

Performance Evaluation and Application of Diesel NO_x-SCR Catalyst by Ethanol Reductant

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ABSTRACT

A catalyst surfaced on Ag/Al₂O₃ substrate for the selective catalyst reduction (SCR) of NO_x by ethanol was evaluated in a diesel engine, and the effect of the catalyst on the reduction of NO_x from the diesel engine under the EURO III ESC test modes was also investigated. The reductant injecting device was designed by means of computational fluid dynamics (CFD) analysis, and the engine test bench including the reductant injection system for the evaluation of the NO_x-SCR catalyst performance was established. On the bench, the SCR catalyst with the ethanol reductant was tested at different temperatures and space velocities (SV), and integrated with an oxidation catalyst to reduce the diesel exhaust emissions of NO_x, HC and CO. Under the conditions of the SV=30,000 h⁻¹ and the exhaust temperature range of 350~420°C, the NO_x conversion efficiency is high over 90% and low beyond the temperature range. The catalyst performance will be greatly deteriorated when the space velocity is large than 40,000 h⁻¹. With the increase of the ethanol injection quantity, the NO_x conversion is increased, but the CO and THC emissions are undesirably increased simultaneously. By optimizing the strategy of the ethanol dosing, the integration of the NO_x SCR catalyst and the CO/HC oxidation catalyst can reduce the emissions from the diesel engine to meet more stringent emission regulations.

INTRODUCTION

Reduction of NO_x and PM is now the focus of diesel emission control to meet more and more stringent emission regulations in the future. But it is quite difficult to solve the trade-off between PM and NO_x by conventional engine modification technologies, most of which sacrifice the power or fuel economy. Therefore, aftertreatment technologies are coming up in the clean diesel engines. The selective catalytic reduction (SCR) is one of the most promising aftertreatment technologies to reduce NO_x emission from diesel engines^[1]. Compared with the lean NO_x trap catalyst, the SCR catalyst has advantages of

higher conversion efficiency, lower cost and less sulfur-sensitivity. Recently, ammonia (urea), hydrocarbons, and oxygenated hydrocarbons are commonly used as NO_x-SCR reducing agents. At the beginning of 1990s, Iwamoto etc^[2,3] first reported that a higher NO_x conversion was achieved at 1%-10% excess O₂ with the light hydrocarbons (CH₄, C₂H₄, C₃H₆ and C₃H₈) as reductants and Cu-ZSM-5 as the catalyst. Later, many other zeolite catalysts such as Cu-Y, Fe-M, Fe-L and Co-Ferrierite^[4,5] were utilized in the removal of NO_x. But the zeolite catalysts have weak thermal stability and are very sensitive to water vapor and SO₂, and not so active in low temperature region, though they are effective in the fresh stage. So, they are restricted for applications. A high NO conversion activity in the low temperature region can be realized by noble metal catalysts (Pt, Pd and Rh) coated on the substrates such as Al₂O₃, SiO₂, TiO₂ and ZrO₂, but these catalysts are less selective in the high temperature region, and easily produce N₂O, and also have high production costs^[6,7]. Miyadera^[8] studied a series of catalysts of Al₂O₃-supported transition metals like Cu, Co, Ag, V, Cr and so on, it was found that the Ag/Al₂O₃ substrate has the most activity in NO_x selective reduction and is not very sensitive to water vapour and SO₂, so it may become a promising NO_x reduction catalyst in diesel engines^[9,10,11].

The selective catalyst of NO_x with oxygenated hydrocarbon reductants such as CH₃OH, C₂H₅OH, CH₃CHO, CH₃COOH, etc over Ag/Al₂O₃ in excess oxygen was comparatively studied by the author H. He^[12]. It was shown that in the whole temperature range, the ethanol (C₂H₅OH) has a higher activity of NO_x conversion than propylene, and also has a wider working temperature range (310~610°C) with the highest conversion efficiency up to 90%. Thus the SCR of NO_x over Ag/Al₂O₃ can meet the working temperature requirements for diesel NO_x converters. With the same concentration, methanol (CH₃OH) and acetic acid (CH₃COOH) are not so effective in NO_x conversion, but acetaldehyde (CH₃CHO) has nearly the same effect as the ethanol in the removal of NO_x. The results above were obtained in the simulated

engine exhaust gas. In this paper, the NO_x SCR catalysts using the ethanol as a reductant^[13] was further evaluated in a diesel engine, and its application to meet more stringent emission standard was also investigated based on the ESC test modes.

