Platinum Catalysts for Diesel Engine Exhaust Purification

By G. J. K. Acres

Research Laboratories, Johnson Matthey & Co Limited

The exhaust gases emitted by diesel engines are frequently both a health hazard and a nuisance to the public. These emissions can be minimised by careful engine design but catalytic combustion provides a more effective method of purification. THT catalysts incorporating platinum have given excellent results in test units. They are suitable for diesel-engined road vehicles and for diesels working in enclosed conditions.

The diesel engine, owing to its efficiency and reliability, has become the basic power unit of many commercial systems. These include units for road and rail transport, lifting equipment, light haulage in mines and factories and power generation. However, despite the diesel engine's many advantages, the exhaust gases it emits create either a public nuisance or a health hazard in many of these applications.

In recent years, as traffic density has increased, the diesel-engined road transport vehicle has become the target for much public criticism. This is currently centred on the nuisance created by the emission of smoke and the odour of the exhaust gases. Petrol-engined vehicles, on the other hand, are much less likely to create these problems and are therefore more acceptable to the public.

The smoke and the odours emitted by diesel engines may be a nuisance but they are not considered to be a health hazard. They are not, however, the only exhaust emissions and such things as carbon monoxide, unburnt hydrocarbons, partially oxidised hydrocarbons and nitrogen oxides are also emitted. All of these compounds are potential air pollutants but – and this is not generally realised – the concentration of these in the exhaust from a diesel engine is significantly less than in that from a petrol engine.

The concentration of pollutants varies from engine to engine and also depends upon the operating mode of the engine. For comparison purposes, figures typical of the two engine systems are given in Table I.

By current American standards of exhaust emission for road vehicles, the concentration in the diesel exhaust is acceptable, unlike that from the petrol engine without substantial modification. However, the problems of smoke and odour remain to be solved for

Table I

Maximum Emission Concentrations in Exhaust Gases from Petrol and Diesel Engines

	Carbon Monoxide %	Hydrocarbons p.p.m.	Nitric Oxide p.p.m.	Sulphur Dioxide p.p.m.	Particulates g/m^3
Diesel Engine	0.1	300	4,000	200	0.5
Petrol Engine	10	1,000	4,000	60	0.01

Fig. 1 Public criticism of diesel-engined road vehicles is centred on the emission of smoke and the odour of the exhaust gases. These are a nuisance but other exhaust gas components constitute a health hazard and their elimination is essential. THT catalysts incorporating platinum are effective in the purification of diesel exhaust gases

the diesel-engined road vehicle to become fully acceptable.

Despite the low concentration of exhaust emissions from diesel engines, when these are emitted into a confined atmosphere they can create a health problem. Particularly hazardous in these conditions is carbon monoxide. Also a problem is the unpleasant odour associated with diesel exhaust gases and the effect of these gases on the eyes and throat. Many diesel engines are operated in confined spaces in units such as mine locomotives, lifting equipment, and stationary electric power generators. For all of these applications it is customary to employ an exhaust purification system, or alternatively to provide adequate ventilation to the enclosed areas.

Exhaust Emissions from Diesel Engines

The origin of the various emissions in diesel exhaust gases stems from the combustion processes occurring in the engine. The reasons for their occurrence, the concentrations at which they appear and the means for reducing them, either by engine modification or by exhaust gas treatment, depend upon the particular emission.

Smoke

The smoke emitted by diesel engines is usually classified by colour. The white smoke sometimes seen when the engine is first started is usually a transition phase which disappears when the engine becomes warm. It can be minimised by increasing the cetane number of the fuel and also by good engine design. Blue smoke is usually caused by misfiring at high speed and this again may be overcome by modifications to the fuel and good engine design.

Black smoke, an unfortunate characteristic of many diesel engines, may arise for a number of reasons, particularly under high load conditions. Black smoke emissions are minimised by good engine maintenance, by limiting the volume of fuel that can be fed to the engine under high load conditions, and by certain fuel additives. In conditions where black smoke is a particular nuisance, for example on public transport vehicles and on mine locomotives, it is customary for the brake horsepower of the engine to be limited.

