Relative Role of H2 and Hydrocarbon in reduction process of HC SCR system driven by on-board plasma reformer


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Abstract: On board reformer for hydrocarbon selective catalytic reduction (HC SCR) system for automobile de-NOx process is suggested. Basically HC SCR catalyst is designed to utilize HC species in engine emission, however de-NOx performance by HC species are rather lower than that of NH3 or H2. In this study, on board plasma reformer is suggested as a possible provider of H2 as a reductant. Suggested plasma reformer is developed for the possible installation in 3,000 cc diesel engine. It has small volume of about 100 cc and consumes less than 100 W of electric power. The reformer can control relative composition of H2 and HC species by changing operating parameter. In engine bench test, relative role of H2 and HC in reduction process is investigated. Plasma reformer showed good de-NOx performance across wide range of operating temperature. Though the operating condition of a SCR system depends much on the characteristic of catalyst used, plasma reformer can follow the need for reductant composition dynamically. It is expected that the application of the plasma reformer is promising.

Keywords: HC SCR, H2, on-board reformer

1. Introduction

NOx is representative hazardous emission of diesel engine. Regulations are getting strict for NOx emission. Euro VI demands 0.08 g/km of NOx emission for passenger cars.[1] And both advanced engine technology and after treatment technology are required for further reduction of NOx.

In this presentation, plasma technology for deNOx is described. Plasma can be used as a provider of reducing agents as an on-board reformer. Among various deNOx technologies, hydrocarbon selective catalytic reduction (HC SCR) system is selected in this work. Though HC SCR has rather lower deNOx performance compared to NH3 SCR or lean NOx trap (LNT), it can be applied with simple configuration and low cost of installation and operation. And advanced engine technology that can level the NOx emission much less than 100 ppm reduces the burden of deNOx performance of after treatment system, HC SCR can be an attractive way of deNOx strategy.[2–5]

Plasma can be easily combined as a HC SCR system, it can be independently operated with engine condition, and plasma reformer developed has small volume of less than 100 cc and consumes only about 100W based on the condition of 300cc engine. Moreover, plasma on-board reformer can produce hydrogen that is kind of deNOx booster in Ag based SCR catalyst.[6,7]

This work focuses the function of reformer especially as a generator of on-board hydrogen for a enhancement of SCR performance.

2. Plasma reforming

Rotating arc already showed its superior performance as a diesel reformer.[8] without additional vaporizer and mixer, rotating arc reformer can produce reformate gas that has hydrogen concentration of up to 10%. Because HC SCR catalyst uses hydrocarbon species as reducing agents, reformer should produce hydrocarbon species that is good at reduction process such as C2H4, C3H8 as well as hydrogen. Figure 1 shows relative production of selective hydrocarbon species according to O2/C ratio.

Figure 1. Hydrocarbon production in the reformer according to the O2/C ratio.
3. Catalyst

Ag/Al2O3 catalyst are tested for HC SCR. The catalyst has been widely studied as SCR catalyst and known to show good performance especially in the case of H2 addition.[6] HeeSung Catalysts corporation provided catalyst for the test and catalyst used in this work has 2.5% Ag/Al2O3 with size of 5.66” × 6” (2.5 L), cell density is 400/6. Figure 3 shows basic test result of the same catalyst with test specimen with dimension of 1” × 2” (Heesung catalyst corp.) with S/V of 50,000/hr.

4. Engine bench test

Engine bench test for the proposed SCR system has been done. Diesel engine of 3L (EURO III) capacity is used. Overall configuration of the test apparatus are given in Fig. 4 NOx sensor before and after SCR catalyst records NOx conversion and AC power supply is used for the operation of the reformer. Fuel flow of 2.7~6 ml/min are supplied to the reformer by precision pump. Air supply is controlled by MFC to match the designed O2/C condition. Emission conditions of the engine according to the temperature in rpm of 2,000 are listed in table 1.

Table 1. Engine emission condition according to the exhaust gas temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>170</th>
<th>220</th>
<th>270</th>
<th>320</th>
<th>370</th>
<th>420</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx (ppm)</td>
<td>133</td>
<td>200</td>
<td>231</td>
<td>224</td>
<td>240</td>
<td>252</td>
</tr>
<tr>
<td>THC (ppm)</td>
<td>27.0</td>
<td>23.0</td>
<td>21.0</td>
<td>19.3</td>
<td>22.3</td>
<td>26.3</td>
</tr>
<tr>
<td>THC/NOx</td>
<td>0.203</td>
<td>0.126</td>
<td>0.098</td>
<td>0.079</td>
<td>0.093</td>
<td>0.104</td>
</tr>
</tbody>
</table>

Figure 5 shows compared deNOx performance according to the exhaust gas temperature for different O2/C ratios. Interesting enough is that in the case of reformer off condition, almost no deNOx is observed even in temperature above 400°C that is why the S/V of the testes catalysts are too high. However, once the reformer is operated, the performance shows totally different results. DeNOx performance in each condition shows much higher rate up to 60%. In the case of O2/C 9.6 shows best deNOx performance in all of the temperature conditions.
The results show that one of the important merits of plasma assisted deNOx process is possible reduction of catalyst volume. The result in this work implies that less than a half of the catalyst may be sufficient for the desired deNOx performance. This is important for the cost of the system can be reduced drastically for the cost of the catalyst has biggest portion in the cost of overall system.

