Car Exhaust Pollution Control

LEAN BURN ENGINES AND THE CONTINUING REQUIREMENT FOR PLATINUM-CONTAINING AUTOCATALYSTS

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Over the past twenty years catalysts containing platinum group metals have become the preferred means of limiting the polluting emissions of carbon monoxide, hydrocarbons and nitrogen oxides from motor vehicles. However, from time to time methods of exhaust control are proposed which appear to offer a viable alternative to autocatalysts. Europe has been slow to adopt emission control standards for vehicles which is, perhaps, surprising bearing in mind that European catalyst manufacturers have been producing autocatalysts and European car producers have been fitting them to vehicles destined for the U.S. and Japanese markets for over fourteen years. This article gives the background to the suggested alternatives, which are in the main different approaches to lean burn operation, and to other engine based controls. It explains why, for the foreseeable future, a platinum-containing autocatalyst will still be required to ensure that the cleanest possible exhaust is emitted under all driving conditions.

Following a lead set by the state of California in the 1960s, automobile emission controls have been progressively tightened throughout the Western World, as the damage caused by pollutants from the exhausts of engines has become more widely understood. At present the most stringent limits are in the U.S.A. and Japan where they have been applied for over 14 years, and in Australia where they have been mandatory for some two years. During this period autocatalysts based upon the platinum group metals have been the established technology employed by the world's motor industry, and this development has been recorded here from time to time (1). To date some 200 million cars have been equipped with such catalysts. The benefits derived from their use in the U.S.A. have been summarised here recently (2).

Following their successful implementation in these countries, similar stringent emission control standards have recently been, or are about to be, implemented in Switzerland, Austria, Sweden, Norway and Finland. In the European Community pollution control standards are governed by a Community directive published in February 1988, which is based upon the assumption that autocatalysts, perhaps in conjunction with lean burn engines, will be used to achieve the proposed standards. However, a number of non-catalyst solutions have been suggested for European use, and some of these are considered here.

All exhaust emission standards set in the world are based on the principle that they are acceptable if the weight of each pollutant emitted does not exceed a stipulated level as the engine is taken through a standard test cycle. The car is "driven" on a laboratory rolling road against an equivalent load to that which it would experience on the open road. The driver follows a strict speed-time protocol using a chart against which he can match the speed of the car. Since road conditions and traffic regulations vary from country to country so do the driving cycles against which the regulations

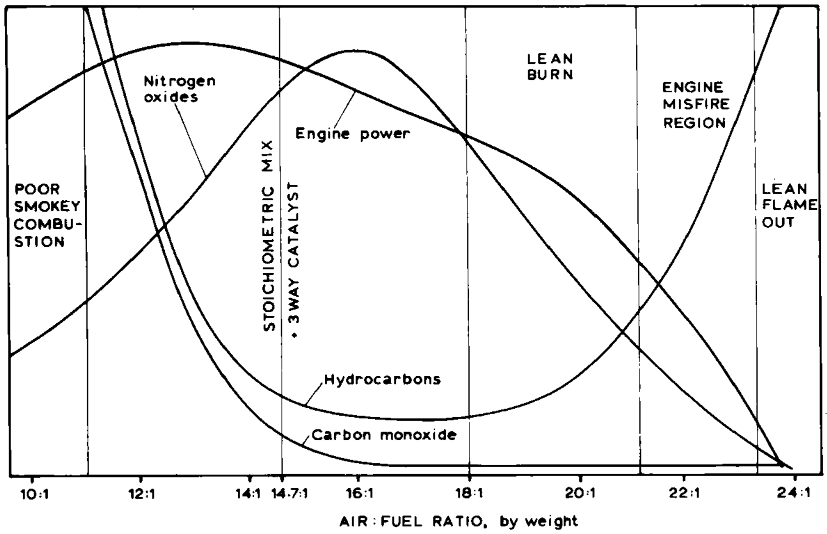

Fig. 1 The four curves shown here only indicate trends, but they apply to any petrol engine. It is apparent that the air:fuel ratio is a most important factor influencing exhaust emissions. When fuel is in excess, at low or rich air:fuel ratios, engine power is high but combustion is poor and high levels 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. In the lean burn region engine power is moderate, carbon monoxide emissions are at a minimum, nitrogen oxides are reduced, but the hydrocarbons are significant

are based. In the European Community the existing test procedure equates to a theoretical drive through a congested city centre, such as Paris, the maximum speed being only 50 k.p.h. (31 m.p.h.) and the average speed 19 k.p.h. (12 m.p.h.). However, a more realistic test procedure incorporating a high-speed element up to 120 k.p.h. (75 m.p.h.) is being considered.