Carbon Monoxide

This is formed during the combustion process when there is insufficient oxygen available for complete combustion. As diesel engines, unlike petrol engines, operate with excess air under all conditions, there is less carbon monoxide in their exhaust gases. Even so, with inefficient mixing of the air fuel mixture and particularly at high load conditions, a significant concentration of carbon monoxide is produced. The problem can be minimised by good engine design and by limiting the power output of the engine. Fuel composition and fuel additives have little effect on carbon monoxide concentrations.

Hydrocarbons and Partially Oxygenated Hydrocarbons

As with carbon monoxide, the emission of these compounds occurs when insufficient oxygen is available for combustion. Again good engine maintenance and design can minimise these emissions.

The odour commonly associated with diesel engines is attributable to the emission of hydrocarbons and partially oxygenated species. Until recently, it was thought to be due solely to the aldehydes present in the exhaust gases. Recent work has now shown that the odour is caused by a synergistic effect of a multitude of components including hydrocarbons, aldehydes, ketones, carboxylic acids, alcohols, phenols and nitrophenols (1).

Although engine design may influence the odour of the exhaust gases it is surprising that there is only a limited amount of work being carried out in Europe at the present time (2).

Oxides of Nitrogen

The oxides of nitrogen which are present in diesel exhaust gases are mainly nitric oxide. This is produced during the combustion process by the combination of nitrogen and oxygen at the high temperatures and pressures present in the combustion chamber. The presence of nitric oxide in the exhaust gases is particularly hazardous when the engine is used in a confined space.

Any engine operating parameter that reduces the combustion temperature will reduce the nitric oxide concentration. For example, retarding the engine, increasing the fuel concentration, reducing the compression ratio, reducing the maximum power output of the engine, and recycling the exhaust gases all lead to a reduction in nitric oxide levels. Unfortunately, a number of these modifications which reduce nitric oxide levels also increase the carbon monoxide and hydrocarbon content of the exhaust gases and therefore cannot be used without an additional exhaust gas purification unit.

Diesel Exhaust Purification Systems

As outlined above, by careful attention to detailed engine design and by limiting the power output, the exhaust gas emissions may be minimised but not eliminated. Engine modifications are particularly effective for reducing the smoke and nitrogen oxide emissions but are not so effective for reducing other emissions. Exhaust gas purification systems have therefore been developed for diesel engines that are used in enclosed areas. The two most common systems are water scrubbing and catalytic combustion. Although an exhaust scrubbing system is effective for the reduction of exhaust emissions, it suffers from a number of disadvantages. These include frequent maintenance, a bulky system and an increase in the emission of water vapour into the atmosphere. An effective catalytic combustion system, on the other hand, may be equally effective at reducing exhaust emissions without suffering from the disadvantages of the scrubber system.

Catalytic combustion is a well-established procedure for the elimination of many of the

Table II **Operating Characteristics of the Test Engine**					
Conditions	Brake horse power	Fuel Rate lb/h	Air rate lb/h	Speed rev/min	Exhaust gas temperature °C
Idling	—	0.51	74.8	600	96
Medium load	7.5	5.14	119.0	1,190	487
High load	11.0	6.20	116.0	1,170	597

components present in the exhaust from a diesel engine. The catalytic system works by promoting the combination of the carbon monoxide, hydrocarbons, aldehydes, etc., that are present in the exhaust gases with oxygen. The products of this reaction are carbon dioxide and water, which of course are odourless and non-toxic. Unlike the petrol engine, there may be up to 20 per cent excess air in the exhaust gases, and this will provide adequate oxygen for the combustion reaction. All that is necessary, therefore, for catalytic diesel exhaust purification is the installation of a catalyst chamber into the exhaust system from the engine. As the catalytic combustion reactions are more effective the higher the exhaust temperatures, it is preferable for the catalytic unit to be installed as close to the exhaust manifold as is practical.

THT Catalyst System

A catalytic combustion system for diesel exhaust purification should take into account a number of limitations imposed by the operating conditions of the diesel engine. These may be summarised as follows:

(*a*) It must be effective over the whole operating range of exhaust gas temperature and must withstand the highest operating temperature without losing its effectiveness.

