Catalysts for Nitrogen Oxides Control under Lean Burn Conditions

THE OPPORTUNITY FOR NEW TECHNOLOGY TO COMPLEMENT PLATINUM GROUP METAL AUTOCATALYSTS

By T. J. Truex
Johnson Matthey Technology Centre

R. A. Searles
Johnson Matthey Catalytic Systems Division, Royston

and D. C. Sun
Johnson Matthey Catalytic Systems Division, Wayne

Regulations to control the exhaust emissions from motor vehicles are being adopted by more and more countries around the world, and in future more stringent regulations will be introduced, particularly in the U.S.A. and Europe. This, together with the need to show good pollution control under real-world driving conditions, has led to the widespread introduction of closed-loop, three-way catalysts based on the use of platinum group metal technology. The increasing concern about emissions of carbon dioxide, as well as the three traditional pollutants, offers an opportunity for catalyst technology to control nitrogen oxides from both fuel efficient lean burn petrol engines and from diesel engines, thus complementing the use of platinum group metals catalysts to control nitrogen oxides and other emissions. This paper reviews the development of "lean-NOx" technology based on the use of zeolite supported catalysts; it highlights the promise shown and the shortcomings still to be overcome.

Over the last 25 years the motor vehicle has increasingly become a cause for concern on environmental issues. This initially led to the control of carbon monoxide, because of the potential build-up of this toxic gas in congested city centres, and of hydrocarbons and nitrogen oxides, both precursors of the photochemical smog and low level ozone prevalent in some regions, particularly in the Los Angeles basin.

Now the motor vehicle is identified as the contributor of around 15 per cent of carbon dioxide emissions. Carbon dioxide is the main "greenhouse" gas contributing to perhaps 50 per cent of the predicted global warming and is of course the inevitable product of burning carbon-containing fossil fuels.

The twin goals of low and efficient fuel use and minimum emissions are increasingly being addressed by research in both the motor and the catalyst industries of the world.

The Lean Burn Engine

In various prototype forms the lean burn engine has been around for nearly 25 years. However, successful and widespread usage of this engine has been restricted by increasingly strict control on the level of pollutants emitted under the full range of engine operating conditions (1). Recent developments have included the evolution of lean operating two-stroke engines (Figure 1).

Lean burn operation involves the burning of

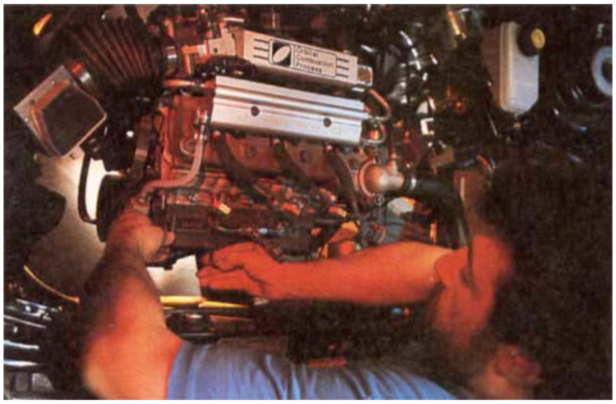


Fig. 1 Among lean burn engines under development that would benefit from using lean-nitrogen oxides catalysts is the Orbital 2-stroke engine, shown here

fuel with an excess of air, in ratios up to 24 parts of air to one part of fuel. Under these conditions nitrogen oxides and carbon monoxide emissions are at a minimum, but hydrocarbons can rise at the onset of unstable combustion, as can be seen in Figure 2. Engine design to increase the swirl of the air/fuel charge can increase the air:fuel ratio at which misfire starts and minimise, but not prevent, hydrocarbon emissions.

The main reason that lean burn engines have not so far had widespread acceptance has been that the power output from an engine falls as the fuelling moves to leaner operation. This means that to meet driver expectations of performance and drivability a rich fuel setting is