An internal combustion engine produces motive power as the hydrocarbon fuel is combusted, but also varying amounts of unwanted carbon monoxide, hydrocarbons and nitrogen oxides emissions. In the case of a spark ignition engine, the fuel comprises a range of hydrocarbons formulated to give the best compromise for performance. For lead-free fuel the octane rating may be increased by the addition of alcohols or aromatic hydrocarbons. Sulphur, left behind during the refining process, will also be present. As the fuel : air mixture is reacted carbon dioxide and water are produced. Additionally, during combustion, some of the hydrocarbon fuel is only partially burned, resulting in the production of carbon monoxide, while a small amount of this is caught in crevices in the engine and so does not get combusted at all. Some of these emitted unburned hydrocarbons are known carcinogens. At the reaction temperature, nitrogen and oxygen from the air combine to form nitrogen oxides. Thus as well as natural constituents of the atmosphere, several harmful emissions are formed. Emitted hydrocarbons and nitrogen oxides can react in the atmosphere to produce photochemical smog and ozone. Both of these contribute to the pollution of our atmosphere and to the damage of vegetation and health.

Combustion Emissions

The emissions from an engine can be influenced by several factors, but mainly by the air : fuel ratio, Figure 1. Here the mechanical and chemical boundaries of engine operation are defined, and the options available for modifying these parameters are limited (3).

At low air : fuel ratios, when fuel is in excess, combustion is poor and emissions of hydrocarbons and carbon monoxide are high. As the fuelling strategy moves towards stoichiometry, the point at which there is exactly the right amount of oxygen from the air to burn the fuel, and which corresponds to an air : fuel ratio of 14.7 : 1, hydrocarbon and carbon monoxide emissions fall but nitrogen oxide emissions rise. Peak engine power occurs just rich of stoichiometry; however, for a conventional engine, peak economy is achieved lean of stoichiometry. Peak combustion temperatures occur just lean of stoichiometry and give rise to the highest emissions of nitrogen oxides. In practice most conventional engines tend to be tuned to operate in the stoichiometric region in order to achieve the best compromise between economy and power.

As the fuelling moves further into the lean burn region, nitrogen oxide emissions fall sharply and carbon monoxide emissions are at a minimum. However, hydrocarbon emissions increase and engine power falls. Ultimately the lean misfire and flame out regions are reached, where hydrocarbon emissions are very high, and the power drops sharply.

In terms of improving engine emissions, therefore, it is possible to tune lean of stoichiometry (18 : 1 to 21 : 1) to obtain low nitrogen oxides and carbon monoxide emissions, moderate engine power and good fuel economy. However, all of these apparent gains are achieved at the expense of increased hydrocarbon emissions to levels that can exceed the emission standard. Thus, from what has been said already it must be apparent that to achieve an acceptable balance of all the features required from an engine, namely, maximum fuel economy, immediate engine response to the driver and minimum production of noxious emissions both engine and catalytic technology must be used; the autocatalyst being used to control the excess hydrocarbon emissions.

Developments in engineering technology have considered both modification of the internal combustion engine and the addition of "bolt-on" devices external to the engine. These include idle mixture adjustment and ignition timing optimisation, such as exhaust gas recirculation (EGR). Within the engine, piston design, sophisticated means for monitoring and mixing the air : fuel charge, and advanced fuel injection systems have all something to offer.

Lean Burn Engines

Lean burn engines have several advantages; such engines are strictly defined as those which run at air : fuel ratios between 18 : 1 to 21 : 1, but this range may be extended somewhat.