(*b*) Because of space limitations and the disadvantages of back pressure on engine performance, the catalyst should combine high activity per unit volume with a minimum resistance to the flow of exhaust gases.

(*c*) The catalyst should be resistant to attrition that might be caused by vibration and it should be possible for the catalyst chamber to be mounted in any position in the exhaust system.

To meet these requirements, we have developed the THT catalyst system for diesel exhaust purification. This catalyst system combines the high activity/low ignition temperature properties of platinum with the unique properties of a honeycomb ceramic support. A detailed account of this catalyst for air pollution control was given in a recent article in this journal (3). In addition to the general information then given, specific data on the performance of THT catalyst for diesel exhaust purification have now been obtained. These tests were carried out on a single cylinder Gardner IL2 laboratory engine fitted with a water brake and set up to reproduce exhaust gases typical of those emitted by diesel engines operating in enclosed areas. The operating characteristics of the engine are given in Table II.

The THT catalytic combustion unit used in these tests was connected to the exhaust manifold by a short length of stainless steel tube. After passing through the catalyst unit, the exhaust gases were emitted to the atmosphere through a conventional silencer. The pressure drop in the catalyst unit was 0.4 inches of water. The experimental system for measuring engine performance and monitoring the exhaust gases before and after the catalyst is shown in Fig. 2. A photograph of the test facility is shown in Fig. 3.

Exhaust emissions before and after the catalyst were measured by conventional techniques. Carbon monoxide and nitric

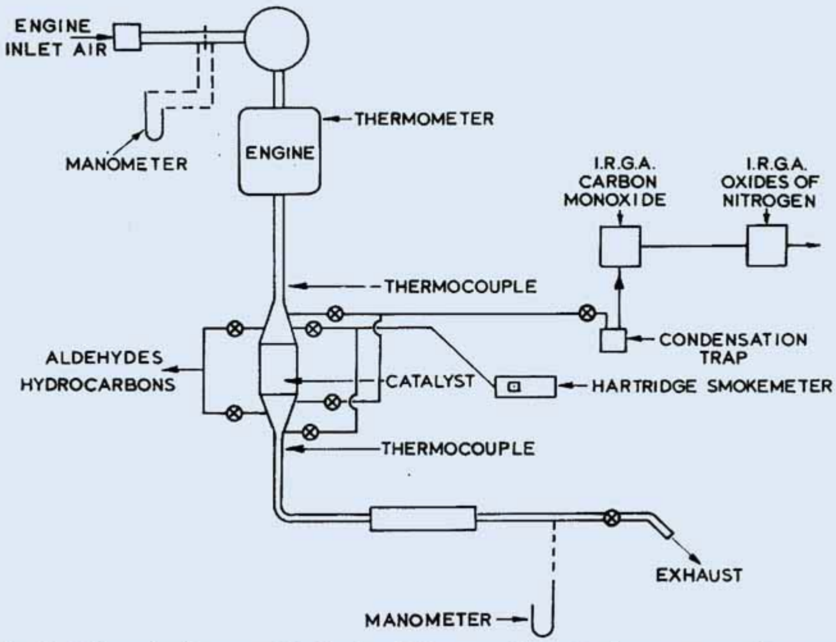

Fig. 2 Schematic diagram of the Gardner IL2 test engine and exhaust gas sampling system

oxide were determined by infra-red analysis. The aliphatic aldehyde concentrations were determined by the MBTH method. The hydrocarbon concentrations were determined by gas chromatography from samples collected in Haldane tubes. Smoke concentrations in the exhaust gases were obtained with a Hartridge Smokemeter.