EXPERIMENTAL SETUP

The experiment was conducted on the test bench, which consists of a Sofim 8140-43C diesel engine, an eddy current dynamometer and the exhaust gas aftertreatment system, as shown in Figure 1. NO_x, THC and CO emissions are measured by AVL CEBII exhaust gas analyzer. The engine specifications can be found in Table 1.

Table 1. Engine Specifications

Engine model	8140-43C
Type	4-cylinder, 4-stroke, in-line, direct injection, turbocharged, intercooling
Fuel pump	Bosch VE4/12F1800 R824-1
Number of valve	2 per cylinder
Displacement	2.798L
Compression ratio	18.5:1
Rated Power/Speed	76kW / 3600r/min
Low idle speed	775±50 r/min
High idle speed	4200±50 r/min

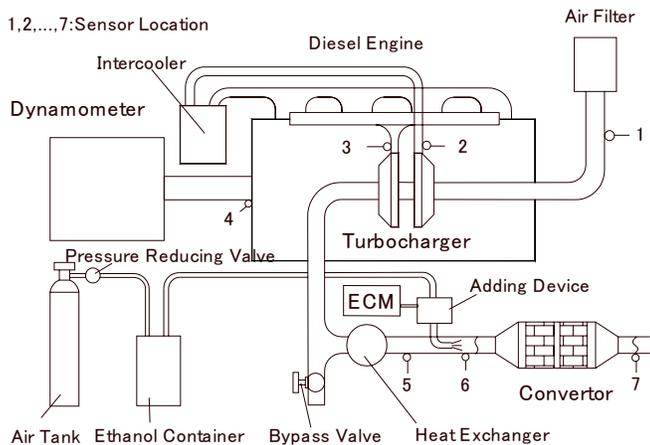


Figure 1. Setup for NO_x-SCR catalyst evaluation

As shown in Figure 1, the ethanol adding system is composed of a high pressure air tank filled with nitrogen gas, pressure control valve, ethanol container, ethanol injector and electronic control module (ECM). By the pressure control valve, the pressure of nitrogen can be reduced to 0.3MPa. Then, the nitrogen gas enters the container to push the ethanol into the injector through a tube connection. According to the engine speed signal and crank position signal, the ECM determines the injecting timing and pulse width to inject certain amount of

ethanol into the exhaust pipe in front of the NO_x catalytic converter.

