Effects of Methanol–Ammonia Blending Ratio on Performance and Emission Characteristics of a Compression Ignition Engine

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Abstract: Sustainable ammonia is one of the leading candidates in the search for alternative clean fuels for marine applications. This paper aims to build a simulation model of a six-cylinder, four-stroke diesel engine to investigate the effects of increasing the ammonia proportion in methanol–ammonia fuel blends on engine performance and emissions. In the present study, the conditions of different speeds and different proportions of ammonia in fuel blends are investigated. The results show that the average effective pressure, brake power, and brake torque increase by about 5% with an increased ammonia substitution ratio. In terms of economic performance, the changes under medium and low speed conditions are not obvious. However, the change in high speed conditions is significant. The brake specific fuel consumption (BSFC) is reduced by 6.6%, and the brake thermal efficiency (BTE) is increased by 4%. It is found that the performance of the engine is best at medium speed. The best performance is achieved with higher efficiency and lower emissions. The present results can provide guidance for the optimization of ammonia–methanol blends and their applications in engines.

Keywords: diesel engine; simulation; methanol; ammonia

1. Introduction

Since the industrialization of human society, the excessive use of high-carbon energy has caused environmental damage and frequent natural disasters, especially air pollution, water pollution, waste disposal, etc. It is urgent that we save energy and protect the environment [1,2]. Diesel engines are the internal combustion engines with the highest thermal efficiency, and they are widely used because of their excellent performance, economic viability, and durability. However, the high emissions of carbon dioxide, nitrogen oxides, and particulate matter have harmful effects on human health, the environment, and the atmosphere. These high emissions have become one of the major factors limiting diesel engine development [3–6]. Governments around the world have adopted various policies to protect the environment. In terms of engines, it is a common practice to limit the emission levels in fuel vehicles. In the face of increasing emission limit standards, it is necessary to increase capital investment [7,8]. The factors that need to be considered when investigating alternative fuels for diesel engines include emissions, fuel stability, fuel availability, and subsequent effects on engine durability [9,10].

Methanol is considered to be a possible alternative to conventional fuels for use in engines [11]. Methanol has a high octane number and good explosion resistance, which can appropriately increase the engine compression ratio and improve the combustion
efficiency of mixed fuel [12]. Methanol is liquid at room temperature and pressure and can be made from any carbon-containing material by thermochemical methods. The preparation cost is low, the existing fuel storage and transportation equipment can meet the basic requirements, and the transformation cost is low [13,14]. However, the latent heat of vaporization is high, so it is difficult to start at low temperatures when it is used in compression ignition engines. Ganesan et al. [15] studied the engine performance of methanol as a main fuel and biodiesel as a combustion aid under different combustion modes. The results show that adding a certain amount of methanol can improve the thermal efficiency and cylinder pressure of the engine as well as reduce the emission of NOx. Wang et al. [16] carried out experiments on diesel–methanol mixed fuel with a high methanol substitution ratio in a high-speed light engine based on a dual direct injection system. The results show that the emission performance and efficiency are better than those of the original diesel engine when the average effective pressure is 0.55 MPa. Adding an accelerant to improve methanol combustion is the choice of most compression ignition engine researchers [15–19].

Ammonia is another clean and renewable fuel which can replace conventional fuels [20]. It contains no carbon and produces water and nitrogen when fully burned, which can be used as fuel to significantly reduce greenhouse gas emissions [21]. Ammonia can be stored in a liquid state at room temperature and pressure and has a mature production, transportation, and storage system. It has a low production cost and can be widely prepared and popularized in a short time [22]. Table 1 shows the comparison of the physicochemical characteristics of ammonia, methanol, and diesel oil. However, the low combustion rate and high spontaneous combustion temperature of ammonia lead to a poor combustion effect of pure ammonia. And, ammonia easily produces harmful NOx under lean combustion conditions [23–25]. The use of exhaust gas recirculation or the addition of other, more reactive fuels as combustion aids, that is, the dual fuel combustion mode [26], can improve ammonia combustion, thereby improving fuel efficiency and reducing emissions. Wei et al. [27] studied the optimization direction and emission reduction potential of an ammonia–natural gas engine. The results show that, with the increase of NH3, the peak value of in-cylinder pressure and the heat release rate decrease, the NOx emission first increases and then decreases, and the CO2 emission decreases. Xu et al. [28] studied the possibility of using ammonia as a carbon-free fuel for marine propulsion in ammonia–diesel dual-fuel engines with reactivity controlled compression ignition. The results show that, in order to ensure the efficient operation of the engine, diesel needs to account for at least 24% of the total fuel, thus reducing greenhouse gas emissions by 70%. Currently, ammonia has proved feasible for blending with diesel fuel to achieve a low spontaneous combustion temperature and fast combustion in CI engines.

