightarrow N_2+HNO$ and $NO+O(+M) \Leftrightarrow NO_2(+M)$, while NO is a product in the chemical reaction $NO+H(+M) \Leftrightarrow HNO(+M)$ and $NO+HO_2 \Leftrightarrow NO_2+OH$. According to the total yield, the main reason for the decrease of NO mole fraction is the formation of N_2 and the further oxidation of NO_2.

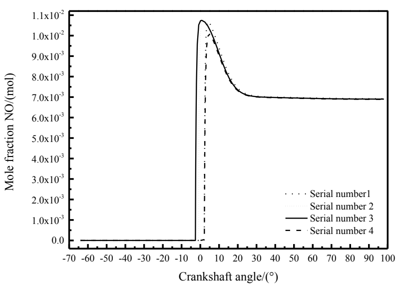


Fig 2 NO mole fraction of different proportion of CH_4 fuel combustion

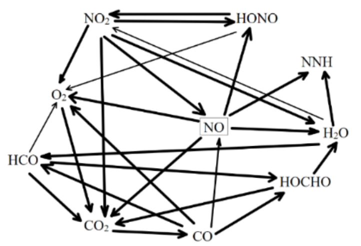


Fig 3 Main reaction pathway of NO

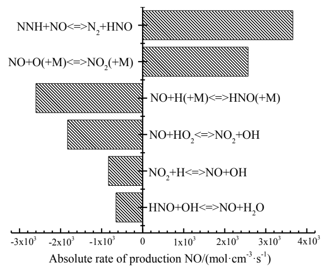


Fig 4 Main reaction equation of NO and its absolute rate of production

Fig 5 shows the relationship between the mole fraction of NO_2 in the reactor and the crankshaft angle in the two-stroke low-speed HCCI. It can be seen from the diagram that the molar fraction of NO_2 in the reactor does not change significantly with the increase of the crankshaft angle under the condition of 75%. When the piston moves to the top dead center, the molar fraction of NO_2 in the reactor rises abruptly. Then, the molar fraction of NO_2 decreases rapidly with the increase of the crankshaft angle. When the crankshaft angle is about 20 °, the molar fraction of NO_2 increases until the exhaust port is opened. The phenomenon that the molar fraction of NO_2 begins to decrease from the top dead center is explained. A is the reaction path, intermediate product and yield required for the formation of NO_2 when the fuel ratio is serial number 3 and the crankshaft angle is 2.24 °. It can be seen from the diagram that the intermediate products that can directly participate in the reaction is: CO, O_2, HNO_2, H_2, H_2O_2, H_2O, HONO, HNO, NO. When the crankshaft angle is 2.42 °, the main reaction equation of NO_2 and the yield of the corresponding reaction equation are shown in C. It can be seen from the listed reaction equations that NO_2 acts as both a reactant and a product in the reaction. NO_2 is the reactant in chemical reactions $NO_2+O \Leftrightarrow NO+O_2$,

$NO+O(+M) \Leftrightarrow NO_2(+M)$ and $NO_2+H \Leftrightarrow NO+OH$, while NO_2 is the product in chemical reactions $NO+HO_2 \Leftrightarrow NO_2+OH$ and $2NO_2 \Leftrightarrow 2NO+O_2$ .According to the total yield, the main reason for the decrease of NO_2 mole fraction is that most of NO_2 decomposes to NO. B shows the reaction path, intermediate product and yield of NO_2 when the fuel ratio is number 3 and the crankshaft angle is 70.46 °. It can be seen from the diagram that the intermediate products that can directly participate in the reaction are : CO, O_2, CO_2, HOCHO, NNH, H_2O, HONO, HCO, NO. The main reaction equations involved in NO_2 and the yield of the corresponding reaction equations are shown in D when the crankshaft angle is 70.46 ° under No.3 and 75 % conditions. It can be seen from the listed reaction equations that NO_2 acts as both a reactant and a product in the reaction, In the chemical reactions $NO+HO_2 \Leftrightarrow NO_2+H_2O$, $HONO+OH \Leftrightarrow NO_2+H_2O$ and $NO_2+O \Leftrightarrow NO+O_2$, NO_2 is the reactant, while in the chemical reaction $NO+O(+M) \Leftrightarrow NO_2(+M)$ and $2NO_2 \Leftrightarrow 2NO+O_2$,NO_2 is the product. According to the total yield, the main reason for the increase of NO2 mole fraction is the production of NO.