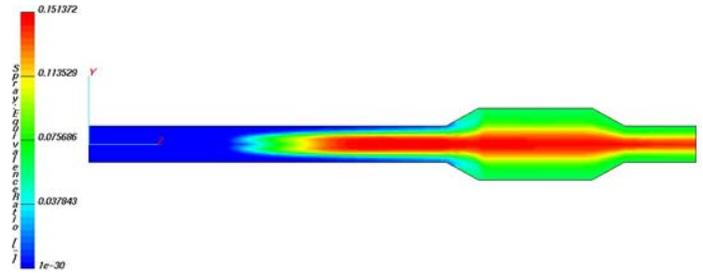


Figure 2. Simulated ethanol distribution

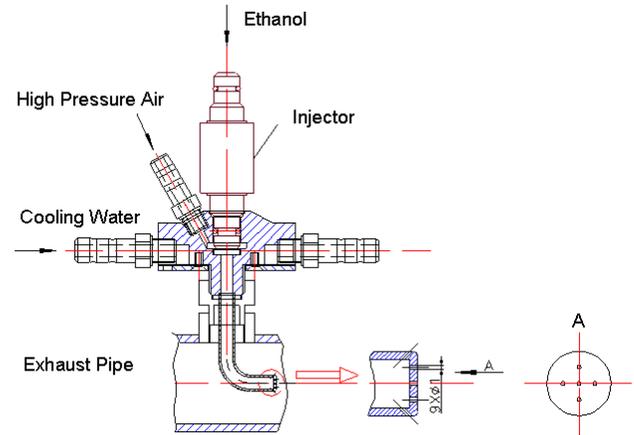


Figure 3. Reductant adding device schematic

For the SCR catalyst, the layout of the reductant adding device has a significant influence on the distribution of the reductant in the exhaust pipe^[3]. In this paper, the reductant adding device was optimized by means of computational fluid dynamics (CFD) analysis^[13]. Figure 2 shows the injected ethanol concentration distribution from CFD simulation. Through CFD simulation, the following optimization design principles are summarized as follows:

- Compared with the pintle valve nozzle, the multiple orifice nozzle can disperse the reductant to cover a wider region. Consequently, the distribution uniformity of the reductant can be improved to get higher NO_x conversion.
- The distribution of reductant is much more homogeneous when placed in the center of the exhaust pipe along the axial direction than that placed at the surface of the pipe vertically.
- The concentration gradient is very small along the axis of the exhaust pipe when the injector is located over 150mm away from the catalytic converter. So, it is not obvious to improve the reductant distribution by increasing the distance between the injector and the catalytic converter.

The ethanol adding device was designed according to the CFD conclusions above. Figure 3 shows the schematic of the ethanol adding device. Since the injector can't bear high exhaust temperature, therefore a conducting bent tube extruded into the exhaust pipe was introduced. The tube exit is of bubble structure with 9 orifices of 1 mm

diameter, through which the injected ethanol and pressured air was pushed into the exhaust. As a result, the bent tube can help the ethanol to be distributed homogeneously in front of the NO_x catalytic converter. Additionally, a water cooling system prevents the high exhaust gas temperature from the injector, and the high-pressure air assists the atomization and diffusion of the ethanol.

CATALYST EVALUATION

It is well known that the activity of NO_x SCR catalyst is closely related to the temperature, space velocity (SV), and THC/NO_x ratio. The exhaust temperature and space velocity vary greatly during the vehicle running. For a diesel engine, the exhaust temperature at part load is about 100°C ~ 200°C, while it may go up to 500°C at full load. The space velocity at high speed will be much higher than that at idle speed. The THC/NO_x ratio in the exhaust was directly controlled by the dosage of ethanol. In order to concentrate on analyzing the influence of these three main factors on the NO_x conversion, the impact of other factors like the exhaust components was neglected. In the experiment, the engine was operating in the same point with engine speed 3450 rpm at full load, meanwhile, the temperature at the inlet of the catalyst was adjusted by the heat exchanger, and the space velocity was regulated by the bypass valve (see also in Fig. 1).

The two assemblies of the catalysts for evaluation are marked A and B, the specifications of which are shown in Table 2. It can be seen that the two catalytic converters have both SCR and oxidation catalysts inside. The oxidation catalyst is 10 wt. % Cu/Al₂O₃ washcoated on Cordierite honeycombs and the washcoated loading was about 110 g/L. In case A and B, the NO_x catalyst and the oxidation catalyst only change in the volume and the catalytic monolith shape. The SCR catalyst was located in front of the converter and the oxidation catalyst in the rear. The oxidation catalyst tried to oxidize the over-injected ethanol and the CO additionally generated in the reduction of NO_x.

Table 2. Specification of the catalytic converters

Case	Shape	NO _x catalyst volume(L)	Oxidation catalyst volume(L)
A	Ellipse	2.4	0.6
B	Circular	0.785	0.26

