INHIBITION AS A METHOD OF AN IN-CYLINDER CATALYTIC COATING TESTING
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Abstract
In-cylinder catalytic coatings are used to improve IC engine performance and emission. Experimental investigations of coatings are normally accompanied with engine reassembly that leads to irreproducibility of results. Coatings can also change the conditions of mixture preparation and combustion. The factors mentioned above make it difficult to assess the catalytic activity of the coating. To eliminate the irreproducibility mentioned above and isolate the effects of a catalyst, an inhibition technique of in-cylinder coating testing has been proposed. The method consists in the “in situ” poisoning of the catalyst by inhibitors. With this method the engine is tested before and after inhibiting without reassembly and the results obtained can be attributed to the coating with more confidence. The applicability of inhibition method has been proved experimentally. An indirect-injection diesel engine with combustion chamber of variable geometry (VG), coated by MoSi₂ and ZrO₂ catalysts was tested using inhibition technique and a positive effect of the coatings on engine emission has been shown.

Key words: IC engine emission, catalyst, in-cylinder coating, inhibition

1. INTRODUCTION
Considerable efforts have been made by investigators to enhance the accuracy of experimental data. When the positive effect of an innovation is comparable with the deviation of experimental results it may be ignored at early stages of an investigation. Who knows how many of innovations otherwise being developed and used have been buried by the experimental inaccuracies?

Apart from common measurement inaccuracies, one more source of data deviation is to be taken into account. Perhaps everybody who has been concerned with engine research and development will agree that one of the most significant problems of engine testing is the reproducibility of the engine performance. Even changes in the pressure, temperature and humidity of the ambient air cause changes in engine performance.

But probably the main reason for the irreproducibility is the engine reassembly which is difficult to avoid in any experimental research.

Another aspect of the problem to be considered here is the search of the factor that predominates over others in the effect achieved.

Such problems can be solved by excluding or at least diminishing the influence of the accompanying factors. A “one at a time” procedure like this has been formulated by Plint and Martyr (1995), when only one factor is varied in a set of experiments the others being unchanged. Again, if the experiment is accompanied by the engine reassembly the deviation of the results will increase due to their irreproducibility. The analyses of and the solution to the problem stated above in one particular application were the objectives of this paper.

The beneficial effect of an in-cylinder ceramic coating on the engine performance and emissions has been investigated for a long time (Bradstreet, 1961; Winkler and Parker, 1993; Klett et al., 1994; Wong et al., 1995; Voss at al., 1997). The authors of this paper have been concerned with an investigation of the in-cylinder coatings as a remedy for nitrogen oxides (NOₓ) emission. Research was aimed at the selection of an appropriate catalyst and providing conditions favourable for in-cylinder catalysis. At the experimental stage of the investigation the base engine was tested and disassembled. Then parts of the combustion chamber were coated; engine was reassembled and tested
again. The first results obtained were difficult to analyse and some of them were contradictory. Several reasons for such contradictions were guessed and analysed. First, the size and volume of the combustion chamber, hence, compression ratio could be slightly changed due to the finite thickness of the coating and engine reassembly. Second, coatings made by the thermal spray technique could change the thermal conductivity and roughness of combustion chamber walls. These and other factors in turn could cause the change in the conditions of mixture preparation and combustion.

Assessment of the deviation of the experimental data due to the engine reassembly has confirmed that this factor alone can be responsible for significant variations. To minimise the impact of engine reassembly on the data deviation an inhibition method suggested by Vasilev et al. (1987) was applied. The inhibition technique has been widely used in studies of heterogeneous catalysis and consists in the poisoning of the catalyst by inhibitors. With such technique the engine was tested before and after inhibiting without reassembly. In this case the results obtained could with more confidence be attributed to the coating, without errors due to reassembly, and since the catalyst layer was still in place, avoiding errors of cylinder size, conductivity and surface roughness variations.