Tests were made of the effectiveness of the catalyst for exhaust gas purification under three operating conditions – idling, medium and high load. Measurements and samples

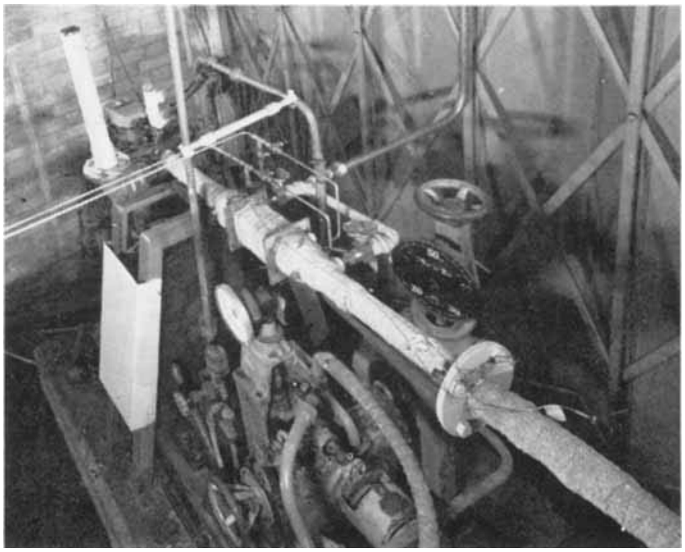

Fig. 3 The Gardner IL2 test engine and water brake with the THT catalytic combustion unit installed in the exhaust system

were taken before and after the catalyst and were taken 10 times for each engine condition. These tests were randomised and a period of 15 minutes was allowed between tests for the engine conditions to stabilise. The results of these tests are given in Table III.

In addition to the exhaust emissions listed in these tables, the aliphatic aldehyde content and odour of the exhaust gases were also determined. Under supposedly stable engine conditions, the aldehyde concentration in the exhaust gases was found to vary and as a result, the catalytic effectiveness for aldehyde removal was only measured under full load conditions. By taking samples simultaneously before and after the catalyst the aldehyde concentration was found to be reduced by 60 per cent. The percentage variation for 95 per cent confidence limits is 41.3 to 78.5 per cent. The odour of the exhaust gases after the catalyst was significantly improved.

Under idling conditions, the exhaust gas temperature of 95°C is too low for the catalytic reaction to occur. The effect of exhaust gas temperature on the removal of carbon monoxide by the catalyst was determined and is

Table III

A **Summary of Exhaust Emissions at Idling (Mean of ten tests)**

Compound	Without catalyst p.p.m. by vol.	With catalyst p.p.m. by vol.	Variation %	Percentage variation for 95% confidence limit
NO_x	<500	<500		not significant
Ethane	15.3	17.0	11.10	not significant
Methane	—		—	not significant
Carbon Monoxide	1,032	1,014	0.17	not significant
Smoke	3.9*	4.0*	2.56	not significant
B **Summary of Exhaust Emissions at Medium Load (Mean of ten tests)**				
NO_x	2,270	2,125	6.4	not significant
Ethane	8.0	1.6	80.0	67.4–88.2
Methane	—	—	—	—
Carbon Monoxide	474	97	79.5	78.5–80.5
Smoke	12.9*	13.1*	1.6	not significant
C **Summary of Exhaust Emissions at High Load (Mean of ten tests)**				
NO_x	2,097	2,281	8.8	not significant
Ethane	8.0	2.4	70.0	50.5–89.6
Methane	15.6	11.8	24.4	5.5–43.2
Carbon Monoxide	1,930	320	83.4	82.7–84.0
Smoke	41.3*	36.7*	11.1	not significant

*Smoke expressed in Hartridge smoke units

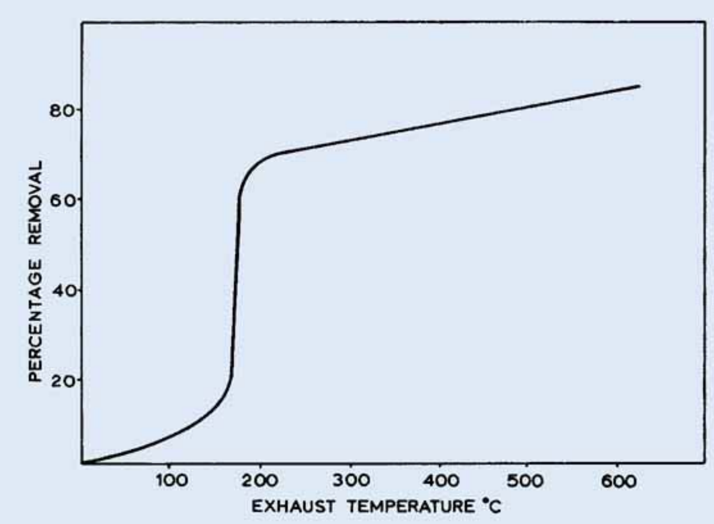

Fig. 4 The effect of exhaust gas temperature on the removal of carbon monoxide with a THT catalytic combustion unit