Table 1. Comparison of physicochemical properties of ammonia, methanol, and diesel oil.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Ammonia</th>
<th>Methanol</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density/g cm⁻³</td>
<td>0.77 (Liquid)</td>
<td>0.79</td>
<td>0.84</td>
</tr>
<tr>
<td>Spontaneous combustion temperature/°C</td>
<td>650</td>
<td>464</td>
<td>316</td>
</tr>
<tr>
<td>Vaporization latent heat/kJ kg⁻¹</td>
<td>1370</td>
<td>1100</td>
<td>260</td>
</tr>
<tr>
<td>Low calorific value/kJ·kg⁻¹</td>
<td>18,610</td>
<td>19,660</td>
<td>42,700</td>
</tr>
<tr>
<td>Octane number</td>
<td>110</td>
<td>110</td>
<td>N/A</td>
</tr>
</tbody>
</table>

As methanol and ammonia are both assessed as alternative fuels, there have been a number of studies on the combustion of ammonia–methanol blends. Li et al. [29] measured the ignition delay time of the NH₃–CH₃OH mixture using a fast compressor. The results show that the NH₃–CH₃OH mixture becomes more reactive with an increase in methanol content. Lu et al. [30] numerically studied the effects of methanol addition on ammonia combustion and emissions under different equivalence ratios. The results show that the
addition of methanol significantly improves the chemical reaction activity of ammonia but leads to higher NOx emissions. Li et al. [31] studied the effect of methanol on ammonia’s spontaneous combustion by using a shock tube. The results show that the ignition delay time of an ammonia–methanol mixture can be shortened by more than 60% by adding 5% methanol. However, there is little research on the application of ammonia–methanol mixed fuel in compression ignition engines at home and abroad, so it is of great significance to explore the feasibility of burning methanol–ammonia mixed fuel. However, most of the studies are fundamental investigations of the combustion of ammonia–methanol blends. Practical engine studies on the application of methanol–ammonia blends are still lacking.

In the present study, a simulation model of a six-cylinder diesel engine is established to investigate the effect of ammonia–methanol blended fuel on practical engine performance. For 11 ratios of ammonia to methanol, the changes in engine performance characteristics (power, torque), economic characteristics (BSFC, BTE), and emission characteristics (CO, CO2, HC, NOx emissions) are analyzed. The optimum operating conditions of the engine using ammonia–methanol blended fuel are analyzed. This study can enrich the simulation research of ammonia–methanol mixed fuels and provides a reference for the related experimental and simulation research of compression ignition engines.

2. Simulation Principle and Model

Simulation technology plays a very important role in combustion engine performance research. By using numerical simulation software, it is possible to make a relatively reasonable experimental design and reduce the time and material costs. In addition, it is possible to pre-simulate the engine to give some guidance on the optimization direction of the engine through simulation. Due to the complexity of the working process of the internal combustion engine, it is necessary to simplify the combustion process of the engine when using simulation software to simulate the working process in a relatively quick and accurate way [32].

GT-Power is mainly used to calculate the one-dimensional gas flow process, which mainly involves the Navier–Stokes equation.