Figure 4 shows the NO_x, CO and THC conversion efficiencies of the catalyst case A changing with the catalyst inlet temperatures under the conditions of SV=30,000h⁻¹ and THC/NO_x ≈ 3.4. It is found that high NO_x conversion efficiency (up to 90%) can be obtained in the range of 350–420°C. But at 270°C and 470°C, the efficiency decreases rapidly to about 50%. The CO conversion efficiency is negative in the whole temperature range, which means the CO is formed in the NO_x reduction process, and the oxidation catalyst has a low

activity in the CO oxidation. The higher the NO_x conversion efficiency is, the more the CO is formed. The suggested mechanism of the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃ had been proposed and discussed in our previous study [12]. The possible reaction of NCO+NO→N₂O+CO can produce small amount of CO. Some intermediate species, such as organo-nitrogen compounds can also be the resource of CO. The production of CO can also be observed during the SCR of NO_x by C₃H₆. And it could be noted that CO production was in direct proportion to the NO_x conversion. It was proposed that CO was not produced from the partial oxidation of THC, but from the SCR-C₂H₅OH of NO_x process. In addition, the HC conversion efficiency is considerably high in the temperature range of 270–470°C and over 90% when the temperature is large than 360°C. Obviously, the oxidation catalyst has a high activity in THC conversion. However, due to the addition of the ethanol, the THC emission absolute value after the catalyst is much higher than that from the original engine, especially at low temperatures about 10 times higher as shown in Figure 5.

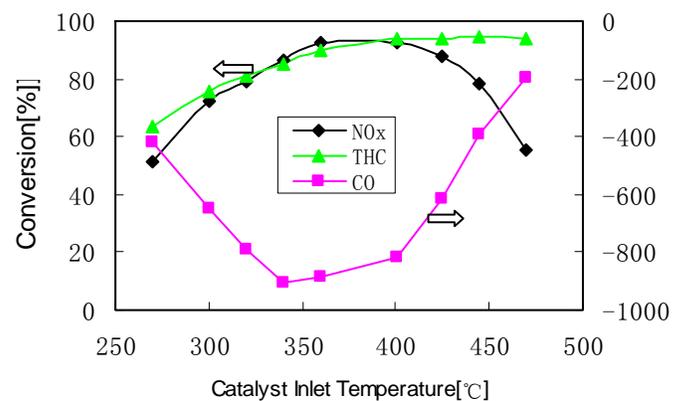


Figure 4 Conversion of catalyst case A (SV=30,000h⁻¹, THC/NO_x ≈ 3.4)

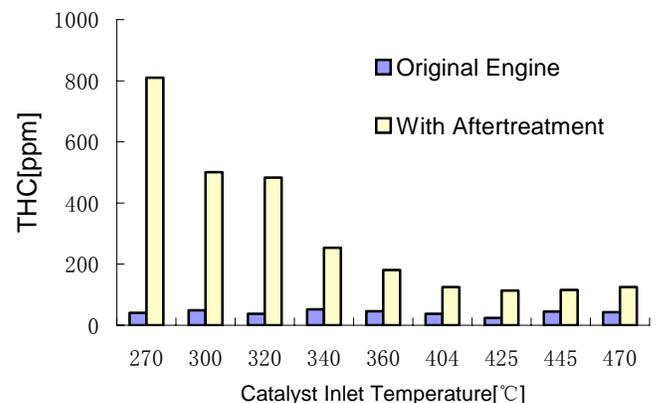


Figure 5 Comparison of THC concentration from original engine with the one after the catalytic converter

To sum up, the NO_x SCR catalyst can reduce NO_x effectively but cause a generation of CO simultaneously. The Cu/Al₂O₃ oxidation catalyst has a low activity in CO

conversion but has a high activity in THC conversion. Oxidation catalyst of higher activity should be integrated with the NO_x catalyst to reduce NO_x, CO and THC simultaneously.

For a practical catalyst, it should maintain a high conversion efficiency even under the high space velocity (e.g. SV=100,000h⁻¹) running conditions. In the real application, the catalyst is also expected to have a high conversion with a small catalyst volume for cost and space consideration. Therefore the conversion efficiency changing with the space velocity is an important characteristic in the catalyst evaluation. Figure 6 shows the sensitivity of NO_x conversion to space velocity of the catalyst case B under the conditions of THC/NO_x=3.4 and catalyst inlet temperature T=450°C. It can be found that the NO_x conversion efficiency maintains above 70% with SV<40,000h⁻¹, while it decreases to about 50% at SV=100,000h⁻¹ and 30% at SV=180,000h⁻¹. It means that the NO_x catalyst can maintain high conversion only in small space velocity region. The catalyst should be improved in SV sensitivity, otherwise it can't be applied well in automobiles.