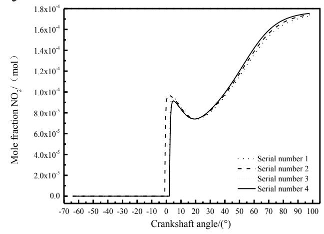
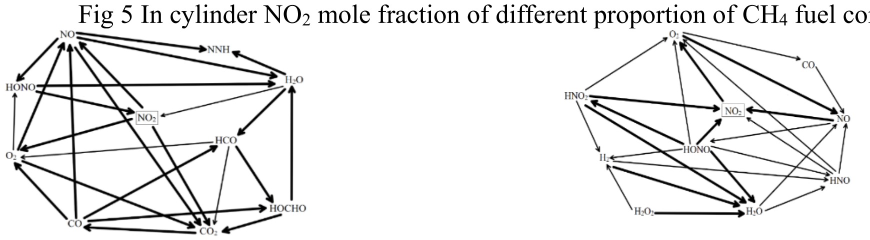
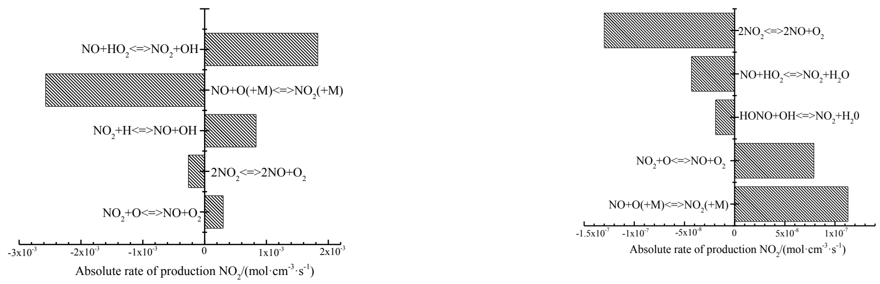


Fig 5 In cylinder NO_2 mole fraction of different proportion of CH_4 fuel combustion



A B

Fig 6 Main reaction pathway of NO_2 when the crankshaft angle is 2.42° and 70.46°



C D

Fig 7 Main reaction equation and absolute rate of production on NO_2 when the crankshaft angle is 2.42° and 70.46°

5.Discussion

When the output power is the same and the air excess coefficient is 1.5, increasing the proportion of CH_4 in the fuel will reduce the temperature when the exhaust port in the reactor is opened. Therefore, the increase of CH_4 in the fuel can effectively reduce the exhaust temperature, and the mole fraction of NO in the exhaust gas increases with the decrease of the proportion of CH_4 in the mixed fuel. Through the analysis of the reaction path and reaction mechanism under 75% operating condition, when the proportion of mixed fuel is 30% n-butanol and 70% methane, it can be seen that the decrease of NO mole fraction is mainly due to the conversion of part of NO into N_2 and part of NO into NO_2 .The decrease of the mole fraction of NO_2 at the crankshaft angle of -2 º~20 º is due to the conversion of NO_2 into NO, and the increase of the mole fraction of NO_2 at the crankshaft angle of 20 ~98 º is due to the conversion of NO. The mixed fuel composed of n-butanol and methane in proportion not only does not change the nature of fuel combustion, but also can reduce the generation of nitrogen oxides and reduce pollution.

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