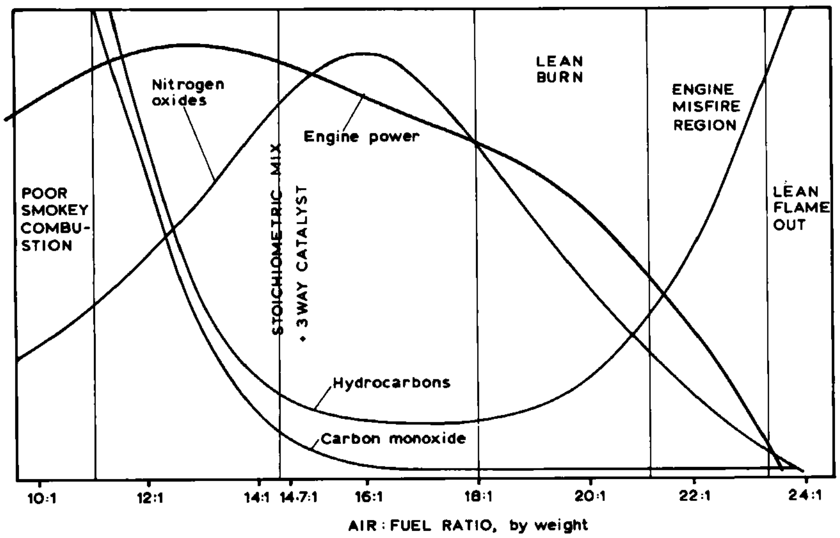


Fig. 2 These four curves indicate trends which apply to all petrol engines. Under lean burn operation fuel is burnt with an excess of air at ratios of up to 24 parts of air to 1 part of fuel, and it can be seen that nitrogen oxides and carbon oxides emissions are at a minimum, but that hydrocarbon emissions can rise at the start of unstable combustion. When there is excess fuel, the engine power is high but high levels of hydrocarbons and carbon monoxide are emitted. Peak combustion temperatures occur just on the lean side of the stoichiometric composition and result in the highest emissions of nitrogen oxides

Table I

European Regulations

1992 Standards in grams/km		
Pollutants	Type approval	Production
Carbon monoxide	2.72	3.16
Hydrocarbons + nitrogen oxides	0.97	1.13
Particulates/diesel	0.14	0.18

On 1/7/92 applies to new models; on 31/12/92 applies to all new registrations

provided for acceleration, high speed cruising and hill climbing, thus causing nitrogen oxides emissions to increase.

The Diesel Engine

The only true lean burn engine in widespread use is the diesel engine. The diesel engine stays in the lean operating region under all engine conditions. The petrol engine is throttled on the air intake, and ultimate power from a given engine is limited by the amount of air that the engine can "breathe". Conversely the diesel engine is unthrottled and its power output is determined by the amount of fuel that is injected into the combustion chamber. The maximum fuel input level is controlled by the onset of unacceptable levels of smoke or particulate formation. To limit particulate emissions to acceptable or legislated levels it is necessary for the diesel engine always to operate in the lean region (2). This means that the diesel engine has a significantly lower power output than a petrol engine of the same capacity.

Three-Way Catalyst Operation

Conventional three-way catalysts, based on the use of combinations of platinum group metals - platinum, palladium and rhodium - can convert over 90 per cent of the three main pollutants carbon monoxide, hydrocarbons and nitrogen oxides (3). They do this by the exhaust gas being controlled by an air:fuel ratio (or lambda) sensor around the so-called stoichiometric point at which neither air nor fuel is in excess at the intake to the engine; for a typical petrol composition this is at a ratio of 14.7 parts of air to 1 part of petrol.

Under lean conditions the three-way catalyst will act as an oxidation catalyst controlling carbon monoxide and hydrocarbon emissions, but the conversion of the nitrogen oxides emissions falls to very low levels.

Limitations to Lean Operation as Legislation Tightens

The introduction of lean burn engines is limited by a number of key factors. The European driving cycle, during which the emissions from motor cars are measured against the legislated levels, has been changed. The original City Test Cycle was based on inner city driving in congested traffic with a top speed of 50 k.p.h. (31 m.p.h.) and an average speed of 18.8 k.p.h. (11.7 m.p.h.). Under these conditions a typical car might need to use only 15 per cent of its maximum available power, so that lean operation would be possible throughout the cycle. However, the realisation that a major contribution to regional and global pollution is made by motor vehicles operating at high speeds on highways led to the addition of the Extra Urban Driving Cycle (EUDC), which includes speeds up to 120 k.p.h. (75 m.p.h.) and needs more power than the City Test Cycle. This causes greater nitrogen oxides emissions.

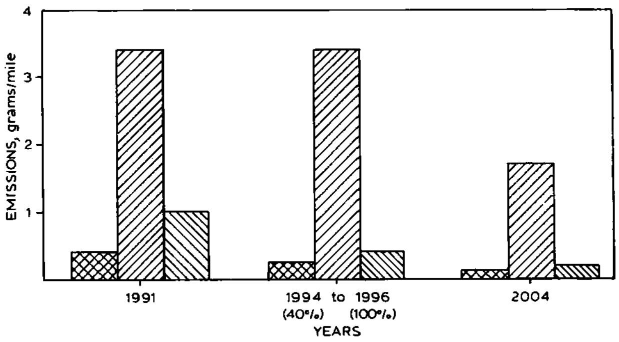
The new European Community directive,

Fig. 3 The U.S. Federal Standards include a timetable for the progressive reduction of pollutant emissions in exhaust gas:

▩ **hydrocarbon reduction from 0.41 g/mile in 1991, to 0.125 g/mile in 2004**

▨ **carbon monoxide reduction from 3.4 g/mile in 1991 to 1.7 g/mile in 2004**

▧ **nitrogen oxides reduction from 1.0 g/mile in 1991 to 0.2 g/mile in 2004**



published on 30th August 1991 (4), sets maximum pollution levels for all sizes of motor cars (Table I) and is based on the combined City and EUDC cycles. The standards will necessitate the use of closed loop, three-way catalysts on all new models sold from 1st July 1992 and on all new cars registered for sale after 31st December 1992.