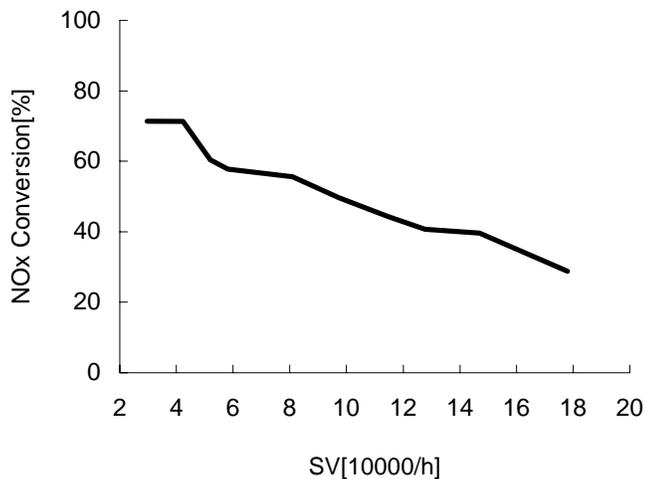


Figure 6 NO_x Conversion v.s Space Velocity (Catalyst case B, THC/NO_x=3.4, T=450°C)

For the NO_x SCR catalyst, it can be imaged that a reasonable reductant addition is necessary to obtain a high reduction of NO_x and meanwhile keep a low increase of THC. Lack of the reductant will no doubt result in a low utilization of the catalyst, while excess reductant will cause an increase of THC emission.

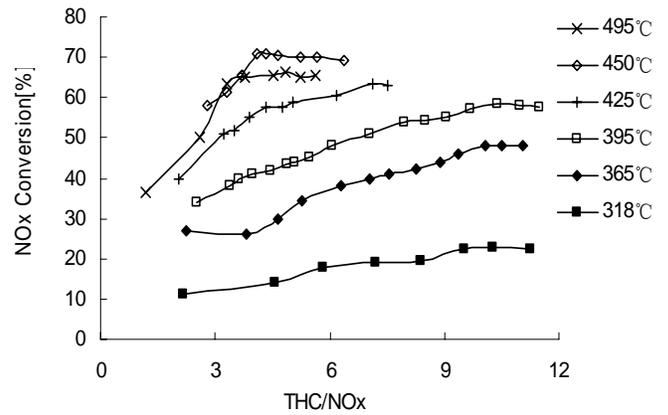


Figure 7 NO_x conversion vs different THC/NO_x ratio (Catalyst B, SV=90,000h⁻¹, 3450rpm, full load)

As shown in Figure 7, the NO_x conversion efficiencies apparently increase with the increasing of the ethanol dosage or THC/NO_x ratio at different catalyst inlet temperatures under the conditions of SV=90,000h⁻¹, engine speed 3450rpm in full load, Considering the exhaust temperatures of 318°C and 365°C, for example, when the THC/NO_x ratio is increased from 2 to 10, the NO_x conversion efficiencies are respectively improved from 11% and 26% to 22% and 48%, nearly twice as much as the previous one. However, the trends of the curves at different temperatures are not fully similar. At the lower temperatures, the conversion efficiency increases slowly until THC/NO_x ratio is about 10, while at higher temperatures, it increases quickly in the low THC/NO_x ratios. For the temperatures of 450°C and 495°C, the conversion efficiency ceases to increase when the THC/NO_x ratio is large than 4. It can be seen from Figure 7 that the catalyst is more active at high temperatures than the case at low temperatures and a very high NO_x conversion can not be available by increase of the THC/NO_x ratio.