The continuity equation is as follows:

$$\frac{dm}{dt} = \sum_{bound} m_{flx} \tag{1}$$

The momentum equation is as follows:

$$\frac{d(me)}{dt} = p dV + \sum_{bound} (m_{flx} \cdot H) - h_g A (T_{gas} - T_{wall}) \tag{2}$$

The energy conservation equation is as follows:

$$\frac{d(m_{flx})}{dt} = [dpA + \sum_{bound} (m_{flx} \cdot u) - 4C_f \rho v^2 dx A - C_p \left( \frac{pv^2}{2} \right) A]/dx \tag{3}$$

where \( m \) represents the mass, \( m_{flx} \) represents the mass flow through the boundary, \( e \) represents the internal energy, \( p \) represents the pressure, \( V \) represents the volume, \( H \) represents the total enthalpy, \( h_g \) represents the heat transfer coefficient, \( A \) represents the flow area, \( u \) represents the boundary velocity, \( C_f \) and \( C_p \) represent the surface friction and the pressure loss coefficient, and \( D \) represents the equivalent diameter.

The model can predict the transient and steady-state behaviors of the engine system, and its computational performance has been confirmed by researchers in relevant scientific research institutes and enterprises.

2.1. Basic Parameters and Model Establishment

The experimental data of the engine are from Li et al. [33]. The engine prototype is a six-cylinder, in-line, four-stroke diesel engine. Its main parameters are shown in
Table 2 [33]. The working environment settings are 1 ATM and 300 K, and the fuels are diesel and methanol, both of which are injected directly into the cylinder by the nozzle. The ignition sequence of the engine is 1-5-3-6-2-4, the combustion model is EngCyl Comb DI Wiebe, and the heat transfer model is Woschni GT. The model is shown in Figure 1.

Table 2. Basic parameters of diesel unit.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression ratio</td>
<td>16.5</td>
</tr>
<tr>
<td>Bore/mm</td>
<td>105</td>
</tr>
<tr>
<td>Stroke/mm</td>
<td>125</td>
</tr>
<tr>
<td>Connecting rod length/mm</td>
<td>220</td>
</tr>
<tr>
<td>Fuel supply advance angle/°</td>
<td>12</td>
</tr>
<tr>
<td>Rated speed/(r/min)</td>
<td>2800</td>
</tr>
<tr>
<td>Rated power/kW</td>
<td>95.6</td>
</tr>
</tbody>
</table>

Figure 1. Model of six-cylinder diesel engine.

2.2. Model Verification and Optimization

2.2.1. Model Verification

To verify the accuracy of the simulation model with reference to experimental data, different fuel injection amounts are set for 10 groups of speed conditions from 1100 rpm to 2900 rpm (Table 3). The model is verified by the output power and the torque change curve. As can be seen from Figures 2 and 3, the simulation of braking power and braking torque of pure diesel and M15 fuel (methanol mass fraction is 15%) is basically consistent with the actual value and trend [33], and the errors in most data are less than 5%. Therefore, it can be considered that this model can be used.

Table 3. Fuel injection at each speed.

<table>
<thead>
<tr>
<th>Speed (r/min)</th>
<th>2900</th>
<th>2700</th>
<th>2500</th>
<th>2300</th>
<th>2100</th>
<th>1900</th>
<th>1700</th>
<th>1500</th>
<th>1300</th>
<th>1100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel injection quantity (mg)</td>
<td>48</td>
<td>47.5</td>
<td>47</td>
<td>46.5</td>
<td>46</td>
<td>45.5</td>
<td>45</td>
<td>44.5</td>
<td>44</td>
<td>43.5</td>
</tr>
</tbody>
</table>
2.2.2. Model Optimization

The cylinder temperature is reduced due to the high latent heat of methanol vaporization. It can cause starting difficulties, combustion deterioration, and other problems, which results in a sharp increase in fuel consumption. Therefore, in order to improve the efficiency of the engine fueled with a high methanol ratio, appropriate measures must be taken. The method of increasing turbocharging is adopted in this paper. The engine model with a turbocharging module is shown in Figure 4.

Figure 2. Comparison of simulation results with experimental results [33] from the literature (pure diesel fuel).

Figure 3. Comparison of simulation results with experimental results [33] from the literature (M15 fuel).
Figure 4. Model of 6-cylinder diesel engine with turbocharging.

Figure 5 shows the changes in power and BTE of diesel–methanol blends with different methanol blends when the engine is turbocharged, or not, at 2000 rpm. Both power and BTE increased by approximately 15%, and by 19% with the highest methanol blends.

Figure 5. Comparison of power and BTE between supercharged and non-supercharged engines.