In the U.S. new, more demanding Federal and Californian standards have been set. The former will reduce the allowed hydrocarbon emissions by 40 per cent and nitrogen oxides emissions by 60 per cent, by 1996 (Figure 3). Californian standards call for increasingly lower and lower emissions, culminating in a requirement for all motor vehicle manufacturers to include 10 per cent of zero emissions vehicles in their fleets by 2003 (Figure 4 and Table II). The Californian standards are also expected to be adopted by 13 states in north eastern U.S.A., which together account for nearly 40 per cent of U.S. car sales.

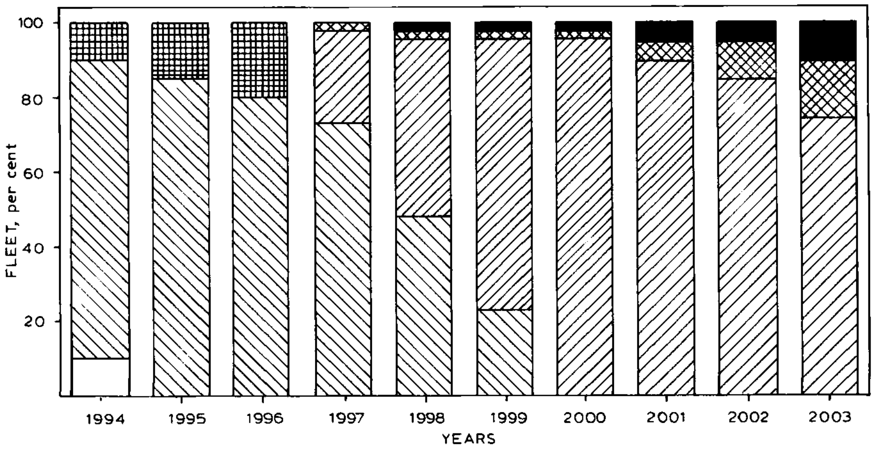


Fig. 4 Californian standards give a timetable for lower emissions and call for motor vehicle manufacturers to include 10 per cent of zero emission vehicles in their fleets by 2003

■ **zero emission vehicles**
▩ **ultra low emission vehicles**
▨ **low emission vehicles**
▦ **transitional low emission vehicles**
▧ **1993 standards**
□ **1991 standards**

Table II

Californian Standards

	Emission limits, grams/mile		
Year and standard	Hydrocarbons	Carbon monoxide	Nitrogen oxides
1991	0.39	7.0	0.4
1993	0.25	3.4	0.4
1994 (TLEV)	0.125	3.4	0.4
1997 (LEV)	0.075	3.4	0.2
1997 (ULEV)	0.04	1.7	0.2
1998 (ZEV)	0	0	0

The European Commission will propose tougher standards for the European Community by the end of 1992, for agreement during 1993 and with implementation expected in 1996. It is anticipated that these will be similar to the new U.S. Federal standards.

These increasing restrictions on nitrogen oxides emissions and the inclusion of real-world driving conditions mitigates against the use of lean burn engines, unless the emissions of nitrogen oxides can be limited in the engine or controlled externally.

Removal of Nitric Oxide under Lean Operation

Nitric oxide is thermodynamically unstable relative to nitrogen and oxygen under the full range of exhaust gas stoichiometries and temperatures encountered in internal combustion engines (5). A number of catalysts were studied during the 1970s, including platinum group metals and metal oxides (6) and some were found to decompose nitric oxide, but none of these had sufficiently high activity to be of practical importance. In their reduced states, these catalysts are rapidly oxidised by nitric oxide, with release of nitrogen. Oxygen is retained on the catalyst surface, however, inhibiting further nitric oxide adsorption and decomposition. Reducing agents are required to remove this surface oxygen and regenerate catalyst activity. Selective catalytic reduction using ammonia as the reducing agent has been utilised for the removal of nitric oxide from industrial boilers and gas turbines under conditions of excess oxygen (7). Careful stoichiometric control of the ammonia must be maintained to assure efficient nitric oxide removal without emission of surplus ammonia. For transportation applications this process is not practical because of the problems associated with the storage of ammonia, and controlling ammonia injection under transient conditions. An active and durable nitric oxide decomposition catalyst, or a selective reduction catalyst utilising reducing species present in the engine exhaust stream would be a major breakthrough for the control of nitric oxide in transportation applications. Recent literature reports and work conducted by Johnson Matthey now indicate that progress is being made towards developing these catalyst technologies employing platinum group metals.

New Nitric Oxide Decomposition Catalysts

Copper-exchanged zeolites have high activity for the catalytic decomposition of nitric oxides according to Iwamoto and co-workers (8). A number of zeolite systems were investigated including Mordenite, Ferrierite, L-type and ZSM-5, with the Cu-ZSM-5 system showing the highest activities (9, 10). Using gas mixtures of 0.5–2.1 per cent nitric oxide in helium, with gas hourly space velocities of 10–80,000

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