Figure 6 shows the result of correlation between de-NOx rate and the supplied reducing agents conditions. In the case of 420°C, deNOx rate follows similarly with the ratio of (HC+H2)/NOx. However, as the temperature decreases, or in the case of 320°C, deNOx rate deviates from the ratio of (HC+H2)/NOx as the O2/C ratio increases. This is why in the relatively low temperature condition, oxidation of HC species is less active than in the case of high temperature. For the H2 has still strongly oxidative in the relatively low temperature condition, deNOx rate in higher O2/C ratio condition shows less deactivation than in the cases of lower O2/C ratio. For the catalyst itself has less oxidative function, the effect H2 amount can be distinguishable as the temperature decreases. If the catalyst has strong oxidative function, H2 will be oxidized before it can work as reducing agents. So as the oxidative function becomes less strong, the dependence of deNOx performance becomes less significant. This can be confirmed from Fig. 7. That shows the result of deNOx performance against O2/C ratio. DeNOx rate does not show much deviation along all the tested O2/C conditions.

The fact that deNOx rate is less dependent on the O2/C ratio is good for robust operation of the system. However, it can be a challenging aspect in view of long term operation. For the oxidative function of the catalyst can be beneficial in the removal of HC deposition. Reformer possibly produces white smoke or heavy hydrocarbon species as well as H2, CO and light hydrocarbon species especially in the start up condition or cold start condition.

Once the heavy hydrocarbon species deposits on the catalyst surface it can reduce the active site of the catalyst and deactivates deNOx performance. if the catalyst has oxidative function, these depositions can be oxidized even to a useful reducing agents even in the low temperature condition. however, if the oxidative function of the catalyst is not so strong, the deposition results in progressive deactivation of the catalyst. To figure out the deactivation characteristics, aging test was done for different O2/C ratio conditions.

Figure 8 shows the aging test results. Increase of O2/C ratio produces oxidative environment in the reforming process and results in more oxidative cracking of heavy hydrocarbon species. Lee et al reported that in the plasma reforming of diesel fuel, increase of O2/C ratio results in the decrease of heavy hydrocarbon species rather than oxidation of hydrogen.[8] and the effect of increased O2/C
ratio is reflected in the result of aging test. Even from the result of the $O_2/C$ ratio of 9.6 shows slight decrease in the deNOx rate. From the result, $O_2/C$ ratio above 12 is required to guarantee the long term operation of the reformer. However, the problem of aging can be solved by changing the operation mode of the reformer. If the $O_2/C$ ratio increases much above the partial oxidation condition, the reformer turn into a plasma burner without change of geometry or any configuration of the system.

One the reformer is operated as a burner, elevated temperature of the exhaust gas can be enough for the oxidation of the deposited hydrocarbon species on the catalyst surface. The procedure is the same with that of DPF regeneration. Plasma burner for the DPF regeneration has been commercialized after field test of more than 100,000km [9] and the plasma burner concept can be successfully applied to the reformer.

Figure 8. Comparison of aging test in each $O_2/C$ condition.

The overall fuel penalty of the system is estimated to be 3%. The fuel penalty is defined to be the ratio of fuel consumption of reformer to that of engine. The fuel penalty can be still be reduced by optimization of the reformer that controls production of reformate to be only necessary amount of reducing agents. Considering that other deNOx technology such as Lean NOx Trap (LNT) generally reports fuel penalty of above 5%, the proposed system in this work can be estimated to have good fuel penalty.

All of the results presented in this presentation verifies that the plasma assisted HC SCR system can be a strong candidate of future deNOx technology.

4. Conclusions

Plasma assisted HC SCR system is proposed and the engine bench test to verify the feasibility of the system has been done. Ag/Al$_2$O$_3$, SCR catalyst is tested. Plasma on board reformer is used for the generation of reducing agents for the SCR system. Rotating arc reactor is used for the reforming or diesel fuel. Plasma assisted HC SCR system shows much enhanced deNOx rate even in much higher S/V condition. Merits of the system can be listed as follows. 1) plasma reformer is best suitable for the on board application. Plasma reactor itself has volume of less than 100cc. and the power supply developed for the plasma generation already went through all the test procedures of electronic device for automobile application. 2) the reformer can be operated as a plasma burner for possible regeneration of the catalyst without any modification or change of the system. Only the change of the reactant condition ($O_2/C$ ratio) can switch the mode of operation. And the plasma burner has been verified for the on board device and commercialized. 3) plasma assisted SCR system can reduce the catalyst volume drastically. S/V of the system can be modulated to be much high by adopting the plasma reformer. Reduction of the catalyst volume means reduction of the cost of the system. Cost for the plasma reformer and power supply can be less than the amount of the cost of reduction. 4) though the proposed system has many merits listed above, the fuel penalty of the system is rather low. Above 50% of deNOx rate can be obtained with fuel penalty of less than 3%.

All of the results strongly supports possibility of commercialization of the proposed system.

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References