3. Results and Discussion

The latent heat of the vaporization of ammonia and methanol is higher, the rate of combustion of ammonia is slow, and the temperature of spontaneous combustion is higher. The calorific value of both is less than half that of diesel. However, the hydrogen element in
ammonia and the high oxygen content of methanol can promote combustion. Therefore, to reduce the negative effect of the excessive latent heat of ammonia and methanol evaporation on combustion, the fuel setting of the simulation model retains diesel fuel with a mass fraction of 5% as the igniter. The intake nozzle is set based on the model with turbocharging components (the model is shown in Figure 6). Methanol and ammonia are premixed and injected into the intake. A total of 11 groups are set to replace methanol with ammonia (in mass fraction) from 0% (N0) to 50% (N50) with an interval of 5% for each group. Three groups of engine speeds and their respective fuel injection amounts are set with reference to the relevant data of the prototype diesel engine, as shown in Table 4.

![Ammonia–methanol engine model.](image)

Table 4. Rotational speed and fuel injection.

<table>
<thead>
<tr>
<th>Speed (r/min)</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel injection quantity (mg)</td>
<td>43.5</td>
<td>46</td>
<td>48.5</td>
</tr>
</tbody>
</table>

3.1. Dynamic Performance

3.1.1. Brake Power

Figure 7 shows the variation in brake power with an ammonia blend ratio under three speed conditions. The power value at low speed shows a fluctuating increase, and the power of the N50 fuel is about 2.5% higher than that of N0. The changes at medium and high speeds are more obvious, the power increase at medium speed is slightly lower, about 3.5%, and the total power is higher than that at high speed. The power increase is the largest at high speed, which is 7%. The overall trend shows increases as the ammonia mixture ratio increases.

When the engine is fueled with the same fuel, the main factors that affect the power are the engine speed, the amount of fuel injected, and the effective fuel consumption. The amount of fuel injected at high speed is more than that at medium speed, but the power is lower. Therefore, it is possible that the combustion of fuel in the cylinder could deteriorate, resulting in a significant increase in fuel consumption.
3.1.2. Brake Torque

The changes in brake torque with an ammonia blend ratio under three speed conditions are shown in Figure 8. Compared with the N0 fuel, the torque under low, medium, and high speed conditions with the N50 fuel increases by 2.5%, 3.5%, and 7%, respectively. The overall trend is that it increases with an increase in the ammonia blending ratio, and the increase range increases with an increase in engine speed, which is basically consistent with the power.

3.1.3. Mean Effective Pressure

The mean effective pressure of an engine is the average pressure of the gas in the cylinder acting on the piston during each work cycle. It directly reflects the power output of the engine. As shown in Figure 9, the overall trend of the mean effective pressure changing with the increase in the ammonia mixture ratio is basically consistent with the torque change. In comparison with the N0 fuel, the average effective pressure increases by about 2%, 2.4%, and 3.7%, respectively, at low, medium, and high speed conditions when the N50 combusts. The range of increase expands slightly with the increase in rotational speed, but the overall range of increase is lower. The use of an ammonia–methanol inlet premixed injection, the use of a small amount of diesel ignition, and the addition of turbocharged components greatly improve the combustion of fuel in the cylinder. This offsets the negative effect of low ammonia calorific value on engine power performance. However, due to the slow combustion rate of ammonia, the effect of low combustion pressure is still limited.
The relative values of mean effective pressure and torque (both of which are closely related to engine cylinder pressure) under three speed conditions are low speed > medium speed > high speed. When the fuel is the same and other parameters are constant, the cylinder pressure of the engine is mainly affected by the speed. As its value decreases as the speed increases, increasing the engine speed causes the average effective pressure and torque to decrease.

![Figure 9](image.png)

**Figure 9.** Mean effective pressure with ammonia blend ratio.

3.2. Economic Performance

3.2.1. Brake-Specific Fuel Consumption

The change in engine BSFC as a function of the ammonia blend ratio for three speed conditions is shown in Figure 10. When burning the same fuel, the BSFC at high speed is obviously higher than that at medium and low speeds. The average value is more than 200% higher than that at low speeds and about 170% higher than that at medium speeds. The BSFC of the three speed conditions decreases with the increase in the ammonia blending ratio, and the decrease increases with the increase in the speed. Compared with the N0 fuel, the BSFC of low, medium, and high speed conditions decreases by 3.1%, 3.5%, and 6.6%, respectively. The BSFC of high speed conditions decreases by about twice as much as that of low and medium speed conditions.