CATALYST APPLICATION

CATALYST INTEGRATION

The final objective of the study is to make the original Sofim 8140-43C diesel engine based on EURO II emission regulations to meet EuroIII by the integration and optimization of the NO_x catalyst system. The engine was tested and checked in the EURO II ECE-R49 running modes, and the emission test result and its comparison with EURO II limits are listed in Table 3. From the Table 3, it can be seen that the original diesel engine can fully meet EURO II.

Table 3. EURO II ECE-R49 test results

Emissions	CO (g/kW.h)	HC (g/kW.h)	NO _x (g/kW.h)
EURO II limits	4.0	1.1	7.0
Test results	1.03	0.38	5.03

Table 4 shows the EURO III ESC test results of the engine integrated with different catalyst assemblies. The NOx SCR catalyst used here is the same as in case A (Table 2), taking SV to be considered. But the integrated oxidation catalyst was changed to an improved one with larger volume and higher activity in CO and HC oxidation (indicated by Oxi. in Table 4). When the engine runs under the ESC modes, the space velocity will change. It should be noted that the ethanol is not injected when the engine runs at idle speed, because the NOx conversion efficiency at idle speed is very low due to the low exhaust temperature (less than 200 °C). It can be seen from the Table 4 that the NOx emission is much lower than the original engine with over 50% of the NOx weight averaged conversion when the SCR catalyst was integrated. In this case, the NOx can meet the EURO III's requirement but CO and THC exceed the EURO III limits. Therefore some measures should be taken to reduce HC and CO simultaneously, such as installing an oxidation catalyst with low light-off temperature after the NOx catalyst, or optimizing the reductant dosing strategy.

Table 4. EURO III ESC test results

Emissions	CO (g/kW.h)	HC (g/kW.h)	NOx (g/kW.h)
EURO III limits	2.1	0.66	5.0
Original engine	1.30	0.35	6.92
SCR	3.48	1.43	2.67
SCR+Oxi.	0.097	0.71	3.65

It can be seen from the Table 4 that the SCR+Oxi assembly not only effectively reduces NOx emission, but also dramatically decreases the CO formed in the reduction of the NOx. The HC emission is also about half reduced by the oxidation catalyst. It should be noted that the NOx emission is a little increased when the oxidation catalyst is introduced. It was reported that the by-products such as NH₃, CH₃CN, HCN, CO and CH₃CHO are produced from the reduction of lean NOx by ethanol over an alumina-supported silver catalyst, and these compounds are easily oxidized to NOx over the oxidation catalyst^[9].

However, HC emission still doesn't meet EURO III standard. Thus, the ethanol dosing strategy was optimized to make the engine completely meet the EURO III based on the SCR+Oxi. assembly.

ETHANOL DOSING STRATEGY

The change of the engine speed and torque will cause the fluctuation of the exhaust temperature which has a great effect on the NOx conversion. Therefore, the optimization method was aimed to control the ethanol injection based on the exhaust temperature.

As discussed above, the SCR catalyst can maintain high conversion efficiency only in the middle range of temperatures such as 360°C-500°C, and its activity drops with the rising of SV. In the low temperature region, since the NOx conversion efficiency is very low (see also Fig. 4), an ethanol injection will cause a great increase of the THC emission without much NOx converted. In this case, the ethanol injection was cancelled. Although the NOx is increased a little, the THC emission will be greatly reduced. In the high temperature region, on the one hand, the activity of the SCR catalyst is reduced, on the other hand, the corresponding SVs are very big (Table 5), so the NOx conversion would be accordingly very low. In this case, ambient air can be introduced to the exhaust pipe to cool the exhaust gas to reach the high NOx conversion range, then the NOx conversion efficiency can be increased.

Table 5. Exhaust gas conditions of ESC 13-modes

Mode	Engine Speed (rpm)	Load Percent (%)	Exhaust Temp (°C)	SV (*10 ⁴ /h)
1	Idle	--	187	2.3
2	2350	100	413	12.
3	2900	50	297	12.
4	2900	75	353	14.0
5	2350	50	278	9.8
6	2350	75	347	11.0
7	2350	25	219	8.7
8	2900	100	427	15.
9	2900	25	225	11.
10	3450	100	489	16.
11	3450	25	306	13.
12	3450	75	428	16.
13	3450	50	364	15.