2. OBJECTIVE AND EXPERIMENTAL

The most significant pollutants from diesel engines are NO\textsubscript{x} and particulate matter (PM). Reduction of NO\textsubscript{x} by catalytic converters is difficult due to high oxygen concentration in diesel exhaust. Fuel injection retarding and EGR are limited by detrimental effect on engine efficiency and soot emission. In-cylinder heterogeneous catalysis is considered to be the one of the promising methods of NO\textsubscript{x} reduction. In the oxygen-lean zones of combustion products the reduction of nitric oxide (NO) can proceed by the reaction

\[ 2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \]

Carbon monoxide can also take part in NO reduction by the reaction

\[ 2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2 \]

Dehydrogenation of the fuel hydrocarbons and NO reduction have been thought to be enhanced by the appropriate catalyst. It is obvious that the rate of reaction will be determined by the rate of delivery of reagents to and the removal of products from the catalyst. To maximize the desirable effect it is necessary to provide an intensive charge motion over catalytic surfaces. Such conditions can be achieved most easily in the indirect combustion engines.

Divided combustion chamber of variable geometry (VG) used in this investigation had the piston with central positioned boss entering the pre-chamber at the top dead center (TDC) (Figure 1). All fuel is injected into the pre-chamber and the first part of combustion occurs with a significant deficiency of air since the pre-chamber volume is as much as half the clearance volume. Up to 75% of burning mixture passes through the clearance between the pre-chamber throat and the piston boss until the boss exits pre-chamber as the piston moves toward the bottom dead center (BTC). The piston boss temperature exceeds 700°C and thus provides the favorable conditions for the performance of the catalyst applied to the surfaces of the throat and the piston boss. MoSi2 has been applied to the piston boss surface by thermal spray techniques. A zirconia based catalyst was reported to promote fuel ignition (Wonnam and Santavicca, 1990) that is why pre-chamber wall was coated by ZrO2.
A single-cylinder research diesel engine with bore of 0.14 m and stroke of 0.14 m was set up on the test bed provided with all necessary equipment. The engine had independent lubricating and liquid cooling systems with the cylinder-block and cylinder head cooled separately. Turbocharging was modelled on the basis of the performance of a six-cylinder diesel engine of the similar design. A piston-type compressor was used as a booster. The two-stage throttle simulated the performance of a gas turbine. NOx concentration in the exhaust was measured by a chemiluminescent gas analyser 344-CL-01. Exhaust opacity was measured by Hartridge-type smokemeter IDS-1.

3. ASSESSMENT OF AN IRREPRODUCIBILITY

In order to assess the change in the engine performance due to reassembly the indirect-combustion turbocharged engine with VG combustion chamber was tested. Not one part of the engine was changed during all the tests. In the test number one the indicated specific fuel consumption (isfc), NOx and carbon monoxide (CO) emissions and exhaust opacity were measured. One week later all measurements were repeated, that was test number two. Test number three was done after taking off the cylinder head, taking out of the pre-chamber and the following reassembly. In the fourth test the piston was taken out and piston rings taken of.

Test results for three values of engine load at 1500 rev/min are provided in Figure 2 and Table 1. Figure 1 show that in general from the test 2 to 4 the fuel consumption increased and the NOx concentration decreased, but with different rates for different loads. Equal drop of NOx emission was accompanied by significant increase of fuel consumption at 50% rated power, but by unchanged economy at 75% power. At rated power the correlation is not so obvious.
Fig. 2. Effect of reassemblage on engine performance.

Data of Table 1 have not been analysed in more details and are provided as they were. These data cannot be used as a reference for the given engine performance analysis but they give an idea of how those parameters may change due to reassemblies.