Operating at leaner air : fuel ratios offers the advantage of improved fuel economy, which is the chief reason for developing such systems. In addition, as shown in Figure 1, lower nitrogen oxide emissions from the engine are obtained. In contrast, higher hydrocarbon emissions occur if the engine is operated in too lean a range when there is not enough fuel for the mixture to burn properly and the engine begins to misfire and run roughly.

Methods of Achieving Lean Burn

To burn a very lean mixture properly, the fuel and air have to be mixed very thoroughly and burned very evenly. As there is so little fuel compared with a conventional engine, there is a greater chance of the flame missing some of the fuel droplets. This causes either a partial burn (misfire) or a "flame out" when no burning occurs and the engine loses power.

To achieve this good mixing and burning, it is necessary to employ sophisticated methods to control the fuel and air metering into the engine, the ignition timing and the spark to ignite the fuel. If any of these are not controlled precisely, the fuel economy and engine performance will suffer and the emissions from the engine will increase.

Air and Fuel Mixing

Most methods attempt to improve mixing of the air and fuel by using devices to make the mixture "swirl" as it enters the combustion chamber. By doing this the mixture is made more homogeneous, and when ignited the swirling motion helps the flame to move across the whole width of the chamber quickly so that more even burning results. This swirl can be caused by changing the shape of the inlet port so that the mixture is forced to take a more tortuous path into the cylinder than normal.

Air and Fuel Metering

To help in controlling the lean conditions closely, the air and fuel have to be metered into the engine very precisely. This is done by an electronic control unit or microcomputer which measures the volume of air passing a fixed point and calculates the amount of fuel needed. Fuel is then metered via injectors (one for each cylinder) into the engine. The microcomputer ensures that each cylinder is fed in turn so that maximum accuracy is obtained.

Ignition

Current lean burn engines use standard spark plugs, sometimes two per cylinder, to ignite the air : fuel mixture. However, a number of new developments are being investigated. For example, these include installing twelve small spark plugs or igniters per cylinder which, it is claimed, allow the engine to run even leaner. Another development is plasma ignition, where a stream of highly charged, high energy particles is injected into the flame to help it burn faster and therefore more efficiently. At present it is too early to say how successful such devices are, but the engines using them are expected to be limited, as are other lean burn engines, by the constraints of chemistry and thermodynamics, and they will produce increased nitrogen oxides as power increases.

Lean Sensors

To improve the control of a lean burn system, a lean sensor can be used which feeds a signal to the microcomputer which in turn controls the amount of fuel metered into the engine. This enables the engine to keep as clean as possible while avoiding lean misfire and allowing rich operation to take place when power is needed.

Thus, the way in which emissions are produced in an engine is the key to realising that total elimination of all pollutants at source is not technically possible at present.

It must be emphasised that, while an engine can cruise under lean burn conditions, when maximum power is needed for acceleration or high speed or high load conditions an increase in power is needed. This results in a reversion to near stoichiometric fuelling with a concomitant increase in nitrogen oxide emissions. A lean burn engine will therefore perform less impressively, in pollution terms, on a test cycle which includes acceleration to high speeds than it will on a low-speed cycle. There will always be a hydrocarbon/nitrogen oxides/power trade-off unless another method of emission control is used to complement the lean burn engine. The new high-speed (up to 120 k.p.h.) addition to the European City Test Cycle provides just such a challenge to lean burn engineers.

Catalysts and Lean Burn Engines

The accurate control of the air : fuel ratio for lean burn engines requires a sophisticated and expensive control strategy. If any of this sophistication is relaxed control will be lost and the air : fuel ratio will drift, and emissions and fuel consumption will both increase. Examples would be the use of single rather than multi-point injection or the use of carburettors.

Even with the sophistication of devices to promote in-cylinder turbulence, better ignition and a lean sensor, hydrocarbon emissions from the engine are still a problem. It is therefore necessary to use an oxidation catalyst, such as platinum-palladium, both with simple and sophisticated lean burn engines to control hydrocarbons to proposed European standards on medium cars and in all probability for the Stage 2 directive proposed for small cars, see Table I. The oxidation catalysts convert hydrocarbons and carbon monoxide to carbon dioxide and water. Thus, when lean burn engines are used in combination with autocatalysts the advantage of better fuel economy can then be

Table I

European Community Emission Standards

	Dates of Introduction		Emissions, grams per test		
Engine capacity	New models	All new cars	Carbon monoxide	Hydrocarbons + nitrogen oxides	Nitrogen oxides
Cars over 2 litres	October 1988	October 1989	25	6.5	3.5
Cars 1.4–2 litres	October 1991	October 1993	30	8	–
Cars less than 1.4 litres Stage 1	October 1990	October 1991	45	15	6
Stage 2	October 1992	October 1993	30	8 (proposed levels)	–

combined with low polluting exhaust emissions.