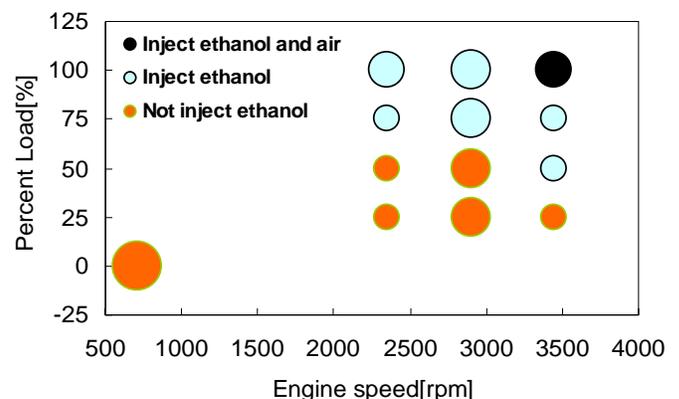


Figure 8 Ethanol dosing strategy

Table 5 shows the 13-mode emission test running conditions for heavy duty diesel engines. As shown in Table 5, the exhaust temperatures at mode 1, 3, 5, 7, 9 and 11 (less than 306 °C) are relatively low, thus the

ethanol is not injected owing to the low NO_x conversion. The exhaust temperatures are at mode 2, 4, 6, 8, 12 and 13 are in the high conversion range, so an adequate ethanol can be injected for NO_x reduction. The exhaust temperature at mode 10 (larger than 489 °C) is too high, therefore the ambient air with low temperature was introduced and the ethanol was injected simultaneously. The optimized ethanol dosing strategy is directly shown in Figure 8.

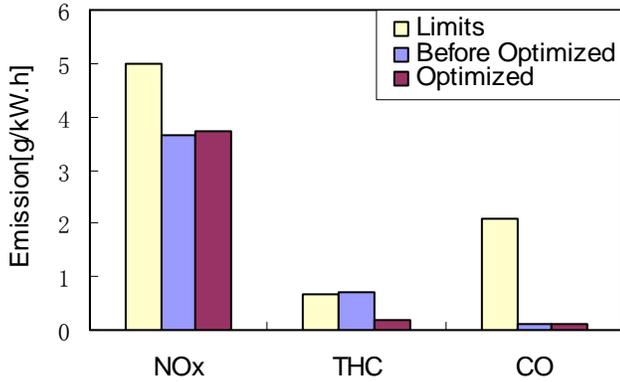


Figure 9 Test results after optimization

The EURO III ESC emission test results after the optimization is shown in Figure 9. It can be found that NO_x and CO are nearly the same, but HC emission is greatly reduced by the optimization of the dosing strategy, making the engine fully meet EURO III standards.

CONCLUSIONS

Through the investigation of NO_x selective catalytic reduction by ethanol over Ag/Al₂O₃ on a diesel engine, the following conclusions can be drawn:

1. The NO_x SCR catalyst in the experiment has the typical volcano-like conversion v.s. the temperature. The conversion efficiency is maintained above 90% with SV=30,000h⁻¹ in the temperature range of 350~420°C, while it is reduced at higher and lower temperatures.
2. The high NO_x conversion is obtained at lower space velocities. When the space velocity is above 40,000h⁻¹, the NO_x conversion efficiency will be greatly reduced.
3. The NO_x conversion efficiency will go up with the increase of the ethanol dosage, but cause the great increase of the THC emission at the same time.
4. A large amount of CO is produced in the reduction process of NO_x, thus a highly effective oxidation catalyst should be mounted integrated with the NO_x-SCR catalyst to reduce CO.
5. In the application test, the NO_x is obviously reduced to below EURO III limit only with the NO_x-SCR catalyst, while THC and CO emissions greatly exceed the limits.
6. The NO_x, THC and CO emissions can be largely reduced with the SCR+Oxi catalysts assembly. Furthermore, through optimizing the ethanol adding strategy, the diesel engine can completely meet EURO III regulations.

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