shown graphically in Fig. 4. The results show that the catalyst becomes effective at 170°C and its activity increases rapidly with increasing exhaust temperature.

The degree of exhaust purification, which is expressed as a percentage variation in these tables, may be increased up to a theoretical value of 100 per cent by increasing the volume of catalyst used in the combustion unit. Increasing the volume of catalyst would also give a significant variation in the smoke concentration before and after the catalyst, but at this stage of catalyst development this would not be economic in a commercial system. Although the catalyst is less effective at reducing smoke than it is at reducing other exhaust emissions, the catalyst does not become coated with smoke particles and

Fig. 5 The effectiveness of the THT catalytic combustion system for diesel exhaust purification has been proved by extensive field tests. The photograph shows a large diesel tractor fitted with a THT unit to enable it to work in the Straight Creek tunnel in the Rockies

therefore rendered ineffective. The smoke particles on the catalyst are continuously removed by catalytic oxidation during the operating life of the catalyst.

Complete Exhaust Emission Control

Under the conditions existing in diesel exhaust gases, namely those of excess oxygen, THT catalyst neither increases nor decreases the nitrogen oxide concentration. It is possible with a two-stage catalyst system, one operation under reducing conditions to remove nitrogen oxide, and a second under oxidising conditions to remove carbon monoxide and hydrocrabons, to achieve complete exhaust gas purification. However, it is probably more practical to achieve these ends by a combination of engine modifications to reduce smoke and nitrogen oxide levels, plus a catalytic combustion unit to reduce the concentration of the other exhaust emissions, including those causing the odour problem.

We conclude that for those applications when diesel engines are used in enclosed locations, the exhaust gases can be made safe and acceptable to people working in the area by incorporating a THT catalytic combustion unit into the exhaust system. Also, the incorporation of catalytic combustion units in the exhaust systems from public transport and other vehicles operating in heavily congested areas would reduce the nuisance caused by exhaust odours.

Acknowledgements

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Measurement of Lunar Heat Flow

A NEW PLATINUM RESISTANCE THERMOMETER

One object of the Apollo programme of lunar exploration is to study lunar heat flow by measurements with temperature probes at depths up to three metres into the Moon's surface. The thermometers for this work must have stability better than 2×10^{-3} deg K/year together with the ability to withstand the shocks of launching into space and landing on the Moon. Workers at Rosemount Engineering Co and Arthur D. Little Inc have developed a rugged differential platinum resistance thermometer for the task (*Rev. sci. Instrum.*, 1970, **41**, (4), 541–544).

The design provides a ±2 deg K differential over the range 200 to 270 K. Isolation from the effects of mechanical and thermal strains is achieved by attaching the platinum wire in the form of a helix to its supporting platinum mandrel by glass insulation of a type which has a similar thermal expansion coefficient. Only 10 per cent of each wire loop is embedded in the glass so that the wire is free to expand or contract while being rigidly supported. To complete the thermometer both wire and mandrel are encased in a platinum tube, the ends of which are sealed hermetically with pure gold solder after the connecting leads of platinum have been passed out through one end.

Each thermometer unit has been calibrated at 42 points (nine differential temperatures and five absolute temperatures between 200 and 250 K). A stability testing programme over one year indicated an average drift of only $+0.45\times10^{-3}$ deg K/year.

Each element has an ice-point resistance of 500 ± 1 ohm. This figure was a compromise between concerns of wire purity, individual coil rigidity, sensitivity, self-heating, and volume.

F. J. S.