Because of the power limitations of lean burn engines, they are unlikely to be used as power units for cars of engine capacity greater than 2 litres, but in this case experience accumulated, particularly in the U.S.A. over the last decade, demonstrates that the three-way catalyst of platinum, palladium and rhodium provides a very satisfactory solution to the control of the three noxious exhaust emissions.

The difference between the oxidation and three-way catalysts is simply in the combination of active components with which the honeycomb substrate is coated. While platinum, palladium and rhodium are required for three-way catalysts, only platinum and palladium are required for oxidation catalysts, and the difference in cost is solely due to the material cost differences.

In the U.S.A. and other countries that have accepted the U.S. standards three-way catalytic emission control in combination with stoichiometric engines is likely to remain the system of choice for the foreseeable future.

Elsewhere in Europe vehicles in the >2 litre and 1.4 to 2 litre range, whether powered by conventional or lean burn engines, will require catalysts to meet emission standards, Table II. Stage 1 legislation in the <1.4 litre category does not yet demand the application of tight

Table II

Possible Ways of Achieving Emission Control Standards

Engine capacity	Engine and emission control
>2 litres	conventional engine + three-way catalyst (as in U.S.A.)
1.4 to 2 litres	some vehicles as above or lean burn + oxidation catalyst or lean burn + EGR + oxidation catalyst or lean burn + EGR + three-way catalyst
<1.4 litres Stage 1	lean tuned conventional engines lean burn
Stage 2	as Stage 1 + oxidation catalysts as Stage 1 + three-way catalysts

Fig. 2 Johnson Matthey has been a major manufacturer of autocatalysts since 1974, with manufacturing facilities in the U.K., U.S.A. and Australia. Autocatalysts are subject to the most rigorous engine testing, and catalyst performance is monitored day and night on computer controlled facilities

emission control. It can be argued, however, that this class of vehicle should not escape stricter controls since it represents 50 per cent of the car pool. When legislation is tightened to the Stage 2 limits for small cars, it is likely that oxidation catalysts will be used in conjunction with lean tuned or lean burn engines.

In the 1.4 to 2 litre class, exhaust gas recirculation (EGR) is mentioned in combination with the lean burn engine and an oxidation catalyst. EGR is used to control the nitrogen oxide emissions from the engine while the catalyst controls hydrocarbons and carbon monoxide. It is shown above that, during acceleration, the fuelling of lean burn engines moves towards stoichiometry, thus it can be possible to take advantage of this situation by using a "clever" oxidation catalyst which can convert some of the nitrogen oxides under these conditions.

Lean burn systems offer the possibility of good fuel economy under part load (city driving) conditions, with acceptably low levels of nitrogen oxides emissions but with high hydrocarbon levels necessitating an oxidation catalyst for their destruction. However, under real driving conditions, transient response and drivability are poor if the system is running too lean. Overall real fuel economy gains have been estimated to be approximately 5 per cent, compared to the 20 per cent sometimes quoted. Also, under real driving conditions nitrogen oxide emissions will increase, as has been shown by results obtained during a proposed high-speed cycle test.

Although some cars can be tuned to meet the proposed limits on the European City Test Cycle without a catalyst this is done at some cost to drivability and fuel economy. It is not expected that this technique will succeed when the new high-speed cycle is introduced into the European test procedure.

Conclusions

The impossibility of keeping the emissions from the internal combustion engine clean under all operating conditions of speed and power means that platinum group metal catalysts have an important role to play in cleaning up emissions after they leave the engine. No matter what type of fossil fuelled engine is developed, its emissions will be cleaner if a catalyst is employed in conjunction with devices to improve combustion or limit nitrogen oxide formation. From an environmental point of view it is now clear that the performance of an engine must be evaluated for all the emissions it produces under all operating conditions.