![Figure 10](image.png)

**Figure 10.** Brake specific fuel consumption rate with ammonia blend ratio.

With all other factors being similar, engine power is positively correlated with the lower calorific value of the fuel. It can be seen from Table 1 that the net calorific value
of methanol is slightly higher than that of ammonia, and both ammonia and methanol decompose upon heating. However, with the participation of oxygen in the air, methanol decomposes into CO\(_2\) and H\(_2\)O, which causes combustion deterioration, and a small amount of hydrogen can be formed. The combustion improvement depends mainly on the hydrogen obtained by ammonia decomposition, which reduces the effective fuel consumption, so the power is slightly increased. This is consistent with the trends shown in the curves of Figures 7 and 10.

### 3.2.2. Brake Thermal Efficiency

Figure 11 shows the changes in brake thermal efficiency of the engine with an ammonia mixture ratio at three speed conditions. In the case of burning the same fuel, the relative effective thermal efficiency of the three speeds is low speed > medium speed > high speed. The overall trend increases with the increase in ammonia content, and the increase in high rotational speed is larger, which is opposite to the change of effective fuel consumption. Compared with the N0 fuel, the BTE at low, medium, and high speed conditions with the N50 increases by 0.26%, 0.66%, and 4.07%, respectively. Although the BTE at high speed is greatly improved, the overall thermal efficiency is still lower than that of conventional engines. The thermal efficiency of the brake is mainly affected by the fuel combustion when the other engine parameters remain unchanged. When the combustion is improved, the thermal efficiency increases, which is consistent with the trend of the curve changes in Figures 10 and 11.

![Figure 11. Brake thermal efficiency with ammonia blend ratio.](image)

### 3.3. Emission Performance

#### 3.3.1. CO\(_2\) Emission

The variations in the engine’s CO\(_2\) emissions as a function of the ammonia blend ratio at three speed conditions are shown in Figure 12. When burning the same fuel, the relative CO\(_2\) emissions of the three speeds are high speed > medium speed > low speed, and the total decreases with the increase in ammonia content. Compared with the N0 fuel, the CO\(_2\) emissions of low, medium, and high speed conditions decrease by 44%, 45%, and 45%, respectively, when burning the N50, which is basically the same. Wang et al. [34] simulated the effect of premixed natural gas–ammonia and diesel ignition on engine combustion. The results showed that the emission of CO\(_2\) decreased significantly with an increase in ammonia content. Other studies also show similar conclusions [35,36].
3.3.2. CO Emission

The variations in the engine CO emission ratios with an ammonia mixture ratio under three speed conditions are shown in Figure 13. It can be seen that, as the ammonia content increases, the relative magnitude of CO emissions under the three speeds is high speed > medium speed > low speed. Compared with the N0 fuel, the CO emissions in the low, medium, and high speed conditions of the N50 decrease by 44%, 45%, and 45%, respectively. This is basically consistent with the change in CO\textsubscript{2} emissions. The sharp decreases in CO\textsubscript{2} and CO emissions are related to the decrease in the carbon content of the fuel, which decreases by about 3.3% for every 10% increase in ammonia content. Similar conclusions can be found in the study of the performance of diesel-ignited ammonia–hydrogen blends in engines by Wang et al. [37].

3.3.3. HC Emission

The variations in the HC emission ratios of the ammonia-blended engine under three speed conditions are shown in Figure 14. Compared with the N0 fuel, the HC proportions decrease by 44%, 55%, and 55% under low, medium, and high speed conditions, respectively. The overall change trend and range of the HC emission percentage is basically the same as those of CO\textsubscript{2} and CO emissions. The decrease in the proportion of HC emissions indicates a decrease in the proportion of unburned and incompletely burned fuels. As confirmed by the change in effective fuel consumption, its essence is an improvement in combustion.
Previous studies have mixed ammonia with fuels such as gasoline and methane and tested it in a single-cylinder engine with a maximum replacement rate of 50%. The results by Vinod et al. [38] show that the addition of ammonia improves the combustion stability of gasoline and methane, and HC emissions can be increased.