Table 1. Engine performance data deviation due to reassemblies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test number</th>
<th>STDEV</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>100% rated power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isfc</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>NOx</td>
<td>1.30</td>
<td>1.14</td>
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<tr>
<td>CO</td>
<td>0.90</td>
<td>1.13</td>
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<tr>
<td>Opacity</td>
<td>0.91</td>
<td>1.09</td>
</tr>
<tr>
<td>75% rated power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isfc</td>
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<td>1.00</td>
</tr>
<tr>
<td>NOx</td>
<td>1.10</td>
<td>1.00</td>
</tr>
<tr>
<td>CO</td>
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<td>1.07</td>
</tr>
<tr>
<td>Opacity</td>
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<td>1.00</td>
</tr>
<tr>
<td>50% rated power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isfc</td>
<td>0.97</td>
<td>1.00</td>
</tr>
<tr>
<td>NOx</td>
<td>1.09</td>
<td>0.99</td>
</tr>
<tr>
<td>CO</td>
<td>0.93</td>
<td>1.03</td>
</tr>
<tr>
<td>Opacity</td>
<td>0.89</td>
<td>1.11</td>
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</table>
Measurement results in Table 1 were reduced to the average values of the corresponding parameters at given loads. It was the authors’ opinion that the standard deviation provided in last column could be reasonably used in analysis to follow.

4. INHIBITION TECHNIQUE

The inhibition method consists of poisoning the catalyst by inhibitors. It has been assumed that inhibitors neutralise catalysts completely and do not act themselves as a catalysts. In chemistry alkalis have been used as inhibitors, and NaOH has been recommended as particularly effective (Navalihina et al., 1971). In order to insure complete inhibition an aqueous solution of NaOH and Na₂S·9H₂O has been used. Na⁺ ions and H₂S resulted from reactions

\[
\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-
\]

\[
\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{H}_2\text{S} + 7\text{H}_2\text{O}
\]

which irreversibly blocked the active centres of catalysts.

The amount of inhibiting solution required has been determined by the technique described by Samahov et al. (1976). Catalyst poisoning was performed as follows. An aqueous solution of the inhibitors was induced into the cylinder through the indicator channel. The engine was then periodically motored with the valve mechanism disabled. The total duration of the inhibiting reaction was 17 hours.

5. RESULTS AND DISCUSSION

VG combustion chamber coated by ZrO₂ and MoSi₂ has been tested using the inhibition technique. Engine was tested before and after inhibition.

The engine tests results after inhibition have been taken as the base-line. Table 2 shows the results from this pair of tests. The values measured were reduced to those of the test after inhibiting, i.e. to the base-line test. The data of Table 2 shows that NOₓ and CO emissions as well as exhaust opacity were significantly reduced due to in-cylinder catalytic coating at slightly improved fuel economy. The effect of coating on the NOₓ reduction increases with the load due to lower air-fuel ratio that provided more favourable condition for catalysis. More details of data obtained in this experiment can be found in paper of Bannikov at. al. (2002).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>% rated power</th>
<th>STDEV from Table 1</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>isfc</td>
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</tr>
<tr>
<td>NOx</td>
<td>0.44</td>
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</tr>
<tr>
<td>CO</td>
<td>0.89</td>
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<tr>
<td>Opacity</td>
<td>0.83</td>
<td>0.42</td>
</tr>
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</table>
Also shown in the table are the values of the standard deviations found in the reproducibility tests of Table 1 (averaged over the 3 values of load). These values illustrate that decrease in fuel consumption due to catalytic effect of coating is comparable with the STDEV and could be unobserved without inhibition. Similarly, emission and exhaust opacity could be under- or overestimated by 10 to 15 per cent if inhibition method was not used.

Similar experiments using this inhibition technique were carried out for an undivided bowl-in-piston combustion chamber coated by MoSi\textsubscript{2}. The effect of coating on engine performance was not as profound as with VG combustion chamber and test results were comparable with the data deviation due to reassembly. However a positive effect observed due to inhibition method was enhanced later by organising local turbulence in the combustion chamber (Figure 3.).

![Fig. 3. Bowl in piston combustion chamber with turbulence generator (Kutenev et. al., 1998)](image)

6. CONCLUSION

Data deviation due to engine reassembly for a particular engine was obtained. This information is unique for a given engine, given equipment and even a given staff, and it cannot be used as a reference. But it gave an idea of how this data can deviate and led to the contrivance of the inhibition technique.

In the case of testing coatings without using the inhibition technique, the data of Table 1 can be used to estimate the confidence level of the effect obtained.

The application of the inhibition technique avoids engine reassembly and allows the direct measurement of the catalytic effect of the coating, separate from other accompanying effects, thus providing authentic and reliable results.
REFERENCES