Acknowledgements

I acknowledge and thank my colleagues Mr. A. J. J. Wilkins of Johnson Matthey Catalytic Systems Division and Dr. B. Harrison of Johnson Matthey Technology Centre for their assistance in preparing this paper.

References

1 For example: G. J. K. Acres and B. J. Cooper, *Platinum Metals Rev.*, 1972, **16**, (3), 74; G. J. K. Acres, B. S. Cooper and G. L. Matlack, ibid., 1973, **17**, (3), 82; M. Shelef and H. S. Gandhi, ibid., 1974, **18**, (1), 2; B. J. Cooper, E. Shutt and P. Oser, ibid., 1976, **20**, (2), 38; A. F. Diwell and B. Harrison, ibid., 1981, **25**, (4), 142

2 M. P. Walsh, *Platinum Metals Rev.*, 1986, **30**, (3), 106

3 House of Lords Select Committee on the European Communities, "Lead in Petrol and Vehicle Emissions", February 1985

Monitoring Impurities in Water

A TECHNIQUE BASED UPON THE HIGH ADSORPTIVITY OF PLATINUM

The widespread pollution of water, be it in the form of rain, groundwater, rivers, lakes, coastal waters or the oceans, is one of the most important environmental challenges facing the world today. A complete solution will only come about when major changes are made to the many contributing factors, which include: mineral extraction and processing, energy conversion and use, industrial manufacturing, intensive methods of farming and sewage disposal. In the meantime many immediate problems must be faced and none, perhaps, is more urgent than the need to analyse accurately and rapidly the impurities in reservoirs, to determine if the water is fit to drink.

A recent communication from researchers at the A. N. Frumkin Institute of Electrochemistry, of the Academy of Sciences of the U.S.S.R., considers in some detail three electrochemical methods of determining impurities in water, and compares them with established methods (V. E. Kazarinov, V. S. Bagotzky, Yu. B. Vassiliev and O. A. Khazova, *J. Appl. Electrochem.*, 1988, **18**, (3), 347–356).

The most suitable of the methods tested is based upon the fact that platinum readily adsorbs organic and toxic metals. Thus the amount of such impurities can be calculated from the degree of poisoning they cause, as determined from the decrease in the hydrogen adsorption capability of a platinum microelectrode. Measurements were made using a conventional three-electrode cell, the working electrode being 2 to 3 mm of 0.5 mm diameter platinum wire and the auxiliary electrode a 1 cm square of platinum gauze. In acid solutions a mercuric sulphate reference electrode may be used. Quantitative determination of individual substances is only possible in limited instances, but organic impurities may be differentiated according to their oxidisability into easy-, medium- and difficult-to-oxidise categories.

The proposed electrochemical method of impurity determination is highly suitable for automatic water monitoring systems, and a number of analysers have been devised.

Oxidation Resistant Iridium Alloys

A requirement for aerospace components which are capable of serving for sustained periods of time at high temperatures has continued to focus attention on the need for suitable materials, and a recently reported study by K. N. Lee and W. L. Worrell of the University of Pennsylvania has identified iridium-containing alloys as promising high temperature oxidation resistant materials. ("The Oxidation of Iridium-Aluminum and Iridium-Hafnium Alloys at 1550°C and 1640°C", Extended Abstracts, Electrochemical Society, Spring Meeting 1988, Vol. **88–1**, Abstr. No. 281, p. 423)

It has long been known that iridium loses weight at a significant rate when it is heated to temperatures in excess of about 1100°C. Now the oxidation behaviour of arc melted iridium alloys containing 5 to 80 atomic per cent aluminium or hafnium has been examined and it has been shown that the formation of gaseous iridium oxides can be restricted on appropriate alloys by the development of a protective oxide scale on the surface. However, if the amount of the second element is too low, any oxide scale which forms is porous and permits the passage of both oxygen and gaseous iridium oxides.

Iridium-aluminium alloys containing 60 to 80 atomic per cent aluminium form a continuous non-porous oxide layer which shows protective oxidation behaviour even when the alloy is exposed to oxygen at a temperature of 1550°C.