![Figure 14. Percentage of HC emissions with ammonia blend ratio.](image)

3.3.4. NO\textsubscript{x} Emission

The variations in the NO\textsubscript{x} emission ratios of the engine with an ammonia mixture ratio under three speed conditions are shown in Figure 15. With an increase in the ammonia blending ratio, the emission at each speed is basically unchanged, and the rate of increase or decrease is about 0.01%. In this study, ammonia and methanol were premixed with air, injected into the intake pipe, and then mixed with diesel fuel in the cylinder. The charging efficiency and the air temperature are improved by turbocharging, which is beneficial to the full combustion of ammonia and methanol. The N\textsubscript{2}O in the tail gas thermally decomposes into NO, which reduces greenhouse gas emissions. However, with an increase in the ammonia blending ratio, the emission proportion of unburned ammonia also increases. In particular, the addition of turbocharged modules exacerbates this trend, which can also explain why the nitrogen in the fuel increases while NO\textsubscript{x} emissions remain basically unchanged. With the increase in the ammonia ratio, the emission densities of CO and CO\textsubscript{2} in the engine exhaust decrease by about 50%. The HC emissions decrease significantly, and the total amount of NO\textsubscript{x} remains basically unchanged. This indicates that the use of ammonia–methanol blends is expected to improve the greenhouse effect emissions from the engine. Wang et al. [35] studied the effects of using the best mixing method and mixing ratio of ammonia–diesel fuel on the combustion and the emission performance of an engine. The results from Wang et al. [35] also show that the emissions of NO\textsubscript{x} can be reduced using ammonia–diesel fuel in engines.

3.4. Application Prospect

Methanol and ammonia are both renewable energy sources with low production costs. They also have a good impact on reducing carbon emissions. The existing system for storing and transporting fuels is perfect and can better adapt to using new fuels. The input cost of the aftreatment system is reduced because only the fuel supply system of the engine needs to be reformed. The transformation cost is low. It is convenient for large-scale popularization. The model of this study improves the combustion efficiency of mixed fuel to a great extent. It ameliorates the negative effect of the increase in fuel consumption due to the decrease in the calorific value of the fuel. The frequency of replenishing the fuel is reduced, the transportation costs and emissions are reduced, and the feasibility of its practical application is improved. In marine transportation, land transportation, and even power generation, it has wide application prospects.
4. Conclusions

In the present study, a numerical model of a six-cylinder diesel engine is established. Different ammonia blending ratios (mass fractions 0–50%) and speed conditions are set up. To improve the combustion in the cylinder, an ammonia–methanol inlet premix injection strategy, a small amount of diesel ignition, and the addition of turbocharging components are set up. The main conclusions of the study are as follows:

(1) The engine power performance parameters can be improved to a certain extent with an increase in the ammonia blending ratio. The brake power and torque of each speed condition increased by 2.5% and 7%. The increase in the mean effective pressure was small.

(2) The increases in the effective fuel consumption and effective thermal efficiency at each speed condition were between 3% and 6% with an increase in the ammonia blending ratio. These increased significantly at high speeds. However, its fuel consumption and thermal efficiency were poor.

(3) The emissions of CO and CO$_2$ in the engine exhaust decreased up to approximately 50% with an increase in the ammonia blending ratio. HC emissions were significantly reduced. The total amount and NO$_x$ remained generally unchanged.

(4) The overall performance of the engine at medium speed was the best. The power output was maximized while maintaining low emissions and high efficiency.

(5) In the simulation, simplified treatments were applied to the heat transfer and the combustion model of the engine. More in-depth studies of chemical reaction mechanisms are needed to further improve the simulation. More experiments are needed for further model calibration.

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**Nomenclature**

- N0: mass fraction of ammonia is 0%
- N50: mass fraction of ammonia is 50%
- BSFC: brake-specific fuel consumption
- BTE: brake thermal efficiency
- CO: carbon monoxide
- CO2: carbon dioxide
- HC: hydrocarbon
- NOx: oxides of nitrogen

**References**


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